PALAEAUX

MANAGEMENT OF COASTAL AQUIFERS IN EUROPE

Palaeowater, natural controls and human influence

FINAL REPORT

JUNE 1999

EC Fourth Framework Programme
(Climatology and Natural Hazards)

ENV4-CT95-0156

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Contents

Contributors

Project Co-ordinator
W.M. Edmunds, British Geological Survey

Report Editors
W.M. Edmunds, British Geological Survey
C.J. Milne, British Geological Survey

Contributing Partners
(figures in brackets indicate chapter numbers of specific major contributions)

Tallinn Technical University, Institute of Geology
R. Vaikmae (2, 11, 17)
L. Vallner (2, 17)

Danmarks og Gronlands Geologiske Undersøgelse
K. Hinsby (3, 15, 16)
W.G. Harrar (3, 13)
P. Nyegaard (3)
P. Konradi (3)
E.S. Rasmussen (3)
T. Bidstrup (3)
U. Gregersen (3)

Universiteit Gent, Lab. for Applied Geology and Hydrogeology
K. Walraevens (4, 14)
M. van Camp (4, 13)
J. Lermytte (4)

Vrije Universitat Amsterdam
C.A.J. Appelo (4, 14)
W.J.M. van der Kemp (4)

British Geological Survey, Hydrogeology Group
W.M. Edmunds (5, 11, 16, 17)
C.J. Milne (5, 14)
D.K. Buckley (5, 15)
W.G. Darling (5, 12)
P.L. Smedley (5)
A.T. Williams (5, 13)
I. Gaus (14)

Université de Paris-Sud, Laboratoire d'Hydrologie et de Géochemie Isotopique
L. Dever (6, 18)
C. Marlin (6)
E. Gibert (6)
F. Barbecot (6, 16)

Université d'Avignon, Laboratoire d'Hydrogéologie
Y. Travi (6, 18)

Universitat Politecnica de Catalunya, Barcelona
E. Custodio(*) (7, 15, 18)
M. Manzano (7, 11, 15)
X. Riera (7)
M.C. Cabrera (7)
J. Custodio (7)
(*) on leave to Geological Survey of Spain, Madrid

Universidade de Aveiro, Departamento de Geociências
M.T.C. Melo (8, 14, 16, 17)
M.M. da Silva (8)

Instituto Tecnológico e Nuclear, Departamento de Quimica, Lisbon
P. Carreira (9)

Institut für Klima- und Umweltphysik der Universität Bern
H.H. Loosli (2, 4, 7, 8, 10, 12, 16)
P. Blaser (2, 8, 10)
M. Juillard (2, 8, 10)
R. Purtschert (10, 12)

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- L. Eichinger (Hydroisotop, Schweitenkirchen)
- C. Bryant, D.D. Harkness (SURRC, East Kilbride)
- L. Savitski (Estonian Geological Survey)
- J. Ivask, R. Karukäpp, E. Kaup, A. Miidel, T. Martma, V. Raidla, A. Raukas, (Institute of Geology at Tallinn Technical University, Estonia)
- P.Raud (Salveesia Ltd, Estonia)
- J. Heinemeier, E. Boaretto* (Institute of Physics and Astronomy, University of Århus, *now Weizmann Institute of Science, Rehovot, Israel)

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- Gill Tyson provided superb cartography

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Preface

This final report summarizes work carried out by a partnership consisting of scientists from UK, Estonia, Denmark, The Netherlands, Belgium, France, Spain, Portugal and Switzerland under the Fourth Framework Programme, contract ENV4-CT94-0156, of the European Union.

The format of the report reflects the country contributions as required by the Commission, but also draws together the main results at the European scale. Chapter 1 provides an introduction to the aims and approach of the project. Chapters 2 to 10 report the detailed regional case studies carried out by the individual partners. Chapters 11 to 17 build on the regional studies to develop key aspects and themes of the study and to take a wider view of the subject at a continental scale. Finally, Chapters 18 and 19 draw out the overall conclusions of the project and discuss the implications for effective long-term management of coastal palaeowater aquifers.

Not all of the large amount of data collected during the project are recorded here. Should clarification be sought the reader is asked in the first instance to contact BGS as co-ordinators of the project.

The results of the project are destined to be published in the open scientific literature and popular channels. However, a major part of the material reported here will, following appropriate peer review, be published in early 2000 as a Special Publication of the Geological Society of London.

Executive Summary

The PALAEAUX project has brought together up-to-date geochemical, isotopic and hydrogeological information on coastal groundwaters across Europe in a transect from the Baltic to the Canary Islands. These data have been interpreted in relation to past climatic and environmental conditions as well as extending and challenging concepts about the evolution of groundwater near the present day coastlines. Freshwater of high quality originating from different climatic conditions to the present day and when the sea level was much lower is found at depth beneath the present coast in several countries. The implications of the scientific results for management of aquifers in European regions are considered.

Results show that information on palaeotemperature, past precipitation and recharge regimes as well as air mass circulation can be deduced from the geochemical and isotopic evidence contained in European coastal aquifers. An age gap can be recognized in some aquifers which indicates that no recharge took place at the time of the last glacial maximum (LGM), for example in UK and Belgium. This indicates that these areas were free of ice cover but sealing due to permafrost was effective. Groundwaters from Estonia have $\delta^{18}O$ values of approximately −22‰ which demonstrates that recharge took place directly beneath the Scandinavian ice sheet during the LGM. Noble gas recharge temperatures supported by stable isotopic data provide convincing evidence in aquifers from northern Europe (UK, Denmark, Belgium, Switzerland) that recharge occurred during the cooler climates prior to the LGM and that recharge temperatures (soil air temperatures) were some 6°C colder than at the present day.

In southern Europe the radiocarbon ages indicate continuity of recharge through the LGM. Noble gas recharge in the Aveiro Cretaceous aquifer also indicate as elsewhere, that atmospheric cooling of 5–6°C occurred before and during the LGM. However in contrast to northern Europe, an enrichment in $\delta^{18}O$ of around 0.6‰ is found in the late Pleistocene recharge waters, and is considered to reflect the enrichment in the Pleistocene ocean water as well as the constancy in the source of moisture from the Azores region of the Atlantic as at the present day. The overall results emphasize that the stable isotope signal in palaeowaters may either reflect the source or the temperature of the precipitation.

For most of the past 100 000 a sea levels considerably below those of the present day provided an opportunity for recharge and movement of groundwater beyond the present coastline as well as emplacement on shore to greater depths than allowed by the present day flow regime. The greatest recorded depth of palaeo-fresh water (to about –500 m) is found in the UK East Midlands aquifer. The timescale of this groundwater movement, shown by radiocarbon data which have been calibrated and extended using chemical tracers, probably represents a continuous sequence of recharge over 100 000 a, supporting the evidence from speleothem growth for infiltration of groundwater through the Devensian glacial period. In Estonia, movement of colder palaeowaters took place to depths of –250 m and excess dissolved gases found in these waters indicate recharge beneath the ice sheet. The model, proposed by Boulton *et al.*, for deep groundwater circulation due to high heads imposed by the ice sheets has been closely examined in the present programme but no evidence can be found from geochemical and isotopic data together with local modelling.

In several regions waters of Holocene age have been recorded at the coast (as in the Dogger aquifer of the Caen and Atlantic coast regions of northern France) which represents recharge of marine or estuarine water during the Flandrian (Holocene) transgression. The use of borehole hydrogeophysical logging has helped to confirm the complex stratification that may exist beneath present day coastlines. Freshwater and saline water (of modern or ancient origins) may be found side by side (as in the south coast of UK) related to structural and palaeohydrogeological controls. Direct as well as indirect evidence is found from the present study that fresh or brackish water, recharged during the late Pleistocene, is found in aquifers currently offshore (off the North Sea coast of Denmark, the Channel coast of UK and Portugal, for example). This is consistent with results from the drilling off the eastern seaboard of the USA where fresh/brackish waters were proven to depths of 300 m to a distance of 100 km from the modern coasts. The results of modelling show that such features may take tens of thousands of years to erase.

The main attribute of palaeowaters in terms of water quality is their high bacterial purity, total mineralization often less than that of modern waters and being demonstrably free of man-made chemicals. As a result of long residence times, some palaeowaters may be enriched in some beneficial trace elements whilst others especially in reducing environments may have high iron or other species requiring treatment.

In Estonia and in the UK freshwaters found at depths up to 300 m in aquifers of Mesozoic to Palaeozoic age, are of lower salinity than the present day recharge. Very low Cl in the East Midlands aquifer is almost entirely the result of pre-industrial atmospheric inputs and the lack of increasing salinity with depth is strong evidence for a lack of cross-formational flow from adjacent formations containing more mineralized waters. Modern waters usually have additional solutes resulting from human impacts. In the Mediterranean coastal areas lower recharge leads to higher salinity conditions in both palaeo and modern waters.

The development of aquifers in Europe during the past 50–100 years by abstraction from boreholes has generally disturbed flow systems that have evolved over varying geological timescales and especially those derived from the late Pleistocene and Holocene. Hydrogeophysical logging has demonstrated time and quality-stratified aquifers resulting in mixed waters which are produced on pumping. A range of specific indicators including ^{3}H, $^{3}H/^{3}He$, ^{85}Kr, CFCs, as well as pollutants have been used to recognize the extent to which waters from the modern (industrial) era have penetrated into the aquifers, often replacing the natural palaeogroundwaters.

In the coastal regions where development pressures are already severe, many problems for management come together including issues relating to quantity and quality of water, seasonal demand, pollution risks and ecosystem

damage. The water balance in many coastal areas may not be fully understood and wells are drilled or deepened without the awareness that palaeowaters belonging to a former recharge regime are being intercepted. In many areas there is induced replenishment as modern (often polluted) waters are drawn in. However in some aquifers the rates of withdrawal exceed the natural recharge and in effect a part of the resource is being mined.

In these areas there is a need for careful drilling to establish the age and quality layering as well as proper well completion. Proper monitoring networks and strategies need to be set up to follow the position of interfaces in both the vertical and lateral planes. Correct management is needed often for seasonal demands: this may be beneficial, allowing winter recovery of water levels. The palaeowater however is a high quality resource and should be treated as a strategic reserve. It should receive priority for potable use and not be wasted for agricultural or industrial purposes which do not require waters of such high purity. Conservation targets are needed to allow for sustainability including ecosystem preservation. Changes may be needed in the administrative and legal framework to safeguard the use of the palaeowater reserves.

1 Introduction

1.1 Concept of the PALAEAUX project

Most of Europe's groundwater resources are found in sedimentary basins ranging from Mesozoic to Quaternary age. Throughout geological time these have been subject to flushing and replenishment with fresh (or saline) water in response to changes in hydraulic gradients brought about by tectonic movement, sea level changes or other processes. Most recently the strong climatic fluctuations of the Quaternary have caused repeated rise and fall of sea levels, producing changes in hydraulic head and changes in the patterns of groundwater flow in both coastal as well as inland areas.

The present day configuration of water resources and water quality is primarily the result of circulation of fresh water to deeper levels in response to lower sea-levels corresponding with the last glaciation. Coastal Europe offers a contrast in conditions for groundwater recharge and evolution during the late Pleistocene. In northern countries the past 100 000 a was dominated by the Devensian glaciation. Recharge was strongly affected by ice cover especially at the time of the glacial maximum and also by permafrost in periglacial areas. However in southern Europe the same period was characterized by highly variable climate with contrasting wet and dry episodes. The lowering of sea level affected the whole European coastline, although to different extents and over much of Europe, the exploitable water resources are considered to occur to depths which are greater than one would expect from present-day hydraulic gradients and recharge inputs. The increasing continentality and fluctuating distances to the coastline may also have influenced amounts and the geochemistry of rainfall as well as recharge.

At the present day aquifers in coastal Europe are under severe pressure due to human settlement, industry and tourism. In addition they are threatened by climate change and the risks of sea level rise. As a background to improved management of groundwater resources in coastal regions it is necessary to have a sound understanding of the processes governing the evolution of aquifers and how they have responded in the recent geological past during periods of glaciation and accompanying sea level change.

The PALAEAUX project has focused particularly on the origins of palaeowaters in coastal areas of Europe and their present day distribution in representative areas along a transect from the Baltic to the Canary islands. Focus is placed on their importance both as possible archives of former climatic and environmental conditions, as well as their potential in certain areas as valuable sources of good quality drinking water, unaffected by impact of the industrial era.

1.2 Context and key scientific issues addressed in PALAEAUX

1.2.1 Palaeowaters - definition and recognition

The term palaeowaters which is used widely in the project, not least to derive the acronym, was first used in the 1960s by isotope hydrologists to categorize fossil waters beneath the Sahara desert following the early success with carbon-14 dating of groundwaters. This is not a generic term in any way but was used especially when it was realized that the climatic conditions of recharge of these fossil

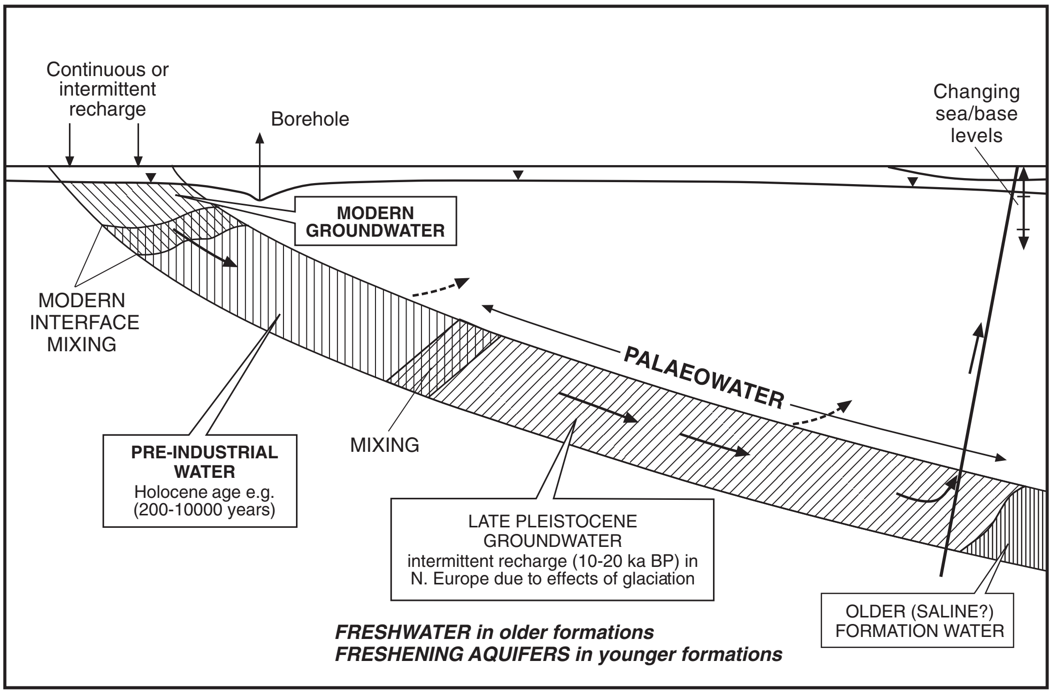


Figure 1.1. Conceptual model of a confined groundwater system to show definitions used in the PALAEAUX study.

waters, as identified using stable isotopes of water, $\delta^{18}O$ and $\delta^{2}H$, was colder than at present and therefore formed a rather unique group of natural waters.

The conceptual approach used in the present study is summarized in Fig. 1.1 considering an aquifer which could have received recharge continuously or intermittently over say, the past 100 ka. which would be the upper residence time for most European groundwaters being considered. Palaeowaters therefore strictly refers to all groundwaters that can be clearly identified in terms of radiocarbon age or other isotopic or noble gas signature as originating in colder climatic conditions of the late Pleistocene.

In several aquifers water which must predate this Devensian cold period may be encountered. These older formation waters are generally saline and may have originated as connate waters of original marine origin or as formation brines where intraformational evaporites are present.

Also considered here are waters of Holocene age (almost exclusively generated after the climatic amelioration. These waters have essentially the same stable isotopic signatures as modern waters but may be dateable to the past 12 000 years. These waters are also termed pre-industrial waters since they are often of similar high chemical quality to the palaeowaters *(sensu stricto),* unaffected by the pollution of 19th and 20th centuries.

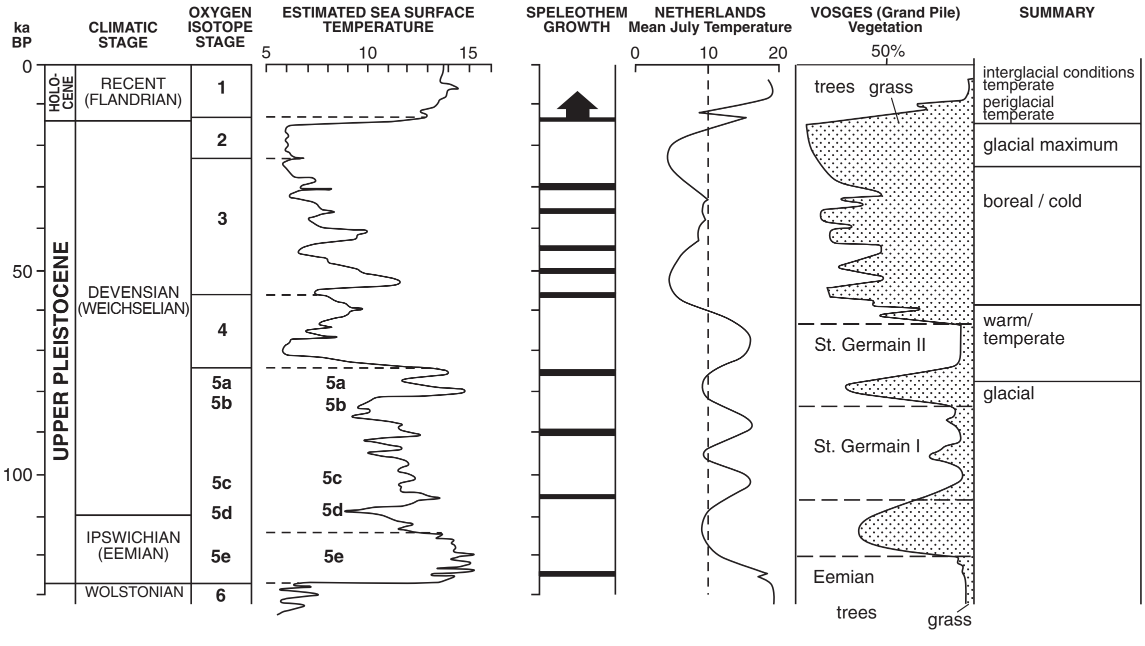
The material presented here is also of relevance in relation to the wider field of palaeohydrology. This term, widely used by earth scientists, is used almost exclusively to consider the mainly sedimentological evidence for surface water history. In the present investigation, the evidence for hydrological changes are contained directly in the waters and may often combine palaeoclimatic evidence. Indeed, groundwater is the only other archive except for ice where one might hope to reconstruct from direct evidence the hydrological history.

1.2.2 Aquifers as archives of former climatic and environmental conditions

A major goal of PALAEAUX is to investigate the extent to which groundwater retains the signature of past recharge events. To date most of the information used to reconstruct the climatic and related history of the Late Pleistocene has come from other archives such as ocean sediment records, especially foraminifera, peats and other terrestrial sediments, speleothems, tree rings, palynology and ice cores. It is proposed that the groundwater evidence can be used as additional proxy data on climatic change, notably direct evidence of former wet episodes, which can be compared and checked with the other marine or continental indicators. The main time scale of interest for the groundwater archive is up to 50 000 years which is the absolute upper limit for radiocarbon dating, which has a potential resolution of measurement of around ±100 years. Hydrogeological and geochemical factors however limit the interpretation and dating resolution to about 30 000 years at best. Several other indicators, for example noble gases, oxygen and hydrogen stable isotope ratios and the relative concentrations of Cl may also be used as indicators of palaeowaters.

1.2.3 Timescales of change in groundwater systems

Groundwater quality and piezometric conditions in coastal regions at the present day differ considerably from those found prior to the onset of exploitation a little less than 100 years in most European countries. Before development, aquifers were in a steady state with hydraulic gradients largely reflecting topography and with changes, for example in spring flows, responding seasonally and with climate. Groundwater residence times in most aquifers would be measurable in the range 10^1–10^5 a, although stratification in ages and in quality would have developed



Shackleton 1987 Core V23 - 82 Sancetta et al. (1973) Gordon et al. (1989) Behre (1989) Woillar (1978) Goodess et al. (1991)

Figure 1.2. The chronology of the late (upper) Pleistocene with key records from Northern Europe that have significance for the emplacement and evolution of groundwater.

related to aquifer properties and lithology. Drilling in the modern era has disturbed this pattern over most of Europe so that spring flows have been disrupted, water levels are on average much lower than before any development and borehole construction has penetrated the layering in age and quality resulting in mixed groundwaters. For the palaeo-reconstruction of the present study this presents problems that are difficult to overcome.

It is considered that the groundwater steady state conditions that existed prior to the industrial era had been maintained for some 7000 years. This corresponds to the rise of sea level to near present levels and the establishment of the recognisable present day coastline of Europe.

Before this the related effects of glaciation and sea level change would have led to significant changes in the hydrodynamics associated with longer flow paths towards the lower sea levels or other base levels, lowering of water levels inland and increase in the volume of the unsaturated zone. In areas close to or beneath ice sheets it is possible that the groundwater was completely reorganized as a result of the very large heads imposed by the ice masses (Boulton *et al.*, 1995, 1996). Over large areas of Europe permafrost may also have interrupted recharge or superimposed other effects on the aquifers. The timescale of the lowered sea levels was of the order of 100 000 years, back to the last warm period (Eemian/Ipswichian). It must also be recognized that other periods of glaciation and climatic oscillations have been recorded during the Middle and Late Pleistocene which would have imposed an earlier cycle of disturbance on the groundwater systems.

Normally a base level or hiatus in the active flow system may be recognized at a certain depth marked by the presence of saline water, creating a saline-fresh water interface. This is taken here to indicate the zone to which groundwater flow on the recent geological timescale (eg below 1 000 000 a in age) has been restricted. Groundwater of the same age as the sedimentary basin (connate or formation water)may still be present in some aquifers where subsidence has been continuous; such a situation has been proposed for the North Sea where water of sea water salinity is present in interstitial waters of the Chalk (Bath and Edmunds, 1981) which has slowly been removed by convection or diffusion over a geological timescale. This same water may also be present in residual amounts in the matrix of dual porosity aquifers (such as the Chalk) and may also give rise to slightly brackish or saline waters.

In the context of the PALAEAUX studies therefore numerous processes may have been involved in the groundwater emplacement. Since the present sea levels are among the highest recorded in the Late Pleistocene (Keen, 1995), sea water intrusion into aquifers is unlikely to have been a common occurrence and the movement of freshwater “offshore” is a more likely scenario.

1.2.4 European climate, glaciation, vegetation and permafrost since ca 120 000 BP

Groundwater evolution in Europe during the Holocene and Late Pleistocene, prior to modern development, has taken place against climatic changes that could have significantly modified the main groundwater parameters of recharge, flow directions and depths, rates of circulation and discharge. The timescale of the past 120 000 years is shown in Fig. 1.2 where some of the more important information from European sources which have a bearing on groundwater evolution is summarized. It should be pointed out that the absolute chronology of some of the events have uncertainties and for full details the source papers should be consulted. For groundwater events however the exact timing is not important, the main thing being the broad climatic trends and the related geomorphological events that are implied.

There are many sources of information which summarise climate change and history of the last glaciation in W Europe (e.g. Dawson, 1992; Goodess *et al.*, 1992) although there is much important new data appearing yearly. The Devensian is now shown to be relatively complex, essentially a cold period, culminating in the maximum glaciation around 18 000 a BP. One of the best indirect indicators relating to groundwater is the well-dated record of speleothem growth (Gordon *et al.*, 1989). This indicates a) the presence of diffuse groundwater recharge and hence the absence of permafrost and b) the biogenic production of carbon dioxide in the soil, both being dependent on temperature. Eight periods of growth are recognized from the UK since the last interglacial (Ipswichian).

1.2.5 Sea level change and groundwater evolution

Sea level changes during the Late Quaternary have varied widely from place to place Pirazolli (1996) and the European cross-section chosen for PALAEAUX - from the Baltic to the Canary Islands probably covers the full range of sea level change that have occurred in NW Europe. The most recent estimate of eustatic sea levels for the past 120 000 years has been obtained from interpretation of the ^{18}O isotopic record of deep sea foraminifera (Shackleton, 1987). This shows (Fig. 1.3) that there has been a maximum sea level rise of around 130 m since the last glacial maximum. Several points are important for considering the impact on groundwaters:

i) that sea levels have been considerably lower than at the present day for well over 90% of the past 120 000 a, allowing establishment of lower water tables as a standard state. In fact climatic conditions in Western Europe are abnormally warm and similar optimum conditions to the present day probably occupied less than 10% of the Middle to Late Pleistocene. Present day groundwater levels may be seen as exceptional.

ii) sea levels have probably not been higher than today during the past ca 100 000 a and earlier studies of marine

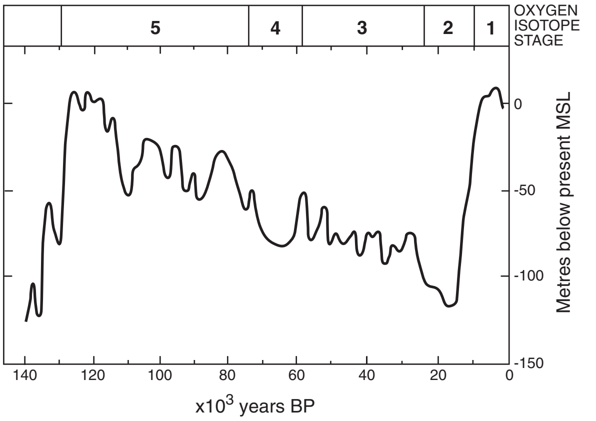
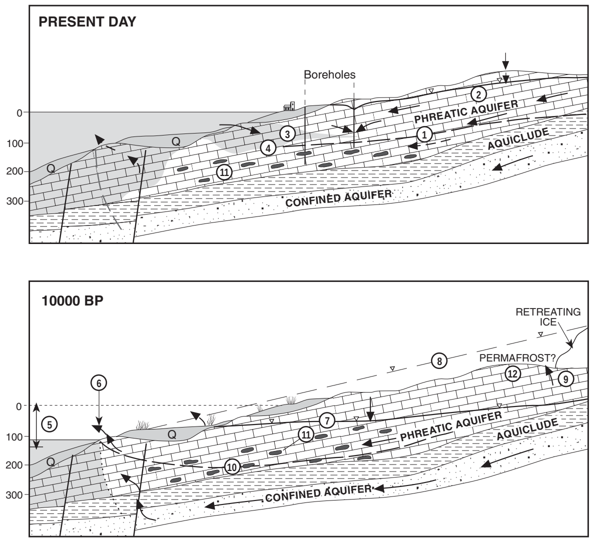


Figure 1.3. Eustatic sea-level curve for the past 140 000 a based on Shackleton (1987) and Pirazolli (1996)



(1) Present day flow restricted to ca. 130 m below msl as observed in temperature gradients and hydrogeophysical logs.
(2) Most rapid flow in upper 50 m.
(3) Modern sea water drawn in along fissures but may overlie freshwater.
(4) Saline-freshwater interface prior to development: depth of sea water penetration unknown offshore but likely to enter aquifer due to density difference, except where permeability barrier.
(5) Maximum lower Late Pleistocene sea level.
(6) Former shore line - Late Pleistocene. Possible sites of modern sub-marine fresh water discharge.
(7) Steady-state water level.
(8) Possible piezometric surface of confined aquifer if controlled by glacier-head up to 500 m higher.
(9) Possible zone of upwelling ahead of stationary front.
(10) Potential depth limit to flow (unconfined) during Late Pleistocene.
(11) Pockets of earlier saline groundwater (ancient sea water or connate formation water) below –260 m in less permeable units (including matrix).
(12) Permafrost and periglacial features possibly controlling groundwater flow and recharge to depth of ca 50 m.

Figure 1.4. Conceptual evolution of groundwater in a coastal aquifer from before the Flandrian transgression to the present day. Based on data for the Channel coast.

transgressions in NW Europe have not been borne out by recent work (Pirazolli, 1996). There are areas of the coastline where marine incursions may have taken place for example as a result of subsidence or change in sedimentation history. The most recent ancient sea water that is likely to be found in groundwaters is therefore likely to be from the Eemian time, when it is possible that sea levels were for a time 5–10 m higher than the present day.

iii) the sea level minima may not be the base levels to which groundwater circulation responded since (eg North Sea) in some areas the sea bed was only tens of metres.

1.2.6 Nature of coastal aquifers

The coastal regions of Europe, as a result of development pressures, have been well explored for groundwater and around much of the coastline, wellfields have been in operation for several decades. The impacts the invasion of sea water have sometimes led to abandonment, although elsewhere good management or favourable water balance (mainly in temperate countries) has allowed limited operation of wells close to the coast (eg. Headworth and Fox, 1986).

Most of the invasion of coastal aquifers by modern sea water is generally derived from shallow depths and may be localized along planes of higher porosity/permeability. The saline/fresh water interfaces at depth in many coastal and inland areas at the present day may be the result of former hydrological conditions unrelated to present day hydraulic heads and involving palaeo-sea water or formation waters. The lower sea levels during much of the Pleistocene encouraged deeper circulation of fresh groundwater, controlled by more distant outlets. The situation that may exist in coastal aquifers at the present day is summarized in Fig. 1.4, which is modelled on the Chalk of the Channel Coast.

It also follows that since the rise in sea level to modern datum was complete only around 7000 years ago over much of Europe, the advance may have covered areas formerly underlain by fresh waters. One of the goals of PALAEAUX was to search for any available evidence that freshwater offshore might still exist. This might occur for example from offshore boreholes drilled for hydrocarbons. Another source of evidence was considered to be sediment recovered from cores obtained from sea bed drilling where salinity, at least, might be recorded. There are also historical records from fishermen and mariners of submarine springs, most of which have been diminished or lost as the result of onshore pumping.

As a result of modern development any high quality palaeowaters may also have been affected by inland pollution from various sources. One of the main goals of PALAEAUX has been to define better the interface between modern polluted and pre-industrial (or palaeo) groundwater resources and to review and test techniques of identification.

1.2.7 European coastline

The familiar outline of the European coastline has only been a recognisable feature for some 7000 a. It is important to consider how changes in the coastline during the climatic and environmental changes of the late Quaternary may have influenced the movement of groundwater. As a basis for the PALAEAUX study a time slice of 10 000 a BP which predates the rapid Holocene (Flandrian) rise in sea levels, is used (Fig. 1.3). Further changes in the coastline and their significance are considered in the text below.

1.3 Key applied issues addressed in PALAEAUX

1.3.1 Impact of past climate change on European water resources

Understanding past hydrological changes is an essential basis for the prediction of the impacts of current future climatic and environmental change on water resources. It has already been pointed out that the reserves of fresh water may be larger than estimated from consideration of the present day water balance, and that fresh water may be found at greater depths, or offshore in several regions.

The focus of this project is primarily on coastal regions of Europe (Baltic, Mediterranean, North Sea and

Atlantic) where human impacts are greatest and the effects are easier to study. By investigating the existing baseline conditions as well as the active controlling geochemical processes taking place near the coast and across the saline/fresh interface both in the past as well as in present day systems it may prove possible to provide guidance for the limits to exploitation of groundwater in coastal regions based on the common European experience. In fact, in the Mediterranean and other southern regions the current resources of brackish water may also be important as a reserve for desalination schemes.

1.3.2 Palaeo-information from groundwater

Specific information may be obtained from the isotopic and chemical records of in groundwater including the palaeotemperature, past precipitation amounts as well as evapotranspiration, former air mass circulation and continentality. The stable isotope records ($\delta^{18}O$, $\delta^{2}H$) in modern rainfall are now well understood at a global scale and the basis exists for interpretation of precipitation characteristics of past climates (Rosanski *et al.*, 1997). The ^{36}Cl contents of groundwaters may also be used in low chloride waters to deduce rainfall and its former composition as well as Late Pleistocene evapotranspiration (Andrews *et al.*, 1994). Noble gas ratios have now been well established as a reliable tool for measuring past groundwater temperatures (Stute and Schlosser, 1993; Loosli *et al.*, 1999b)

1.3.3 Global context of PALAEAUX

This is among the first studies which has paid attention to groundwaters at a continental scale, both as possible archives of the effects of glaciation and sea level change as well as the impacts on modern water resources in these economically important coastal regions. Many high resolution studies are available for palaeo-reconstruction (ice-core, tree rings, marine sediments) which are of international significance. Groundwaters are generally not considered of importance on account of their low resolution signals. However they record regional events of long duration, especially episodes of recharge (evidence of wetter than average climates). The information retained in the groundwaters especially if these can be radiometrically dated, is likely to be robust and representative of certain climatic events which can be correlated at the continental and global scale. For example, the possibility of using noble gas ratios to record palaeotemperatures at the global scale has been shown for example by Stute and Talma (1998).

Drilling of Pleistocene and Miocene sediments on the Atlantic coastal plain of the USA has proved the existence of freshwater (<5 g L^{-1}) to depths of -200 m OD and as far as 100 km offshore (Hathaway *et al.*, 1979). These waters are suggested as remnants of fresh palaeowaters when the coastline was ca 130 km off the present shoreline. Modelling suggests that it would take 30 000 years to reach a new equilibrium and that the offshore interface is moving landward at about 0.32 m ka^{-1}.

At the scale of groundwater exploitation the European region is a type area at the global scale of an advanced society who have been exerting tremendous development pressure around its highly varied coastline. These aquifers and their past and present evolution can be used as case studies of possible wider impacts for other regions of the globe.

1.3.4 Human intervention in coastal aquifers

Coastal aquifers have been the subject of recent interest for intervention activities including management of sea water intrusion (de Breuck, 1991), disposal of toxic including radioactive wastes (Bath *et al.*, 1996) as well as aquifer storage and retrieval (Pyne, 1995).

Water supply in coastal regions is often difficult to manage due to the combined effects of seasonal demand and sea-water intrusion. One approach to mitigating these difficulties that is becoming more widely practised is the cyclic storage of freshwater in deep saline aquifers. The design of such schemes depends on an understanding of the hydraulic and geochemical conditions in such aquifers, including their former evolution, since the various types of intervention are often accelerated versions of the natural analogues that have taken place during the late Pleistocene.

The extent of palaeowater occurrence at a regional scale across Europe has not been previously examined. The extent and total quantity of palaeo-freshwater resources are liable to overestimation since palaeowaters are grouped together with those being replenished today from active recharge systems. However, the impact of the late Pleistocene events means in effect that deeper fresh waters are being mined. In other areas, especially in coastal zones, new fresh water resources may be found which are relict of the former lowered sea level and groundwater circulation.

1.4 Regional scope of the PALAEAUX project

The PALAEAUX project investigates evolution of palaeowaters in a transect across Europe extending from the Baltic to the Atlantic (Fig. 1.5). It involves 10 partners from 9 countries. The work has been restricted to representative sedimentary basins which are considered to contain the best preserved palaeo-groundwater sequences. Other studies have been carried out on crystalline basement and hard rock aquifers, especially in connection with the containment of radio-active wastes. This is the first such study of the main sedimentary aquifers which are important in the context of European water resources. The main aquifers chosen for the project are shown as numbered in Fig. 1.5 and with details below:

Estonia (1)

The Cambrian-Vendian aquifer, the lowermost of the six aquifer systems extending under most of Estonia, has been the main target of study. The groundwater has a strongly depleted stable isotopic signal and low radiocarbon values, and appears to be an excellent example of European periglacial recharge at a relatively high latitude. The overlying aquifers are polluted in many places, principally in the north-eastern mining area, and as a result of heavy exploitation of the Cambrian-Vendian aquifer, pollution is beginning to leak through the overlying clay strata. Saline intrusion from the Baltic Sea is also an issue.

Figure 1.5. Probable extent of the European landmass around 10 000 BP, showing the reach of the Last Glaciation Maximum (LGM). The study areas of the PALAEAUX project are outlined, numbers refer to the descriptions in the main text.

Denmark (2)

South-western Jutland. This area is the focal point for the intake of new groundwater resources for the town of Esbjerg. The Ribe Formation, the target of the PALAEAUX study, is an aquifer system within a relatively flat-lying succession of Tertiary (Miocene) sands as well as Quaternary fluvio-glacial sands. The individual aquifers are separated by clays, locally cross-cut by deep buried channels which provide hydraulic continuity. This region is little known and palaeowaters are likely to be present at depth and may extend westwards beyond the coastline.

United Kingdom (3, 4, 5, 6)

The East Midlands Triassic Sandstone aquifer (4) which was previously the subject of detailed geochemical investigation (*e.g.* Andrews *et al.*, 1983; Edmunds *et al.*, 1982) has been further investigated and updated. Fresh waters of Pleistocene and Holocene age are found to a depth of around 600 m below sea level. The extensive data set has also been used as the basis for developing modelling approaches.

The Cretaceous Chalk has been investigated in coastal southern and eastern England facing the English Channel (6), within the Thames Estuary and North Kent (5), and North Sea coasts of Yorkshire and Lincolnshire respectively (3). Near the Channel coastline, fresh water has been proven to a depth of −300 m OD at Brighton and also in Dorset to >200 m OD. Temperature logs on these coastal boreholes indicate undisturbed geothermal gradients below around −100 m which is likely to represent the present day base of groundwater movement; there is the possibility that offshore reserves of freshwater may exist here

Netherlands/Belgium (7)

The Ledo-Paniselian is a Tertiary aquifer confined beneath the Boom clay. This aquifer spans the Dutch/Belgian border in Zeeland and is the subject of exploitation for drinking and irrigation water. This aquifer shows excellent chromatographic freshening patterns (Appelo, 1994) and has been used as the main focus of research on the rates and processes of fresh water migration in the Pleistocene and Holocene. Comprehensive chemical and isotopic data exist for many parts of this aquifer (Walraevens, 1990), but in the northern part of the aquifer information is sparse and some borehole drilling (not on project funds) was carried out to fill in the gaps.

France (8, 9, 10).

In France, three aquifers have been studied mainly on their respective connection, past and present, with the sea water, *i.e.* the Channel (8), the Atlantic Ocean (9) and the Mediterranean Sea (10).

(i) Dogger aquifer (N of France). The aquifer of the Middle Jurassic carbonates in the Caen region is a well-fissured reservoir, presently connected with the Channel. It is largely exploited for drinking water needs and agriculture supplies by ca. 600 boreholes. However, once confined under the clayey Callovian and the Flandrian deposits, the increase in groundwater salinity limits the exploitation of the aquifer to the area where the water-bearing formation is unconfined or slightly confined. Located on these clayey formations, the main tourist town on this coast, Cabourg, can not be supplied by water taken from local boreholes due to high mineralization caused by marine water intrusion. The geochemical investigations on this system are mainly focused on (1) the identification of processes leading to the evolution of salinity (major and minor elements) and (2) the chronology of the aquifer recharge by fresh and/or sea waters.

(ii) Dogger aquifer (W of France). The Dogger aquifer is one of the main water-bearing formations in Vendée along the Atlantic coast. Southward, the Toarcian and the Callovian marls sandwich the Dogger aquifer which thus becomes confined under the "Marais Poitevin". Although this aquifer is largely exploited for fresh water supplies in the unconfined area of 1–2 km in extension, the presence of saline waters, Cl-Na type, in its confined part limits their use southward. In this aquifer, the evolution of salinity and its relationship to recharge (past and present) are studied. The impact of human activities on the saline wedge, identified in the confined part of the aquifer, is also investigated.

(iii) Astian aquifer (S of France). Located in southern France, the Astian calcareous sands are one of the most important aquifers for the fresh water supplies in the Valras and Agde areas. Over a surface of 438 km^2, this coastal aquifer only outcrops over 17 km^2, elsewhere being covered mostly by Plio-Quaternary continental formations. A fault isolates the southern part from the northern part of the aquifer**.** Almost 580 boreholes are recorded in the Astian sands. Some of which may be artesian during low population density season, i.e. in winter. This coastal area is a key touristic region in summer, with impacts on the water resources, including decreasing piezometric level and increasing groundwater salinity. In this system, previous work indicated the presence of fresh water (Holocene recharge) in the western part of the aquifer with brackish groundwaters in its eastern part.

Spain (12, 13, 14)

In Spain, three areas, described below, have been the subject of significant new investigation. Discussion has also been presented on the important but previously studied coastal aquifers of the Llobregat delta area, near Barcelona.

(i) Mallorca (12). An area on the east coast (S'Albufera d'Alcudia) has been selected. This is an area with brackish/saline water of unknown age. There is strong local interest in view of pressure on the resources.

(ii) Iberian peninsula (13). In the Guadalquivir delta, now sustaining the Doñana National Park marshes, dense evaporated marine water has been able to cancel vertical flux in the aquitard.

(iii) Gran Canaria (14). A study has been made of the Amurga Massif, a phonolite block extending from near the centre of Gran Canaria towards the sea, forming an important aquifer of Pliocene age. All recharge goes directly towards the sea. Groundwater is brackish due to climatic effects, low present day rainfall and airborne marine salts. Some of the groundwater yields radiocarbon

ages of 11 000–12 000 a, as a result of low recharge (3–12 mm a^{-1}) through thick unsaturated zones. This area provides good opportunities to study palaeowater characteristics of a European arid coastal area and with maximum sea level impacts.

Portugal (15, 16)

The Aveiro confined aquifer (Cretaceous) represents the main water resource of an important industrialized area with high population density and intense agricultural activity (15). It has been extensively exploited over the last thirty years, and is threatened with pollution by shallow groundwaters and seawater intrusion. Hydrogeochemical and isotopic studies have shown that this aquifer holds a considerable quantity of palaeowater, and is so far unique in Europe in showing evidence of downgradient stable isotopic enrichment rather than the normal depletion.

The Lower Sado/Lower Tagus aquifer (Tertiary), located in the Setubal-Lisbon area, is another important groundwater resource serving a dense population (16). While this aquifer is less well characterized than the Aveiro, preliminary indications are that deep wells are exploiting palaeowaters, and that salinization by mixing with deep brines is occurring in places.

Switzerland (17)

The University of Bern has contributed to PALAEAUX on the basis of its unrivalled noble gas expertise. A case study of the Glattal aquifer (17) is given here which acts as a reference study of a shallow system containing known palaeowaters from a continental rather than a coastal environment. Noble gas measurements and interpretation play a crucial role in this study because they are the only absolute palaeothermometer against which to calibrate stable isotopic depletions. In addition, where palaeowater ages reach beyond the range of radiocarbon, argon and helium isotopes measurements have been carried out to provide more secure estimations of age

1.5 East Midlands aquifer as a model for Palaeowater evolution

The East Midlands Triassic sandstone has been used a model for the present study and some key results from earlier studies are summarized here to illustrate the type of data being sought in other European systems. The Sandstone is a single hydraulic unit confined by a thick sequence of mudrocks (Mercia Mudstone) which locally contain evaporite minerals. The aquifer is underlain by a sequence of Permian mudstones, marls and dolomitic limestones which form an impermeable base to the aquifer. The Triassic aquifer contains freshwater and any upward leakage from the Permian can be ruled out, although losses of water through the overlying mudstones is considered probable. The groundwater chemistry is influenced by the presence of minor carbonate minerals (calcite and dolomite) as well as small contents of anhydrite/gypsum at depth (Edmunds *et al.*, 1982).

A selection of some of the geochemical and isotopic indicators is shown in Fig. 1.6 relative to corrected radiocarbon age with a summary of halogen data in Fig. 1.7 plotted relative to groundwater temperature as a proxy for distance along flow lines. The relevance of these and other indicators can be summarized:

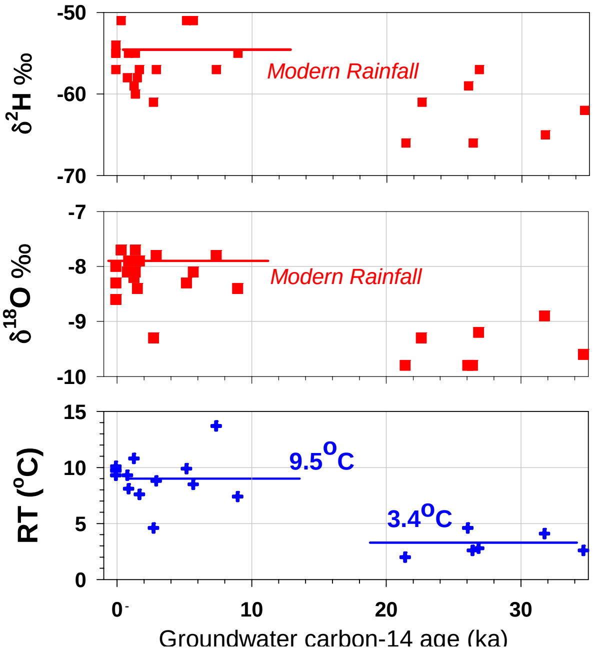


Figure 1.6. Noble gas and isotopic indicators of palaeowaters in the East Midlands aquifer.

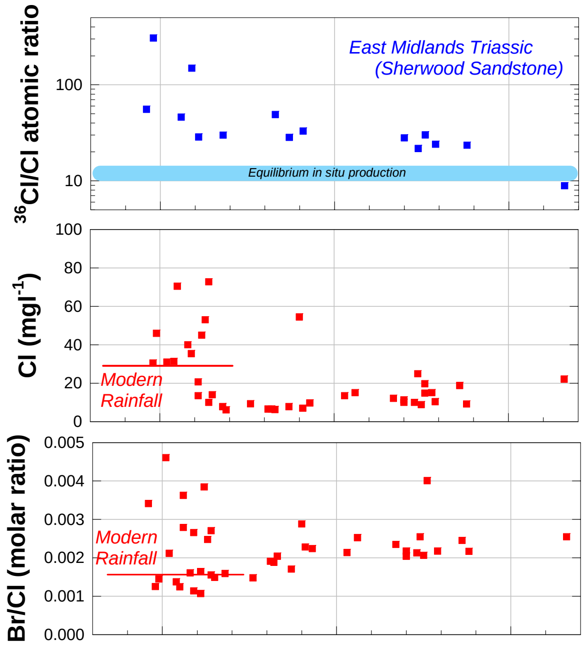


Figure 1.7. Chloride, Br/Cl and ^{36}Cl as indicators of former climatic conditions in the East Midlands aquifer.

Carbon isotopes and groundwater age. Groundwater radiocarbon activities measured on selected samples have been converted to groundwater ages using ^{13}C as well as supporting pH and chemical data. These modelled ages have been supported during international calibration studies using other dating tools (^{85}Kr, ^{39}Ar, ^{32}Si, ^{3}H as well as ^{4}He and uranium series) such that the East Midlands aquifer is one of the best calibrated in Europe, if not the world. Groundwater recharge occurred during the Holocene as well as during the Devensian (the oldest waters are be-

Table 1.1. Isotopic and related tools applied to project.

Tool	Function / Significance in study	Equipped Laboratories
Radiocarbon (^{14}C, AMS and/or radiometric)	Primary technique for age determination to ca 30 000 a	Paris, East Kilbride (Scotland), Lisbon, Madrid
Helium isotopes (^{4}He) and ($^{3}He/^{4}He$)	Residence time indication. Aquifer or deep source of gases.	Reading, Zurich
Carbon isotopes ($\delta^{13}C$)	Radiocarbon/age interpretation. Extent of rock-water interaction	Paris, Wallingford (UK)
Oxygen/ hydrogen isotopes ($\delta^{18}O$, $\delta^{2}H$)	Palaeowater indicators	Wallingford (UK), Paris, Lisbon, CEDEX (Madrid)
Sulphur isotopes ($\delta^{34}S$)	Palaeowater evolution	Paris, Barcelona
Noble gas ratios (Ne, Ar, Kr, Xe) and isotopes (^{85}Kr, ^{39}Ar)	Recharge temperature of palaeowater and age determination	Reading (UK), Berne (Switzerland)
CFCs	Recognition of modern inputs	Copenhagen
Major ion and trace elements	Characterization of palaeowaters, evolution of quality, qualitative residence time indication	All. Trace element at Wallingford
Tritium (^{3}H)	Confirmation of palaeowater, absence of recent component	CEDEX (Madrid), Lisbon, Barcelona

yond the limits of radiocarbon dating), but an age gap indicates that no recharge occurred during the period approximately 10 000–20 000 a BP, corresponding to the recharge areas being frozen during the glacial maximum. There is a good relationship between groundwater age and water temperature and the latter may be used as a proxy for age (Fig. 1.6).

Noble gases, stable isotopes of water ($\delta^{18}O$, $\delta^{2}H$) and palaeotemperatures. The ratios of the heavy noble gases (Ne, Ar, Kr and Xe) as well as oxygen and hydrogen stable isotope ratios have been used to indicate palaeotemperatures relative to those of the present day (Andrews and Lee, 1979). Noble gas ratios indicate that recharge temperatures close to modern occurred during much of the Holocene but during the Devensian (Wurm) period the soil and shallow groundwater temperatures were some 6°C cooler. This is also borne out by the difference in $\delta^{18}O$ and $\delta^{2}H$ between the Devensian and the Holocene age groundwaters (Fig. 1.7) where a difference of 1.7‰ in $\delta^{18}O$ supports the evidence for a colder climate; similarly groundwaters with $\delta^{2}H$ more negative than −8.4‰ all have groundwater ages in excess of 10 000 a BP.

The halogen elements as indicators of rainfall source and amount. Chloride can be regarded for practical purposes as an unreactive solute and therefore serves as an ideal inert tracer in palaeoenvironmental studies since it largely reflects input conditions from atmosphere and other sources (Fig. 1.7). The ratio Br/Cl may also be used to help to constrain the origins of Cl. Br is relatively inert but may be depleted in evaporite minerals and geochemically enriched in organic sediments.

The high Cl at outcrop mainly defines the extent of groundwater pollution including modern rainfall input(from the industrial period) which, after evapotranspiration, has an input concntration to groundwater of ca. 27 mg L^{-1}. The palaeowaters (including those of pre-industrial age) have Cl concentrations well below modern values. Values as low as 6 mg L^{-1} are thought to have originated from precipitation when a more continental climate existed, especially during periods of lower sea levels when the coastline was essentially to the west of Ireland. The Br/Cl ratio (Fig. 1.3) provides a further indication of this. The steady increase of Br/Cl above its modern maritime value of 1.56×10^{-3} in the early Holocene and waters from the interstadial is also an indication of increasing continentality in the past. A similar trend is also seen in the I/Cl ratio where the variations are also likely to be due to atmospheric changes comparable to Br.

The ^{36}Cl concents of the East Midlands groundwaters have been used to deduce rainfall amounts, its chlorinity and palaeoevapotranspiration on the assumption that all the Cl is atmospherically derived and also that the cosmogenic fallout of ^{36}Cl at this latitude has been constant over the late Pleistocene (Andrews *et al.*, 1994). There is a relatively constant atomic ratio of $^{36}Cl/Cl$ with a mean value of 30.6 atoms m^{-2} s^{-1} in the palaeowaters (Fig. 1.7). Using the chemical and isotopic information and substituting in the water balance equations it is estimated that infiltration was reduced by around 40 mm a^{-1} during the late Pleistocene as compared with the present day.

1.6 Methods used in PALAEAUX

The PALAEAUX consortium was selected to include partners with complementary skills in the fields of hydrogeology, hydrochemistry and isotope hydrology. The interpretation of palaeo-environmental and palaeo-hydrological conditions has required an integrated approach of these skills (as well as other disciplines). The use of state-of-the-art tools for age determination and characterization of palaeowaters has formed a particular strength of the project. Exchange of know-how on the tools used in the different countries of the project has enhanced dissemination and ensured technological equality throughout the participating countries. Collectively the partners also cover well the fields of geochemical and physical modelling of aquifers.

1.6.1 Hydrogeological investigation

For most of the aquifers selected a basic hydrogeological framework already existed. A major shortcoming was found to be the need for improved depth characterization of the flow regime and aquifer evolution. Therefore hydrogeophysical profiles have been obtained for representative sites in certain aquifers. In particular high-resolution conductivity and temperature logging has been conducted forming the basis for depth sampling for chemical and isotopic analysis in some countries. The temperature and conductivity logging also allows major discontinuities in the aquifer to be recognized, notably the interface between actively circulating groundwaters and deeper palaeowater; a separate chapter of the report refers in more detail to the background and lessons learned from these investigations. Where possible, advantage has been taken of ongoing or new drilling programmes to obtain customized information of relevance to PALAEAUX. This has included the obtaining of core material for extraction of interstitial waters.

1.6.2 Isotopic techniques

The isotopic techniques used in this study are summarized in Table 1.1 and are detailed in Chapter 12. The conventional and widely used δ^2H and $\delta^{18}O$ measurements provide signatures of the climate conditions and temperature at the time of recharge. Dissolved noble gas contents can also provide an indication of recharge temperature as the solubility is temperature dependent.

Other measurements provide indications of residence time or age of the groundwater. Radiocarbon (^{14}C) dating is the best known of these methods but several other (often more complex) techniques, have been applied where appropriate within the PALAEAUX study. The different isotopes, including ^4He, ^{39}Ar, ^{81}Kr, ^{226}Rn, have different half-lives and hence provide age information on a range of timescales form 10s to 1000s of years.

1.6.3 Inorganic chemistry

For each aquifer system chosen for the project, sets of high quality hydrochemical data have been obtained:

(i) to allow refinement of age or residence time interpretation.

(ii) to identify past atmospheric inputs.

(iii) to characterize the water - rock interaction over the timescales in question.

(iv) to detect the presence of modern groundwater.

In particular the hydrogeochemical data have also been used to derive qualitative information on residence times. Time-sensitive geochemical processes such as ion-exchange and incongruent mineral dissolution have been considered and these results compliment the absolute dating using ^{14}C. This approach is detailed in the chapter on isotopic and chemical methods The hydrochemistry has also been used to examine water columns in boreholes and to decide which samples can be used as representative of the native groundwater and which are mixtures, helped by the use of hydrogeophysical logging. The principal measurements have been:

(v) Field determination of pH, HCO_3, DO, Eh, SEC.

(vi) Analysis of major cations and anions to determine the main trends in chemical evolution.

(vii) Minor and trace element analysis. A wide spectrum of indicator elements has been analysed using ICP-OES, ICP-MS and GFAAS, as well as ion chromatography and automated colorimetry for Br, I and other trace anions. These data have been used to support the overall geochemical models and provide additional information on solute sources and residence times.

1.6.4 Modelling

Hydraulic and geochemical modelling have been carried out as an integral part of most regional studies, although the methodological aspects are considered further in Chapters 13 and 14. In these chapters some of the case studies are also brought together so that an integrated report is given.

2 Palaeogroundwater of glacial origin in the Cambrian-Vendian aquifer of northern Estonia

2.1 Introduction

The main objective of the PALAEAUX programme in Estonia was to study the Cambrian-Vendian (C-V) aquifer system, which is the most important source of public water supply in northern Estonia. In the frame of earlier studies it has been established that the groundwater in the Cambrian-Vendian aquifer system has a strongly depleted stable isotope composition and low radiocarbon concentration, which is unique at a European scale and indicates most probably the recharge in glacial or periglacial conditions (Punning *et al.*, 1987, Mokrik & Vaikmäe, 1988, Vaikmäe & Vallner, 1989). However, the time and mechanism of the recharge as well as the extent of the palaeogroundwater in space are still in dispute. As a coastal aquifer with intensive abstraction, the possibility of saline sea-water intrusion into the Cambrian-Vendian aquifer has also been an important issue.

2.2 Programme of work

The main components of the working programme were an extensive isotope study of groundwater from the Cambrian-Vendian aquifer system (mainly ^{18}O, ^{13}C, ^{14}C) and the analysis of the palaeohydrological situation in Estonia at the end of the last glaciation in order to find out the explanation regarding formation and preservation of the isotopically unusual light freshwater in the northern part of the aquifer system, whereas in South Estonia the water in the Cambrian-Vendian aquifer has high salinity (1 to 22 g L^{-1}). Sampling wells were selected in those areas where only a few or no data of earlier studies existed. Many of studied wells belong to the monitoring network of the Estonian Geological Survey, which means, that the background information for those was also available. Advantage has also been taken of participation in the PALAEAUX project of the Swiss group from the Physics Institute, University of Bern, and a number of colleagues from EAWAG and ETHZ, having the expertise and the laboratory capacity, which made it possible also to include in the working programme the noble gas analysis and the analyses of gas content and composition in the Cambrian-Vendian aquifer.

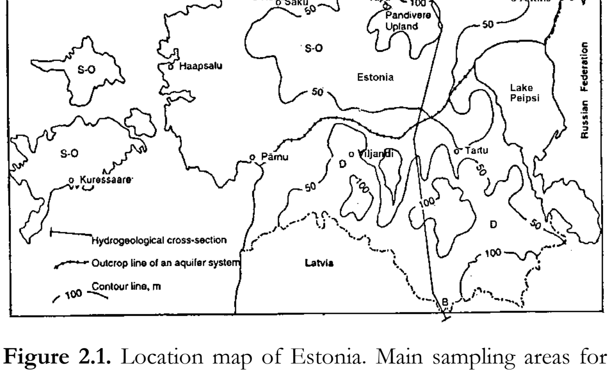


Figure 2.1. Location map of Estonia. Main sampling areas for PALAEAUX project were surroundings of Tallinn, Pakri peninsula and Rakvere. Line A-B marks the location of hydrogeological cross-section

2.3 Hydrogeological setting

Estonia, covering 45 000 km^2, is a flat country, where plateau-like areas and groups of small hills alternate with lowlands. The average absolute height is 50 m and only 10% of the territory have elevations between 100–250 m above sea level (Fig. 2.1). The Baltic Sea with the Gulf of Finland is the main drainage basin. The climate is moderately cool and humid. Average annual precipitation ranges from 500 to 700 mm. The mean surface runoff from Estonia is 270 mm a^{-1}.

Geologically, Estonia is situated on the slope of the crystalline Baltic Shield sloping southwards at about 3–4 m km^{-1}. Here the Lower-Proterozoic gneisses and migmatites of the basement are overlain by Upper Proterozoic (Vendian) and Palaeozoic (Ordovician and Silurian) sedimentary rocks covered by Quaternary deposits (Fig. 2.2)

Quaternary deposits (Q) consist predominantly of glacial till and glaciolacustrine sandy loam. Their thickness usually ranges from 3 to 30 m, but 100–150 m (Perens & Vallner, 1997). In South Estonia, Quaternary deposits cover the Devonian aquifer systems (D_3, D_{3-2}, D_{2-1}), which are represented chiefly by sandstone and siltstone (Fig. 2.2).

In North and Central Estonia, and also in the West-Estonian islands, the Quaternary deposits mostly lie on the outcrop of the Silurian-Ordovician aquifer system (S-O) consisting of fissured limestones and dolomites interbedded with marls. The upper portion of the carbonate formation is significantly karstified and cavernous to a depth of 30 m from its surface. In the depth range from 30 to 100 m several water yielding strata usually alternate with aquitards of local extent. Deeper than 100 m below the bedrock surface, the fissures are almost closed in carbonate strata. The latter form an effective aquitard (S-O) extending all over Estonia. The underlying Ordovician-Cambrian aquifer system (O-C) is represented chiefly by fine sandstone separated by siltstone interbeds. This aquifer system is the first groundwater system encountered beneath the land surface, which is relatively well protected against pollution.

The next confining stratum (Fig. 2.2), the Lükati-Lontova aquitard (Lk-Ln), consists of clays and siltstones, which extend under most of Estonia. This aquitard has a strong isolation capacity as its vertical hydraulic conductivity is predominantly only 10^{-7} to 10^{-5} m/d.

Below this comes the main study target within the PALAEAUX project, the Cambrian-Vendian aquifer system (C-V), the terrigeneous rocks of which occur all over Estonia, except the Mõniste-Lokno uplift area. There is an obvious difference between the cross-sections of the aquifer in western and eastern Estonia (Fig. 2.3). East of the Rakvere-Põltsamaa-Otepää line, clays of the Kotlin For-

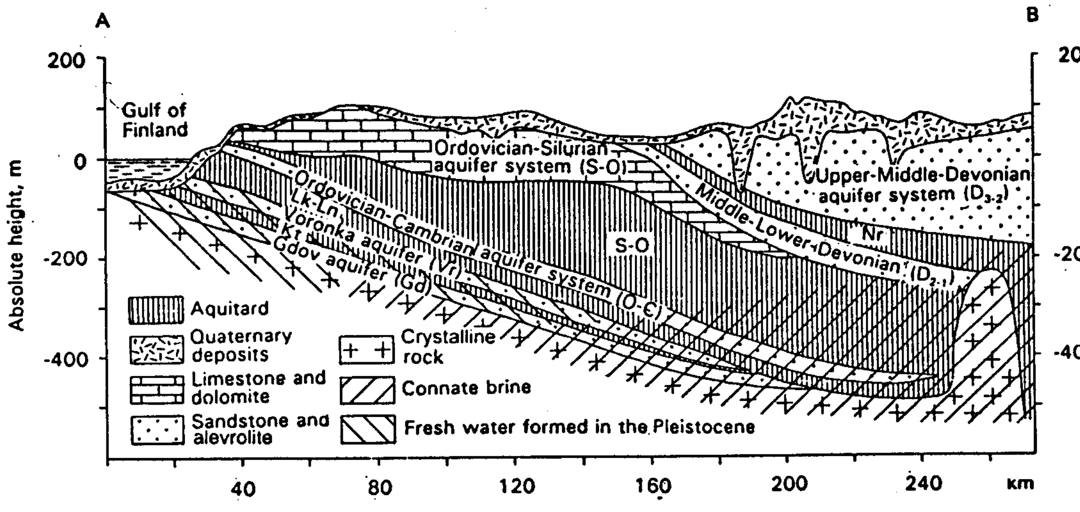


Figure 2.2. Hydrogeological cross-section of the Estonian bedrock; Voronka and Gdov aquifers form the Cambrian-Vendian aquifer system.

mation (V2kt) up to 53 m thick, divide the aquifer system into two. The upper, Voronka aquifer, consists of quartzose sand- and siltstone with a thickness of up to 45 m in north-eastern Estonia. The conductivity of rocks ranges from 0.6 to 12.5 m/d, being 2 to 6 m/d on average. Transmissivity decreases from 100 to 150 m^2/d in northern Estonia to 50 and even less m^2/d in the southern direction. Under natural conditions, the potentiometric level in the coast of the Gulf of Finland is about 1.5 to 5.5 m asl

The lower, Gdov aquifer is formed of a complex up to 68 m thick of mixed-grained sand- and siltstone and lying directly on the Precambrian basement. The clay of the Kotlin Formation serves as an upper confining unit. In northern Estonia, the conductivity of water-bearing rocks is 0.5 to 9.2, average 5 to 6 m d^{-1}. Transmissivity in north-eastern Estonia is 300 to 350 m^2 d^{-1}; decreasing in southerly and westerly directions to <100 m/d. The potentiometric surface is about 3 to 5 m asl under natural conditions in the coastal area of northern Estonia. Westward from the line where the Kotlin clays are pinching out (Fig. 2.3), the Cambrian and Vendian water-bearing rocks form the steady Lontova-Gdov aquifer.

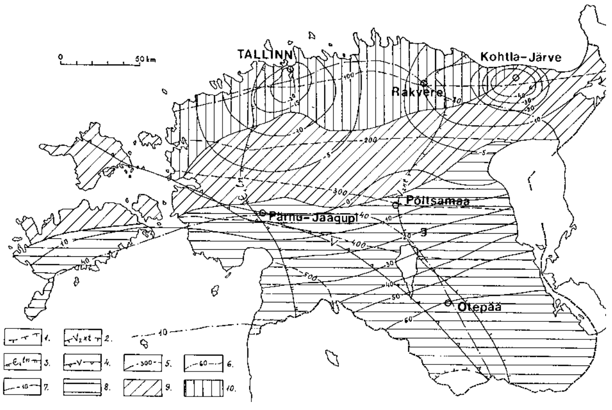


Figure 2.3. Cambrian-Vendian aquifer system: 1 - boundary of the aquifer system; 2- western boundary of the clays of the Kotlin Formation; 3 - western boundary of the clays of the Lontova Formation; 4 - boundary of Vendian rocks; 5 - isoline of the height of the roof of the aquifer system asl, m; 6 - isoline of the thickness of the aquifer system, m; 7- isoline of the height of the potentiometric surface asl in 1995, m; 8 ÷10 - transmissivity, m^2/d: 8 - up to 100, 9 - 100 to 300, 10 - more than 300. *Compiled by R. Perens.*

The Cambrian-Vendian aquifer system thins out in South and West Estonia but in North Estonia its thickness amounts to 90 m. This aquifer system outcrops along the northern coast of Estonia on the bottom of the Gulf of Finland. In northern Estonia, the aquifer system is, as a rule, confined by 60 to 90 m thick clays of the Lontova Formation. However, in places the bedrock formations are penetrated down to the crystalline basement by ancient buried valleys, filled mostly with loamy till but sometimes glacio-fluvial gravel occurs in the lower portion of the valleys. Westwards from the Tallinn-Pärnu-Jaagupi line, the Lontova Formation is gradually replaced by interbedding clay and sandstone of the Voosi Formation, which attain a thickness of 90 m in south-western Estonia. On the West-Estonian islands, the Vendian deposits have also been pinched out and the water-bearing terrigeneous rocks consist only of Cambrian sand- and siltstones with interlayers of clay.

The Cambrian-Vendian aquifer system is the most important source of public water supply in northern Estonia. Intensive water extraction has led to the formation of two extensive depressions in the potentiometric level (Fig. 2.3).

Cracks and fissures of the Lower-Proterozoic crystalline basement contain a small amount of water, which is not now exploited. The lower portion of the basement serves as an impermeable base for all overlying aquifer systems.

2.4 Groundwater flow

In order to estimate the possibility of preservation of palaeogroundwater in the Cambrian-Vendian aquifer system, the present day and palaeo-flow conditions have to be considered. According to the groundwater flow model (Fig. 2.4, Vallner, 1997), the Cambrian-Vendian aquifer system belongs mostly to the regional flow system, with recharge in southern Estonia, in those parts of the Haanja and Otepää heights (Fig. 2.3) where the groundwater table is 180 to 280 m asl In this location the head declines with depth attesting to the existence of downward groundwater flow. This flow reaching the completely impermeable portion of the crystalline basement changes its direction and bends towards the discharge areas which are situated in the depressions of the Baltic Sea and the Gulf of Finland. The length of deeper branches of the regional flow system can reach 250 km between the Haanja and Otepää heights and the central part of the Baltic Sea.

While the potential direction of the groundwater movement is marked by the flow systems described above, the actual quantity and velocity of subsurface flows depend on permeability of layers. Various co-influences of head distribution and permeability are expressed by the vertical zoning of the groundwater flow. In general, the velocity of the groundwater movement decreases with the flow depth. In this respect the Cambrian-Vendian aquifer system north of the recharge area belongs to the slow flow subzone of the zone of passive water exchange according to the vertical zoning of the Estonian hydrogeological cross-section (Vallner, 1997). The lateral hydraulic gradient of groundwater flows there ranges from 0.0001 to 0.0003. The calculated velocities of deep groundwater movement in the Cambrian-Vendian aquifer system are between 5×10^{-4} and 5×10^{-3} m/d, which means that during the last about 10 ka the deep groundwater could only have moved forward about several tens of kilometres and a complete water exchange along flow branches would not have been possible. Therefore it is possible that, in natural conditions, the groundwater recharged during the last glaciation has been preserved in the Cambrian-Vendian aquifer system. However, at present the water consumption from the subzone of slow flow is about 110 000 m^3/d. Pumping wells are mostly situated in the coastal area of northern Estonia within 20 km from the sea. Pumpage is most intensive in Tallinn and Kohtla-Järve where local centres of piezometric depression have formed and the maximum drawdowns reach 25 and 50 m, respectively (Fig. 2.3). At the present time, the water moves to the centres of piezometric depressions in the subzone of slow flow. North of groundwater intakes, the direction of flows is from the sea to the mainland. i.e. contrary to that in pre-development conditions. Therefore, an encroachment of salty sea water into coastal aquifers is taking place in the near-shore area of northern Estonia.

2.5 Results and discussion

Isotope investigations were combined with other studies on the Estonian groundwater in order to understand:

- the processes and climate conditions during the palaeorecharge;
- the age structure of deep waters;
- the mixing components and their variation.

The following isotopic and geochemical tools were applied:

^{3}H	^{4}He	Noble gas concs
^{85}Kr	^{40}Ar/^{36}Ar	for RT (Ne, Ar, Kr, Xe)
^{39}Ar	N_2/Ar	
δ^{13}C	^{15}N/^{14}N	Amount & composition
^{14}C	δ^{18}O/δ^{2}H	of extracted gases

2.5.1 *Isotopic investigations*

Samples were collected from 31 wells and in many cases repeatedly. In addition to the Cambrian-Vendian aquifer system, samples were also collected for comparison from Ordovician (O), Ordovician-Cambrian (O-C) and from Devonian (D) aquifers. Sampling wells were selected mainly in areas were only a few or no data were available from earlier studies. In respect of radiocarbon data on Estonian groundwater, the existing database was very limited and therefore intensive sampling for radiocarbon analysis was organized in the frame of PALAEAUX project. ^{18}O, ^{14}C concentration and in most cases also ^{13}C was measured in all collected samples. Measurements were done in the Laboratory of isotope-palaeoclimatology of the Institute of Geology at Tallinn Technical University. In selected samples, also ^{3}H concentrations were measured in the laboratories of Lithuanian Geological Survey. As many of the sampled wells belong to the groundwater monitoring network of the Estonian Geological Survey, their database on groundwater chemistry was used for some interpretation. A set of selected stable isotope and radiocarbon data of Estonian groundwaters is presented

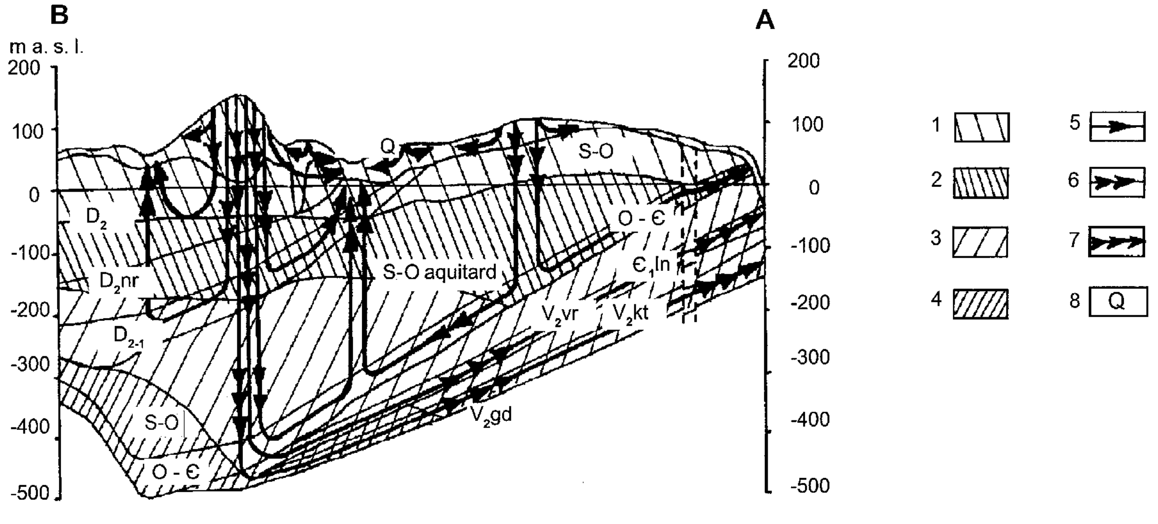


Figure 2.4. Vertical zoning of groundwater flow: 1 - subzone of fast flow; 2 - subzone of moderate flow; 3 - subzone of slow flow; 4 - subzone of very slow flow; 5 - 7 - systems of groundwater flow: 5 - local, 6 - intermediate, 7 - regional. (compiled by L.Vallner).

Table 2.1. Stable isotope and radiocarbon data for groundwater from different aquifers.

Sampling date	Locality	Well No	Aquifer system	Depth m	^{18}O ‰	^{13}C ‰	^{14}C ppm
08-May-97	Ahtme, Estonia mine	PK 265	C-V	270	-18.4	-19.3	3.30
08-Sep-97	Ahtme, Estonia mine	PK 2	C-V	290	-18.1	-18.8	3.94
27-Aug-97	Keila	PK 18	C-V	218	-21.1	-14.1	3.30
17-Aug -95	Kohtla-Järve, Toila	PK 897	C-V	214	-14.8	-16.9	38.91
03-Jun-98	Pakri pen.	PK 54	C-V	200	-20.9	-13.8	4.33
22-Aug-96	Rakvere	PK 6803-5	C-V	220	-20.3	-18.8	1.55
20-May-97	Saku, brewery	PK 7	C-V	105-200	-20.8	-15.2	3.01
23-May-97	Sillamäe, Viivikonna carry	PK 27	C-V	53-180	-19.3	-17.7	1.40
23-May-97	Sillamäe, Viivikonna carry	PK 879	C-V		-18.7	-17.8	1.89
23-May-97	Sillamäe, Viivikonna carry	PK 15	C-V	56-150	-18.5	-21.7	2.71
01-Jun-95	Tallinn, Toompuiestee	PK 705	C-V		-14.9	-13.9	60.34
30-Aug-95	Tallinn, Haabneeme	PK 647	C-V		-21.5	-14.9	3.65
28-Sep-95	Tallinn, Haabneeme	PK 646	C-V		-21.3	-15.0	12.76
30-May-95	Tallinn, Kopli pen.	PK 632	C-V		-19.9	-14.9	3.87
15-May-97	Tallinn, Kopli pen., Dekoil	PK D1	C-V	98-107	-21.5	-15.3	4.00
21-May-97	Tallinn, Kopli pen., Dekoil	PK D3	C-V	51-60	-19.7	-13.3	3.07
19-May-98	Tallinn, Kopli pen., Dekoil	PK D2	C-V	52-60	-20.3	-14.0	4.80
30-Aug-95	Tallinn, Pak-Terminal	PK 821	C-V	70-75	-20.0	-17.6	2.95
12-Aug-96	Tallinn, Pak-Terminal	PK 825	C-V		-22.0	-15.4	2.36
08-May-97	Ahtme, Estonia mine	PK 4	O-C	130	-17.5	-8.9	2.56
27-Nov-96	Keila, Mudaaugu	PK M1	O-C	88	-18.9	-10.4	3.27
03-Jun-98	Keila, Uus-Raba	PK 6015	O-C	90	-18.5	-10.2	4.42
04-Sep-96	Pakri pen.	PK T2	O-C	24	-11.4		82.71
22-Aug-96	Rakvere	PK A2	O-C	84	-14.8	-8.6	2.40
16-Oct-97	Tamsalu	PK 2854	O-C	227	-15.1		3.33
26-Sep-97	Viljandi	PK 4717	O-C	480	-12.2		18.62
22-Aug-96	Rakvere	PK E2	O	49	-12.2	-9.5	43.77
16-Oct-97	Tamsalu	PK 3869	O	65	-11.7		90.91
26-Sep-97	Viljandi, Karksi-Nuia	PK 39	D	250	-11.0		38.64
26-Sep-97	Viljandi	PK 4120	D	65	-11.2		66.78
26-Sep-97	Viljandi	PK 3782	D	200	-11.0		55.61

in Table 2.1. and in Fig. 2.5.

Based on the data from Table 2.1, the characteristic isotopic values for main aquifers are presented in Table 2.2. The oxygen isotope composition of groundwater in most of aquifer systems in Estonia ranges from −11.0 to 12.2‰. However, the groundwater in the Cambrian-Vendian aquifer system has a heavily depleted oxygen isotope composition. The values of ^{18}O vary mainly from −18.1 to −22‰. At the same time, the long term mean annual ^{18}O values in contemporary precipitation in Estonia are −10.4‰ (Punning *et al.*, 1987). Low ^{18}O values in the Cambrian-Vendian aquifer are indicative of recharge in cold conditions, whilst low ^{14}C concentrations are indicative of long residence time of groundwater (Fig. 2.5). However, in this context it is difficult to explain very low ^{13}C values in many wells (Table 2.1 and Fig .2.6), which seems to be rather typical for water in the Cambrian-Vendian aquifer system in Estonia. Analyses of the gas composition in some samples showed rather high concentration of methane (Table 2.3). This is indicative of the influence of biogenic reactions in the groundwater, which could cause the low ^{13}C values. Results of ^{13}C analyses in two methane samples (Table 2.5) also show, that the methane has most probably biogenic origin (see for example Chapter 5 in Clark & Fritz, 1997).

Low ^{3}H concentrations in most of studied wells confirm that, as a rule, no detectable intrusion of modern water (including sea water) into the Cambrian-Vendian aquifer has been occurred during approximately the past 45 years. However, data from two wells (PK 705 and PK 897) show, that groundwater there is affected by mixing with infiltrated modern water. Both wells are located near the buried valleys, cutting through the aquitard, which normally protects the Cambrian-Vendian aquifer system from upward infiltration. The intrusion of modern water through those valleys has been detected earlier also by the change of Cl$^-$ concentration in groundwater of the Cambrian-Vendian aquifer system (Groundwater State, 1994). On average, the chlorine concentration in the Cambrian-Vendian groundwater is in the range between 100 and 600 mg L^{-1}. Through the mixing with infiltrating modern water the chlorine concentration has decreased to values less then 100 mg L^{-1}.

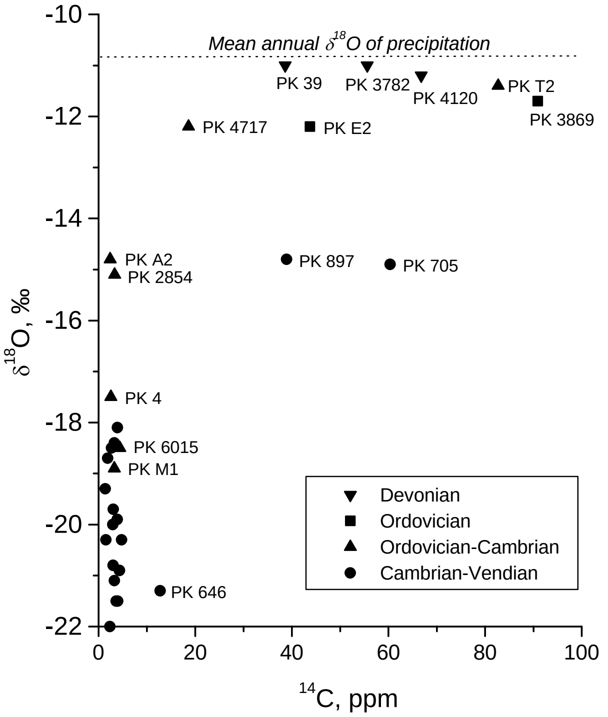


Figure 2.5. Distribution of ^{18}O values of groundwater from different aquifers in Estonia according to their ^{14}C concentrations. ^{18}O values from two wells (PK 705 and PK 897) indicate the mixing with infiltrated modern water.

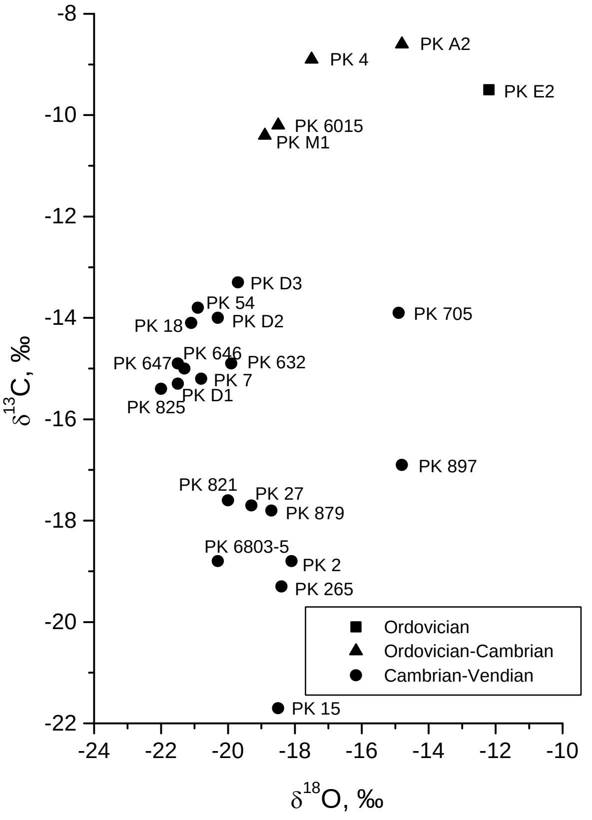


Figure 2.6. ^{18}O versus ^{13}C values of groundwater from different aquifers in Estonia.

Table 2.2. The characteristic isotopic composition of the groundwater in the main aquifer systems in Estonia

Aquifer system and Lithology	^{18}O ‰ SMOW	^{14}C pmc	^{3}H TU
Ordovician limestones, dolomites	−11.7 to −12.2	43.77 to 90.91	13.1 to 21.0
Ordovician-Cambrian detritical sandstones	−11.4 to −18.9	2.40 to 18.62	1.8 to 21.3
Cambrian-Vendian sandstones	−18.1 to −22.0	1.40 to 12.76	0.5 to 2.1

The water in the overlaying Ordovician-Cambrian aquifer is also depleted by ^{18}O (Tables 2.1. and 2.2). However, as a rule, the rate of depletion is several per-mil smaller than in case of the Cambrian-Vendian aquifer and the range of ^{18}O variations between different wells is also greater (Fig. 2.5). At the same time the ^{14}C concentrations are low also in most investigated wells in Ordovician-Cambrian aquifer, indicating the long residence time. It is likely, that both aquifers have received the palaeorecharge at about the same time, but being less protected from downward infiltration from the ground surface, the water in the Ordovician-Cambrian aquifer is slightly mixed with younger water. As the radiocarbon concentration in wells of the Ordovician-Cambrian aquifer is still low, the infiltration rate of modern water is probably rather modest.

2.5.2 Noble gas investigations

Sampling for the radionuclides ^{85}Ki, ^{37}Ar and ^{39}Ar (method A).

1 to 5 m^3 of water are degassed in a vacuum system; the extracted gases are compressed and transported to the laboratory, where argon and krypton are separated and purified for activity measurements. This extraction procedure produces gases with average gas composition and content; single bubbles are not important

Sampling for noble gas recharge temperatures (NGRT) (method B).

Small water volumes are enclosed in Cu -tubes or in a stainless steel cylinder of about 1 L volume. The gas content may depend on the chance how many gas bubbles of an oversaturated water are captured.

Gas Concentrations.

In some samples unexpectedly high gas concentrations have been found (Table 2.3). Excess air up to about 50% is common (Wilson & McNeill, 1997), but factors 2 to 5 for the oversaturation are very unusual and need special processes and explanations. One interesting question is if the needed pressure to produce high oversaturation could originate on the bottom of a (melting) ice sheet.

Four samples, marked in *italic* in Table 2.3. were collected for ^{39}Ar measurements (method A) and six samples were collected for excess air determination by method B, using the 1 L sampling device. Reproducibility of results certainly is limited by the sampling procedure (Juillard, 1999). The O_2-content in all gas samples is low and demonstrates, that the high gas concentrations are not due to contamination by air during sampling.

The data in Table 2.3. suggests, that large CO_2 or CH_4 contents do not account for the high gas content. The best indicators of the atmospheric air composition of excess gas are the N_2/Ar ratio, the $^{15}N/^{14}N$ ratio and the noble gas contents (see Chapter 12).

Table 2.3. Data on amount and concentration of extracted gases. Italics indicate samples collected for ^{39}Ar measurements by degassing samples in a vacuum system. Asterisks indicate two parallel samplings to provide a reliability check of the data. See Table 2.1. for location of sampled wells and for aquifers.

Sampling date	Well No.	Extracted gases (cc L^{-1})	O_2 (%)	CO_2 (%)	CH_4 (%)	$\delta^{18}O$ (‰)	N_2/Ar	$\delta^{15}N$/ $\delta^{14}N$ (‰)
30.08.96	*PK 705*	*70*	*0.18*	*1.6*	*1.1*	*–15*	*80*	–
03.09.96	*PK 6803-5*	*109*	*0.08*	*0.15*	*15*	*–20.7*	*92*	–
07.11.97	PK 6803-5*	75	1.1	6.4	14.6		57	0.2
07.11.97	PK 6803-5*	71	0.5	5.9	15.2		54	0.5
05.09.96	*PK 54*	*130*	*0.05*	*0.11*	*0.02*	*–21*	*81*	*–0.7*
03.11.97	PK 54*	58	0.7	1.9	<0.1		55	–0.1
03.11.97	PK 54*	60	0.9	2.7	<0.1		56	0.6
10.06.98	PK D2	60	1.85	5.8	9.4	–20.1	49	0.2
10.06.98.	PK 821	59–68	1.95	3.7	1.25	–20	54	–0.4
06.09.96	*PK 6015*	*62*	*0.45*	*0.5*	*0.2*	*–18.9*	*65*	*–0.1*
Air							83	0
ASW (0°C)		20			–		37	

Some of the gas samples extracted by the vacuum degassing procedure show atmospheric N_2/Ar ratios within the uncertainties, others indicate more a mixture of air saturated water (ASW) and air. Fig. 2.7. shows in a schematic way the difficulties in collecting reliable gas samples. However, it also shows clearly that all old Estonian samples have large oversaturation of N_2 and Ar compared to normal samples (e.g. Spain, Australia, Oman, Glattal). The N_2/Ar ratio depends still very much on the present sampling technique. Fractionation may have happened; this is demonstrated by the circumstance that the measured values in area B are partly below the curve ASW + EA. A mixing between air saturated water without excess air and an end member with air composition and high oversaturation seem a possible explanation.

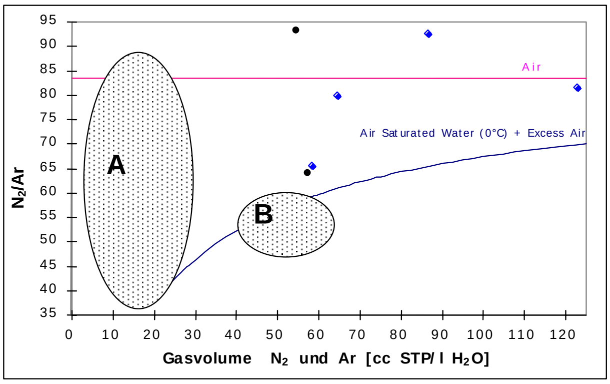


Figure 2.7. Extracted gas volumes versus N_2/Ar. Area A summarizes measured values for samples extracted by method A with "normal excess air"; fractionation and addition of biogenic N_2 may increase the N_2 /Ar ratio. Area B represents samples extracted by method B. Higher N_2 + Ar contents and N_2 / Ar ratios are measured. Gas loss and fractionation cannot be excluded. Asterisks are measured values for samples extracted by method A. An extraction yield of 80% is assumed; fractionation again can not be excluded.

Noble gas recharge temperatures.

Water samples for NGRT were collected by the usual Cu-tube technique first for the 4 samples with high oversaturation from Cambrian-Vendian and Ordovician-Cambrian aquifers (Table 2.4). The results indicate that high oversaturation and consequently uncontrolled degassing happened. Since the calculated RT show very large errors, they seem unreliable and have, therefore, not been included in Table 2.4.

The main conclusion drawn from these calculations is that the excess gas has air composition as assumed in the calculation models for NGRT. This means also that degassing of the samples from Rakvere and Paldiski did not substantially disturb the gas content, although excess air in these 3 samples is between 240 and 400%. Within the errors of the calculated temperatures, infiltration took place at temperatures around the freezing point. For the other 3 samples (with moderate excess air) infiltration temperatures correspond to the present-day average yearly temperatures in Estonia.

Age structure of deep groundwaters.

Based on the above mentioned possibility that part of the groundwater may have infiltrated below a glacier, it is concluded that traditional ^{14}C-models may not be appropriate for the conversion of a ^{14}C -activity into an age. Air bubbles in the ice would contain an atmospheric ^{13}C value. The measured ^{13}C value, e. g. for PK 6803-5 (Table 2.5) of −18.8‰ seems to be in contradiction with the subglacial infiltration model. However, the recently measured δ^{13}C values in CH_4 open the possibility of isotope exchange (see Table 2.5). Therefore, ages are difficult to calculate even if most of the measured ^{14}C activities are below 5 pmc.

In Table 2.5 results of the isotope studies are summarized. The interpretation of all results for PK T1 indicates a young water, although the small depth, which is only about 7 m, would allow gas exchange between the atmosphere and the groundwater through the unsaturated zone. This exchange may have increased the ^{39}Ar and ^{85}Kr ac-

Table 2.4. Reliable data on NGRT (see Juillard, 1999). See Table 2.1. for location of sampled wells.

Sampling date	Well No.	Aquifer system	Extracted gases cc L^{-1}	Ne excess %	RT °C	$\delta^{18}O$ ‰
02.09.96	PK E2	O	20	32	4.0 ± 0.5	−12.2
04.09.96	PK T2	O-C	18	8	2.3 ± 0.5	−11.4
04.09.96	PK T1	O	18	14	4.4 ± 0.5	−11.1
07.11.97	PK 6803-5	C-V	75	400	1.0 ± 1.6	−19.5
07.11.97	PK 6803-5	C-V	71	270	4.7 ± 2.1	−19.5
03.11.97	PK 54	C-V	60	240	−4.5 ± 2.9	−21.3

Table 2.5. Isotope and noble gas data from selected wells. See Table 2.1. for location of sampled wells and for aquifers.

Sampling date	Well No.	Depth m	^{4}He Vol %	$^{40}Ar/^{36}Ar$	$\delta^{18}O$ ‰	^{85}Kr dpm/cc	^{3}H TU	^{39}Ar % mod.	^{14}C pmc	^{13}C ‰
04.09.96	PK T1	6.9	<0.01		−11.0	63 ± 3	17.9± 1.3	90 ± 5		
03.09.96	PK 6803-5	220	0.12		−20.7		2.0± 0.5	<8	1.55	−18.8
05.09.96	PK 54	200	0.1	294.2± 2.2	−21.4	0.48± 0.04	0.5± 0.2	8 ± 4	12.53	−13.8
10.06.98	PK D2	52–60			−20.1				4.80	−78.8*
10.06.98	PK821	70–75			−20.1				2.95	−74.2*

* ^{13}C measured in CH_4

tivities but would not have influenced the ^{3}H activity. For deeper samples this limit of the noble gas dating methods is not important. Samples from Rakvere (PK 6803-5) and Pakri peninsula (PK 54), both from the Cambrian-Vendian aquifer, are older than 800 years based on ^{39}Ar, but their ^{18}O values indicate cooler climatic conditions during infiltration, i.e. an age older than about 11 ka. A high age is qualitatively also supported by the increased ^{4}He content in the extracted gas samples.

2.6 Palaeogroundwater formation

Consideration of the new data obtained in the course of PALAEAUX project and also the results of earlier studies leads to the convincing conclusion, that isotopically depleted groundwater in the Cambrian-Vendian aquifer in Estonia is of glacial origin. Based on the radiocarbon data and on the results of noble gas analyses, and considering the palaeoclimatic and palaeoenvironmental situation in the study area during the late Weichseilian time (see Ch 16 and 17), the most probable candidate for the source of heavily depleted groundwater in Estonia is the Fennoscandian ice sheet. However, so far there is no convincing answer to the question how and when the meltwater of the Fennoscandian ice sheet reached the aquifer system. The results of some earlier studies have provided a basis for the conclusion, that the meltwater penetrated into the Cambrian-Vendian aquifer system after the continental ice had retreated from Estonia's territory and during the formation of the Baltic Ice Lake about 11 to 12 ka BP (Yezhova *et al.*, 1996). However, the low ^{14}C concentrations below 5pmc may suggest that the age of the water is about 15 to 30 ka, which suggest, that the meltwater intrusion took place much earlier, at the time when the Estonian territory was still covered by ice sheet.

According to Mokrik (1997) the freshwater in the Cambrian-Vendian aquifer complex in the North Estonia formed mainly through the cryogenic metamorphism. He proposes, that during the Pleistocene glaciation the aquifers went through several freezing-refreezing cycles down to the depth of 200 to 250 m, which could lead to the freshening of the originally highly mineralized groundwater in the Cambrian-Vendian aquifer complex. In accordance to his model the permafrost zone developed southwards by the belt of 100 to 150 km wide from the cropping of aquifers on the surface of the Baltic Shield (Mokrik, 1997). However, the existence of thick permafrost layer under the Fennoscandian ice sheet in the Estonian territory seems unrealistic. According to Kleman *et al.* (1997), frozen conditions existed only under the central area of the Fennoscandian ice sheet, while most of subglacial area reached melting temperature due to frictional, strain and geothermal heating.

Considering that and taking into account also the recent works of Boulton *et al.* (1995, 1996) and Piotrowski (1994, 1997), the recharge of aquifers by subglacial meltwater seems to be more realistic explanation of formation the isotopically light freshwater in Estonian aquifers. During the Late Weichselian the base of the ice sheet at the Cambrian-Vendian outcrop area in Estonia would have been in a molten state for about 11 ka (Jõeleht, 1998). During this time the hydraulic head was controlled by thickness of ice. Although the Cambrian-Vendian aquifer system itself has high hydraulic conductivity, it is surrounded by areas of low hydraulic conductivity and therefore the hydraulic head in outcrop area of aquifer system was probably close to floating point, e.g. about 90% of ice thickness (Piotrowsky, 1977). Taking into account also the postglacial uplift and the present depth of Cambrian-Vendian aquifer system (about 100 m bsl), the hydraulic gradient was around 0.0031 (Jõeleht, 1998). Thus, the recharge of the Cambrian-Vendian aquifer most probably occurred during the glaciation, preferentially by subglacial drainage through the tunnel valleys.

2.7 Conclusions

Strongly depleted stable isotope composition and low radiocarbon concentrations are the main indicators of glacial origin of groundwater in the Cambrian-Vendian aquifer in the northern Estonia.

The Cambrian-Vendian aquifer system is mostly well protected from downward infiltration of modern water by the Lükati-Lontova aquitard, having a strong isolation capacity. This is confirmed by absence of ^{3}H in most of sampled wells. Intrusion of modern water into the Cambrian-Vendian aquifer system has been detected through the changes in isotopic composition and increasing concentration of radiocarbon near the buried valleys. The noble gas analyses allowed to conclude, that palaeorecharge took place at temperatures around the freezing point.

In some places unexpectedly high gas concentrations have been found (Table 2.3). Excess air up to about 50% is common, but factors 2 to 5 for the oversaturation are very unusual and need special processes and explanations. One explanation could be, that oversaturation indicates the recharge in the high pressure conditions, e.g. by subglacial meltwater recharge through aquifers.

However, in this context it is difficult to explain very negative ^{13}C values in many wells. Analyses of the gas composition in some samples showed also a rather high concentration of methane. This is indicating the influence of biogenic reactions in the subsurface, which could cause the rather negative ^{13}C values. Results of ^{13}C analyses in two methane samples also show, that the methane has most probably biogenic origin. This versions, however, has to be confirmed by further studies.

Based on the isotope data, on the results of noble gas analyses, and considering the palaeoclimatic and palaeoenvironmental situation in Estonia during the late Weichseilian time, we came to the conclusion that palaeorecharge of Cambrian-Vendian aquifer most probably occurred during the last glaciation preferably by subglacial drainage through the tunnel valleys.

High quality groundwater of glacial origin in the Cambrian-Vendian aquifer system is distributed throughout all northern Estonia at least up to 50 km south from the coast of the Gulf of Finland. Due to the heavy consumption of the groundwater in the densely populated areas of northern Estonia the potentiometric surface of the Cambrian-Vendian aquifer system has subsided quickly showing maxima of depressurization in Tallinn and Kohtla-Järve. In these places the head was withdrawn to a depth of 30 and 56 m bsl., respectively. Due to that, the groundwater inflow into the Cambrian-Vendian aquifer system from adjacent strata has grown significantly. The downward flow provides the Cambrian-Vendian aquifer system mostly with fresh water, but the rising flow may be connected with upconing of brines from the crystalline basement, and the lateral flows induce the transport of connate brines from deeper portions of the aquifers or sea water intrusion to groundwater intakes.

As the glacial water in the Cambrian-Vendian aquifer system is not renewable, special regulations for sustainable consumption of the water has to be settled.

3 The Ribe Formation in SW-Jylland, Denmark: Holocene and Pleistocene groundwaters in a coastal Miocene sand aquifer

3.1 Introduction

To meet the objectives of the PALAEAUX project, the largest regional aquifer in Denmark, The Ribe Formation, a deep-seated Miocene quartz sand aquifer, was selected for the main part of the Danish studies. The study includes three coastal areas but focuses on an approximately 50 km long cross-section through the Ribe Formation in Southern Jylland (Figs 3.1 and 3.2). The cross-section is constructed on the basis of the well log database at the Geological Survey of Denmark and Greenland and extends through the area with the most dense concentration of water supply and irrigation wells in The Ribe Formation. The wells investigated at the two other sites at St. Darum south of Esbjerg, and at Fjand north of Ringkøbing Fjord are water supply and monitoring wells from small waterworks. The study area includes the island of Rømø, a popular summer vacation area, areas around the city of Esbjerg at the western coast of Jylland, and extends to the Main Stationary Line (MSL) of the last glaciation in the eastern part of Jylland.

The Ribe Formation is an important aquifer for water supply and irrigation in large parts of Jylland, and some counties have put considerable effort into mapping the extent of the Ribe Formation (e.g. Thomsen and Friborg, 1992).

3.2 Geological and palaeogeographical setting

3.2.1 Geology of SW Jylland

The geology of SW-Jylland consists of a westward dipping succession of Tertiary clastic sediments overlain by Quaternary glaciofluvial and marine deposits. The Tertiary consists of a thick sequence of Eocene and Oligocene clays overlain by Miocene fluvial, lacustrine and marine deposits. The Miocene sediments are generally coarser grained in the east and fine to the west. The unit of primary interest in this study is the Ribe Formation which forms the most regionally extensive aquifer in Denmark. It consists of fluvial quartz sands which dip to the west and are present at a depth of 100 to 200 m below ground surface. Towards to the west, the Ribe Formation is overlain and locally interbedded with fine grain sediments. Seismic surveys indicate that in some areas the Ribe Formation sands extends offshore below the present day North Sea (see Fig. 3.2.). The Quaternary sediments are comprised predominately of meltwater sands and gravels, sandy and clayey tills and lacustrine clays. The Quaternary sequence is typically 20 to 40 m thick. Deep valleys filled with Quaternary sediments occur in eastern and western Jylland. Some Holsteinian marine deposits are present within Quaternary valleys in western Jylland. Faults are present in some areas disturbing the hydraulic connectivity of the Ribe Formation e.g. by replacing parts of the Ribe Formation with Quaternary deposits. In large parts of the study area, the Ribe Formation is overlain by Tertiary and Quaternary (Holsteinian) marine sediments. This has led to salinization of the fresh water sediments of the Ribe Formation at times of high sea levels, followed by freshening (Appelo, 1994) during the Quaternary glaciations, interglaciations and interstadials. Generally the freshening seem to be completed in the Ribe Formation. Slightly elevated chloride concentrations are observed in a few wells, but these are attributed to diffusion form adjacent marine sediments.

3.2.2 Cenozoic geology of Jylland and the Danish North Sea

During the Late Cretaceous and early Tertiary marine fine grained sediments were deposited in the Danish North Sea sector and in large parts of Jylland. Through the Danian the depositional environment was characterized by deposition of cool-water shallow marine carbonates in the Danish Basin (Surlyk, 1997). From the late Palaeocene clastic deposition prevailed and during the late Palaeocene and most of the Eocene fine-grained sediments accumulated in a marine environment. The variation in depositional conditions was caused by changes in sea level or circulation patterns in the North Sea (Bonde, 1979, Pedersen and Surlyk, 1983, Heilmann-Clausen *et al.*, 1985, Rasmussen, 1994).

The transition from Palaeogene to Neogene (Oligocene-Miocene) in the Tertiary period is an important phase in the sedimentary development of the eastern

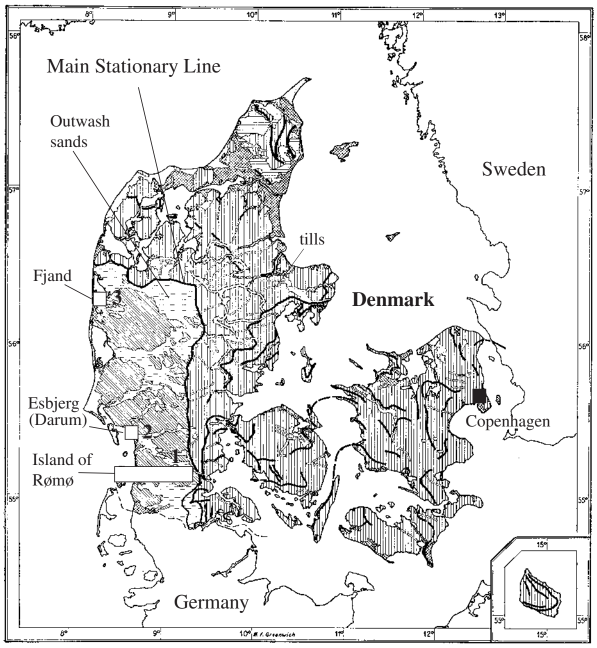


Figure 3.1. Quaternary geology map of Denmark with the location of the Main Stationary Line (MSL) and the described study sites, showing (1) 50 km long cross section through the Ribe Formation from the MSL in the east to the Island of Rømø in the west; (2) St Darum south of Esbjerg where a water supply investigation well was recently completed; and (3) Fjand where 2 waster supply wells and 8 small monitoring wells at different depths have been investigated.

North Sea Basin. The distinct uplift of Fenno-Scandia, up to 1200 m in eastern Denmark (Japsen, 1993), resulted in a marked increase of coarse-grained clastics in the south-western part of the Danish area. Minor salt movements also occurred during the Oligocene and resulted in a smooth topography in the sedimentary basin. A complex succession of alternating terrestrial/near-shore and shelf deposits were laid down in the Miocene and the coast line was occasionally displaced more than 100 km basinwards (towards the west). In the Langhinian the subsidence pattern changed dramatically and strong subsidence of the central North Sea occurred. The overall stacking pattern of the Miocene and Pliocene succession correlates to glacio-eustatic sea-level changes (Rasmussen, 1996; Sørensen *et al.*, 1997) and the most prominent displacement of the shoreline, into the basin, occurred in the early Miocene (the Ribe Formation) and in the uppermost Miocene (Messinian). The general sediment supply was from the north and northeast and changed to a more westerly directions after the Langhinian tectonic event (Cameron *et al.*, 1993; Sørensen *et al.*, 1997).

In the Paleocene and most of the Eocene the climatic conditions were warm and humid (Buchardt, 1978; Bonde, 1979; Collison *et al.*, 1981). At the end of the Eocene a cooler period started and continued during most of the Oligocene. Warm-temperate and humid climatic conditions prevailed in most of the Miocene (Sorgenfrei, 1958; Radwanski *et al.*, 1975; Koch, 1989) and in the early Pliocene. However, a marked temperature drop occurred in late Miocene, and especially during the Pliocene (Buchardt, 1978; Miller *et al.*, 1987) and caused ice-cap growth to increase. More rapid climatic fluctuations occurred in Quaternary and caused the well-known glaciations during the Quaternary.

In general the Cenozoic succession in the Danish on- and offshore areas dips towards the west and thickens from ca. 200 m in the easternmost part to more than 2500 m in the western part of the Danish North Sea sector.

The Palaeogene is subdivided into 3 stratigraphic packages; the Thanetian stage, the Eocene and the Oligocene series. These packages are dominated by clay-rich hemipelagic deposits in this part of the Danish area. Shallow marine upper Oligocene sand-rich deposits is, however, found in the eastern part and is referred to as the Vejle Fjord Formation.

The Neogene succession consists of a series of prograding depositional systems, of which the Ribe Formation is one, that demonstrate successively infill of a basin. The Neogene has been subdivided into 8 stratigraphic packages representing the Aquitanian, Burdigarlian, Langhinian, Serravallian, Tortonian, and Messinian stages for the Miocene and Zanclean and Piacenzina stages for the Pliocene (Fig. 3.3). The Miocene succession consists of alternating marine and terrestrial deposits. Sand-rich intervals in the Miocene mainly occur in the Aquitanian and Burdigarlian shallow marine and fluvial sediments known as the Klinting Hoved and Ribe formations, respectively, and Langhinian fluvial deposits referred to as the Odderup Formation. The succeeding Upper Miocene Gram Formation is dominated by marine clays, but gradually becomes more silty and sandy in the early Pliocene. The most sandy part of the Pliocene is known as the Sæd Formation and occurs in the south-western-most part of Jylland and on the adjacent small islands. The silty and sandy Pliocene deposits can be traced as prograding deltaic systems towards the centre of the North Sea (Sørensen *et al.*, 1997; Gregersen, 1997).

Quaternary deposits top the succession. These are especially thick in the western part of the geoprofile and in incised valleys (Fig. 3.3). Strong Quaternary glaciotectonic disturbances by thrusting of upper parts of the Miocene and Pliocene successions occur onshore and in adjacent offshore areas.

3.2.3 Palaeogeographic model of Southern Jylland and the adjacent North Sea during the LGM

During the Last Glacial Maximum the sea level was in a lowstand of about 121 m below present sea level, Fairbanks, 1989. The southern part of the North Sea as well as most of the Central North Sea was above sea level in that period. The base level for erosion and for the ground water table therefore was situated at the rim the Norwegian Channel and the Devil's Hole area. The melt water from the southern rim of the Scandinavian ice sheet drained via the Elbe Urstromtal and its tributaries to the sea. The Elbe-Urstromtal crossed the southern North Sea in what is now the depression of the Heligoland Channel from the present mouth of the Elbe, passed south-east of Heligoland and continued in north-westerly direction and passed between the Turbot Bank and the Tail End Bank. From there it most probably continued to the Devil's Hole.

In southern Jylland the landscapes was made up of Saalian glacial deposits, both tills and glaciofluvial sediments. During the Weichselian this old landscape was eroded by the glacial meltwater rivers and vast sandurplains were deposited in the erosion valleys and partly on the adjacent Saalian landscapes (Friborg, 1996). Friborg indicates the base of the Weichselian erosion (= top of Saalian sandurplains) to be about 15 m below the present surface. In south-western Jylland by Tønder Eemian marine interglacial deposits are identified with the top in 10–15 m below sea level (bsl.) indicating the base Weichselian erosion. These are underlain by Saalian glaciofluvial deposits and overlain by Weichselian meltwater deposits. Around the city of Ribe the top of the Eemian marine deposits are found about 20–25 m bsl. indicating the Weichselian erosion level in the extramarginal Gram Å valley (Mertz, 1977). The interglacial deposits are topped by Weichselian glaciofluvial sands.

In the German part of the Heligoland Channel the base of the Holocene has been mapped seismically, (Figge, 1980). Southwest of Heligoland the base is found around 35 m bsl. whereas at the border to the Danish sector the base is at 64 m bsl. At this position (H. Hartmut, pers. comm., 1990) a reflector is identified below base Holocene at about 75 m bsl. Unpublished Danish reports from two east-west profiles at ca. 55°45'N indicate the base Holocene in the Heligoland Channel at around 72 m bsl and another reflector below that at around 75 m bsl. In a borehole at 55°48'N in the Heligoland Channel the base of the Holocene is at 72 m bsl. A seismic reflector coincide with a shift in the fluvial sediments in the borehole at 93 m bsl. This change in the sediment, including a shift in the reworked foraminifera, from fine sand below to medium sand above with scattered clasts and with gravel at the base, is thought to mirror the basal probable erosion level for the Elbe Urstrom in the Weichselian. The base of the erosion of the Elbe Urstrom therefore is expected to

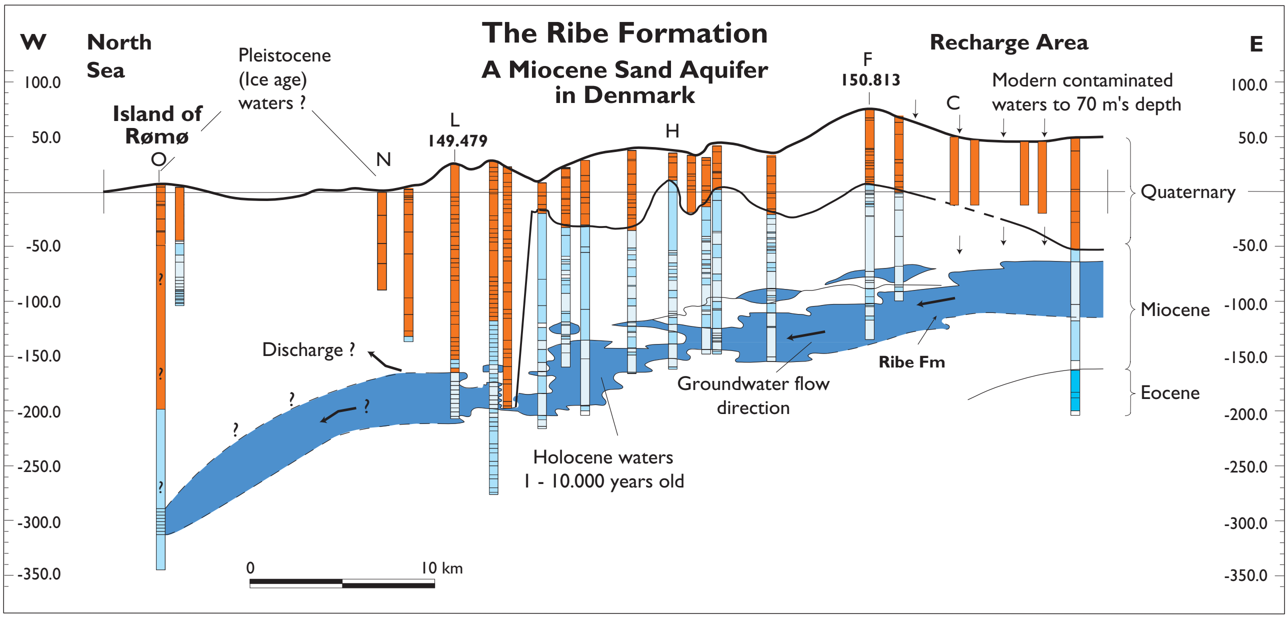


Figure 3.2. An East-West cross section through the upper 250 to 350 m of the Quaternary and Tertiary sediments in Southern Jylland. The shaded layer marks the quartz sands of the Ribe Formation which is situated at depths between approximately 100 to 200 m below the surface and dips towards the west and pinch out offshore. The main recharge area to the Ribe Formation is in the eastern part of the cross section just outside the MSL of the last glaciation. Six of the wells listed in Table.3.1 (C, F, H, L, N, O) are marked on the cross section. Well C is above the Ribe Formation in the recharge area. The groundwater flow is towards the west. Pleistocene waters from the last glaciation seem to be present in the discharge area at the coastline above the Ribe Formation (well N) and deep below the island of Rømø (well O). Groundwaters of Holocene age (100–10 000 a) are generally found in between the recharge and the discharge areas.

be some meters (15–20 m) below the base of the Holocene.

The above mentioned unpublished Danish reports also show that the area between the coast of Jylland and the Heligoland Channel to a large extent is made up of glaciofluvial sediments but highs and ridges of glacial till in places also reach the Holocene subsurface.

In general the sea floor in the southern part of the Danish North Sea sector is rather smooth. Only two areas rise from the flat sea floor. West of the westernmost point of Jylland the Horns Rev rises as a ca. 4 km long ridge about 20 m above the general smooth sea floor. The Horns Rev is interpreted to be a moraine ridge. About 20 km west of the island of Rømø the shoal Røde Klit Sand rises about 10 m above the flat sea floor. This structure is also thought to be remnants of an old glacial landscape.

In the German sector the seabed sediments are mapped (Figge, 1981 & 1983). Here the subsurface below the Holocene is expected to be made up of glacial deposits, tills as well as glaciofluvial deposits.

In the North Sea morphological features from the Saalian glacial period as well as features ascribed to the Weichselian are both levelled by the marine processes: erosion , reworking and deposition. These processes have been active during the Eemian interglacial North Sea as well as in the present Holocene North Sea.

Only few boreholes from the North Sea gives information of the sediments. In the borehole BH 89/6 at 55°30'N, 6°10'E the sediments down to 207 m bsl primarily consists of sand with gravel and with silty intercalation's, Pleistocene and possibly Pliocene in the lower part. In borehole BH 89/9 at 55°10'N, 6°48'E, the sediments down to 160 m bsl are made up primarily of sand with gravel, Pleistocene in the upper part and Pliocene in the lower part.

3.3 Hydrogeological conceptual model

A conceptual model of the regional hydrogeology of southern Jylland is developed based upon geological cross-sections, observed groundwater levels, base flow measurements, extraction rates and climatic data. Two types of flow systems exist within the study area: 1) shallow aquifers consisting of Quaternary glaciofluvial and interglacial sediments and 2) a deep regional aquifer system consisting of Tertiary freshwater and marine sediments. The areal extent of the shallow aquifer systems is within the order of 10s to 100s of km^2 and aquifer boundaries often coincide with those of surface water catchments. Recharge is from the infiltration of precipitation and is estimated to be 250, 275, and 180 mm a^{-1} in western, central, and eastern Jylland, respectively. Discharge from the shallow aquifers is to streams, wetlands, lakes, exraction wells and to the deeper regional aquifer system. Discharge to surface water bodies accounts for 70 to 90% of the total recharge. The transmissivity of the Tertiary sediments controls flow paths and the depth of circulation in the shallow aquifer system. The Tertiary sediments consist of clays in eastern Jylland, predominately sands in central Jylland and sand and clay in western Jylland. The hydraulic conductivity of the Ribe ranges from about 1.3×10^{-3} to 2.0×10^{-4} m/s with an average of 7.7×10^{-4} m s^{-1}. Hydraulic conductivity is generally greatest in central Jylland and decreases to the west. Recharge to Ribe Formation occurs primarily in central Jylland

Table 3.1. Selected parameters and estimated ages from selected wells in and above the Ribe Formation. Wells in italics (A,B,C) show indications of human impact. Wells in bold (C,D,E,F) illustrate the importance of correction for fossil organic matter oxidation. Negative ^{14}C "ages" indicate post-bomb waters (^{14}C concentrations above 100 pmc). The wells are listed in alphabetical order from the recharge area in east towards the discharge area in west. Six selected wells (C,F,H,L,N,O) are marked on the cross section in Fig. 3.2. The wells J,N and O seem to be Pleistocene waters recharged during the last glaciation.

1 well no.	**2 screen mbs**	**3 pH**	**4 Eh mV**	**5 O_2 –**	**6 Cl –**	**7 SO_4 –**	**8 NO_3 –**	**9[(a)] DIC mg/L**	**10 H_2S –**	**11 CH_4 –**	**12 DOC –**	**13 ^{14}C pmc**	**14 $\delta^{13}C$ ‰**	**15 ^{18}O ‰**	**16 ^{3}H TU**	**17[(b)] ^{14}C pmc**	**18[(c)] ^{14}C pmc**	**19[(b)] age 1 a**	**20[(c)] age 2 a**	**21[(d)] age 3 a**
A	9-18	7.65	-20	3.88	27	73	0.25	95.4			2.1	42.1	-10.0	-7.95		105	149	-423	-3297	-
B	31-51	7.11	120	2.00	48	23	43.2	86.7			3.4	75.5	-15.1	-7.82		125	170	-1845	-4373	-
C	**65-73**	**7.31**	**-80**	**0.01**	**26**	**58**	**1.6**	**104**	**0.03**		**1.1**	**41.0**	**-12.30**	**-7.99**	**18**	**83**	**123**	**1507**	**-1733**	**-**
D	**89-92**	**6.87**	**-22**	**0.02**	**16**	**36**	**0.3**	**58**	**0.03**		**1.5**	**35.2**	**-13.30**	**-8.19**	**1.1**	**66**	**143**	**3414**	**-2930**	**-**
E	**140-167**	**7.06**	**-106**	**0.05**	**16**	**14**	**0.1**	**94**	**0.03**	**.007**	**1.9**	**34.7**	**-13.00**	**-7.86**	**0.74**	**67**	**101**	**3344**	**-58**	**-**
F	**180-209**	**7.34**	**-102**	**0.04**	**17**	**7**	**0.1**	**158**	**<0.02**	**.026**	**1.6**	**46.6**	**-13.10**	**-7.58**	**<0.04**	**89**	**111**	**970**	**-871**	**-**
G	161-173	7.59	-99	0.01	22	7	0.1	126	<0.02		1.0	38.2	-13.60	-7.58		70	92	2922	645	730
H	174-195	7.42	-145	0.03	24	6	0.3	151	0.03	.016	1.3	37.8	-14.10	-7.52		67	83	3308	1522	970
I	180-202	7.65	-125	0.01	25	4	0.1	163	0.03	.013	1.9	34.0	-14.10	-7.49		60	73	4184	2547	1340
J	184-224	9.02	-	0.00	196	12	0.4	172	<0.02	.11	130	0.6	-12.90	-8.73		1	1	36822	35113	14100
K	202-222	7.89	-151	0.01	55	8	0.3	133		.012	0.9	27.0	-13.10	-7.44		52	68	5481	3239	1740
L	192-232	7.89	-145	0.02	83	7	0.0	158	<0.02	.020	3	23.2	-13.40	-7.41		43	54	6922	5127	2360
M	120-126	7.73	-108	0.04	185	6	0.4	(154)	0.04	.019	3.7	14.0	-13.0	-8.29	<0.04	27	34	10800	8900	3900
N	60-90	8.24	-37	0.00	109	12	0.5	(196)	0.05	.019	41	1.1	-13.0	-8.23	0.25	2.1	2.5	32000	30000	12200
O	292-304	7.78	-164	0.00	3400	36	0.3	(631)		6.9	156	0.7	-5.8	-9.23#		3.0	3.4	29000	28000	11200

(a) as CO_2, calculated from field alkalinities by NETPATH (Plummer *et al.*, 1994) except numbers in parenthesis which are measured at the ^{14}C lab. at Århus University.

(b) $\delta^{13}C$ correction (Ingerson and Pearson, 1964)

(c) $\delta^{13}C$ correction and maximum correction for O_2 oxidation of fossil ^{14}C "dead" organic matter (Boaretto *et al.*, 1998)

(d) As in column 20 but with correction for oxidation of fossil OM. by only half the original O_2 (6 mg L^{-1}) content and correction for aquifer/aquitard diffusion after Sanford (1997) – assuming an average aquifer thickness of 20 m and an aquitard thickness of 50 m, porosity values of 0.33 for both, and a diffusion coefficient $D = 1 \times 10^{-10}$ m^2/s.

(e) Corrected for seawater mixing assuming $\delta^{18}O = 0.0$‰ for seawater.

through the overlying Quaternary sediments. Here it is estimated that 10 to 20% of the recharge to the shallow aquifer system ultimately discharges to the Ribe Formation. Groundwater then flow westward within the Ribe Formation and discharges to the North Sea through deep Quaternary valleys located along the coast.

3.4 Results and discussion

3.4.1 *Hydrochemistry, isotopes and groundwater ages*

Human impacts as indicated by relatively high concentrations of nitrate, sulphate and tritium have been recognized in shallow aquifers within the recharge zone of the Ribe Formation in eastern Jylland. This influence can be recognized to depths of 60 and 73 m below the surface. The geochemical results from analyses of groundwater samples from the Ribe Formation show no evidence of human influence as indicated by the very low nitrate and sulphate concentrations. This is in accordance with the isotope tracers tritium and ^{14}C, which have values of less than 0.04 TU and between 0.6 and 47 pmc, respectively, indicating that the groundwater in the Ribe Formation generally was recharged during the Holocene (100–10 000 a BP). Groundwater becomes progressively older towards the discharge area along the west coast of Jylland. The very low ^{14}C values (≤ 1 pmc) measured in samples from western Jylland indicate some Pleistocene groundwaters recharged during the last glaciation may be present within the aquifer system towards the coast (Table 3.1, Fig 3.2.).

No severe salt water problems have been recognized in the Ribe Formation within the study area although, chloride concentrations increase slightly towards the coast. Locally, elevated chloride concentrations and even brackish waters associated with high dissolved organic matter content are encountered in western Jylland. The source of the Chloride and DOC is thought to be primarily from marine and lagoonal sediments adjacent to the Ribe Formation (Rasmussen, 1995, 1996), while lignite in the aquifer itself may also contribute to the DOC. To the north, the dissolved organic matter present in the Ribe Formation was found to be of terrestrial origin from adjacent lacustrine sediments (Grøn *et al.*, 1996).

The ^{14}C content in wells J, N and 0 (Table 3.1) is very low (<1 pmc) indicating that these groundwaters are potentially of Pleistocene age. The high DOC and/or Sodium-Chloride concentrations in well J and O are capable of influencing the inorganic carbon pool either directly through production of CO_2 from the fermentation process and/or indirectly through the triggering of carbonate dissolution/precipitation processes (Appelo, 1994). Evaluation of the groundwater chemistry of the two wells indicate that these processes seem to be insignificant in well J, but in well O they clearly affect the dissolved carbon pool as shown by the high DIC and CH_4 concentrations and the relatively enriched ("heavy") $\delta^{13}C$ value.

Chemical and physical processes and ^{14}C estimated residence times.

One of the main issues in ^{14}C age-dating of groundwater is to correct for all the significant chemical and physical processes that affect the dissolved inorganic carbon in the groundwater. It has been shown that substantially different age dates than those obtained from classical correction models (For review see e.g. Fontes and Garnier, 1979; Plummer *et al.*, 1994; Clark and Fritz, 1997) in some cases can be obtained when recognized chemical processes in the aquifer are considered (e.g. Plummer *et al.*, 1990; Plummer *et al.*, 1994; Kalin and Long, 1994; Aravena *et al.*, 1995). Similarly, significant corrections for physical processes (diffusion) in the aquifer are sometimes needed in order to estimate reasonable groundwater ages (e.g. Neretnieks, 1981; Maloszewski and Zuber, 1991; Sanford, 1997).

Effects of geochemical reaction/mass transfer on ^{14}C age estimate.

The two most important and common types of geochemical reactions affecting the inorganic carbon pool in groundwater are carbonate dissolution/precipitation and oxidation of fossil ^{14}C "dead" organic matter (e.g. Ingerson and Pearson, 1964; Münnich, 1968; Pearson and Hanshaw, 1970; Dörr *et al.*, 1987; Clark and Fritz, 1997). No carbonate dissolution, however, is generally expected to occur in the Ribe Formation because carbonates are absent in most parts. This is confirmed by sediment chemistry analyses and the relatively constant DIC and $\delta^{13}C$-values in most of groundwaters in the Ribe Formation. Likewise no significant oxidation of organic matter seems to occur in the Ribe Formation. In the Ribe Formation the redox-environment seems mainly to be post-oxic (Berner, 1981; Appelo and Postma, 1993), because oxygen is reduced to very low concentrations in the layers above (Table 3.1), and the relatively inert character of the Ribe Formation sands. Slow sulphate reduction, though, is indicated by the relatively low sulphate concentrations and redox potentials in the Ribe Formation, and has been suggested in an earlier study on the basis of H_2 measurements (Jakobsen, 1995). However, no clear trend is observed and the low concentrations could be a result of much lower sulphur deposition in pre-industrial times (Graedel and Crutzen, 1993). If slow sulphate reduction does occur, the rate is generally too slow to considerably affect the carbon pool. Only in the case of fresh and salt water mixing (well O, Table 3.1) does carbonate dissolution/precipitation and oxidation of organic matter by sulphate and methanogenesis seem to affect the inorganic carbon pool in the Ribe Formation.

In the recharge zone carbonates present in the Quaternary sediments are most certainly dissolved and the oxygen originally present in the groundwater might have been reduced primarily by fossil organic matter before the groundwater reaches the Ribe Formation. The effect of these processes on the ^{14}C age dating results has to be evaluated. Studies in other similar Danish aquifers show that the process mainly responsible for the reduction of oxygen might vary significantly. Boaretto *et al.*, (1998) argue that the oxidation of fossil organic matter affect ^{14}C age dating results in an aquifer in eastern Jylland. Postma *et al.* (1991) demonstrate that pyrite oxidation is the dominant process for oxygen reduction at the Rabis Creek study site, and finally Hinsby (1988) estimate that both processes are of approximately equal importance at a third study site close to the Rabis Creek test site. Therefore the effect of carbonate dissolution and fossil organic matter oxidation have to be evaluated and taken into account.

In columns 19 and 20 of Table 3.1 the two processes have been included in the estimation of the ^{14}C age. Column 19 presents age dates based on the correction for the dissolution of carbonates in the aquifer by the $\delta^{13}C$ method described by Ingerson and Pearson (1964). It is assumed that the ^{14}C and $\delta^{13}C$ concentrations in the initially dissolved soil-CO_2 was 100 pmc and $-25‰$, respectively, and that the dissolved carbonate had ^{14}C and $\delta^{13}C$ concentrations of 0 pmc and 0‰. Column 20 includes the $\delta^{13}C$ correction as well as maximum correction for the oxidation of fossil organic matter (0 pmc, $-25‰$) by oxygen. The $\delta^{13}C$ values measured in the Ribe Formation indicate that about half of the dissolved inorganic carbonate in fact is from the dissolution of carbonates in the recharge zone above the aquifer. This is in accordance with what theoretically would be expected for the dissolution of carbonates under closed conditions (e.g. Appelo and Postma, 1993, Appelo, 1994). This justifies the use of the Ingerson and Pearson (1964) correction as a first approximation to a corrected ^{14}C age. In column 20 of Table 3.1 a fossil organic matter correction is added assuming that all oxygen originally present in the groundwater (approx. 12 mg L^{-1}) is used to oxidize fossil organic matter in the aquifer. This reaction would produce about 17 mg L^{-1} CO_2 with $^{14}C = 0$ pmc i.e. the effect of the "oxygen correction" is significant especially for waters with low DIC contents. The difference in the results in column 19 and 20 illustrates the importance of selecting the right corrections for geochemical reactions in the aquifer. Note that the negative "ages" in Table 3.1 indicate postbomb waters as these are a result of corrected ^{14}C values above 100 pmc. When evaluating all tracer and geochemical results in Table 3.1 it is clear that some correction for the oxidation of fossil organic matter seems to be needed in order to obtain postbomb ^{14}C values in some high tritium waters (e.g. well C). However, it is also indicated that not all oxygen could have been reduced by fossil organic matter (e.g. well F). For well F the most up-gradient well in the Ribe Formation fossil organic matter oxidation by up to 5–6 mg L^{-1} O_2 seems to be reasonable. This indicates that about half of the oxygen originally present might have been reduced by fossil organic matter and that other processes also take part in the reduction of oxygen. High sulphate concentrations in some wells indicate that pyrite is another important reducing agent that at least locally reduces significant amounts of oxygen and nitrate.

No attempt will be made here to define the needed geochemical corrections more precisely. Geochemical modelling by NETPATH (Plummer *et al.*, 1994) and PHREEQC (Parkhurst, 1995; Parkhurst and Appelo, 1997) will probably be able to constrain the age ranges further and these will be performed at a later stage. Only the corrections described in the section above are applied for groundwaters from well O, although redox-reactions e.g. sulphate reduction by dissolved organic matter definitely has a significant influence on the dissolved inor-

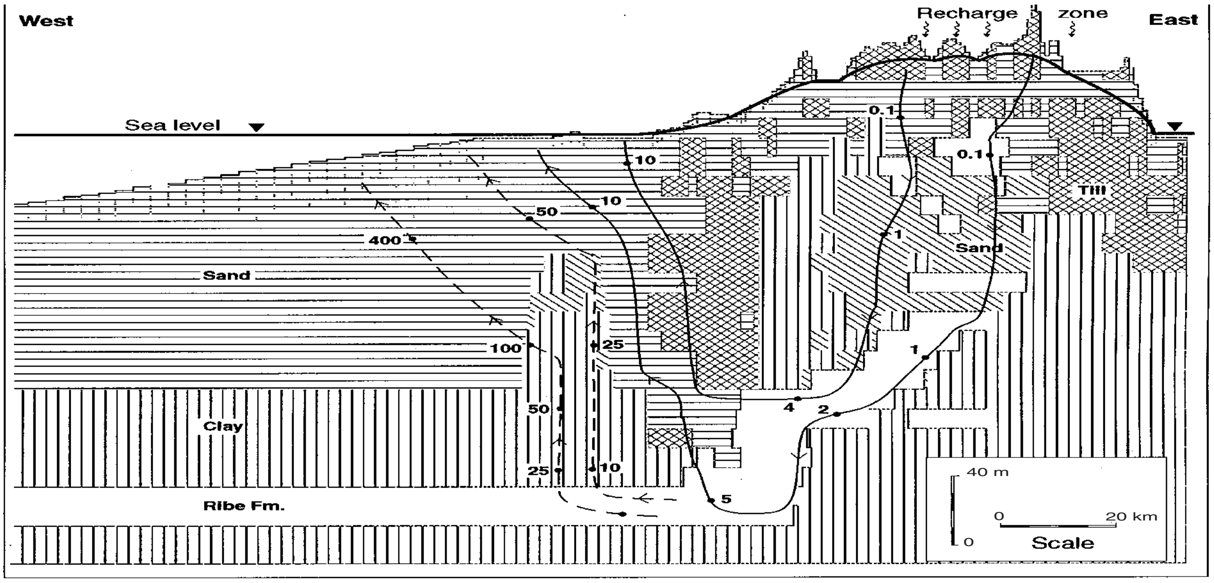


Figure 3.3. Simulated groundwater flow paths and age dates (ka) for present base level conditions. Solid line indicate flow paths of groundwater recharged under present base level conditions. Dashed lines indicate flow paths of groundwater that was emplaced at depth within the Ribe Formation under low base level conditions.

ganic carbon. This is because ^{14}C age-dating at such low ^{14}C values involves a significant uncertainty due to a relatively large uncertainty on the estimation of initial ^{14}C and δ^{13}C values (Van Kemp *et al.*, 1998; Taylor, 1999), the risk of significant contamination by modern carbon during sampling and analysis is relatively high and finally the uncertainties related to the effect of aquifer/aquitard diffusion (see section below). Geochemical processes as well as fractionation and diffusion processes will affect the estimated ^{14}C age considerably at the Rømø well making the groundwater appear much older than it is.

However, noble gas results from the well calculate a mean recharge temperature of approx. 2.7°C (Poole, 1998) indicating that the annual mean temperature at the time of recharge for this water was 5–6°C lower than present day temperatures. This is in accordance with temperature differences between present day and late Pleistocene temperatures observed in other studies (e.g. Andrews and Lee, 1979; Plummer, 1993; Stute *et al.*, 1995; Clark *et al.*, 1998; Loosli *et al.*, 1999a) confirming that the sampled groundwater indeed seem to be of a Pleistocene age. This conclusion is also supported by a slight depletion of about 1.5‰ in ^{18}O in the Rømø water compared to the ^{18}O values generally observed in the Holocene waters in the Ribe Formation. This value is comparable to values observed in studies in the British Isles (Darling *et al.*, 1997).

Effect of aquifer/aquitard diffusion on ^{14}C age estimates

Diffusion will affect solute transport and age dating results e.g. using ^{14}C and other tracers in fractured and layered aquifer and aquitard systems (e.g. Foster, 1975; Barker and Foster, 1981; Neretnieks, 1981; Sudicky and Frind, 1981; Maloszewski and Zuber, 1991; Sanford, 1997). The significance of diffusion of ^{14}C from the Ribe Formation to surrounding aquitards and the impact of this process on ^{14}C age estimates is evaluated below using the method presented by Sanford (1997).

The DIC is assumed to be only slightly affected by hydrodynamic dispersion and diffusion in the recharge zone above the Ribe Formation. However, during the flow towards the coast the DIC content of the groundwaters in the relatively thin Ribe Formation is potentially affected to a significant degree by diffusion to the surrounding clay and silt sediments. The effect of diffusion from the Ribe Formation to the surrounding aquitards was calculated by the equations described by Sanford (1997), assuming a uniform thickness for the Ribe Formation of 20 m, a thickness of the surrounding aquitards of 50 m, and a porosity of the aquifer and aquitard of 0.33. The results of these calculations are shown in column 21 in Table 3.1. The results show a significant influence of the diffusion process resulting in diffusion corrected ^{14}C ages nearly three times lower than without the correction. This correction factor is of the same order as the correction factors needed for the correction of the geochemical processes (mainly carbonate dissolution) for most of the wells in the Ribe Formation. This indicates that the groundwaters of the Ribe Formation probably are between 3 and more than 10 times younger than uncorrected ^{14}C ages would estimate, depending primarily on to what extent the geochemical reactions have modified the dissolved inorganic carbon pool and the variation of the thickness of the Ribe Formation and the surrounding aquitards.

3.4.2 Groundwater flow modelling

A cross-sectional numerical groundwater flow model was developed and calibrated for the study area. Steady-state flow simulations using MODFLOW (McDonald & Harbaugh1988) and particle tracking using MODPATH (Pollock, 1989) were performed along the cross-section presented in Fig. 3.2. The objectives of the modelling are to simulate flow paths and residence times within the regional Miocene aquifer and to compare these results with groundwater age dates estimated from isotopes. Simulations show active groundwater circulation and age dates of 100s to 1000s of years within the Ribe Formation under the recharge zone. Flow paths within the Ribe Formation are then towards the west and ultimately to Quaternary deposits within the deep valley located along the coast. Simulated groundwater ages dates within the Ribe Formation near the Quaternary valley range from 2000 to 5000 years. Groundwater then flows upward through the Quaternary deposits and discharges to the North Sea within several kilometres of present coast line. Simulated groundwater ages within the Quaternary valley range from several thousand to over 10 000 years. Simulations also indicate that groundwater located in deep Miocene sands beneath the island of Rømø are essentially isolated from the present day flow system. Groundwater flow from the recharge zone seaward beneath the Island of Rømø was simulated only under conditions of lower sea levels. The simulated age dates within the regional groundwater flow system are in general agreement with the isotope results (Fig 3.2, Table 3.1).

3.4.3 *Geochemistry and grain sizes of quartz sands*

The geochemical analyses made on 16 samples of Ribe Formation quartz sands from about 5 different levels in three different wells in the cross section (Fig 3.2)show that the sands generally is composed of more than 95% quartz, the rest is mainly composed of phyllosilicates ("clay minerals") from the weathering of feldspars and mafic minerals. The Carbon content is mainly organic and constitutes generally less than 0.5% of the sands. These pure quartz sands result in a relatively inert geochemical environment in the Ribe Formation, and geochemical reactions are limited.

Grain size analyses on 20 samples from the same three wells mentioned above show that the Ribe Formation mainly is composed of medium to coarse grained sands with a few examples of gravel and fine sands. The geometric mean of the hydraulic conductivity estimated from the grain size analyses is 7.7×10^{-4} m s^{-1}. This value is in accordance with the hydraulic conductivity value found in pumping tests (7×10^{-4} m s^{-1}), which have been used in the groundwater flow simulations in this study and in other groundwater flow simulations in the Ribe Formation.

3.4.4 *Geophysical logging*

Geophysical logs have been performed at 4 sites in the project mainly to indicate active groundwater flow zones, lithology and salinity. Summarized versions of the logs performed at the 4 sites are shown in the data appendix. At the Skaerbaek site (in the western part of the Ribe Formation profile, Fig. 3.2) a flow log that was run in the completely screened Ribe Formation showed that the whole thickness of the aquifer was contributing to flow. At this site sampling at fixed levels in the bottom, middle and top of the aquifer showed no significant differences between the groundwater quality and age (Buckley *et al.*, this report). At the Fjand site (site 3, Fig. 3.1) the geophysical logs were especially helpful in defining important flow zones and the mixing between waters from separate aquifers e.g. due to short-circuiting wells (Buckley *et al.*, this report/volume). At the Fjand site some differences are observed in the water quality when pumping from different depths of the aquifer, high TOC ("brown") and older waters are present in the deepest part of the aquifer resulting in problems for the local water works. No problems with saline waters however have been observed although the well is located less than one km from the coast line.

3.4.5 *Porewater salinity in offshore wells*

The porewater chloride contents have been estimated in two offshore wells from the Danish and the German sector, with continuous cores down to depths of 206 and 160 m below the sea floor, respectively. The two investigation wells were cored in a former EC project (Sha *et al.*, 1989) investigating Quaternary sediments in the North Sea, at or close to the left banks of the Heligoland Channel (the Palaeo-Elbe Valley) in the south-eastern North Sea. The estimated chloride concentrations in the porewaters of the cores range from about 2000 mg L^{-1} chloride to 25 000 mg L^{-1} chloride (see data appendix). Most of the estimated chloride contents in the porewaters indicate a fresh water component and that the sediments below the North Sea have not been completely salinized after the sea-level rise. However, there is a large variation in the estimated chloride concentrations and no clear trend is observed with depth in the profile, indicating that the porewaters of the cores have been influenced too much during sampling and storing to be used for any certain conclusions on the possible influence of fresh waters in the cores.

3.5 Conclusions

Hydrochemistry and isotopes (^{14}C, ^{13}C and $\delta^{18}O$) show that the Ribe Formation generally contains high quality fresh groundwaters of Holocene age with no signs of human impact. However, noble gas data indicate 5°C lower recharge temperatures for two coastal wells. These data in combination with carbon and oxygen isotope data suggest that Pleistocene waters occur in discharge areas around the coast and locally in hydraulic isolated parts of the Ribe Formation. Groundwater flow modelling results indicate that the deep emplacement of Pleistocene age groundwaters occurred under low sea level conditions during the late Pleistocene. Modelling also suggests that these waters are essentially isolated from the present flow system and that fresh groundwaters may be "trapped" in deep sand aquifers offshore.

Seismic surveys show that the Ribe Formation continues beyond the coastline below the present day North Sea in some areas along the west coast of Jylland and e.g. probably has a thickness of 40–50 m 15 km west of the coastal water supply wells at the Fjand site. The combined results from hydrochemical, geophysical, isotope and groundwater flow modelling studies suggest that high quality Pleistocene groundwaters may be present in some offshore parts of the Ribe Formation. This probably decreases the risk of salt water intrusion into coastal water supply wells.

Seismic sections and the investigation well on the island of Rømø that was drilled in the project show that glaciotectonic features and tunnel valleys are common on- and offshore and probably influence the groundwater flow and aquifer continuity. Glaciotectonic deformation and deep tunnel valleys may create conditions favourable for cross flow between aquifer systems and the presence of Holocene and Pleistocene age groundwaters in the coastal discharge zone.

4 The Ledo-Paniselian aquifer in Flanders, Belgium: a model of a freshening aquifer

4.1 Introduction

The Eocene Ledo-Paniselian aquifer occurs in the Belgian provinces of East- and West-Flanders. It extends across the Belgian-Dutch border into the Dutch province of Zealand, where it is found at greater depths. This aquifer presents a model example of a freshening aquifer, consisting in initial marine conditions being freshened by precipitation recharge. The freshening comprises two main processes: dilution and cation exchange. The latter gives rise to a well-expressed chromatographic pattern upflow of the fresh/salt-water interface.

4.2 Geology and hydrogeological structure

The Ledo-Paniselian aquifer is part of a sequence of alternating clayey and sandy Tertiary deposits that are gently dipping towards the north. In its semi-confined part, the aquifer is overlain by Bartonian clay. Underlying the aquifer, a thin layer of Paniselian clay is found, followed by the Ypresian (or Ieperian) aquifer, which in turn is underlain by the Ypresian clay (the equivalent of the London clay). The sequence is shown in a cross-section (Fig. 4.1) extending from the unconfined/semi-confined boundary of the Ledo-Paniselian in the south, towards the north. The Ypresian clay layer reaches over 100 m thickness, and has been considered impervious for modelling groundwater flow and chemistry in the Ledo-Paniselian aquifer. However, it has been shown (Walraevens *et al.*, 1990) that underlying aquifers are recharged through it, although at a very slow rate.

4.3 Groundwater flow

Piezometric levels demonstrate that recharge of the Ledo-Paniselian aquifer takes place in the areas with a higher topography, where the aquifer is semi-confined and covered by the Bartonian clay (Walraevens, 1987). Outflow occurs in part to the south, in the unconfined area, where the Ledo-Paniselian crops out beneath the Quaternary sediments. The other part of the recharged groundwater flows in the opposite direction to the north, where the depth of the aquifer increases.

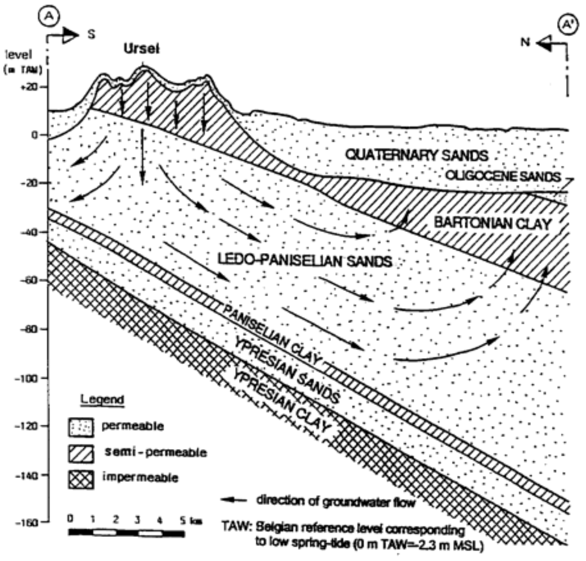


Figure 4.1. Schematic hydrogeological profile A-A'

Groundwater flow in the aquifer has been modelled, both with a Q3D flow model (Walraevens, 1988) and along cross-sections. Some flow lines are given in Fig 4.1. The Q3D simulation has been done both for natural conditions and for the present situation, which shows substantial changes in piezometric levels due to groundwater exploitation by industry (and also by private households). The recharge areas under natural flow conditions coincide with topographically higher regions (Fig. 4.2; cf. Fig. 4.1). Groundwater flow within the main part of the aquifer then continues to the north or north-west.

4.4 Groundwater chemistry

The Tertiary sediments have all been deposited in a marine environment. At the end of the Tertiary the sea regressed from the area, and the present-day topography developed due to fluvial erosion. Groundwater flow was induced by precipitation recharging in the higher regions. Calcite dissolved in the infiltrating water, and freshening took place, consisting in dilution of the marine pore solution and cation exchange, the latter mainly in the Bartonian clay in the recharge areas (Walraevens, 1987). In an upstream direction, progressively more freshened watertypes are found in the groundwater (Fig. 4.3). The chromatographic sequence of cation exchange is found in the subsequent surplus of Na^+, followed by K^+ and finally Mg^{2+}, resulting in $NaHCO_3$ and $MgHCO_3$ watertypes (classification after Stuyfzand, 1991). Upstream of the latter, Ca^{2+} is the dominant cation, leading first to a $CaHCO_3^+$ watertype (showing still evidence of cation exchange) and finally to a $CaHCO_3^0$ watertype (without cation exchange evidence) (Walraevens, 1990). The distribution of groundwater types on a regional scale still reflects

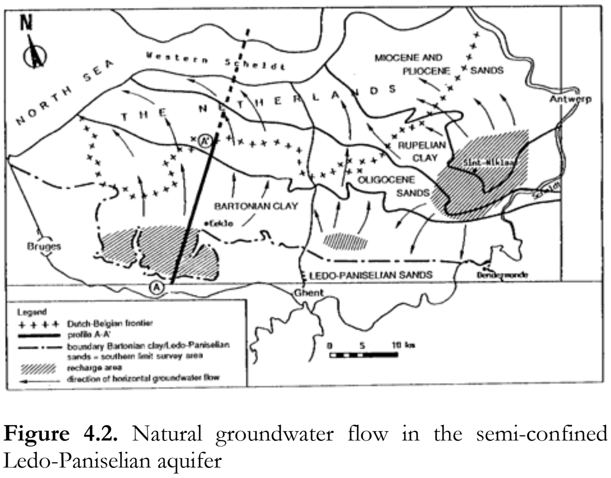


Figure 4.2. Natural groundwater flow in the semi-confined Ledo-Paniselian aquifer

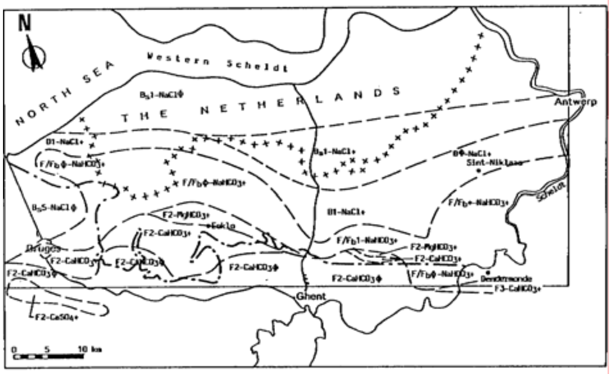


Figure 4.3. Distribution of groundwater types in the Ledo-Paniselian aquifer

the flow pattern under natural conditions.

Measurement of adsorbed cations in the Bartonian clay of the recharge area, showed a very clear depletion of adsorbed Na^+, compared to a boring outside the recharge area, while adsorbed Ca^{2+} is higher (Walraevens & Lebbe,1989). The model PHREEQM (Appelo & Postma, 1993) has been used to model the freshening of the Bartonian clay and of the Ledo-Paniselian aquifer along the cross-section in Fig 4.1 (Walraevens & Cardenal, 1994; Cardenal & Walraevens, 1994). The modelling results have confirmed that the observed water qualities are due to ion chromatography.

A remarkable feature is the steady increase of HCO_3^- along the direction of groundwater flow in freshening groundwaters. The HCO_3^- concentration shows a positive correlation with the extent of cation exchange, expressed by the increase of Na^+ (Walraevens, 1990; Appelo, 1994). Adsorption of Ca^{2+} in exchange for marine cations, has apparently initiated a second phase of calcite dissolution. However, the modelling with PHREEQM has shown that cation exchange alone can not account for the high HCO_3^--values observed. Including sulphate reduction has given agreement between observed and modelled data (Cardenal & Walraevens,1994).

4.5 Data collection

4.5.1 *Hydrochemical and isotope analyses on pumped groundwater samples*

A new sampling campaign for hydrochemical and isotope analyses on Ledo-Paniselian groundwater extracted from wells was performed. Most sampled wells were chosen in those regions where the density of existing data was the lowest. Some samples were also taken from wells that had been sampled before. The locations of isotope data that were already available (Walraevens, 1990) and of the newly sampled wells for isotope analyses, have been indicated in Fig 4.4.

The new hydrochemical data were in agreement with the regional pattern that had been described on the basis of the existing data. The available data base for isotope analysis had however been fairly limited, and several uncertainties had remained, both for radiocarbon and for stable isotopes.

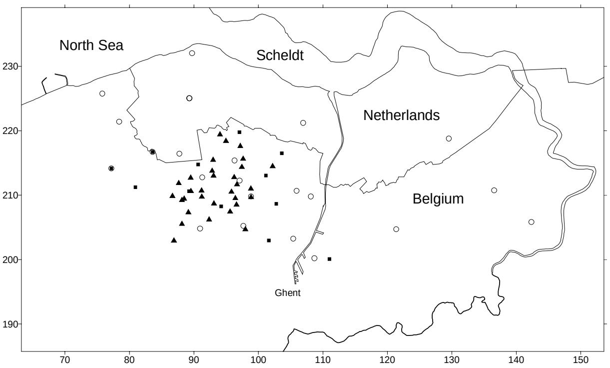


Figure 4.4. Sampling locations for the different isotope sampling campaigns (filled squares: 1984, open circles: 1997, filled triangles: 1998). Co-ordinates in km.

Isotopic data and interpretation

During the period 1997-1998 two sampling campaigns were organized. Each one involved sampling for stable isotopes and for radiocarbon. Almost all sampled wells are production wells. Stable isotopes were measured at ITN (Lisbon) and at Hydroisotop. A data set from 1984 was already available (analyzed at laboratory of M.A. Geyh in Hannover).

When all data are plotted in a δD vs. $\delta^{18}O$ graph, three groups of data can be recognized, depending on the laboratory where the samples were measured (Fig. 4.5). All values are corrected for the seawater contribution, calculated from the Cl^- concentration, presuming a seawater component with $\delta^{18}O$ and δD equal to SMOW.

The evident distinction between the three groups rises questioning. As the samples were taken in the same way and in the same recipients, a difference because of sampling handling can be excluded. From the hydrogeological point of view only one trend should be found as all samples are derived from the same aquifer. Further sampling should be done to clear the difficulties arising from these different results.

Each data set can however be explained. Data obtained from 1984 were explained by a precipitation originating in colder regions of the ocean than it does today (Walraevens, 1990). Data from 1997 plot close to the meteoric water line and can simply be explained by recent and palaeorecharge in a colder period.

Data from the 1998 sampling campaign can be ex-

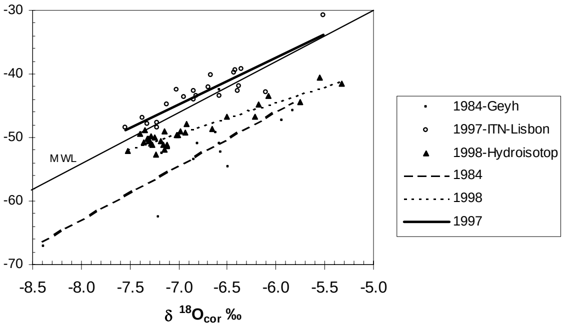


Figure 4.5. $\delta\ ^{18}O$ – δD relationship for the different sampling campaigns. The values are corrected for seawater contribution with an isotopic composition equal to SMOW.

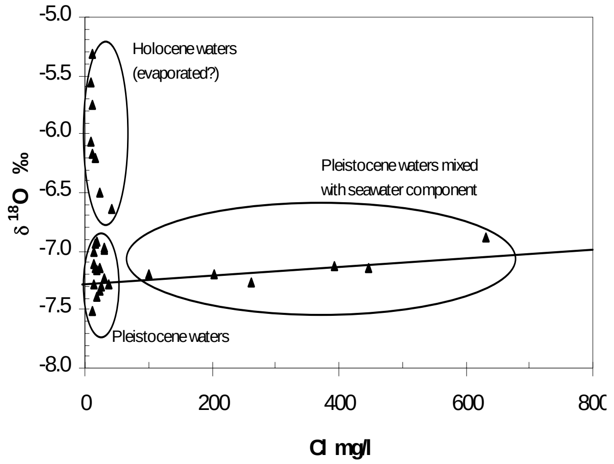


Figure 4.6. $\delta^{18}O$ – Cl^- relationship for the 1998 sampling campaigns. Line: isotopic mixing line between seawater (SMOW) and palaeowater ($\delta^{18}O = -7.3‰$).

plained by a combination of two effects. In the first place there is both recent and palaeorecharge, and secondly an evaporation effect. During the colder period evaporation was less strong than in the warmer period, which explains why the palaeowaters lie closer to the meteoric water line.

By plotting the uncorrected $\delta^{18}O$ data vs. Cl^- content for the 1998 dataset, three groups can be distinguished (Fig.4.6). The (more strongly) evaporated Holocene waters, the (less evaporated) Pleistocene waters and a mixing between Pleistocene and ancient seawater component with a $\delta^{18}O$ value equal to modern seawater.

During the 1998 sampling campaign, samples for radiocarbon dating were taken. The results show that the youngest waters contain around 50 pmc. The older waters range from 20 to 0.5 pmc with $\delta^{13}C$ values between −8 and −10‰. Some samples show suspiciously high $\delta^{13}C$ values. This will be studied further.

4.5.2 Noble gas analyses

A total of 36 wells have been selected for noble gas analyses, in collaboration with EAWAG-Switzerland. Only preliminary results are as yet available. They indicate that recharge temperatures for Pleistocene waters to be about 7°C cooler than for Holocene waters, which show a present-day recharge temperature of around 10–11°C.

4.5.3 Cored drillings

Three cored drillings were executed at Ursel, in the western recharge area, where the Ledo-Paniselian aquifer is recharged by percolation through the overlying Bartonian clay. A first attempt was unsuccessful. A (second) test drilling had to be ended at a depth of 7.5 m, in the clay. The porefluid from the cores was analyzed for main cations and anions. A third drilling reached a depth of 21 m, piercing through the clay, well into the aquifer. The lithological and lithostratigraphical description of this boring is given in Fig 4.7. The porefluid of the cores has been analyzed. The adsorbed cations and CEC of the sediments have been determined by various methods.

4.5.4 Hydrogeochemical analyses on core porewater from the Bartonian clay and the Ledo-Paniselian aquifer recharge area

Porewaters from the core were obtained by the squeezing method. The porewaters were analysed for main cations and anions, pH and conductivity. The results are presented in Fig 4.7. There is a clear bipartition in the chemistry of the waters from the Bartonian clay compared to those from the Ledo-Paniselian sand.

The high sulphate concentrations in the clay porewater (around 60–70 meq L^{-1}) can be explained by the dissolution of gypsum, which is observed in the core. These gypsum crystals are due to pyrite oxidation in conditions where the watertable was lower than at present. Furthermore, the morphology of the gypsum crystals (radial needles) indicate important diffusive transport following the pyrite oxidation.

As a result of gypsum dissolution, Ca^{2+} cations enter the pore solution. The Ca^{2+} cations are subsequently exchanged for the marine cations (Na^+, K^+ and Mg^{2+}) which are adsorbed to the clay. In the present situation, almost all Na^+ has already been flushed from the clay surfaces, as Mg^{2+} and Ca^{2+} are the most important cations in the solution. The decrease of the sulphate concentration in function of depth in the clay is controlled by the solubility of gypsum, as can be deduced from Fig 4.7.

As soon as the aquifer is reached, the saturation index of gypsum falls bellow zero and sulphate concentrations decrease drastically to about 11 meq L^{-1}, indicating that mixing occurs of sulphate rich and of sulphate poor waters. A possible explanation is the existence of preferential flow paths through the clay, in which the once existing gypsum has already completely disappeared by dissolution, whereas the less favoured flow paths still contain gypsum and thus elute sulphate rich waters. The cored boring must be part of a slower flow path. In contrast, porewaters from the test drilling reaching only 7.5 meters depth, executed close to the groundwater divide, shows sulphate concentrations of only about 4 meq L^{-1}. This test boring is likely to represent a preferential flow path.

Another possible sign for the existence of preferential flow paths is the higher Mg^{2+}/Ca^{2+} ratio in the porewaters from the clay (around 1.5 on the average) compared to those from the aquifer (around 0.6), indicating that cation exchange in the clay of the cored drilling has not yet evolved as far as in other parts, where waters with lower Mg^{2+}/Ca^{2+} ratios are eluted from the clay (Walraevens & Cardenal, in press). Indeed the porewaters from the test drilling show a Mg^{2+}/Ca^{2+} ratio of about 0.5, meaning that the clay has been flushed more strongly.

The most evident sign for the existence of preferential flow paths in the clay, is the difference between the magnitude of total concentrations of dissolved ions. In the clay the total cation concentration is between 50 and 80 meq L^{-1} whereas the concentration in the aquifer is around 20 meq L^{-1}, clearly indicating that the water from the aquifer did not elute from the clay just above, but is a mixture with waters from different flow channels with strongly varying salt contents.

The existence of preferential flow paths does have implications for geochemical modelling. The different flow paths result in mixing of waters originating from both less flushed and more strongly flushed parts of the recharge area, corresponding to zones in the Bartonian clay that contain gypsum, and other zones that do not. Not only the geographical distribution of gypsum is relevant for

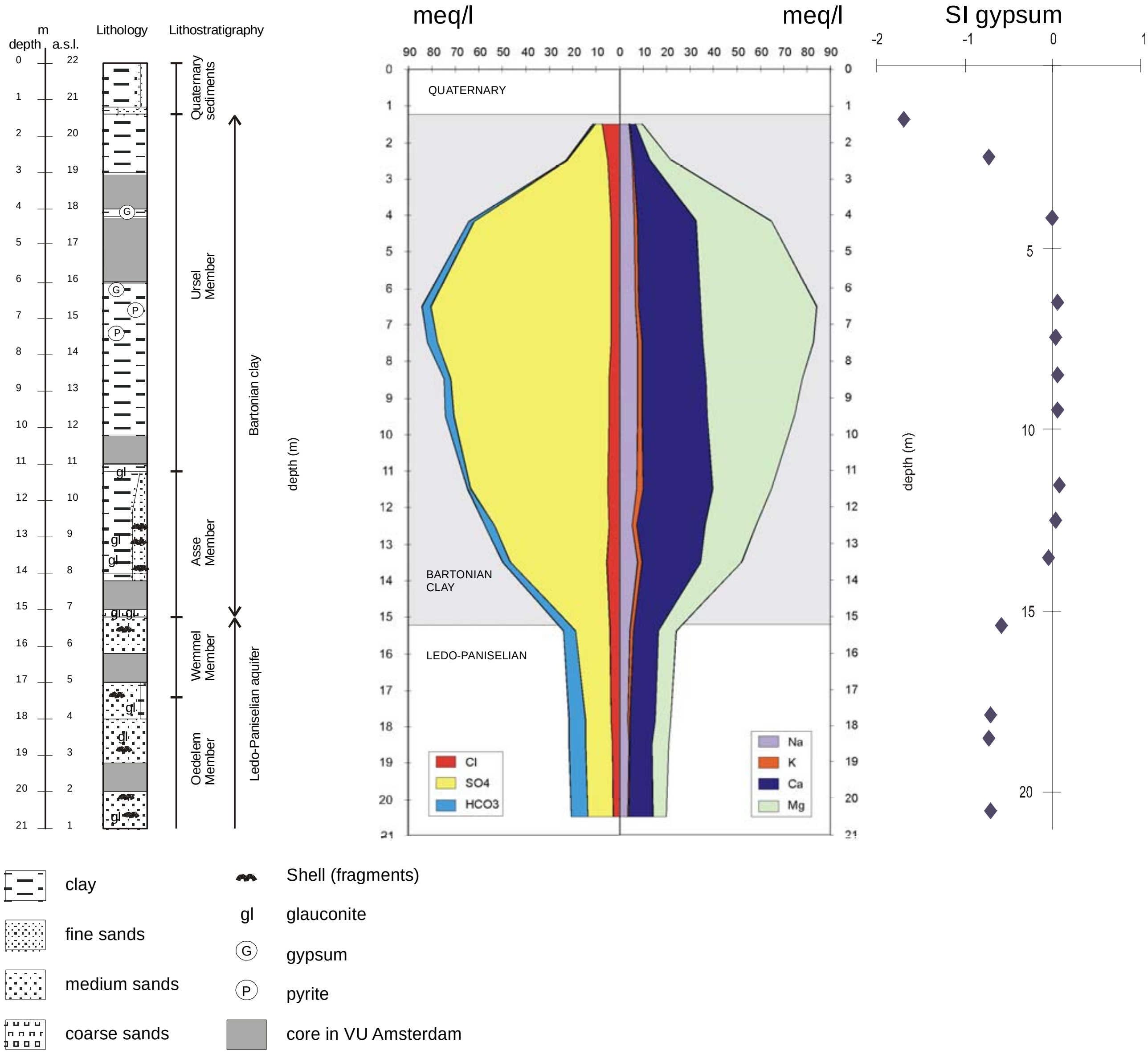


Figure 4.7. Lithology, pore solution composition and saturation index for gypsum of the cored drilling in the recharge area.

geochemical modelling, but also its occurrence in time. Probably the gypsum crystals were formed in conditions when the watertable was lower than today, maybe in a cold and dry climate.

4.5.5 *Determination of Cation Exchange Capacity and adsorbed cations*

The chemistry of the Ledo-Paniselian waters is in the first place determined by cation exchange coupled to the freshening of the aquifer. The cation exchange capacity (CEC) of the sediments, that are in contact with water along its flow path, determines the chemical composition of the water in terms of space and time. An increased CEC means that more pore volumes of fresh water are needed to flush an exchanger that was initially in equilibrium with seawater. Therefore a reliable determination of the CEC and the adsorbed cations is a major issue in the investigation of the groundwater quality of the studied aquifer.

Samples from the cored drilling were used to determine the CEC of the sediments and the adsorbed cations. Different methods were applied.

The first method involves flushing of the adsorbed cations with a NH_4OAc 1M solution and subsequently determining the adsorbed NH_4^+ by steam distillation. The second and third method (British Standard 7755/ss3.3 & 3.12) involve flushing of the adsorbed cations with a $BaCl_2$ 0.1M solution. Method 3 is the same as method 2 but the $BaCl_2$ solution in the former is buffered at pH 8.1. After Ba^{2+}-saturation of the exchanger the Ba^{2+}-cations are removed by a known volume of a $MgSO_4$ 0.02 M solution. Excess Mg^{2+} is measured as Ba^{2+} is removed by precipitation with the sulphate ions. Finally, the fourth method involves flushing of the adsorbed cations once with a NaCl 1M solution and once with a NH_4Cl 1M solution (method proposed by Appelo). Subsequently the flushing cation is desorbed by a $MgCl_2$ 0.2M solution and is measured.

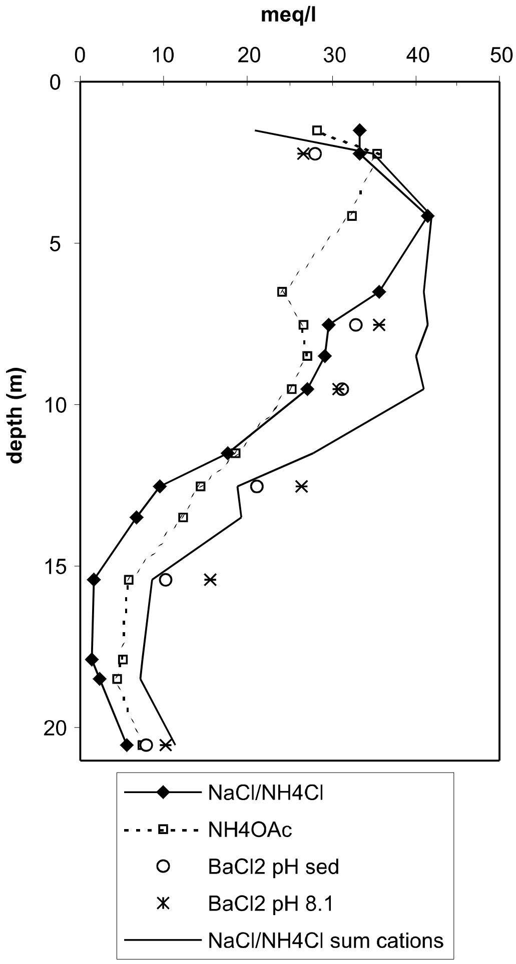


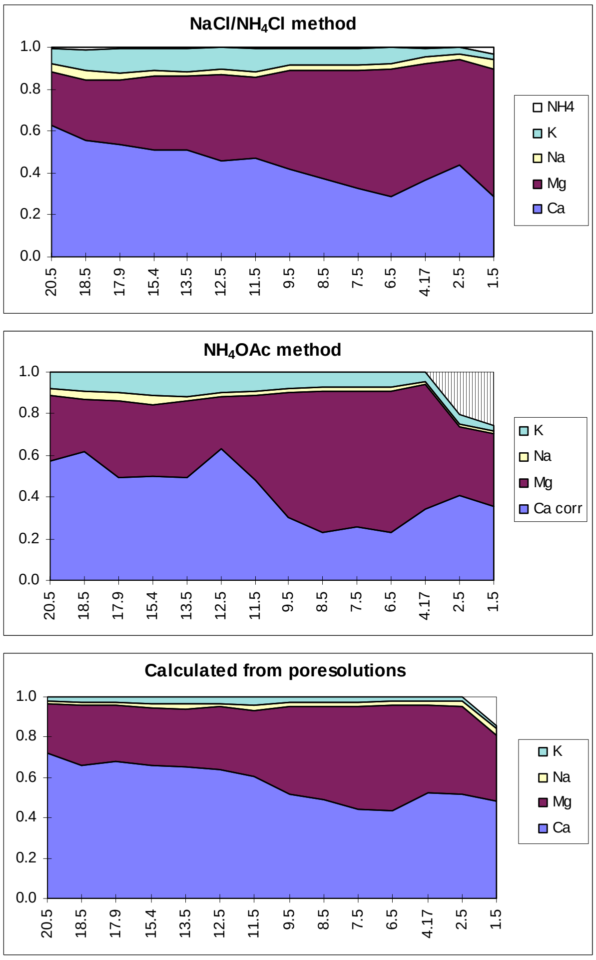
Figure 4.8. CEC and sum of adsorbed cations according to the different methods in function of depth.

Each method needs some correction for the dissolution of minerals as gypsum or calcite. Furthermore contributions of the pore solution have to be subtracted. Porewater contributions can be calculated from measured porewater concentrations and porewater quantity or by flushing the (dried) sediment with demineralized water, and measuring the concentrations.

It is quite remarkable that the sum of the adsorbed cations is always higher than the measured CEC. This can be explained by extra dissolution of calcite or gypsum in the flushing solutions. Therefore the adsorbed Ca^{2+}-concentrations were adjusted so that the sum of the adsorbed cations equals the CEC. These corrections can be very large resulting in a lower accuracy. Results for the CEC measurements are represented in Fig 4.8.

Although all methods show the same trend, large differences exist between them. The $BaCl_2$ methods generally result in the highest CEC values. The buffered method produces higher values than the non- buffered one, probably due to deprotonation of the complex because of the high pH. The method of Appelo leads to unreasonably low results for the aquifer material, and relatively high values for the clay.

The method proposed by Appelo is the only one in which the adsorbed Ca^{2+}-concentration is corrected by the measured sulphate and bicarbonate concentrations, and not by matching the sum of the adsorbed cations with the CEC. However, the sum of measured cations (after correcting the adsorbed Ca^{2+} for gypsum and calcite dissolution) is far larger than the measured CEC.


NaCl/NH$_4$Cl method

NH$_4$OAc method

Calculated from poresolutions

Figure 4.9. Measured and calculated equivalent fractions (fraction of CEC) of the adsorbed cations in function of depth (m). NH_4OAc method: crosshatched area: difference between CEC and sum of adsorbed cations. Calculated from pore solution: blank area: NH_4^+ and Fe^{2+}.

Comparing the measured equivalent fractions of the different adsorbed cations on the exchanger (Fig. 4.9) with those calculated from the pore solutions with PHREEQC, using the standard exchange coefficients, one can conclude that the method of Appelo produces the best results, although the CEC values are far too low for the sandy material. CEC values should therefore not be taken from the Appelo method but rather from the NH_4OAc method.

The uncertainty concerning CEC and adsorbed cations is rather high, and should be accounted for in geochemical transport modelling, by choosing a lower and higher limit for the CEC values.

4.5.6 Determination of Proton Exchange Capacity of decalcified sand from Member of Oedelem

The Member of Oedelem is the upper part of the Ledo-Paniselian aquifer. It consists of fine sand with many shell fragments and glauconite. A mixed sample of this sand in the depth range 19–20 m from the (third) cored drilling at Ursel was decalcified with 0.1 M hydrochloric acid at pH 5. Decalcification was done in a glove-box under nitrogen atmosphere. After decalcification the sample con-

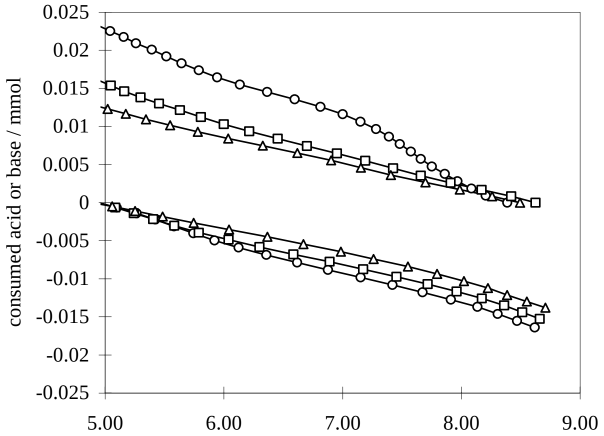


Figure 4.10. Titration of 1.000 g of pretreated (see text) sand of the Member of Wemmel with 0.1000 M hydrochloric acid and sodium hydroxide. Circles: initial ionic strength 1 mM, squares 3 mM, triangles 10 mM. The consumed amount of acid or base is corrected for a distilled water background.

tained less than 0.2% calcite. The samples were kept under nitrogen atmosphere and titrated using the Wallingford autotitrator as described by Kinniburgh *et al.*, (1995). Titrants were 0.100 M sodium hydroxide and hydrochloric acid. Titrations were performed at 25°C and initial ionic strengths of 1, 3 and 10 mM sodium chloride (Fig. 4.10).

The first titration started at pH 8.4 with titrant hydrochloric acid. The deviant behaviour of this curve is possibly caused by traces of calcite. In the pH range 5 to 8.5 the proton exchange capacity of the decalcified sediment is in the range 1 to 1.5 meq/100g. Assuming a porosity of 0.35 and a grain density of 2.65 g cm^{-3}, this leads to a proton exchange capacity of 49 to 74 meq L^{-1} porewater solution.

4.6 Impact of late-Pleistocene and Holocene palaeo-environmental changes

The freshening of the Ledo-Paniselian aquifer was reconstructed using a solute transport model along a 40 km long profile (Fig 4.2), which extends from the outcrop of the layer in the south, crossing the recharge area and low-lying polders, to the north bank of the Western Scheldt river. The calculations were performed with a modified version of the USGS MOC-model (KONIKOV and BREDEHOEFT, 1978) which was adapted for variable density flow, heterogeneous aquifer storage, time-varying constant head boundaries and a direct solver for the flow equation.

The treated profile comprises Quaternary deposits and underlying Eocene and Oligocene layers. The substratum of the model is formed by the Ypresian clay. The salinity distribution as observed in the water quality shows that rather fresh water occurs far northward under the present polder area. At the Braakman and Groede sites, close to the Western Scheldt river, salinity is only around 15%.

A first model simulation reconstructed the freshening of an initially completely salty Ledo-Paniselian aquifer under the actual flow regime. Boundary conditions were derived from piezometric level observations, present topography, as well as present surface water and sea levels. This Holocene flow regime was introduced when sea level had risen to its present position after melting of the glacial ice sheets and the shoreline was positioned near the polder boundary. It has therefore been valid only for the last 10 000 years or so. The results of this simulation show that even when this situation should continue for 30 000 years, fresh water infiltrated in the recharge area will never flow so far to the north as it is encountered today. This is mainly because the groundwater flux decreases in downstream, northward direction by loss of water by upward flow, especially under the polders and coast. Flow velocities become so small that the freshwater front doesn't advance significantly on the Holocene timescale. It should require hundreds of thousands or even millions of years to move the freshwater front to its actual position. This latter statement was derived from a simplified, two layer advective model of flow under a constant drainage level.

It is obvious that the observed fresh/salt water distribution is to be seen as the result of different flow regimes in the past, most likely due to completely different palaeoclimatological conditions, which affected the groundwater flow in the aquifer system. The pre-Holocene history shows that during the ice ages, sea levels were much lower (up to 150 m) than today and consequently, coastlines had moved, especially in regions with a rather flat topography like North Belgium and the North Sea basin.

The next step was to try to model the evolution of flow and salinity during the last glacial period, the Weichselian. This period started around 115 ka ago and lasted for more than one hundred thousand years. A palaeo-environmental model was constructed, which describes the palaeo conditions of hydrology, climatology and topography during the successive phases of the glacial period, and which could provide the necessary data for defining the boundary conditions in the model. Special attention was given to specific features like:

- Impact of low sea levels. Because the shoreline moved to the north the discharge section in the profile can have been displaced to the north, resulting in a continuing groundwater flux to the north. It is assumed that under the sea hydraulic heads in the Ledo-Paniselian are the same as sea level. This is built into the model along the north side of the profile.
- The topography in the profile changed throughout the Weichselian: first an extensive valley was eroded in the Tertiary substratum (the “Flemish Valley”) to a depth of more than 20 m below the present surface, later this valley was filled up again. This erosion has changed the base level in the profile between 115 and 70 ka BP.
- The occurrence of a permafrost layer. During the last glacial maximum (25–13 ka BP) climate conditions were so severe that in North Belgium a permafrost layer could develop. This can have altered the recharge and discharge of the aquifer system dramatically.
- Today the recharge of the Ledo-Paniselian is 40 to 50 mm a^{-1}, which is small compared with the precipitation rate of around 800 mm a^{-1}. This is mainly because the combination of the hydraulic conductivity of the overlying Bartonian clay layer with the topographic elevation of the ground surface in the recharge region (which defines an upper limit to the position of the water table) limits the percolation rates. Because the limiting criterion is not the precipitation (most of it doesn't contribute to the recharge), it is thought that during the Weichselian recharge rates were more or less the same as today. Only a severe reduction of the precipitation can influence the recharge rate of the Ledo-Paniselian.

The results of the simulations are integrated in the synthetic profiles at the end of this paper and can be summarized as follows:

- During the Early Weichselian (116–70 ka BP) the base drainage level in the profile was 20 m lower than today and groundwater flowed much further to the north. At 70 ka BP the freshening front was nearly at the position where it is found today.
- During the Early Pleni-Weichselian (70–25 ka BP) the Flemish Valley was filled up again and topographic surface and drainage levels were rising. This caused a decrease in groundwater flow velocities and the position of the fresh water front was stabilizing.
- The Upper Pleni-Weichselian (25–13 ka BP) had very cold conditions (LGM) and a permafrost layer was developing. The calculation of the thickness of a permafrost layer for given surface temperatures is treated elsewhere (Chapter 11). These calculations show that in a time interval of 12000 years, even for an average temperature of a few degrees below zero, the permafrost can occupy the upper half of the modelled profile. The first effect of a permafrost layer is suspension or reduction of the recharge of the water table. This will cause a lowering of piezometric levels under the permafrost layer, although the situation can be more complex in the early stages because of the disappearance of discharge to surface waters. This process was modelled with a separate hydrodynamic model and the results hereof are discussed elsewhere (Chapter 13).
- After the LGM, during the Late Weichselian (13–8 ka BP) climate conditions were improving and the permafrost layer started to melt, although it may have required a few thousands of years before the whole layer had disappeared. During melting the aquifer system may have been divided in an upper aquifer system above the deeper permafrost, where normal recharge has restarted, and a lower aquifer system under it. Because of the melting of the glacial ice sheets sea level was rising and during the Holocene (8–0 ka BP) the present level was reached and the shoreline was moved to its present position.

Although North Belgium was never covered by an ice sheet, the possibility that, during the second last glaciation, the Saalian ice sheet influenced the flow was investigated with a separate model simulation using a longer and deeper profile. During the Saalian, the glacial ice sheets had their southernmost extension and reached the central part of the Netherlands. Because of high pressures under the ice cover, groundwater flow can have been reversed to a southward direction. The results of this model are discussed elsewhere (Chapter 13).

4.7 Synthetic profiles

The results of the observations, analyses and modelling research are summarized in the form of four synthetic profiles. Both first ones illustrate the present-day situation, the other two visualize old flow regimes during the Weichselian period before, during and after the Last Glacial Maximum.

4.7.1 Profile1: present day groundwater flow situation

- The aquifer is recharged in the south where young fresh water percolates through the overlying clay layer (Fig. 4.11).
- From the recharge area, most of the infiltrated water flows to the north; a small part flows to the outcrop area in the south.
- To the north water is discharged upwards to the low lying polders (mainly in The Netherlands). Flow velocities become smaller and further northward there is virtually no flow, even in a part where fresh water is found today.
- When the fresh water replaces salt water, cation exchange processes occur, affecting the groundwater composition.
- In the north, more saline water is found, although at the moment it is not clear how far freshening has influenced groundwater composition in the aquifer. Around 25 km from the recharge area, the groundwater is composed by 85% of the fresh end member.

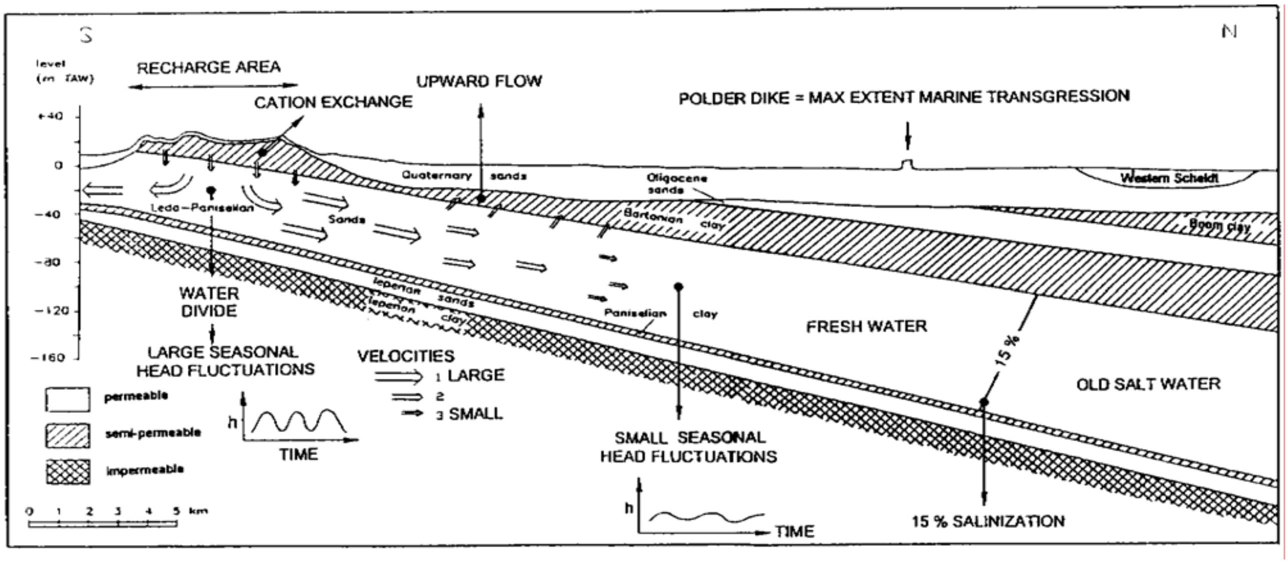


Figure 4.11. Present day (0 BP) groundwater flow situation

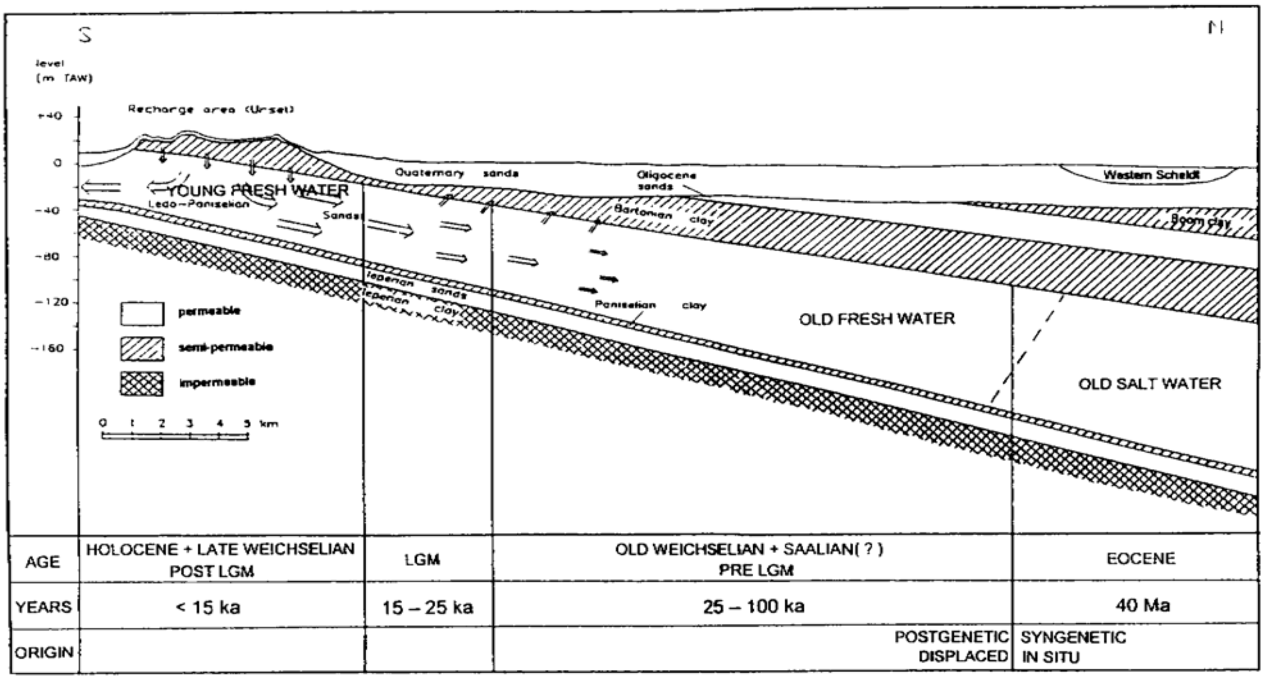


Figure 4.12. Age and origin of the groundwater

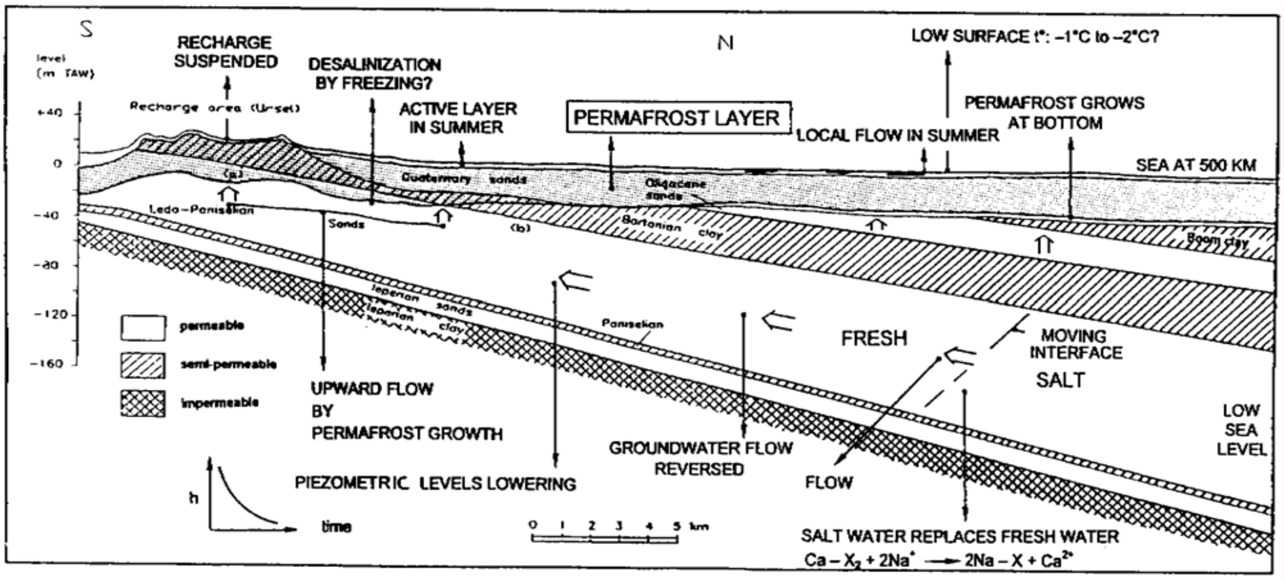


Figure 4.13. Groundwater flow during permafrost development

4.7.2 Profile 2: age and origin of the groundwater

- Under the recharge area and in the upstream part of the aquifer the fresh water is young and has infiltrated after the last glacial maximum (< 15 ka BP) (Fig. 4.12)
- Further to the north the water has probably infiltrated during the colder part of the last glacial period (15–25 ka BP)
- Even more to the north the fresh water becomes older and has infiltrated before the last glacial maximum (>25 ka BP)
- The saline water in the north is very old: it is the connate sea water from the Eocene period and is around 40 Ma old.

4.7.3 Profile 3: groundwater flow during permafrost development

- This situation occurred before the Last Glacial Maximum (> 25 ka BP) when average annual surface temperatures dropped below zero. (Fig. 4.13).
- Sea levels were much lower than today and the shoreline was positioned far to the north-west.
- A permafrost layer starts to develop at the surface causing a suspension or at least a reduction of the recharge of the aquifer system and a consequent lowering of piezometric levels.
- As long as summer temperatures are above zero, the top of the permafrost can melt in summer and in the active layer, local groundwater flow cycles exist.

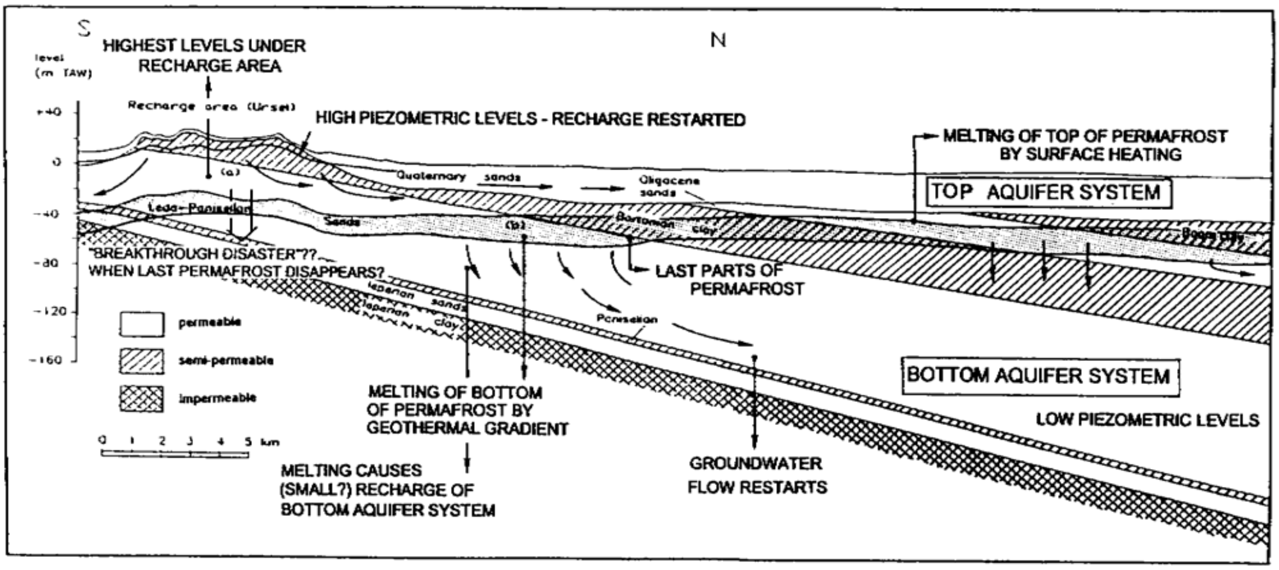


Figure 4.14. Groundwater flow during permafrost melting

- Beneath the permafrost, maybe an upward flow occurs by the growth of the permafrost layer.
- This upward flow can displace the fresh/salt water interface in upstream direction causing cation exchange processes, which can affect the composition of the water.
- During the Last Glacial Maximum (15–25 ka BP) surface temperatures were very low; the thickness of the permafrost layer may have reached 100–200 m This suspended the recharge of the aquifer system. As a result the hydraulic heads became very low.

4.7.4 Groundwater flow during permafrost melting)

- This situation occurred after the Last Glacial Maximum (< 13 ka BP) when average annual surface temperatures became above zero. (Fig 4.14).
- Melting of the permafrost layer occurs both at the top by the increased surface temperature and at the bottom by the geothermal flux. The aquifer system is then divided in a top aquifer, which is recharged again and in which normal groundwater flow occurs and a bottom aquifer separated from the upper one by the last part of the permafrost layer. The deeper layer is recharged by the bottom melting of the permafrost layer although recharge rates are probably lower than in present conditions.
- It can have taken a few thousands of years before the whole permafrost layer has disappeared.

4.8 Conclusions

The following conclusions have been drawn from the study of the Ledo-Paniselian aquifer:

It may take a very long time for the groundwater reservoir to reach a steady state after a new pumping has started. This indicates that piezometric measurements for the present-day pumped situation should be considered with caution, when calibrating hydrodynamic models on the present-day observations. Indeed, in semi-confined, rather low permeability porous media from which groundwater is being pumped at several locations, like the Ledo-Paniselian aquifer, the steady state is very unlikely to be observed, especially when pumping rates are still increasing. Impact on the water table will only occur many years after groundwater extraction from the deeper aquifers has been started.

Model calculations show that the observed fresh/saltwater distribution is not the result of the present freshwater flow conditions, but the result of different flow regimes during the ice ages when sea levels were much lower. Occurrence of a permafrost layer during cold periods could have a dramatic impact on the groundwater flow system by (at least temporarily) decreasing the recharge of the aquifers. The existence of the Saalian ice sheet in the Netherlands could have influenced the flow in the deeper Eo-Oligocene aquifers. The high pressures which existed under the ice sheet could have reversed the flow direction from northward to southward.

The distribution of groundwater types in the Ledo-Paniselian aquifer is determined by two end members: fresh Ca-HCO_3 water recharged into seawater saturated sediments. Hydrogeochemical modelling has allowed to confirm that mixing of the end members and cation exchange are the main processes; calcite dissolution is important as well. Cation exchange consists in the first place in desorption of the adsorbed marine cations (Na^+, K^+ and Mg^{2+}) in exchange for the fresh-water cation Ca^{2+}. Moreover, older samples, that are less freshened, are depleted in Mg^{2+}, as a result of charge effects during cation exchange.

Analysis of core porewater of the Bartonian clay shows the existence of preferential flow paths in the clay: quicker flow paths are more strongly leached, leading to low total dissolved solids, low sulphate concentrations and low Mg^{2+}/Ca^{2+} ratios; the slower pathways still contain gypsum, increasing the sulphate concentrations and TDS, and Mg^{2+}/Ca^{2+} ratios are higher because cation exchange resulting from freshening has not yet progressed so far.

Four methods for determining CEC and adsorbed cations have been compared: the NH_4OAc-method, two $BaCl_2$-methods (one in unbuffered and the other in buffered conditions) and the $NaCl/NH_4Cl$-method proposed by Appelo. Reasonable CEC-values are obtained with the NH_4OAc-method. Comparing the measured equivalent fractions of the adsorbed cations with those calculated from the pore solutions with PHREEQC, one can conclude that the method of Appelo produces the best results.

The proton exchange capacity of decalcified sand from the Ledo-Paniselian aquifer was determined to be in the range of 1 to 1.5 meq/100g.

The interpretation of ^{14}C is complicated by the corresponding variation of ^{13}C: decreasing ^{14}C is accompanied by a strong increase in $\delta^{13}C$, indicating chemical dilution of ^{14}C along a flow line.

Although the validity of a $\delta^{13}C$-correction may be questionable for the very high values (up to +0.1‰), this correction has been applied to the ^{14}C-data. The model data suggest the presence of Pleistocene groundwater in the downstream part of the aquifer, apart from Holocene groundwater in the upstream part.

The isotopic composition of soil-CO_2 is a function of the soil-CO_2 pressure. This relation was used for inverse chemical modelling and subsequent radiocarbon dating of the Ledo-Paniselian groundwaters. Higher CO_2-pressures clearly correlate with less negative $\delta^{18}O$, implying warmer conditions.

5 Palaeowaters in coastal aquifers of southern and eastern England

5.1 Introduction

The British Isles lie in a strategic position for the consideration of the impacts of Late Quaternary climate change on the landscape in general and water resources in particular. The land surface and near shore areas have been strongly affected by glacial advances and permanent ice cover, by permafrost, especially in southern Britain, and by sea level change. Glacio-isostatic changes have had a strong impact on the coastline, especially along the western seaboard, in addition to the global eustatic changes in sea levels. In the present PALAEAUX studies, an emphasis is placed upon the effects of these major changes on groundwater systems in southern and eastern England adjacent to the English Channel and the southern North Sea.

The probable maximum advance of the two principal ice masses (Anglian and Devensian) into central and southern Britain and adjacent coastal areas are shown in Fig. 5.1 (Bowen, 1986) and both of these have led indirectly, through permafrost development, to modifications to the near surface properties, especially jointing and the spatial variability of permeability in the Chalk (Younger, 1989), which forms the main aquifer of interest in the present studies. The presence of thick ice cover over or adjacent to the outcrop of both the Chalk and the Triassic sandstone aquifers in northern England during the Devensian glacial maximum could have had significant impacts on the directions and depths of groundwater flow (Boulton *et al.*, 1995, 1996). The presence of outwash drainage may also have influenced the nature of recharge during the periglacial periods. The duration of ice sheet cover was probably restricted to around 10 000 years yet the much cooler Devensian climate (see Goodess *et al.*, 1990) lasted prior to the glaciation back to around 65 000 BP. Despite this, there is evidence from speleothem growth that diffuse groundwater recharge must have taken place at intervals throughout the Devensian (Gordon *et al.*, 1989).

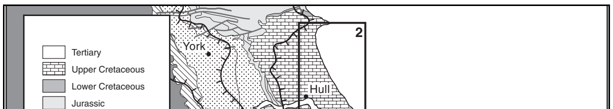


Figure 5.1. Site and location map of PALAEAUX investigations in England. 1) East Midlands, 2) East Yorkshire, 3) Lincolnshire, 4) Thames Estuary (North Kent), 5) South Downs, 6) Dorset and Poole Harbour

In the context of the present study, sea level change has probably had the strongest impact on the groundwater evolution. The English Channel and the North Sea were completely drained in the near shore regions for most of the last 100 000 years and the base levels for hydraulic purposes were around −65 m OD and −30 m OD respectively, well above the maximum fall of ca 125 m. This decline in sea levels also had the effect of increasing the continentality of UK and Europe as a whole with the nearest open sea around 150 km to the SW of Brighton. This would for example have affected the precipitation chemistry. For most of the Devensian the Channel floor was an area with forest/grassland and a zone with a developed freshwater cycle and with land connections across the palaeovalley (see Ch 17) with France. The present day coastline has only been in place for the past 7000 years. This is especially evident when onshore drainage maps are compared with those offshore, as preserved in buried and infilled valleys (Bellamy, 1995). This reveals that the drainage relates to deeper base levels and present onshore catchments are merely the exposed upper 30–50% of catchments developed during the Pleistocene.

The objective of the UK PALAEAUX studies has been to examine evidence for the presence of palaeowaters in the aquifers of the southern and eastern coastal regions, their possible offshore extent and to establish the controls on groundwater emplacement and movement as well as development of the water quality, against the wider studies of late Quaternary evolution of the UK.

5.2 Programme of work

The scientific programme has concentrated mainly on the Chalk aquifer adjacent to the North Sea and English Channel coastlines. These areas, underlain by confined and unconfined Chalk, represent contrasting hydrogeological conditions exposed to the changes in sea level as well as the north to south gradients of the impacts of glaciation (Fig 5.1). Advantage has been taken of commercial or research drilling projects to obtain core material (North Kent, Wessex and Yorkshire) for investigation of interstitial water profiles as an accurate method of depth sampling of the matrix water. Hydrogeophysical logging has been used extensively to define the stratification in water quality and to indicate horizons suitable for detailed chemical and isotopic work. This is necessary since preferential flow may occur in boreholes allowing mixing (see

Table 5.1. Stable isotope and radiocarbon data for Chalk groundwaters from Yorkshire and Lincolnshire.

Locality	Distance to coast km	$\delta^{18}O$ ‰	$\delta^{2}H$ ‰	$\delta^{13}C$ ‰	Activity ^{14}C pmc
Yorkshire					
Bluekeld Spring	16	−8.1	−51	−12.7	52.0
British Gas 3	2	−8.1	−58	−9.1	52.1
Britax	1	−7.7	−49	−11.2	51.5
Grimston	0	−8.0	−50	−9.3	3.65
Needlers, Hull	3	−7.5	−47	−8.5	12.0
Flamborough Maltings	1.5	−7.7	−48	−8.5	47.8
Carnaby	2.2	−8.1	−52	−13.6	67.7
Lincolnshire					
Heneage Road 2	2.5			−10.3	57.9
Dixon Ltd No 1	3	−7.5	−51	−11.9	55.2
Middle Farm	2	−7.3	−50	−6.8	8.62
The White Bungalow	9	−7.3	−49	−13.1	17.0
Bleak House Farm	0.5	−7.5	−51	−10.9	16.7
Mumby 2	1.5	−7.4	−53	−14.6	39.1
Thurlby 2	4.5	−7.4	−46	−12.3	38.4

Chapter 15); hydrogeophysical logging provides the necessary control for interpretation.

Further investigation (modelling studies and geochemical re-interpretation) has been made of the well-studied East Midlands Triassic sandstone aquifer which has provided a model for the PALAEAUX project as a whole. The Cretaceous sandstones underlying the Chalk in coastal areas of Lincolnshire and on the south-coast near Brighton have also been sampled.

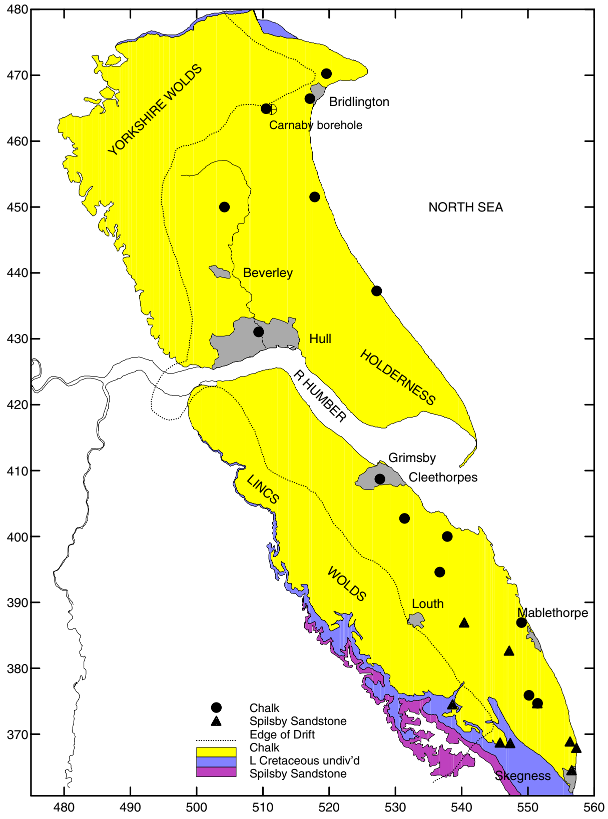


Figure 5.2. The Yorkshire and Lincolnshire Chalk study area

5.3 Results

The UK results are considered separately by area. A large data base has been produced with only selected data shown here.

5.3.1 Yorkshire and Lincolnshire

Chalk

The Chalk is the main aquifer and an important source of water supply for Lincolnshire and east Yorkshire (Figs. 5.2 & 5.3). The Formation outcrops in the Wolds escarpments in the western part of the region and dips gently north-eastwards where it is covered and in places confined by Quaternary Drift deposits. The Chalk surface retains the record of a fossil cliff line and wave-cut platform of Ipswichian age which is particularly marked in the northern and southern parts of the Chalk but has little topographic expression in the vicinity of the Humber Estuary. The Quaternary Drift cover is particularly thick to the east of this feature, reaching up to 45 m of dominantly impermeable clay in the Holderness Peninsula of north Humberside. Drift deposits are patchiest in the Humber Estuary.

The Drift cover has an important impact on groundwater flow and chemistry in the Chalk aquifer. Recharge occurs in the western outcrop area and natural flow is dominantly eastwards along the structural gradient, although flowlines are modified significantly by high abstraction rates in the Humberside urban centres of Hull, Immingham and Grimsby. Groundwater flow is restricted by the Drift deposits, especially where these are thickest to the east of the fossil cliff line. In the confined aquifer, groundwater flow rates are sluggish, particularly in Holderness and the southern part of Lincolnshire. The groundwaters show evidence of chemical evolution along flowlines with aerobic, often polluted groundwaters at outcrop and older, reducing and non-polluted groundwaters in the confined aquifer.

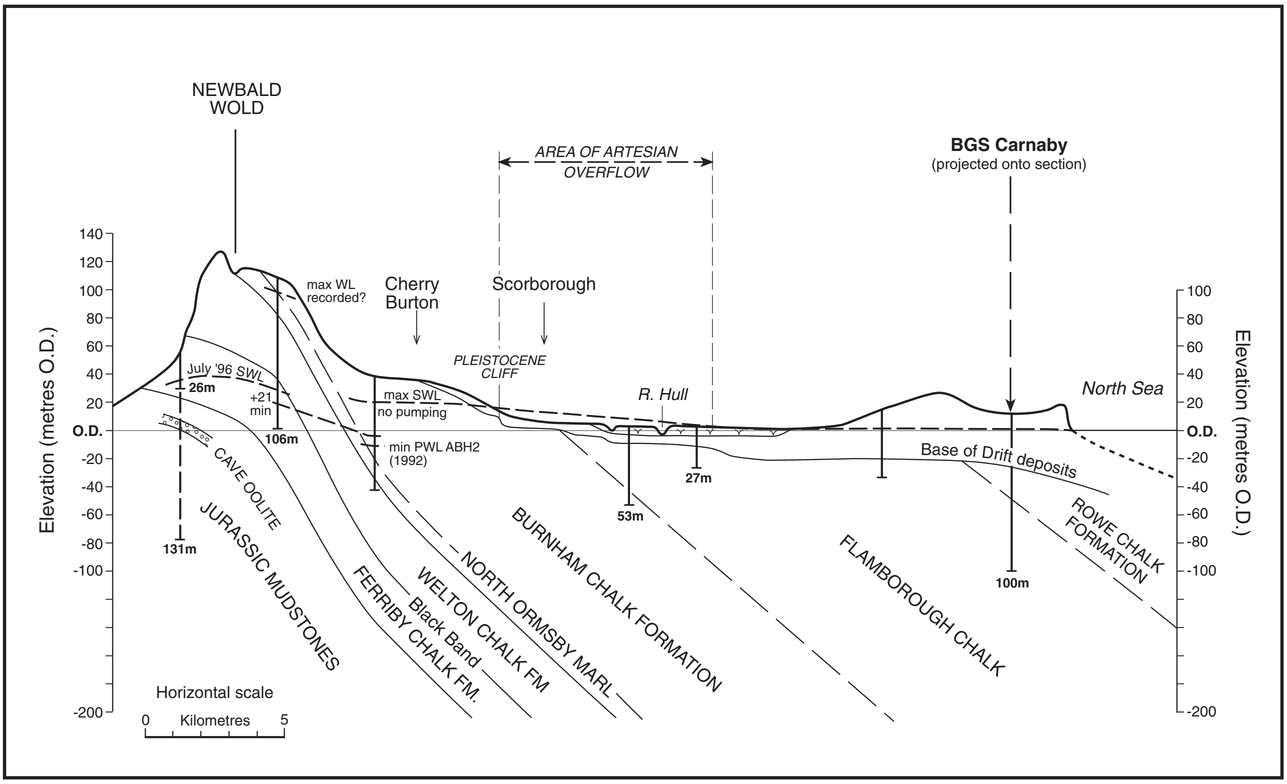


Figure 5.3. Cross section across Yorkshire, showing site of the Carnaby cored borehole

Table 5.2. Radiocarbon results for groundwaters from the Spilsby Sandstone of Lincolnshire with model ages calculated by correcting for mineral reaction after Evans *et al.*, (1979).

Sample	Well depth	Dist to coast	$\delta^{13}C$	Activity modern C	Corr. age
	m	km	‰	%	years
Driby 4	64	15.5	−12.1	61.66	modern
Candlesby 1	58	11.5	−11.6	27.63	4000
Welton le Marsh 1	77	10.0	−13.0	27.53	4900
Manby	?75	9.0	−14.9	45.40	2000
Maltby le Marsh 3	172	4.5	−12.8	18.97	7900
Mumby 1	162	1.5	−12.5	17.02	8600
Whitestacks	123	0.5	−10.6	3.38	20600
Butlins North	?83	0.0	−9.2	1.94	24000
Fenland Laundry	115	0.0	−10.5	0.33	>35000

Chalk structure also has a major impact on groundwater flow. The Chalk is of the order of 300 m thick but groundwater flow is largely restricted to the upper 50 m of the formation where fracturing is most well developed. Flow is also strongly influenced by localized folding: the N-S trending Hunmanby Monocline in Yorkshire and the E-W Caistor Monocline in Lincolnshire impose local restrictions on groundwater flow.

In the upper parts of the Chalk aquifer, groundwater movement along fissures has been relatively rapid and there has not been widespread preservation of palaeowaters. Saline zones are present in the coastal fringes of the Chalk, most notably in the Holderness Peninsula, Humber Estuary, Grimsby-Immingham areas and southern Lincolnshire. Combined radiocarbon, stable isotope and tritium (University of Birmingham, 1978) evidence indicates that saline intrusion is of relatively recent origin in the urban areas of the Humber and Grimsby-Immingham.

Stable isotope compositions of confined groundwaters investigated in the present study (Table 5.1) are mostly indicative of relatively modern recharge: $\delta^{18}O$ compositions are typically around −7.4‰, $\delta^{2}H$ typically −50‰ and $\delta^{13}C$ values mostly −14 to −11‰, although in coastal areas some of the groundwaters are affected by mixing with intruded seawater and stable isotope enrichments have therefore occurred. Activities of ^{14}C of >20 pmc typify the groundwaters of the confined Chalk aquifer (Table 5.1) and support the evidence of a relatively modern, though pre-industrial, age.

Saline groundwater of an older generation appears to exist in the Holderness Peninsula and southern Lincolnshire (University of Birmingham, 1978; Hiscock and Lloyd, 1992) where ^{14}C activities of less than 20 pmc are present (e.g. Table 5.1). Saline water present in the Chalk in southern Lincolnshire was taken as a body of seawater intruded during the Ipswichian Interglacial (ca 110 000 BP) by Lloyd and Howard (1978) but as groundwater with a significant component derived by upward leakage from the underlying Carstone by Hiscock and Lloyd (1992). Trace-element evidence (notably As) from the present study lends some support to the latter hypothesis.

Interstitial waters and bailed samples were taken from a cored Chalk borehole at Carnaby, 2 km from the coast, in Yorkshire (Fig. 5.2) which penetrated 72 m of Chalk below 28 m of Drift. The log of the borehole shows decreasing fissuring with depth, notably below 72 m but the temperature profile is effectively constant at 10.3±0.1 to depth indicating present day groundwater movement to −100 m. The conductivity profile also is nearly constant at 370±5. Interstitial water profiles also show relatively small

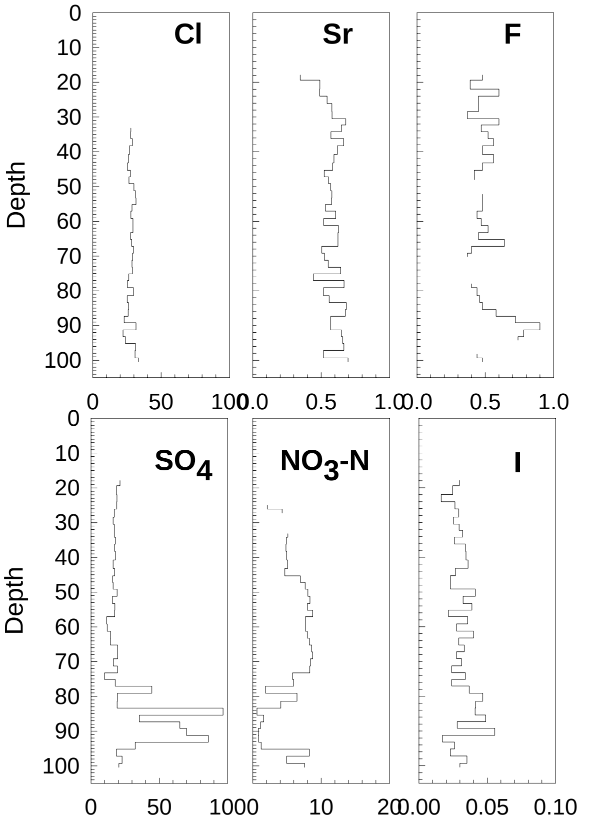


Figure 5.4. Interstitial water profiles from Carnaby No 1 borehole. Note the zone from 85 to 95 m depth containing slightly more evolved (probably older) water.

variation in Cl (25±5 mg L^{-1}). However several other indicators suggest that relatively older water is present between 80–95 m depth (Fig 5.4). Strontium which has been used as a key indicator in the southern UK Chalk shows no significant increase, but F, I and SO_4 increase with NO_3 decreasing to background levels. The $\delta^{18}O$ (−7.8±0.0‰) and $\delta^{2}H$ (−50±2‰) values are also almost constant. These results probably indicate that modern water (with high nitrate) is penetrating selectively to 100 m but the profile in general below 80 m may contain water of pre-industrial age. A ^{14}C activity of 68 pmc was found in bailed groundwater from near the base of the borehole at 96 m.

Unlike the Chalk of southern England, there is little evidence for the occurrence of freshwater at depth beneath the zones of saline intrusion. Lloyd and Howard (1978) mention the existence of borehole conductivity logs from Lincolnshire showing freshening of groundwater profiles with increasing depth but give no data and provide no information on their location.

Spilsby Sandstone

In Lincolnshire, minor aquifers of glauconitic sandstone of Lower Cretaceous and Upper Jurassic age (Carstone and Spilsby Sandstone Formations) are also used for water supply but abstraction volumes are comparatively small. Only the Spilsby Sandstone is exploited for public water supply. This formation outcrops in the west, to the west of the Chalk escarpment and dips north-eastwards conformably with the overlying Chalk (Fig 5.3). The Spilsby Sandstone is separated from the Chalk by some 70 m of largely impermeable clay, marl and ironstone deposits. It is also underlain by impermeable Jurassic Kimmeridge Clay. It therefore comprises a thin (ca 10 m) aquifer without hydraulic connection to other strata. Most groundwater abstraction is from the confined aquifer.

Chemical compositions of groundwater in the Spilsby Sandstone demonstrate evolution along the flow gradient from recently recharged, oxidizing and often polluted waters at outcrop, through to reducing non-polluted groundwaters beyond the redox boundary. Groundwaters show evidence of decreasing Ca and Mg and increasing Na down the flow gradient, considered due to ion-exchange reactions with clay minerals, especially glauconite, in the sandstone (Smedley *et al.*, 1994). Salinity increases slightly along the flow line, due mainly to increasing residence time and rock reaction rather than saline intrusion. On the coast at Skegness, Cl concentrations are still less than 200 mg L^{-1} (SEC values around 1300 μS cm^{-1}) and demonstrate that fresh groundwaters occur in the aquifer even on the coastal margins and probably also offshore.

Stable isotope and radiocarbon techniques have been used to assess the evolution of groundwaters along the flow line. Radiocarbon data are particularly diagnostic in demonstrating a relatively simple pattern of increasing residence time with distance along the line of groundwater flow. At the coastal margins, groundwaters in excess of 35 000 years old have been detected (Table 5.2). These are just 15 km or so from the outcrop area and indicate that groundwater flow (mainly intergranular) in this aquifer has been extremely slow. The aquifer has been unaffected by saline intrusion during Quaternary sea-level fluctuations.

5.3.2 North Kent

Two boreholes were drilled on the shoreline of the Thames Estuary at Reculver in North Kent near Herne Bay. The first borehole drilled to 205 m depth penetrated 32 m of Palaeogene strata overlying Chalk. The second borehole 1.8 km east of the first was only drilled to 104 m depth. These boreholes were partially cored and were geophysically logged to characterize the lithostratigraphy, vertical salinity variation and groundwater movement. These results have been compared with groundwater in the Chalk at boreholes up to 8 km inland (Fig 5.5).

Geophysical fluid logging of the first borehole showed a complex time-varying salinity profile which was caused by invasion of the lower part of the borehole by waters from the upper part. Fluid logging at intervals throughout a 204 day pumping test showed how the invaded waters were slowly recovered and a tripartite salinity profile became established which matched that obtained from centrifuged pore fluids from core material.

The salinity profile (Fig. 5.6) confirms an upper brackish zone from –30 to –52 m (OD) with Cl 4000 mg L^{-1} overlying a zone of higher salinity –52 to –94 m (12 000 mg L^{-1} Cl) overlying a basal zone of steadily decreasing salinity (4000 mg L^{-1} Cl) from –94 to –200 m OD. Borehole flowmeter logging showed there were 7 main water inflows from the Chalk. The flow logging demonstrated the upper brackish, middle saline and lower brackish zones transmitted flow in the ratio 4:2:1. Comparison of the geological and geophysical logs with the inland boreholes resolved the stratigraphy and revealed the northward dipping Chalk aquifer was interrupted by

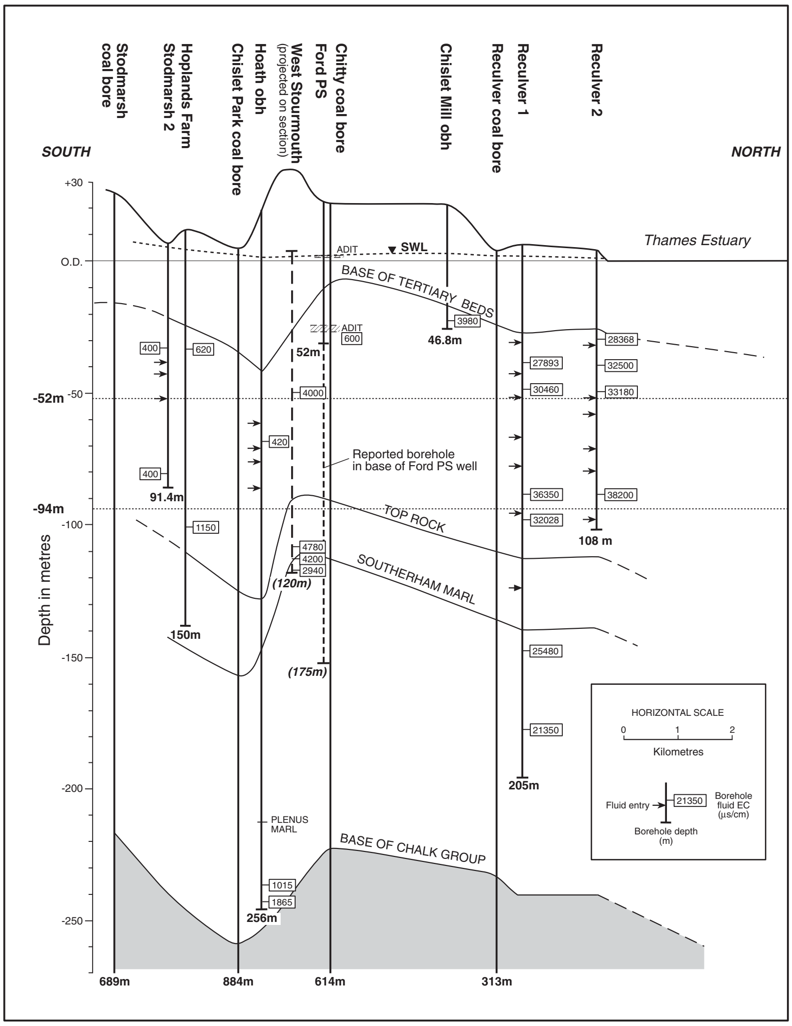


Figure 5.5. North to south cross-section though NE Kent showing the position of the Reculver boreholes

E-W trending fold axes and showed that the coastal borehole site was immediately downgradient of an anticlinal fold structure representing a barrier to groundwater flow from inland. The combination of unconfined Chalk at the coast further east and the anticlinal fold barrier to throughflow provides the framework for the tripartite salinity distribution observed.

Pumped groundwaters and porewaters of the upper brackish zone have low tritium content (<0.7 ± 0.2 TU) and are not modern recharge. Model ages and ^{14}C activity support the idea that fissure water in the upper zone is <2000 years but is of mixed origin and therefore could represent a mixture of much older matrix water and younger fissure water. There was no evidence of any component of modern seawater or water from Tertiary strata in the pumped water during the short period of pump testing of both boreholes.

Groundwaters of the upper zone down to −52 m OD are consistent with throughflow refreshening of a body of older Holocene seawater. This sea water could have entered and partially contaminated the aquifer during the sea level rise in the Thames estuary area although no other evidence of sea levels higher than the present is available. The freshening is thought to be associated with the maximum fissuring and porosity development that has occurred down to that depth which is recognized by the geophysical logging. The morphology and depth of the buried channels immediately offshore reported by Bridgland and d'Olier (1995) strongly suggests a link between the developed permeability of the upper zone and the hydraulic base level at –50 to −60 m OD.

Groundwater of the middle saline zone is isotopically similar to that of the brackish zone above. This has only 50% of the throughflow of the upper zone, and so has not undergone the same amount of freshening. This is probably due to its lower porosity and permeability at depth. The zone of lower chloride water below –100 m, having a depleted δ^{18}O signature (–8.2‰) is considered to be an older generation of fresh groundwater emplaced during the colder climatic conditions of the Devensian and when sea level was much lower. This lower zone water has elevated Sr, Ba and F concentration consistent with the geochemical model found elsewhere in UK (Edmunds *et al.*, 1987) for evolved groundwater in the Chalk.

Groundwater inland at Ford PS contains detectable tritium (1.5 TU) and is dominantly pre-1950 water with a small quantity of modern recharge. On pumping it draws in more saline (older) water from the low-lying coastal area to the north. Groundwater at Hoath observation borehole (EC ~1200 µS/cm) has no detectable tritium and is isotopically depleted. It is also considered to be a fresh palaeowater recharged in the Devensian.

Hydrogeochemical investigations of the area to the west of Reculver have revealed the occurrence of palae-

Table 5.3. Isotopic data for groundwater samples from the confined Chalk and Lower Greensand aquifers of the Medway area of Kent. Greensand samples are from below the Chalk outcrop.

Locality	Distance from Chalk outcrop	$\delta^{18}O$	$\delta^{2}H$	$\delta^{13}C$	Activity ^{14}C
	km	‰	‰	‰	pmc
Chalk					
Sheppey Ltd, Rushenden	8	−7.8	−51	−14.2	38.5
Funton Brickworks	4	−7.6	−49	−6.7	4.14
Co-Steel, Sheerness	10	−8.4	−56	−14.8	10.6
Sheerness Port	10.5	−8.4	−56	−14.3	2.95
MC Air Filtration	3	−7.2	−48	−16.4	79.3
Motney Hill WTW	2	−8.1	−48	−14.5	40.1
Lower Greensand					
Akzo Nobel	0	−8.5	−54	−12.5	1.32
Capstone PS	0	−7.9	−49	−16.8	26.5
Luddesdown PS	0	−7.2	−45	−16.5	38.9

owaters in the Chalk and Lower Greensand aquifers, though of limited regional extent. Chalk outcrops in the uplands escarpments of the North Downs but towards the Thames Estuary (northwards) becomes partially and then completely confined in turn by Tertiary silts, sands and clays of the Thanet Beds and the London Clay. Groundwaters from the deep confined Chalk aquifer (>150m depth) on the Isle of Sheppey (Table 5.3) have ^{14}C activities of less than 5 pmc with slightly negative $\delta^{18}O$ values (−8.4‰). This groundwater is relatively fresh (SEC 1000 µS/cm). Groundwaters from closer to the feather edge of the confining Tertiary beds (Table 1.3) are of more recent origin with higher ^{14}C activities and modern stable isotope signatures. Some groundwaters from the deeper Lower Greensand aquifer (ca. 300 m depth) are also fresh palaeowaters (SEC <900 µS/cm) with radiocarbon compositions of 1 pmc and light stable isotope compositions.

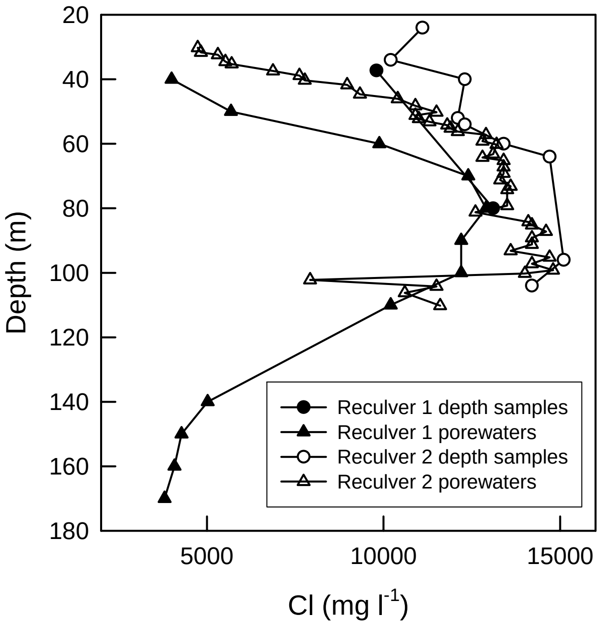


Figure 5.6. Variation in Cl content in depth samples and interstitial waters in Reculver 1 borehole

5.3.3 South Coast – Brighton to Chichester

The geological structure of the south Downs has a marked impact on the hydrogeology of the area. A number of east-west folds cross the area, the most important being the Chichester syncline which has a gently dipping south limb (2–3°) and a steeply dipping north limb. It is bounded to the south by an anticlinal structure – the Portsdown anticline which becomes the Littlehampton anticline in the east. Up to 160 m of Tertiary sediments and drift cover the Chalk surface near the syncline axis, preventing or restricting groundwater flow from north to south. These structures continue offshore but are flexures of the larger regional Hampshire-Dieppe Basin (see Chapter 6) which brings the Chalk to outcrop in the Channel some 30 km offshore. The base level for the area during the Devensian was controlled by the large palaeovalley (at about –60 m) some 20 km south of the present coastline (Hamblin *et al.*, 1992) and there is evidence that the immediate offshore area was subject to erosion and sediment deposition, including peat, during the periglacial to temperate oscillations of the Devensian (Bellamy, 1995).

The aquifer of the South Downs has been studied in detail from Brighton to Chichester in the west (Fig 5.7). This is an area with a high population density and which relies almost entirely on groundwater resources. In the east the unconfined chalk aquifer forms the coastline and since the turn of the century intrusion of saline water up to 500 m inland has been recorded (Monkhouse and Fleet, 1975) causing some abandonment of boreholes. This necessitated the replacement by sources further inland, although in later years one source, Eastbourne has been reinstated. Hydrogeophysical logging has revealed that the saline water moves inland along discrete horizons yet at the same time freshwater may be moving seawards. Careful management of the aquifer in recent years has led to the optimum use of the coastal zone, restricting the pumping (and sea water invasion) during times of lower water levels in summer (Headworth and Fox, 1986).

Geological cross-sections based on geological and geophysical logging data shows that groundwater recharged on the South Downs flows south towards the Channel but is also interrupted by E-W trending fold structures in a mirror-image of the geological structure

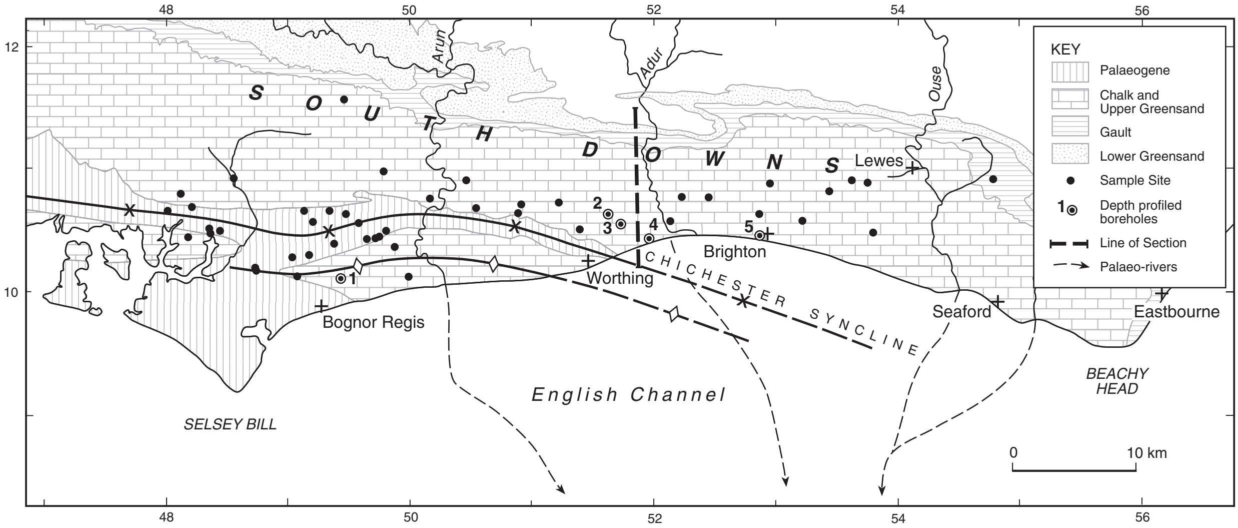


Figure 5.7. The area of South Downs with sites investigated during the PALAEAUX project. Depth profiles have been obtained from1) Shripney, 2) Sompting, 3) Lancing (Crowshaw) 4) Lancing, 5) Brighton.

seen in the North Downs in N.Kent. Detailed lithostratigraphic comparisons in the Chichester area show the groundwater is moving up-sequence through the New Pit, Lewes, Seaford, Newhaven and Tarrant Chalk units as it flows south towards the coastline where it is confined by drift. The physical properties of these Chalk units differ and this affects the aquifer properties and introduces variation in well yields.

In the Brighton area the Chalk aquifer is unconfined at the coastline and modern seawater can enter the aquifer. Fluid logging shows water movement is greatest in the top 50 m and fluid temperature logs again show cooler faster circulating groundwaters above –55 m OD and –95 m OD corresponding to offshore river valley base levels.

A new geochemical database for the regional Chalk aquifer within 10 km of the coastline has been obtained with sites shown in Fig 5.7. The sampling was concentrated on the area around the Chichester syncline where there was evidence of saline waters and variable hydrogeological conditions relating to structure have been inferred. Several wells that were accessible were geophysically logged and depth sampled. In the Brighton area, wells in the Lower Greensand were also sampled. No hydrogeological evidence was available from wells immediately offshore and interpretation of conditions is conjectural. There are however records of freshwater in Tertiary sediments in a well at Spithead fort near Portsmouth at a depth of 100 m (Whitaker, 1910).

The isotopic and radiocarbon results obtained in this study are shown in Table 5.4. Freshwater was identified at a depth of 230 m beneath Brighton with Cl of 22 mg l^{-1}, considerably lower than the near surface (modern recharge) groundwater. The lowest groundwaters (below 180 m depth) have δ^{13}C of around −1‰, indicating significant water-rock interaction. This water also has a light δ^{18}O and δ^{2}H (−7.8 and −51‰ respectively), compared with local modern water. The lowest ^{14}C value in this aquifer is 1.52 pmc; other depth samples have rather higher and may have undergone some mixing in the borehole profile. It is likely from these data that late Pleistocene palaeowater is still be present at depth and that this water has been part of the general movement towards the centre of the Channel, especially during the time of lowered sea level.

The overall evolution of the groundwater in the South Coast region is summarized using strontium relative to chloride (Fig. 5.8). Strontium has been used elsewhere in the study of the UK Chalk as a good indicator element for groundwater evolution (Edmunds *et al.*, 1987). Whereas Mg solubility may be limited by the solubility of dolomite, strontium solubility is only limited by celestite and its increase in groundwaters should be related to the progressive water-rock interaction. The upper limit of Sr is controlled by celestite and these maximum values are found in some of the most saline waters from Shripney. However these have a different chemistry to dilute sea water in the Chalk at Lancing (Edmunds *et al.*, 1999). The waters with very high Sr are considered to represent a modified connate water where strontium was derived from aragonitic

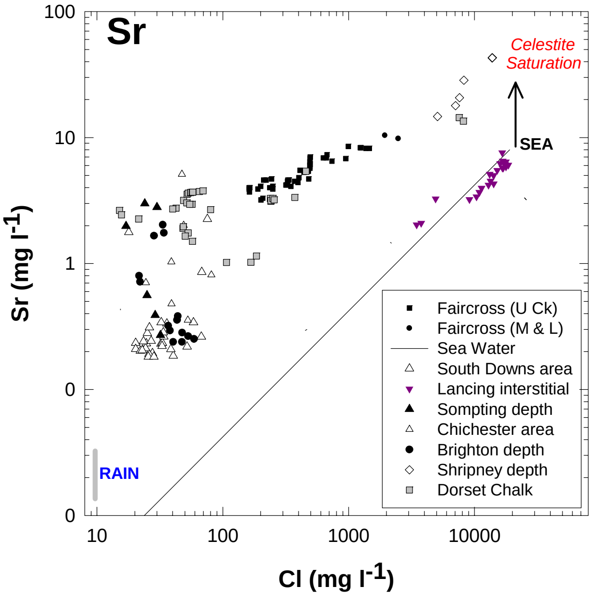


Figure 5.8. Sr vs Cl plot for groundwaters from the South Downs. Also shown for reference are published data from Berkshire (Faircross) from Edmunds *et al.*, 1987.

tests and/or high-Mg calcite in the early chalk sediment. This situation has been described in East Anglia (Bath and Edmunds, 1981). Where such compositions are found it is concluded that little or no movement has taken place in the aquifer since its time of formation.

The fresh groundwaters have evolved from rainwater, reacting congruently with chalk during recharge to give Sr concentrations around 0.2 mg L^{-1} within the unsaturated zone. The water retains the input Cl concentrations but show an increase in Sr resulting from incongruent reaction of chalk. Thus the increase in Sr/Cl ratio also represents a qualitative residence time indicator.

This model for evolution of the Chalk groundwater chemistry can be applied to the South Downs area as well as much of the UK Chalk. The interstitial waters from Sompting show strong enrichment in all elements although Cl concentrations in this borehole do not exceed 51 mg L^{-1}. The deepest waters found in the Chichester syncline have a Cl maximum of 202 mg L^{-1} which is the highest value found in this area.

The Albian sands beneath the Chalk near Worthing (Fig. 5.9) were investigated by pumping tests, hydrogeophysical logging and geochemical sampling on a borehole at Sompting (Buckley and Edmunds, 1998). This borehole penetrated the Lower Greensand (Albian) sequence from 404–457 m with a static water level of 26 m OD. This water (Table 5.4) is of low mineralization and contains freshwater with an uncorrected age of ca. 7800 BP. The very light $\delta^{13}C$ composition indicates soil CO_2 to be the main carbon source and that reaction with carbonate is incomplete. The uncorrected age therefore is considered close to the true age of the groundwater. The stable isotope analyses ($\delta^{18}O$, $\delta^{2}H$) as well as the low helium confirm that these waters are of Holocene age.

The situation on the south coast area is summarized in cross section (Fig. 5.9). As well as modern saline intrusion found locally and exemplified in the data from the cored borehole at Lancing, residual salinity may also be derived from connate water still present in the Chalk matrix (as demonstrated in the case of Shripney). Fresh palaeowater is found at depth in several locations in the Chalk and probably offshore beneath confining beds, as well as in the Albian (Lower Greensand).

Table 5.4. Isotopic and chemical data for the Chalk of the South Coast area. * – ^{14}C data awaited.

Locality	Depth	$\delta^{13}C$	^{14}C	Sr	Cl	$\delta^{18}O$	$\delta^{2}H$
	m	‰	pmc			‰	‰
South Downs							
Northhmundham		−12.1	*	6.36	202	−14	−49
Park Farm		−13.5	*	0.86	68.1	−6.2	−34
Groves Farm		−13.4		0.34	58.5	−6.2	−38
Wicks Farm		−16		0.26	67.5	−6.2	−39
Hollards Farm		−13.3		2.26	75.3	−6.1	−42
Fishbourne		−15.5		0.28	25.1	−6.2	−42
Funtington		−16		0.23	20.3	−6.5	−42
Lavant		−17.3		0.23	24.7	−6.9	−39
Chichester							
Shripney	32		*	17.9	7070	−4.6	−30
	64		*	20.7	7610	−4.2	−30
	92		*	28.5	8240	−4.2	−30
	162		*	42.9	13800	−3.4	−26
	190		*	43.0	13900	−3.8	−24
Poole Harbour							
Stoborough	120	−4.7		3.17	48.8	−7.2	−42
	130	−4.1		1.90	48.2	−6.9	−42
	180	−3.3		1.96	48.5	−7	−42
	195	−1		3.03	51.8	−7	−42
	240	−0.3		1.75	53	−6.9	−42
Wareham C'mon	120	1.5	1.64	3.27	240	−7	−41
	195	−0.2	1.84	3.28	239	−6.9	−38
	210	0	63.5	3.35	373	−7.1	−46
	240	−0.4	2.8	3.12	241	−7	−42
	266	−0.2	4.99	3.16	242	−7	−45
	280	−0.8	2.09	3.28	250	−7	−45
	299	−0.7		3.20	256	−6.8	−41
Brighton							
St. Peters Church	24	−9.5	72.95	0.24	47.3	−6.1	−43
	36	−6.6	82.36	0.24	40.3	−6.2	−42
	58	−9.6	75.38	0.29	38	−6.2	−41
	73	−3.9	1.53	0.32	36.8	−6.4	−40
	150	−6.2	43.68	1.66	28.4	−6.6	−41
	180	−0.1	20.12	0.80	21.6	−7.2	−46
	230	−1	14.94	0.72	22	−7.8	−51

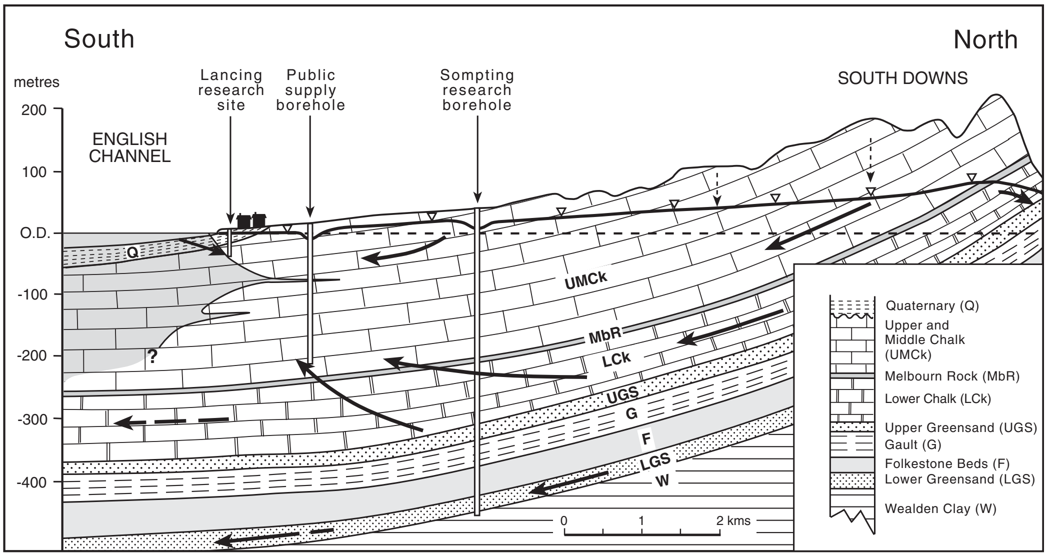


Figure 5.9. Hydrogeological cross section through the South Downs near Worthing

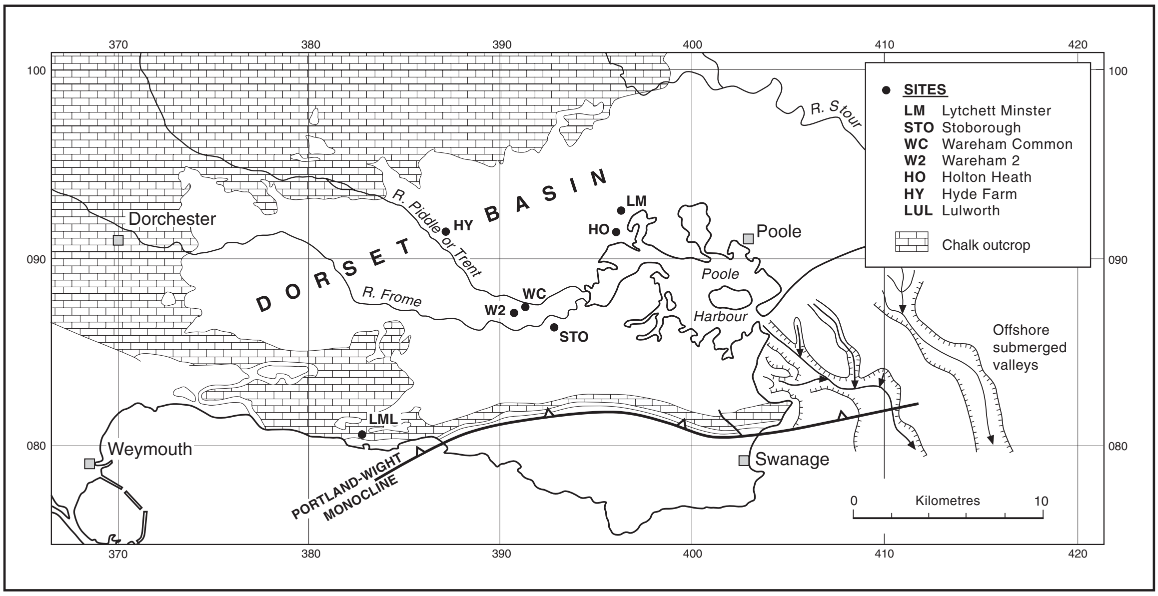


Figure 5.10. Hydrogeological map of the Dorset Basin showing samples refered to in PALAEAUX

5.3.4 South Coast – Dorset and Poole harbour

The Chalk groundwater evolution has also been investigated at two sites a) Lulworth adjacent to the Dorset coast which shows fresh water to a depth of –170 m. and b) several sites in the centre of the Dorset Basin where newly drilled boreholes provided access to about 300 m below OD (Fig 5.10).

At Lulworth, the unpublished data for interstitial waters from a research borehole completed in the late 1970s have been compiled and the results are shown here (Fig. 5.11) in conjunction with a new geophysical log carried out during the present study. It is found that the base of the present day flow system is around –65 m OD as defined by the temperature. Below this depth also a very slight decrease in conductivity is noticed and these quality variations correspond to the interstitial profile analysed some 20 years earlier. High nitrate is found above 65 m and below this depth baseline values occur. No radiocarbon data are available for this water but stable isotope results give a modern signature. Some suggestion of a more mature water is indicated in the pore water profile below 140 m.

Groundwater in the confined aquifer at Wareham is relatively fresh (<1000 µS/cm down to −240 m depth in Stoborough borehole). Fluid temperature logs suggest a depth of –170 to –180 m OD is a local base for present day groundwater circulation in the Chalk aquifer. This is considerably deeper than seen elsewhere along the South coast and is believed to be due to local geological structure (the Lulworth monocline) which has prevented groundwater from discharging to the normal hydraulically controlled base levels, and the fact that the Palaeogene strata are in excess of 100 m thick in places so that permeability development to base levels was mostly within the Palaeogene strata. Results of pumping tests of the Poole Harbour area boreholes each show low yields with drawdowns in excess of 70 m indicating low permeability for this area of the south coast.

Interstitial waters from terminal core also indicate fresh water to depths of 250 m below surface and there is no evidence of any seawater contamination of the area or residual saline formation water (as found elsewhere in the Chalk). One possible explanation is that much of the original saline formation water was expelled from the sediment during the Alpine orogeny, which affected this part of Britain 20–40 million years ago. However the radiocarbon data are given in Table 5.4 and suggest that the bulk of the water from the depth profiles is late Pleistocene in age. The geochemical characteristics of the water (high F, Sr and enriched ^{13}C) confirm that despite the freshness of the water it is of considerable age.

Some modelling work was carried out using SUTRA to investigate the timescales for density driven inundation of the underlying aquifers following a rise in sea level. The model geometry was simplified, but was designed to give an indication of whether it is reasonable to expect freshwater to exist in the deeper aquifers following the rise of sea-level following the last glaciation. The results show that the density difference between fresh and sea water is a sufficient driving force to allow sea water to penetrate into coastal sediments over timescales that are relevant to the timescale since the Flandrian transgression. Using realistic values for aquifer and aquitard thicknesses and permeabilities it was shown that sea water can penetrate the full thickness of the modelled system at the coastline (to 400 m) in a period of about 30 000 years. The model also shows that it would be reasonable to expect to find freshwater offshore near the coast in the Lower Greensand formation at the present time, as this formation is protected from the sea water by the low permeability Gault clays.

This modelling work also shows that the predicting water quality from physical models is difficult as the results are very dependant on the values used for, particularly, vertical permeability. This parameter is very difficult to measure and very few values exist for most aquifer and aquitard materials.

5.3.5 East Midlands

The East Midlands (Sherwood) Sandstone in central England is a typical red-bed aquifer which has been the sub-

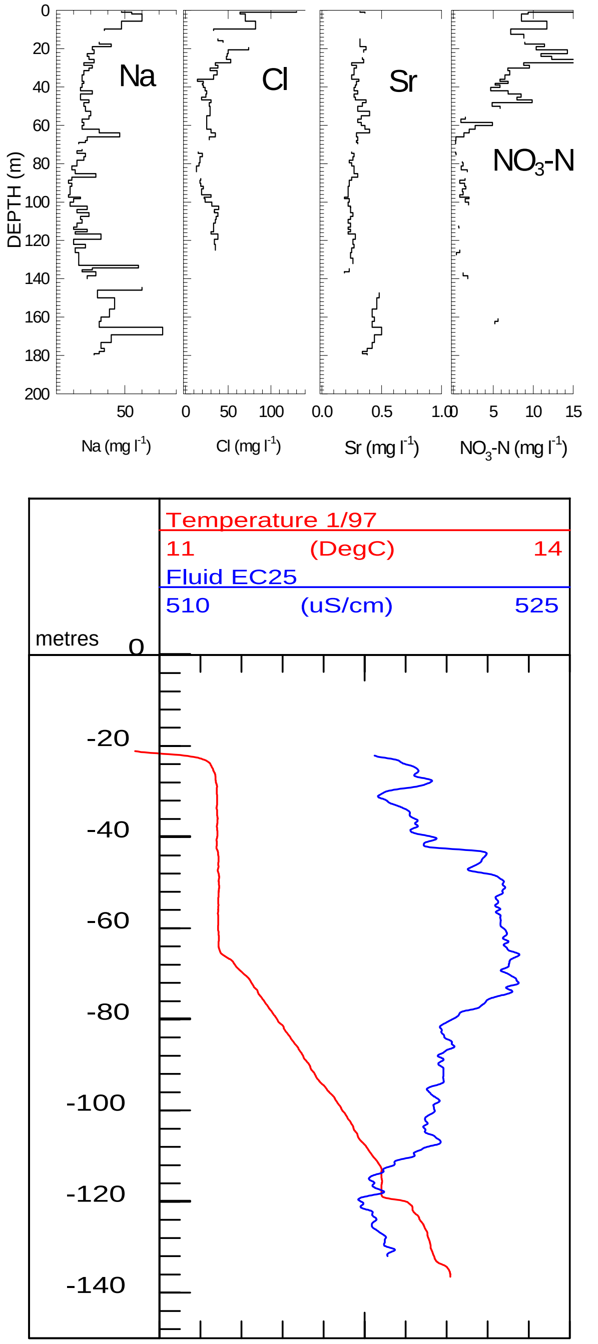


Figure 5.11. (a) Interstitial water profiles and (b) recent geophysical logs for the Lulworth borehole

ject of detailed hydrogeological investigations (see Ch 1). It is the main model for the PALAEAUX investigations since it is considered that fresh groundwater resources which persist to depths in excess of 500 m could have been influenced by sea level changes and/or the presence of the Devensian ice sheet with a stationary front within a few tens of km of the aquifer. The results are updated in this report. New work has included:

(viii) depth sampling profiles proving stratification with palaeowaters at depth;

(ix) reinterpretation of data to investigate palaeoclimatic information and the use of chemical trends as age indicators;

(x) modelling of the impact of glaciers on the groundwater recharge conditions at and around the last glacial maximum.

New depth profiles

Two boreholes, Hayton and Grove, were sampled to investigate any age stratification in the aquifer. The sampling intervals were based on information obtained from hydrogeophysical logging. Hayton was a newly drilled borehole, although Grove was an established pumping station within the confined aquifer which had been in use for more than 30 years.

Selected data have been plotted for both boreholes on the same depth scale relative to mean sea level (Fig. 5.12). Two distinct water types are seen at Hayton. Water with a Holocene isotopic signature (around −8.0‰) but with low Cl (6.0 mg L^{-1}) is found to a depth of at least 200 m. Below this, a zone of isotopically light (around −9.2‰) water is found also with high sulphate concentrations (similar to groundwater in the deeper confined zone) and slightly higher Cl as well as other chemical indicators (Li and Sr for example) indicative of longer residence time. Although possibly distorted by the modern groundwater development it is clear that residual cooler late Pleistocene water is found at depth overlain by Holocene (pre-industrial water); despite being close to outcrop no evidence of modern water is found. Radiocarbon data confirm that the upper section is water of Holocene age, although one spurious age at 200m (maybe inflow from adjacent pumping borehole) is discounted for interpretation; the radiocarbon values of the three deeper groundwaters range from 4.6 to 17.3 pmc (with corresponding δ^{13}C values from −7.8 to −10.8‰). The lowest value is considered to be the most representative water giving a corrected age of 17.1 ka BP.

At Grove where pumping has taken place for over 30 years no significant stratification remains but the stable isotopic composition of the water (δ^{18}O −8.3‰) lies just within the Holocene range and this is confirmed by the radiocarbon analyses which give an average of 31.7 pmc which correspond to a corrected age of 7.2 ka BP. The

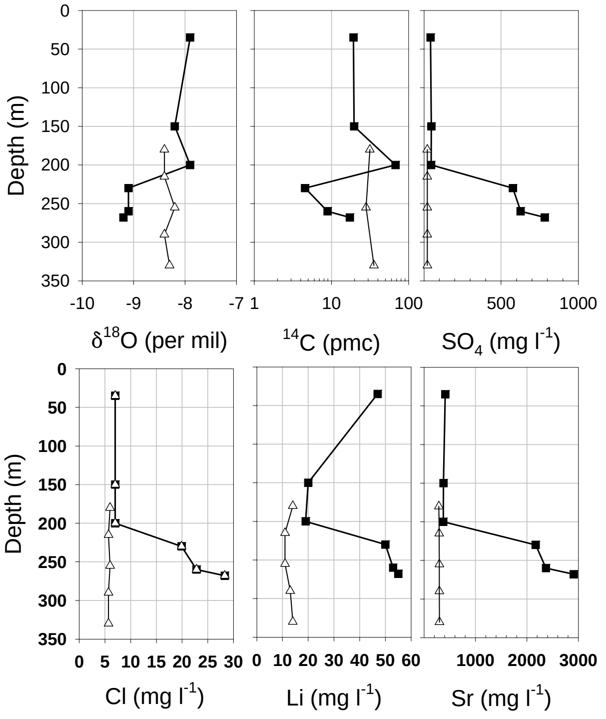


Figure 5.12. Geochemical logs of depth profile obtained from the Hayton borehole, East Midlands

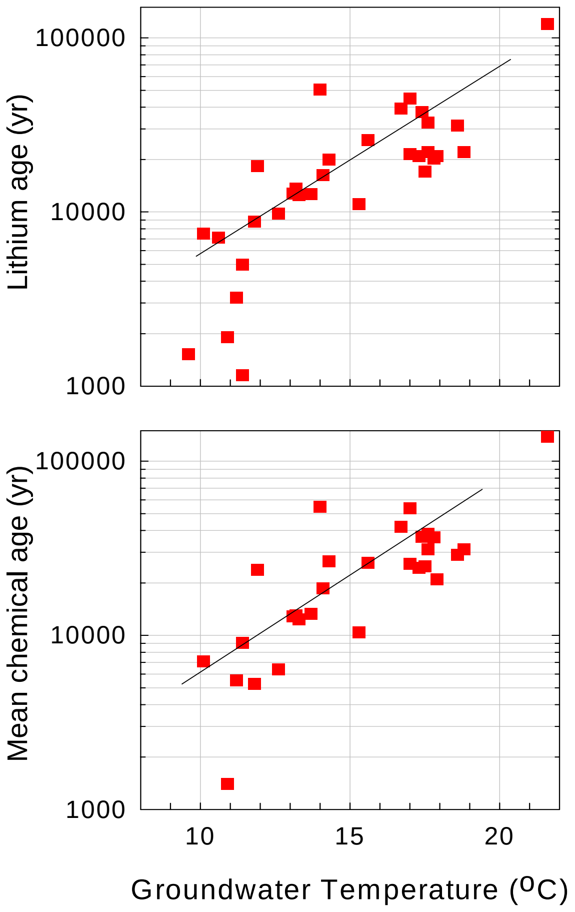


Figure 5.13. Chemical ages, calculated from the individual ages based on five of the parameters with the highest regression coefficients (Li, Rb, Mn, Mo and Sr), and lithium ages for groundwaters in the East Midlands aquifer.

other indicators are generally intermediate between the two waters at Hayton. The Cl concentration of 6.1 mg l^{-1} is one of the lowest in the aquifer, but there is no suggestion of the high sulphate water that is preserved at Hayton.

Residence time indicators

The possibility has been examined during the re-examination of the East Midlands data that time-dependent water-rock reactions give rise to "linear" build up of reaction products, especially inorganic major and trace elements which can be used to estimate groundwater residence times up to and beyond the range of radiocarbon (Edmunds and Smedley in press). Radiocarbon ages and other indicators of palaeowaters, verified in previous studies, have been used to explore the increase in concentration of various ions and isotope ratios along the flow lines as water moves down-gradient. The use of Cl and the halogen elements as inert, qualitative residence time indicators in this aquifer has also been considered. Chemical data for groundwater which have no corresponding radiocarbon measurements are then used to derive groundwater ages and to expand the understanding of residence time distributions in this aquifer.

Eight parameters (Rb, Cs, Sr, Na/Cl, Li, Mn, Mo and $\delta^{13}C$) were considered as potential residence-time indicators. These mainly comprise trace elements which are progressively released by incongruent or disproportionation reactions from carbonate, silicate or oxide minerals and ideally they are unaffected by solubility controls to limit upper concentrations neither have they reached plateaux controlled by partitioning between the solid and aqueous phases.

The indicators when plotted against corrected carbon-14 age increase progressively across the aquifer, indicating that reactions continued during times of low flow or during glacial or permafrost conditions.

The "chemical ages" were calculated from the individual ages based on five of the parameters with the highest regression coefficients (Li, Rb, Mn, Mo and Sr). In Fig. 5.13 the chemical age as well as the Lithium age is shown plotted against temperature as a proxy for distance down-gradient. Only those results for the pre-industrial waters are shown since the modern (polluted) waters generally give negative ages. The age range for fresh groundwaters is then extrapolated beyond the effective limit of radiocarbon dating (30 ka) and an age range of up to 160 ka is indicated.

The overall timespan indicated for the current main episode of fresh water recharge, taking freshwater to a depth of around 500 m is consistent with the relatively cool period of the Devensian from ca 110 000 BP to the start of the glacial maximum, when throughflow was controlled initially by lower sea levels, assisted by access to the surface through faults or glacial channels although these only reach 60 m in the area. Continuous evolution of the hydrochemistry is considered to have taken place, but there is a hiatus between the main group of fresh groundwaters and the deeper saline waters.

Hydrodynamic Modelling

Modelling was performed using MODFLOW to assess the impacts of ice cover over the East Midlands area. The model of present day conditions shows, as expected that the predominant flow direction is from the outcrop area towards the sea. The extent of the flow towards the sea, and the velocities, depend on the position of the no-flow boundary used to imitate the coastal boundary condition but under present day conditions the model shows that freshwater can flow to great depth in the aquifer. The effective "end" of the flowline is controlled by the permeability of the overlying aquitard which also affects the groundwater velocity.

As a glacier passes over or near to the region it immediately alters the direction of groundwater flow in the aquifer. The flow is changed from a predominantly E-W direction to a N-S direction, with water recharging beneath the glacier and discharging in front of the permafrost region. As the glacier advances water flows further south. When the glacier retreats, the heads soon regain the same pattern as before the onset of glaciation. Thus the overall effect of the glaciation on the aquifer is to displace the water southwards, rather than eastwards towards the coast. There is some eastwards movement at the edge of the outcrop area. Particle tracking shows that, over a period of about 500 years, water originating immediately below the confining layer will move about 20 km southwards and up to 6 km eastwards as the permafrost region moves directly above. This compares with a maximum water movement of 5 km eastwards in 500 years under present climatic conditions.

In the modelling various assumptions have been made about the position of the glacier and the effect and position of the permafrost region. The uncertainties in these processes are such that it is not possible to accurately predict the movement of water in the aquifer under glaciated conditions. It is possible that the glaciers would have moved water further into the aquifer than under present climatic conditions, but the extent of that movement is uncertain.

The modelling has highlighted the difficulty of using physical models to constrain the possible age of groundwaters . The conclusion from PALAEAUX suggests that the water chemistry and isotopic composition is needed to constrain the aquifer parameters used in the physical modelling.

5.4 Isotopic overview

Radiocarbon data from Chalk aquifers may not readily give residence time information owing to the dilution with carbonate-derived carbon as well as uncertainty over the correct value for initial carbon activity (Kloppmann *et al.*, 1998; Elliott, 1999). The data from the present programme are summarized in Figure 5.14. Most of the groundwaters from the Chalk show an exponential increase in ^{13}C in line with incongruent reaction with the host carbonate. Evolution along this pathway is likely to be at most a qualitative indication of residence time. By contrast, groundwaters from the Lower Greensand are less affected by carbonate exchange and can more readily be modelled to provide a quantitative indication of age.

An alternative method of assigning an approximate age range to Chalk groundwaters is available. In Britain and elsewhere, Holocene and Devensian (late glacial) groundwaters can be distinguished on the basis of their oxygen and hydrogen stable isotope ratios. Devensian groundwaters are characteristically depleted in ^{18}O and ^{2}H compared to waters recharged in modern times. Figure 5.15 shows data for Chalk groundwaters collected during

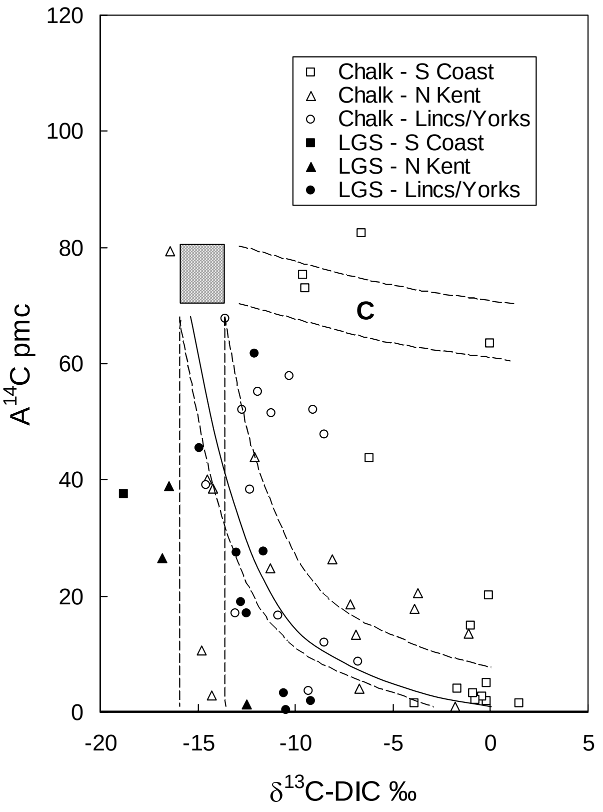


Figure 5.14. Plot of radiocarbon activity in % modern carbon (pmc) versus δ^{13}C-DIC in ‰ for samples collected during the study from the Chalk and Lower Greensand aquifers. The shaded box shows the range of carbon isotopic starting compositions in typical groundwaters. **A** indicates the trend for evolution by radioactive decay alone from the initial value. **B** indicates reaction via the incongruent dissolution pathway (solid median line indicates the situation in the London Basin). **C** indicates mixing.

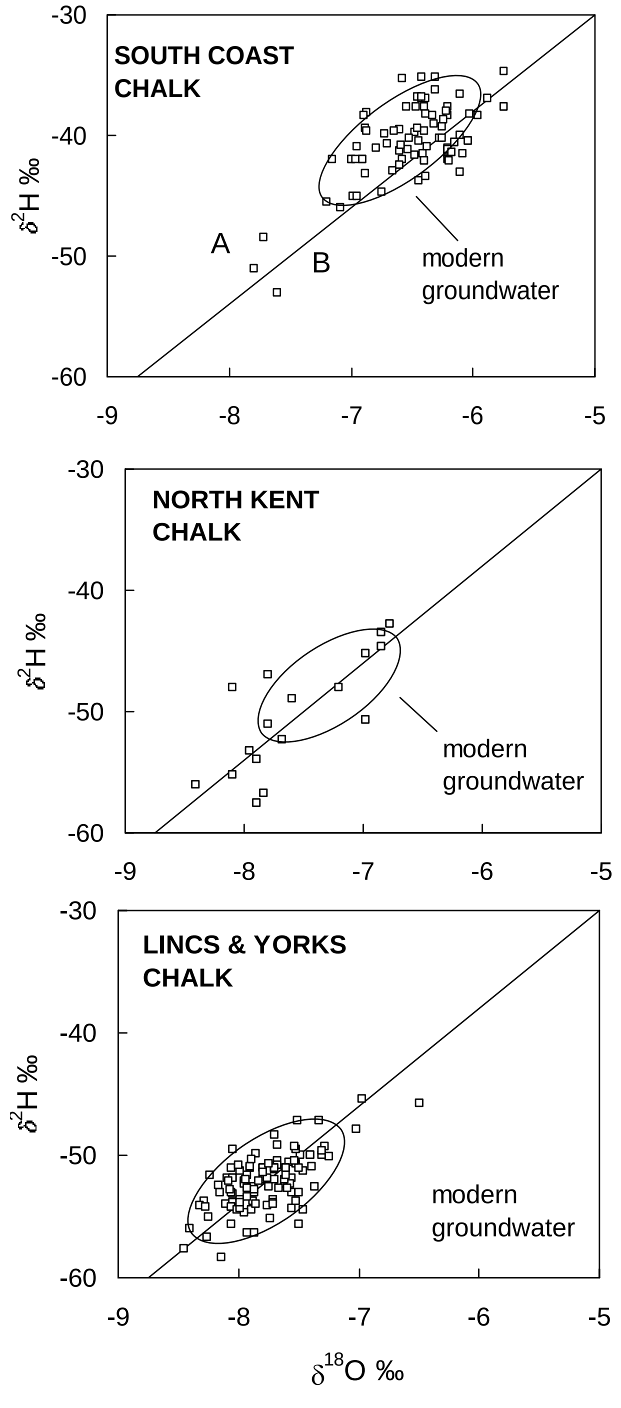


Figure 5.15. Plots of δ^{2}H versus δ^{18}O for Chalk groundwaters collected during the study. For each region the compositional envelope for modern recharge is shown. Relatively few samples have the depleted isotopic composition typical of pre-Holocene waters.

the study. Samples from Dorset and the Chichester-Brighton area are included in the South Coast plot, those from the Reculver and Sheppey areas in the North Kent plot, and samples from north Lincolnshire, Humberside and east Yorkshire in the Lincs & Yorks plot. In each case a field showing the compositional range for modern groundwaters in the region is shown. The Chalk is not an ideal aquifer type for preserving palaeowater compositions because of the amount of fissuring, and the data reflect this in that isotopically-depleted waters are relatively rare.

In the south coast (Fig 5.15) the few unequivocal palaeowaters, recognized on the basis of stable isotopic data were found at depths below –200 m OD in boreholes of the Chichester-Brighton area although from radiocarbon data the Poole Harbour area also must contain palaeowaters. In North Kent the area inland of Reculver also yielded palaeowater signatures. In contrast few palaeowaters are recognized in the Chalk from the Lincolnshire and Yorkshire Chalk. This is mainly due to the absence of sample availability from boreholes as deep as those available at the south coast. Structural controls play an important part both in the emplacement of palaeowaters in the Chalk and in their preservation. This is shown especially by the preservation of saline (modified connate water) in the borehole at Shripney.

5.5 Conclusions

The main conclusions may be drawn concerning the evolution of groundwaters

- In coastal N Kent there is evidence that fresh water of Late Pleistocene age, having an isotopically light signature was invaded by sea water or estuarine water during the Flandrian transgression. Fresh palaeowater is also preserved at depth inland and has not been flushed due to E-W folding parallel to the coast.
- Confined Chalk groundwaters in the Thames estuary at depths of ca −100 m OD have been shown to be palaeowaters with a $\delta^{18}O$ −8.4‰ and ^{14}C down to 3 pmc.
- There is a complex distribution of freshwaters and saline waters in the Chalk along the Channel coast (South Downs area)where it is concluded, that depth of circulation of modern water controlled by sea level does not exceed −100 m OD. Modern sea water invasion is also recognized. Fresh palaeowaters to −250 m OD represent groundwater which was recharged under lower heads controlled by the Central Valley of the Channel and preserved at depth.
- Both in Kent and along the south coast, the migration of groundwater in the N-S direction both in former times and at the present day, has been controlled by E-W structures. At one location, Shripney, the geochemical evidence indicates that original connate water may be trapped by these structures.
- Fresh water found at a depth of −450 m OD in the Albian (Lower Greensand) near the south coast with an age of ca 7000 a BP. The age of this water probably records the timing of the sea level rise and implies that freshwater may also exist offshore.
- Fresh water is also found in Tertiary strata beneath the Solent at a depth of −122 m providing evidence of Late Pleistocene ‘offshore’ groundwater movement and aquifer development.
- Freshwater is found to a depth of 300 m in confined Chalk beneath Poole Harbour. This water has moved towards the former lower base level in the channel via a breach in the monoclinal structure which developed in the late Pleistocene. At Lulworth further west, there is evidence of freshwater, probably palaeowater to a depth of –160 m OD.
- The absence of recharge during the period 10 000–20 000 a BP is interpreted as due to permafrost cover. This in turn indicates the absence of ice in the east Midlands area.
- In the East Midlands Triassic aquifer, depth stratification showing modern (Holocene) or palaeowater has been preserved near to outcrop as indicated by isotopic as well as chemical parameters which are then observed downgradient in the confined aquifer.
- Reactive species (Li, Rb, Cs, Mo and Mn) have been used as additional indicators of residence time in the East Midlands aquifer as a means of extending the radiocarbon timescale. The recorded chemical ages suggest that recharge was probably continuous during the cold conditions of the Devensian interstadial. Although recharge did not occur during the last glacial maximum (as shown by the ^{14}C data gap), chemical indicators show that water-rock interaction was uninterrupted.
- The isotopic and chemical evidence show conclusively that freshwater of Devensian age has reached depths of ca –500 m OD. This aquifer is a classic model of piston flow movement with velocities slowly decreasing due to upward leakage via the mudstones.
- In the Chalk of North Yorkshire fresh water is found to a depth of at least –100 m OD.
- Elsewhere in South Yorkshire and Lincolnshire palaeowater emplacement and movement around the time of the last glacial maximum was restricted by glacial deposits from earlier glaciations (as well as low gradients and structural barriers) so that brackish waters are common.

6 Evidence for palaeowaters in the coastal aquifers of France

6.1 Introduction

Within the program PALAEAUX, three aquifers have been studied, respectively along the Atlantic, Channel and Mediterranean coasts of France, with the aim of establishing conceptual models, essentially based on chemical and isotopic compositions of groundwater. The main concerns were: (1) the origin of mineralization and recharge, (2) the identification of possible mixings, (3) the relationship with sea-water and (4) an estimation of a chronology of the events which have occurred during the Late Quaternary at the different studied locations.

The three systems studied have been chosen to explore the various topics as follows:

- the potentialities of the geochemical tools for a wide range of hydrodynamic and geological situations;
- the specific responses of the aquifers to Holocene sea-level variations and consequently their vulnerability to sea-water intrusion (natural or/and anthropogenic processes);
- the identification of human impact (influence of water supply increasing demand on the water salinization), in order to provide to local authorities and end-users, a sound knowledge of the baseline conditions and geochemical evolution of these coastal aquifers.

The work done during the whole duration of the project has focused on:

(xi) the development of an efficient depth-sampler, for a step-by-step collection of stratified groundwater up to 150 m deep; more than 100 samples were collected, according to the chemical stratification painted out by the in situ measurements (pH, Temperature, Eh, Electric Conductivity, dissolved O_2);

(xii) the evaluation of pumping and sampling disturbances on the water stratification via the temperature logging associated with a complete sampling of boreholes and a global sampling in the whole aquifers ;

(xiii) the completion of chemical and isotopic measurements performed on a set of groundwater mainly selected by their mineralization. Specific chemical and isotopic tracers chosen according to the previous chemical results while establishing the data set (major elements, Br and F contents performed at the University of Avignon, France), were applied on different samples:

- $^{18}O_{water}$, $^{2}H_{water}$, $^{18}O_{diss.\ sulphate}$, $^{34}S_{diss.\ sulphate}$, $^{13}C_{TDIC}$ contents, $^{14}C_{TDIC}$ activity by conventional or AMS methods (University of Paris-Sud, France);
- ^{3}H analysis (HYDROISOTOP GmgH, Germany);
- Trace elements contents (BGS, UK);
- $^{226}Ra/^{234}U/^{238}U$ disequilibria (GEOTOP, UQAM, Montreal, Canada).

(xiv) the interpretation of the whole data set in relation to geological and hydrogeological maps, past sea level variations already known, and geochemical modelling of water-rock interaction processes.

The main results and interpretations are synthesized in Table 6.1.

6.2 Dogger aquifer (North of France)

The aquifer of the Bathonian (Middle Jurassic) in the Caen region is a well-fissured carbonate reservoir, gently deepening toward the Channel (Fig. 6.1). It is largely exploited for drinking water needs and agriculture supplies by ca. 600 boreholes in its unconfined part.

This aquifer corresponds to the Middle Jurassic formations of the Mezozoic marine series which belongs to the western margin of the Paris Basin. The whole series lies on a schistose-gritty Paleozoic bedrock, weathered in the upper part and covered by up to 8 m of clayey to calcaro-marly layers from the Lias (Rioult *et al.*, 1989). The aquifer consists of oolitic and sponge-bearing carbonates (up to 20 m thick) of Bajocian age and of pure marine carbonates and marly calcareous layers (110 m thick) of Bathonian age, these two formations being hydraulically connected. .The insoluble residues of the aquifer matrix are mainly quartz, smectite and illite as major components, and phosphate and pyrite as trace minerals.

All layers dip toward the N-E with a slope close to 1% and the main structural feature is horst trending N110° across the Dives valley. In the Caen area, the aquifer is more confined eastward under the Callovian marls (up to 100 m thick). However, the confining Callovian marls have been completely eroded away in some parts of the lower valley of the Dives river, forming "windows" lead-

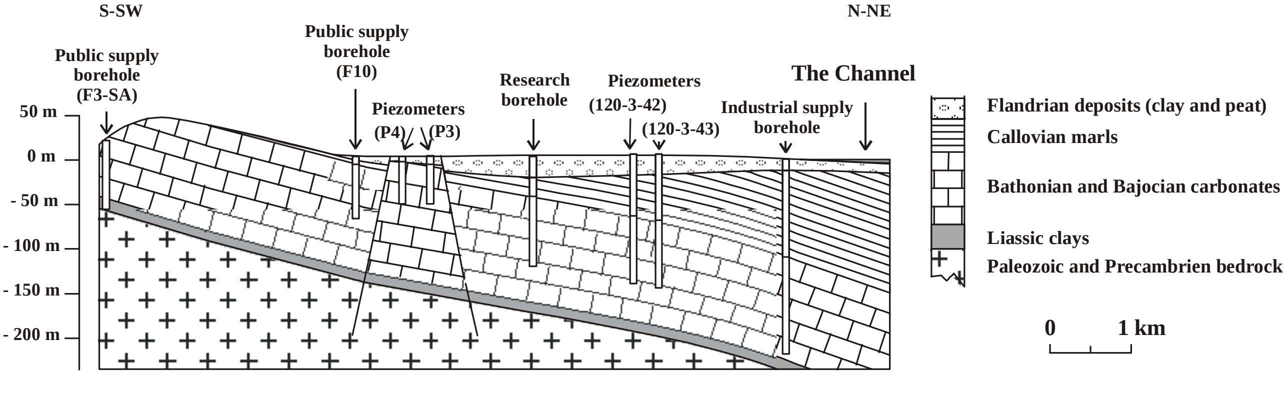


Figure 6.1. Cross-section of the Dogger aquifer in the Caen area

Table 6.1. Summary of evidence for saline intrusion in French coastal aquifers

	Channel coast	**Atlantic coast**	**Mediterranean coast**
Aquifer	- Dogger carbonates (Basse Normandie) - Fissured reservoir	- Dogger carbonates (Vendée) - Fissured reservoir	- Astian micaceous sands (Languedoc-Roussillon) - Interstitial porosity reservoir
Salinization features	- Restricted area (< 20 km^2, 6 km inland) - Confined aquifer under Flandrian and Callovian deposits - Low salinity (<650 mg L^{-1})	- Large area (from coastline to 40 km inland) - Limit between unconfined and confined aquifer (under Flandrian and Callovian deposits) - High salinity (up to 15 000 mg L^{-1})	- Limited to the eastern part (40 km^2) - Aquifer confined under Pliocene marls - Median salinity (up to 4600 mg L^{-1})
Mechanism	- Transgression	- Transgression	- Upward fault flow - Leakage
"Age"	- Flandrian	- Flandrian	- (Past) / Present day
Mixing process	- Density gradient	- Density gradient	- Difference of hydraulic heads - Fugacity
End-members	- Flandrian groundwater - Sea water	- Ante-Flandrian groundwater - Sea water - Recent fresh water	- Groundwater - Old sea water
Geochemical tools of specific interest	- Halogen geochemistry (Cl, F, Br)	- $\delta^2H/\delta^{18}O$ and C geochemistry	- C geochemistry (deep CO_2) - ^{226}Ra, ^{234}U, ^{238}U
Carbon geochemistry	- Simple mixing of C - Negligible sea water contribution	- Mixing of fresh and sea water - Carbonate dissolution/precipitation	- Contribution of deep CO_2 in the C budget. - Chronology of the mixing validated by U and Ra geochemistry
Management	- Refreshing via increasing uptakes	- Possible refreshing by artificial output in the confined part of the aquifer - Consequence : increasing fresh water resources	- Increasing uptakes likely enhance water salinization - No evidences of refreshing with reduced uptakes

ing to hydraulic continuity between the calcareous aquifer and the recent Flandrian deposits which are composed of marine clayey layers alternating with peat. High sea level periods may thus have allowed direct recharge of the Bathonian aquifer by marine water because two marine Holocene transgressions have been interpreted to have occurred over the study area (Hualt, 1972).

The aquifer permeability generally increases according to the fracture density; the transmissivity is 2.0×10^{-3} m^2 s^{-1} for the whole aquifer; and increases to 3.0×10^{-3} m^2 s^{-1} in the most fissured zones, with an associated storage coefficient of 10^{-4} to 10^{-5}.

The study area is submitted to humid and temperate climatic conditions with a mean annual rainfall of 710 mm (1961–1990). As in the whole Paris Basin, the main recharge of the unconfined aquifer occurs from September to March, although the rainfall is well-distributed over the year (Dever *et al*., 1990). The mean annual temperature is 10.5°C (From Météo-France).

A piezometric map of the unconfined zone indicates that the major water flow, from the S-W to the N-E, follows the slope of the geological units at the regional scale and largely contributes to the river pattern (Pascaud and Mauger, 1991).

Once confined, the increase of the groundwater salinity limits the exploitation of the aquifer to the area where the water-bearing formation is unconfined or slightly confined. Located on these clayey formations, the main tourist town on this coast (Cabourg) cannot be supplied by local boreholes since groundwater presents a mineralization higher than the WHO specifications resulting form a marine water intrusion and dissolution of fluoride minerals. The differentiation and the extension of the water bodies have been revealed by a study of the water stratification of the aquifer through in situ measurement (EC, T, pH, Eh) and depth water-sampling on piezometers along the flowpath (Barbecot *et al*., 1997).

On the western part of the Dives valley, the salty intrusion, recognized in the aquifer, is restricted to a 20 km^2 area, 6 km inland, and characterized by salinity up to 2100 mg L^{-1}. The chemical and isotopic analyses gathered so far have shown that this salty water originates from mixing between fresh water and sea water which has overflowed during an oceanic highstand. However, the sea-water fraction needed for such a salinity which is calculated on the basis of chloride contents, is low and does not reach more than 4% for the most saline water (Table 6.2).

In the central and eastern part of the Dives valley, the total mineralization remains constant both with depth and along the flowpath, with values between 800 and 890 mg L^{-1} for boreholes in the most confined part of the aquifer, while pH increases with the distance to the re-

Table 6.2. Chloride contents and isotopic data for the Channel French aquifer

Sample	$\delta^{18}O_{water}$ ‰ SMOW	δ^2H_{water} ‰ SMOW	^{14}C activity pmc	Cl^- mg L^{-1}
F1	−6.51	−41.5	33.1±0.5	18.2
F3	−6.47	−43.3	67.3±0.4	60.6
F4	−6.78	−43.3	54.5±0.5	175.9
F7	−6.63	−44.1	67.7±0.6	106.4
F10-20	−7.31	−49.1	13.0±0.2	142.4
F10-45	−6.89	−45.8	25.6±0.6	276.8
F10-48	−6.61	−44.0	25.4±0.3	240.7
P4-7	−6.88	−46.3	—	188.9
P4-27	−6.83	−45.6	29.2±0.4	184.2
P4-45	−6.56	−45.3	28.5±0.3	236.9
P3-6	−7.02	−46.4	—	278.9
P3-12	−6.79	−45.2	27.5±0.3	294.1
P3-20	−6.31	−43.2	27.5±0.3	377.6
P3-21	−6.31	−43.2	—	486.4
P3-23	−6.19	−42.8	—	656.8
P3-42	−6.13	−43.8	25.8±0.2	639.5
F41-55	−6.99	−46.2	0.4±0.3	216.7
F41-90	−7.24	−46.9	0.4±0.2	238.9
F42	−7.08	−44.2	5.5±0.2	216.3
F43-75	−6.95	−45.7	0.7±0.4	253.6
F43-110	−7.10	−44.5	—	—
F43-135	−7.02	−45.4	0.8±0.2	221.7

Table 6.3. Fluoride contents and saturation indexes with respect to fluorite for groundwater of the Channel aquifer

Sample	F mg L^{-1}	Fluorite S.I.
F1	0.79	−0.54
F3	0.41	−0.98
F4	0.87	−0.35
F7	0.72	−0.49
F10-20	6.70	0.94
F10-45	2.56	0.50
F10-48	2.08	0.43
P4-7	8.33	1.17
P4-27	8.67	1.15
P4-45	8.49	1.14
P3-6	3.85	0.65
P3-12	3.64	0.59
P3-20	2.51	0.37
P3-21	2.50	0.44
P3-23	2.34	0.41
P3-42	2.36	0.43
F41-55	7.80	0.78
F41-90	8.59	0.86
F42	7.43	0.98
F43-75	9.38	0.54
F43-135	9.24	0.58

charge area. This evolution is confirmed by the chemical analyses which show a trend from a calcium bicarbonate type in the unconfined area toward a bicarbonate to sodium chloride type for deep water.

As soon as the aquifer becomes confined, the fluoride content of groundwater exceeds 2 mg L^{-1} and reaches 9 mg L^{-1} in deeper parts of the aquifer. The high F contents are associated with groundwater characterized by a Na-HCO_3 to Na-Cl/HCO_3 geochemical facies. As the content of F gradually rises with increasing distance from the outcrop, two main primary sources of F can be invoked: (1) incongruent dissolution of fluorapatite and (2) leaching of marine clay (Travi, 1993). Moreover, the fluoride content linked to the saturation with respect to fluorite (Table 6.3), gradually rises with increasing distance from the outcrop. This evolution is thus controlled by the dissolved calcium content, itself affected by time dependent water-rock interaction (Fig. 6.2). The concentrations of Ca decrease downgradient by cation exchange on phyllosilicates. Indeed, the aquifer is made up of an intercalation of pure Ca-carbonate layers and calcaro-marly layers. This is in agreement with an excess of Na with respect to a seawater dilution line and with the relative mobility between Na and Ca, Na being known to be more mobile than Ca under such a system (Barbecot *et al.*, 1998a).

The $A^{14}C$ compared to chloride contents allow us to define two groups of groundwater (Fig. 6.3). The first one concerns groundwater for which a wide range of $A^{14}C$ is correlated with a slight increase in chloride contents from 140 to 240 mg L^{-1} (Fig. 6.3). The interaction between water and calcareous rock of marine origin may explain the mineralization of the water. Conversely, the second corresponds to groundwater with a wide range of chloride contents (from 180 to 640 mg L^{-1}) while $A^{14}C$ remain quite constant. Considering the sea water TDIC and its low proportion in the mixing, the sea water radiocarbon input is negligible and represents, at most, 2% of the dissolved carbon. The fresh water end-member involved in the mixing is thus characterized by Flandrian ^{14}C ages (7500–4500 a BP) (Barbecot *et al.*, 1998b). The marine intrusion corresponding to the salty water recognized in the system, is thus well defined in time by the ^{14}C age of the most ancient freshwater implied in the mixing, and would have occurred around 7500 a BP at the latest.

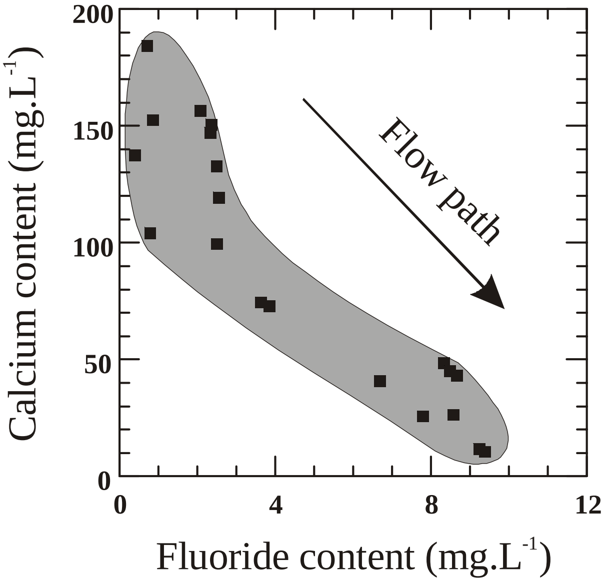


Figure 6.2. Calcium and fluoride content of groundwater from the Dogger aquifer in the north of France.

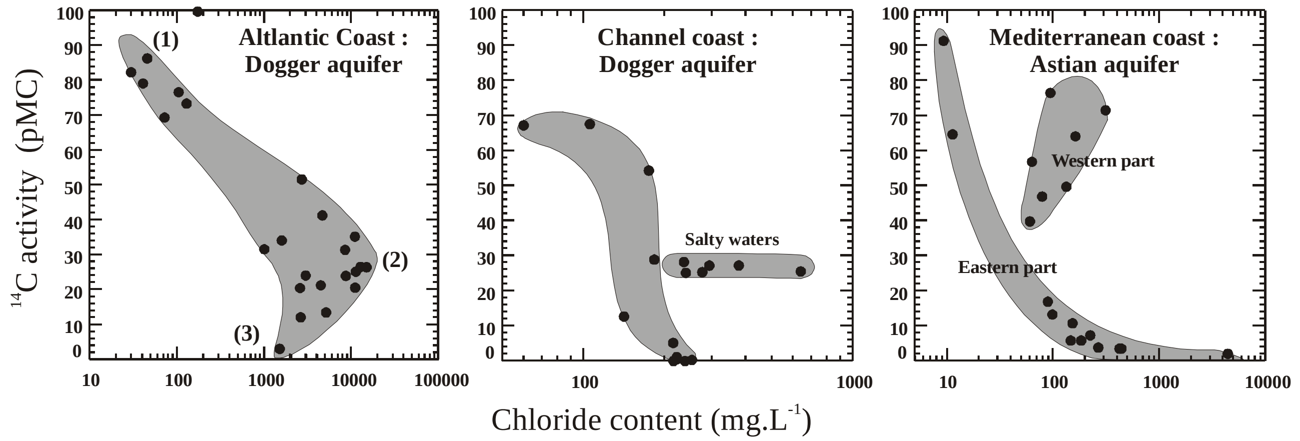


Figure 6.3. ^{14}C activity as a function of chloride content for the French coastal aquifers.

6.2.1 *Management perspectives*

At present, no freshening has been observed since the ^{14}C ages remain constant whatever are the mixing proportions. Moreover, the boreholes situated in between the salty area and the sea do not present any fingerprint of a salty intrusion and thus evidence that the saline wedge is disconnected from the sea. In such a case, the saline wedge could disappear by high pumping rates. This groundwater management would bring the opportunity to solve the problem of the high fluoride contents through the increase of the groundwater renewal rate.

6.3 Dogger aquifer (West of France)

The Dogger aquifer consists of calcareous formations, more or less altered and fissured over the first 10 m. Under this highly permeable zone, the existence of a fault network is one of the main conditions enhancing the groundwater circulation (Roy, 1987). The basement of the reservoir is made of the Upper Toarcian marls which act as an aquitard. These marls, like the whole sedimentary series, are gently deepening toward the Atlantic ocean. Under the "Marais Poitevin" (Fig. 6.4), the Dogger aquifer becomes confined under Flandrian clayey and Callovian marly deposits (Dupuis *et al.*, 1975; Verger *et al.*, 1975).

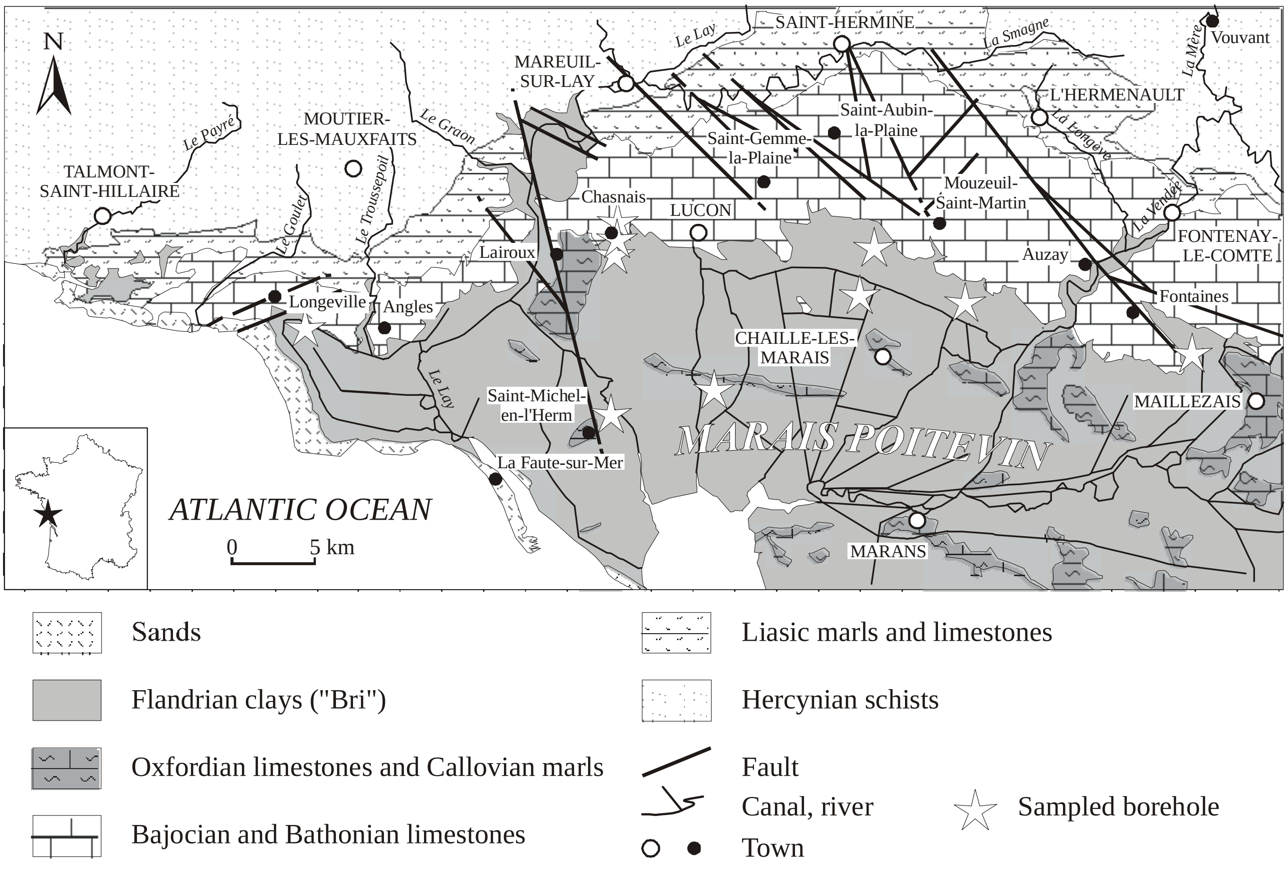


Figure 6.4. Geological map of the Dogger aquifer site in western France

Outcropping over 470 km^2, the unconfined aquifer is intensively exploited for fresh water supplies over only a narrow belt, of 2 km wide, surrounding the confining limit (Mondain, 1995). Although this aquifer reaches a maximum of 40 m in thickness in its confined part and would thus be considered as an important potential resource, the presence of saline waters prevents its exploitation.

The study area is under oceanic climatic influences. The monthly rainfall amount is rather quite constant over the year (mean of 66 mm; σ = 17 mm), and reaches a total amount of 794 mm a^{-1}. The mean air temperature of 11.9°C is bounded by 5°C in January and 19.5°C in July and August. In this region, the potential evapotranspiration is 690 mm a^{-1}. The aquifer recharge mainly occurs from October to March (Roy, 1987).

In the study system, fresh water is found in the unconfined aquifer and in the upper part of the confined aquifer along the northern extension limit of the Flandrian clays. In this latter area, the vertical sampling of groundwater and the *in-situ* measurements logging have allowed the identification of both the hydrochemical vertical stratification of groundwater and the interface between two water bodies, *i.e.* fresh and saline waters. Since the boreholes intercepting the salty deep part of the aquifer are few, the study has thus focused on the unconfined and "slightly" confined parts of the aquifer. The whole study area extends from the Atlantic coast to almost some 40 km inland. This area is characterized by annual alternation between aquifer recharge during winter and aquifer overexploitation during summer. This seasonal alternation modifies the hydraulic gradients and leads to the displacement of the salty-fresh water interface either towards the North or towards the South under the "Marais Poitevin". Then during the Summer, when the aquifer is highly pumped for agricultural supply, the unconfined aquifer containing fresh water-body can be encroached by brackish/saline water from the confined aquifer. However, the great difference in water density limits the mixing between fresh- and salty-water masses during the displacement of the saline wedge.

In this aquifer, groundwater with Cl contents up to 15 g L^{-1} has been found (Table 6.4). The chemical contents indicate that the increase in TDS comes from a simple mixing between fresh water and a salty end-member. The salty groundwater presents ionic ratios, for both major elements and bromide, similar to those of the modern Atlantic ocean (e.g. weighted Br/Cl ratio equal to 3.4×10^{-3}). This mixing thus involves an intrusion within the aquifer of up to ca. 80% of sea water.

Although the chemistry suggests a simple mixing between fresh water and marine water, the ^{18}O and ^{2}H compositions do not account for a simple mixing and evidence a multi-step encroachment of the aquifer with marine solutions. The cross-checking of the ^{14}C activities (ranging from 12 to 100 pmc, Table 6.4), the ^{13}C contents (ranging from −5.0 to −16.5) and the Cl contents (ranging from 40 to 14800 mg L^{-1}) paints out a mixing with three end-members (Figure 6.3; Marlin *et al.*, 1998): (1) the modern fresh water characterized by low Cl/ high NO$_3$ contents/detectable ^{3}H contents, and located in the unconfined part of the aquifer and above the fresh-saline water interface, (2) a Flandrian marine water (chemical composition similar to that of modern sea water), and (3) an old fresh water ($A^{14}C < A^{14}C_{sea\text{-}water}$ and $\delta^{13}C > \delta^{13}C_{sea\text{-}water}$). The presence of the latter water body indicates that the aquifer was probably filled by fresh water before the transgression.

Table 6.4. Chloride contents and isotopic data for the French Atlantic aquifer

Depth (m)	δ^{18}O$_{water}$ ‰ SMOW	δ^{2}H$_{water}$ ‰ SMOW	^{14}C activity pmc	Cl^{-} mg L^{-1}
La Bonde du Coteau				
11.5	−4.81	—	21.7±0.6	—
18.5	−3.53	—	—	—
23.5	−4.05	—	20.6±0.8	10918
31.5	−3.51	—	—	—
39.5	−2.71	−23.0	26.6±0.6	12593
Champagné				
5.0	—	—	—	—
10.0	−2.12	—	—	—
17.0	−2.21	—	—	—
27.0	−2.32	−20.2	26.5±0.3	14768
Langon				
10.0	−4.53	—	—	1691
21.0	−4.90	−25.0	—	4783
28.0	−4.73	−21.6	—	7395
46.0	−3.76	−18.2	35.3±0.7	10827
Doix				
17.0	−5.10	—	84.5±0.9	1049
36.0	−4.21	−27.8	31.5±0.5	8365
47.0	−3.77	−21.6	24.0±0.6	8523
Booth de l'Homme				
17.0	−4.78	−24.4	51.8±0.8	2653
37.0	−4.17	−24.1	41.4±0.6	4585
Longeville				
5.0	−5.61	—	99.9±1.2	178
11.0	−4.75	—	—	3705
19.0	−3.75	—	—	9236
37.0	−3.73	−18.7	25.2±0.8	11124
Beugne-l'Abbé				
—	−5.22	−33.4	82.6±0.5	28.9
Lairoux				
—	−5.20	−33.9	76.9±0.4	101
Tournebride				
5.0	−5.19	−32.9	—	39.1
11.0	−5.01	−34.0	—	39.0
15.0	−5.11	−33.9	79.4±0.5	39.6
21.0	−5.05	−34.1	—	39.8
32.0	−5.06	−33.7	73.6±0.7	125
33.0	−4.84	−33.8	—	1393
34.0	−4.86	−33.4	34.2±0.3	1561
37.0	−4.70	−31.2	12.1±0.2	2584
Les Salines				
4.0	−5.23	−35.4	69.6±0.6	70.0
33.0	−4.47	−29.5	—	1323
33.5	−5.22	−34.1	—	2615
34.0	−3.90	−23.6	24.1±0.3	2946
36.0	−3.76	−19.2	—	6104
46.0	−3.18	−16.5	13.5±0.6	5053
Le Rondo				
15.0	−5.20	−34.5	86.6±0.5	44.2
33.0	−4.50	−30.9	20.5±0.3	2532
35.0	−4.42	−27.7	—	3739
43.0	−4.32	−26.1	21.3±0.3	4393

The marine intrusion recognized in this coastal aquifer can be related to successive marine overflows during the

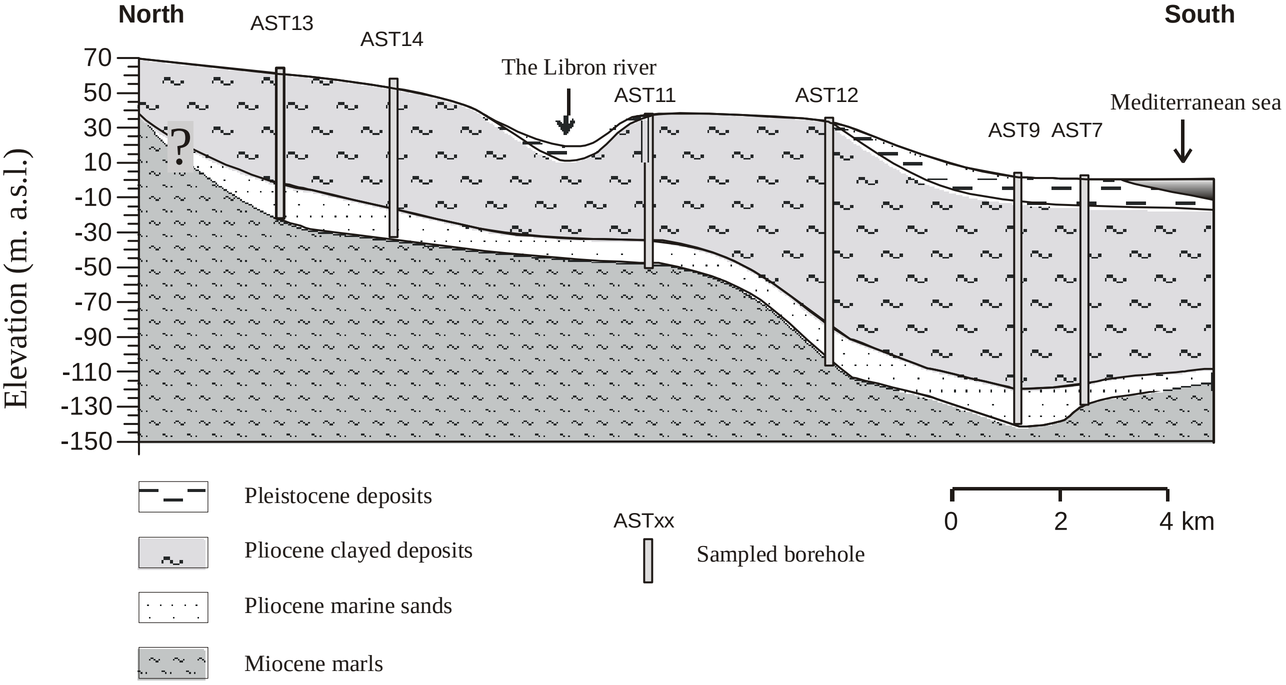


Figure 6.5. Cross-section of the Astian aquifer (southern France)

Flandrian transgression, over the wide palaeo-plain made of calcareous Dogger formations before the deposits of the Flandrian clays.

6.3.1 Management perspectives

The mixing between end-members (2) and (3) characterizes a salty water end-member located under the fresh-saline water interface while a more complex mixing between the three water bodies is likely to occur at the interface salty water/fresh water (1), due to the annual anthropogenic displacement of the saline wedge. Thus, the water uptakes mainly related to agricultural activities in this area enhance the water salinization.

Anyway, since the saline wedge is trapped in the confined aquifer, a break in water uptakes would not have any or very low influence on the aquifer refreshing. However, a possible and significant refreshing might occur through artificial discharge of saline groundwater from the confined aquifer.

6.4 Astian aquifer (South of France)

The study aquifer is contained in micaceous, quartzose sands of Astian age over a surface of 450 km^2. Overlying more than 100 m thick Miocene clays, this 20 m-thick aquifer outcrops on the northern part of the study area over less than 20 km^2. Southward, it becomes confined under clayey layers of Upper Pliocene age, this latter formation reaching 80 m in thickness near the coast (Fig 6.5) (Berger *et al.*, 1978).

The present-day hydro-climatic conditions of the study area are of Mediterranean type, with irregular rainfall amounts from one year to the other. However, the annual rainfall averages 606 mm (σ = 23 mm), mainly spread over autumn and spring mainly through heavy storm showers. Temperature varies between 7.7 and 23.2°C throughout the year (mean annual value of 14.9 ± 5.4°C).

Hydraulic gradients defined in this aquifer induce a groundwater flow from the North (recharge area) to the South (Mediterranean sea). At present, these gradients are enhanced by recent water uptakes concentrated along the coastline, implying that the present-day hydraulic conditions are not representative of those having existed in the past.

The isotopic and chemical analyses (major elements, Br and trace elements), and *in-situ* measurements carried out on 22 boreholes point out:

- the existence of three different recharge areas, the western and eastern areas being separated by the Herault river and the Herault river area itself;
- that at present this aquifer is under severe human pressure and water uptakes would have largely influenced groundwater circulation (Leduc, 1985). However, as the Herault river contains water slightly depleted in ^{18}O and ^{2}H compared to that of the local precipitation, those isotopes indicates that the hydraulic gradients direction and recharge of the Astian aquifer may have been conserved since some thousands of years;
- that the highly mineralized groundwater is limited to the south-eastern and eastern part of the Astian aquifer, along the Thau pond. This increase in TDS is well-correlated with high TDIC contents and low ^{14}C activities (Table 6.5). This can not be explained by a simple modern sea water intrusion, but implies a mixing with a ^{14}C-free water body.

According to groundwater chemical composition, the study aquifer can be divided into two parts from one side of the Herault river to the other. In the western part of the aquifer, the total dissolved solid content (TDS) of groundwater remains low with a mean of 0.670 g L^{-1} (σ of 0.170), while it rises to 10.3 g L^{-1} in the eastern part of the aquifer (mean value of 2.49 g L^{-1}, σ of 3.33).

Table 6.5. Chloride contents and isotopic data for the French Mediterranean aquifer

Sample	$\delta^{18}O_{water}$	$\delta^{2}H_{water}$	^{14}C activity	Cl^-
	‰ SMOW	‰ SMOW	pmc	mg L^{-1}
AST-96-1	−5.88	−34.7	—	20.9
AST-96-2	−6.56	−39.4	92.1±1.4	9.2
AST-96-3	−6.01	−33.1	16.4±0.3	89.9
AST-96-4	−5.98	−35.4	6.5±0.2	227.3
AST-96-5	−6.15	−34.7	57.2±0.5	63.6
AST-96-6	−7.12	−36.3	65.3±0.5	11.2
AST-96-7	−5.59	−33.1	47.1±0.6	79.3
AST-96-8	−6.02	−38.1	77.3±0.5	94.9
AST-96-9	−6.03	−36.2	49.9±0.5	134.6
AST-96-10	−5.90	−34.8	<0.5	4599
AST-96-11	−6.31	−39.1	72.2±0.7	318.0
AST-96-12	−6.19	−37.7	64.7±0.5	164.2
AST-96-13	−5.87	−35.9	—	83.4
AST-96-14	−6.20	−38.4	—	219.7
AST-97-15	−6.89	−40.3	2.6±0.2	449.0
AST-97-16	−6.79	−38.7	2.9±0.2	271.2
AST-97-18	−6.02	−33.1	39.6±0.4	60.8
AST-97-19	−6.78	−38.3	2.6±0.2	430.2
AST-97-20	−6.63	−38.8	5.0±0.2	148.0
AST-97-21	−7.00	−41.0	9.1±0.3	154.4
AST-97-22	−6.66	−35.9	4.9±0.2	186.4
AST-97-23	−6.83	−39.1	12.6±0.2	99.2

The western part of the aquifer, unaffected by processes of mixing with marine solution, has been used to identify the baseline conditions of groundwater circulation. In this area, groundwater is of Ca-HCO_3/Cl-type, and chemical contents are quite constant along the flow path. However, dissolved K and Mg increase along the flowpath as consequences of water-rock interaction (implying Mg-carbonates and phyllosilicates contained in the aquifer matrix). Anyway, this evolution does not lead to water quality deterioration (Laurent, 1993). In this part of the aquifer, the modelled ^{14}C ages have been confirmed by the ^{226}Ra measurements (Joffroy *et al.*, 1997). The ^{226}Ra can be used as a tracer of water residence time within the aquifer using a model taking into account (Barbecot *et al.*, 1999a):

- the initial ^{226}Ra coming from carbonate dissolution in the recharge area;
- the ^{226}Ra in-situ production in the aquifer itself.

The mean residence time of groundwater within the aquifer ranges from Present in the recharge zone to 6000 a BP near the coast (Barbecot *et al.*, 1999a).

Groundwater from the eastern part of this aquifer is characterized by salinization increasing from the recharge area towards the sea. This increase is likely due to the mixing with a marine water solution as shown by the bromide, sodium and chloride relationships (Figs. 6.6a,b). At the same time, groundwater is enriched in both TDIC (up to 0.13 mol L^{-1}), and $\delta^{13}C$ (up to +0.24‰ *vs* PDB). Moreover, this area of the aquifer is affected by an approximately N 40–50° fault that may constitute ways for water and/or deep CO_2 upward leakage. This is demonstrated by the relationship existing between the TDIC and ^{13}C contents of CO2 in equilibrium with these groundwater (Fig. 6.7). In this diagram, the $\delta^{13}C_{gas}$ values are plotted along a mixing line between soil CO_2 (−23.3‰ as measured on field), and a CO_2 bounded by −4‰ vs PDB. Such a ^{13}C-enriched isotopic signature is consistent with the endogenous carbon domain values already defined for the peri-Alpine arc (−10 to −2‰ vs PDB; (Maisonneuve and Risler, 1979). The carbon mixing can thus be associated to deep CO_2 diffusion, accompanied by carbonate dissolution due to the increase in dissolved CO_2 proportion, since the saturation indices with respect to calcite are conserved for all the samples (Barbecot *et al.*, 1999b).

The groundwater mineralization increases according a binary mixing between (1) the fresh water as recognized in the western part of the Astian aquifer, and (2) a deep salty water with a high carbon content. Moreover, after correction of the carbon excess, the ^{14}C activities indicate that the salty end-member is likely over the ^{14}C time scale, attesting that the salinization can be associated with water leakage from the underlying formations (Fig. 6.3). Furthermore, the ^{226}Ra deficit with respect to U isotopes indicates that the salinization process of the groundwater is

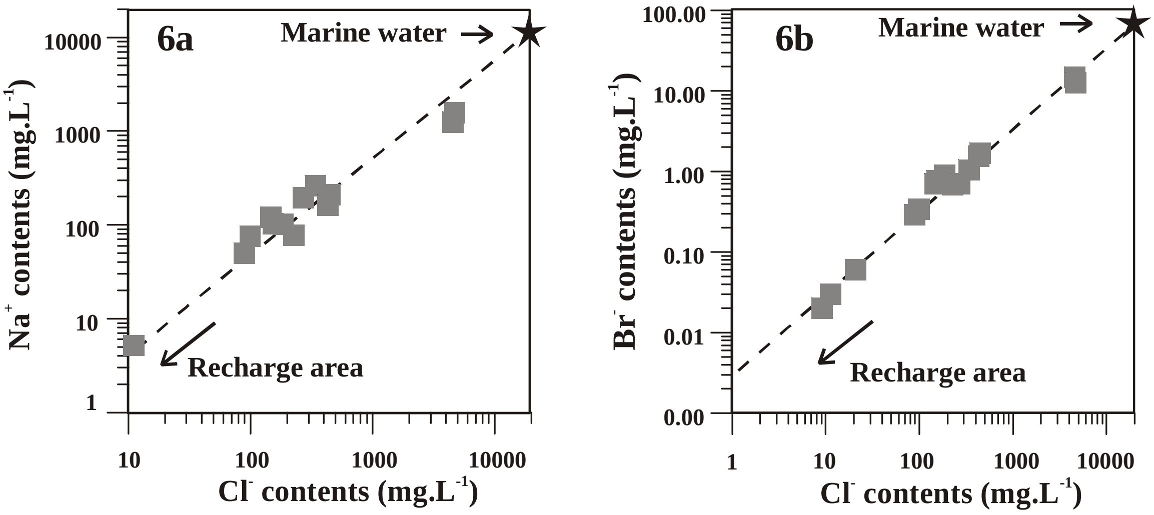


Figure 6.6. Sodium versus Chloride, and Bromide versus Chloride contents diagrams for groundwater sampled in the eastern part of the Astian aquifer.

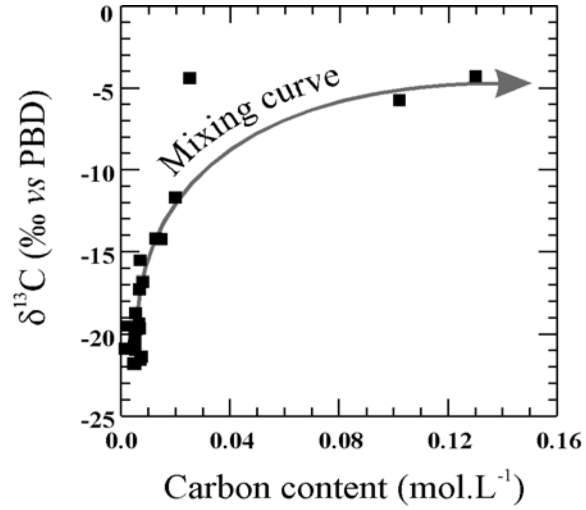


Figure 6.7. $\delta^{13}C$ of the TDIC as a function of carbon content for samples from the Astien aquifer, southern France.

probably not a natural evolution at steady state but can be associated to exploitation of this groundwater resource.

6.4.1 Management perspectives

As a conclusion, the increase of water uptakes from the Astian aquifer will likely enhance the water salinization, since it will increase the salty water leakage. In the present circumstances, no evidence of rapid refreshing linked to reduced pumping rates exists.

6.5 Conclusions

The three coastal aquifers systems studied in France show a great variability in the evolution of isotopic and chemical compositions of groundwater, these latter depending on past sea-water intrusions. More than the global variation of the sea-level, the salinization processes of the French coastal aquifers performed in this program are shown to be mainly related to the local geology, and to the elevation of past and present recharge areas.

In the recognized salty water bodies, the proportions of marine water vary from 4 to 80% without any direct relationship with the aquifer geology or/and morphology of the study sites. However, these parameters are closely related to the salinization mechanism. The aquifers studied along the Atlantic coast and the English Channel coast (Dogger) indicate a marine solution encroachment related to sea water overflows in flat palaeo-valleys at low elevations. These aquifers thus constitute accurate and sensitive archives of the Flandrian transgression.

On the other hand, the aquifer confinement does represent a real barrier to salinization by sea water overflow, but leads to assume a different salinization process as water-leakage. This latter mechanism is generally enhanced by the aquifer over-exploitation.

The geochemical approach of coastal aquifers allows the identification of the main processes controlling the water quality and its time and spatial variations. Afterwards, the understanding of salinization processes give the opportunity to establish relationships between human activity impact and coastal aquifers salinization/refreshing.

7 Palaeowater in coastal aquifers of Spain

7.1 Introduction

The most important aquifers along the 5000 km of peninsular and island coastal areas in Spain are mainly unconsolidated sedimentary Plio-Quaternary formations and Triassic to Miocene carbonate massifs. The first consist of deltas, filled up ancient estuaries and coastal lowlands, which are mostly present in the SW Atlantic strip and along the Mediterranean shore. The carbonate massifs are common features along the Mediterranean coast of the Iberian Peninsula and the Balearic Islands, as well as in some areas of the N coast. Both the sedimentary and the carbonate formations constitute highly permeable and often extensive and thick aquifers, usually intensively developed for agricultural, industrial, urban and touristic uses.

To a minor extent, the fractured granite and shale Palaeozoic formations along the N and NE Spanish coast are also permeable enough as to be considered aquifers of local significance. In the Canary Islands, volcanic formations and the associated sediments, of Miocene age to recent, may constitute good coastal aquifers.

At the Last Glacial Maximum most of the Iberian Peninsula coastline and also that of the Balearic and Canary Islands were between 100 and 120 m below present sea level, with the coastline not far away from the present situation. Sea level rise started some 15 to 12 ka ago and stabilized some 6 ka ago. Due to the configuration of most of the coastal aquifers, it can be expect that fresh Pleistocene and early Holocene groundwater can still be present in some areas, especially in the sedimentary formations, where highly permeable alluvial layers are confined by estuarine and prodeltaic clayey wedges. These wedges may or may not isolate or not the offshore end of the aquifer below.

In most of the cases relatively high fresh water head has induced the Pleistocene water being replaced, and only Holocene and recent fresh water is found. This is the case of the small Mediterranean deltas like the Llobregat river delta. Currently the natural situation has often been dramatically changed due to intensive development, and the existing freshwater may be totally or partially replaced by recent freshwater and marine water. In other cases fresh water head was not high enough to flush away the sea water encroached during the rising sea level, and late Pleistocene or early Holocene salt and brackish groundwater is still present, often mixed in different proportions with recent water. This is the case of the biggest deltas (e.g. the Ebre river and the Guadalquivir river deltas), and also of some carbonate formations filling grabens open to the sea, like the Inca-Sa Pobla system on Mallorca island.

In very arid zones, like the S flank of Gran Canaria island, the influence of arid conditions during recharge combined with the supply of marine airborne salts has to be taken into account to explain the existence of saline Pleistocene to Holocene groundwater above sea level in hydraulic conditions preventing marine intrusion. This is the case of the Amurga Massif.

In the PALAEAUX study the Llobregat delta is used as a reference and the Doñana, the Inca-Sa Pobla and the Amurga aquifers are introduced. These four aquifers are representative of the Spanish coastal areas and have been selected to show typical situations to which many of the other coastal aquifer systems can be referred to.

7.2 Llobregat river delta aquifers, NE Iberian Peninsula

The Llobregat river delta lies at the SW boundary of the city of Barcelona, in its Metropolitan area, within the NE Mediterranean coast of Spain (Fig. 7.1). It is a small sedimentary formation of about 80 km^2 which extends into the lower river lower valley up to some 20 km upstream. The alluvial aquifers in this area are an important piece of the local water resources system in spite of being so small. Under intensive exploitation most of the recharge comes from river water, both by channel infiltration and recharge of irrigation excess water along the lower valley. The river drains a basin of about 5000 km^2 and contributes a mean flow close to 20 m^3 s^{-1}, which may vary between 4 and 2000 m^3 s^{-1}.

The intensive development of the alluvial aquifers started late in the last century, first in the lower valley to supply Barcelona, and then in the delta where deep wells were overflowing. There were industrial settlements making intensive use of groundwater at the delta boundaries and around 1925 they started to abstract large quantities of groundwater from the delta itself. The massive use of groundwater to supply factories peaked in the 1970s. The use of groundwater for irrigation, although important is a minor term since a large part of the area is served by irrigation canals taking river water upstream.

In 1955 a river water treatment plant to produce drinking water was put into operation and the supply wells for Barcelona changed their use from continuous exploitation to emergency use, to respond to peak demands, river droughts, serious river pollution events and failures. Also artificial recharge has been operated to increase river infiltration and to inject excess treated river water into the supply wells. Total groundwater abstraction peaked in the 1970s at about 4·5 m s^{-1} of equivalent continuous flow, but currently it is about 2·5 m s^{-1}, although variable from one year to another.

The quality of river water is rather poor due to the large and increasing population and industrialization of the basin and especially due to the disposal of brines in the central part of the basin, resulting from potassium chloride mining and processing. At some times of low flow river water was brackish. Late in the 1980s a pipeline was constructed to divert part of the brines directly to the sea, and the problem was alleviated. The alluvial aquifers are affected by river water salinity, as well as threatened by contamination from diverse sources resulting from previous decades of poor environmental control. Recharge is also threatened by the reduction in flood plains and rural areas due to the progressive urbanization of the area. The costs involved if the aquifer system fails is concerning some citizen groups and the already operating Groundwater Users' Association, which demand action of the water authorities, and help in environmental control.

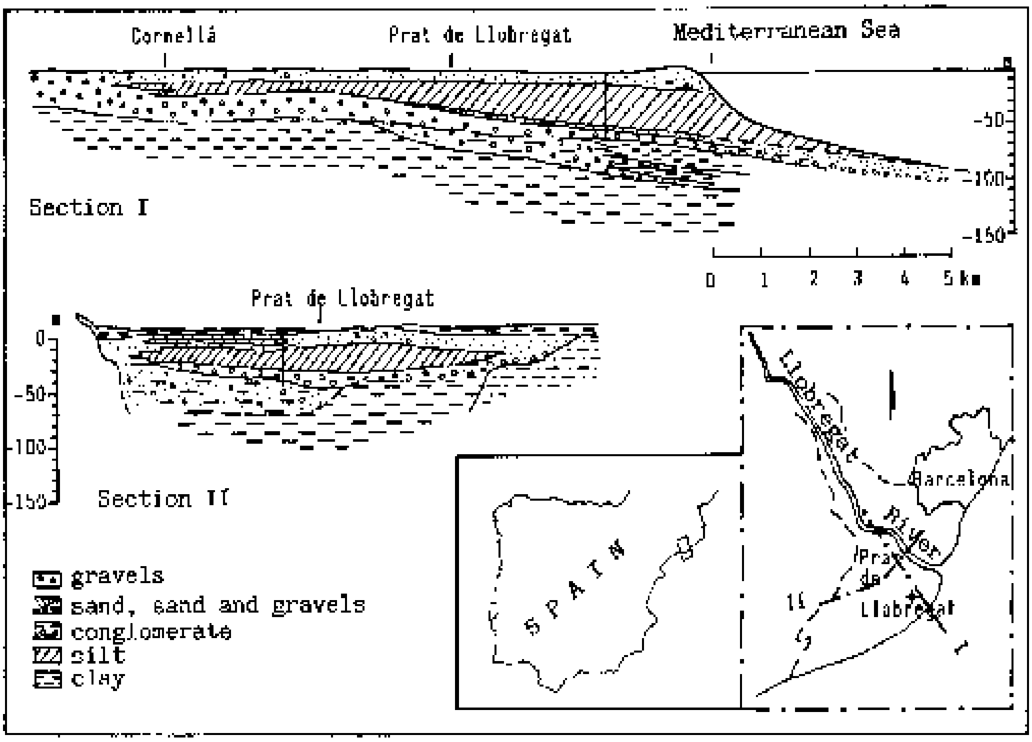


Figure 7.1. Geographical emplacement and geological structure of the Llobregat river delta (after Custodio *et al.*, 1992).

The first study, carried out by the Geological Survey of Spain, dates from early the 20th century (Santa María and Marim, 1910) but detailed studies did not appear until the second half of the 1960s, led by the Water Authority and its Geological Service. The were joined by the Polytechnical University of Catalonia and what is now the Foundation International Centre for Groundwater Hydrology. A series of exploration and research studies have been carried out. (see Custodio, 1981; 1992c for details). As a result a large amount of groundwater data is available which is of value in illustrating the processes the coastal aquifer in the context of the PALAEAUX project.

7.2.1 *Geology and hydrogeology*

The delta (see Fig. 7.1) is a Pleistocene and Holocene formation that consists of three layers:

(xv) a deep confined layer of Pleistocene alluvial sands and gravels,

(xvi) an intermediate prodeltaic silty-clayey aquitard with a high organic matter content wedge,

(xvii) an upper water table aquifer of sandy deltaic plain and overstepping Holocene sediments.

The silty intermediate wedge and the sandy upper layer were grown up under the sea level rise of the Flandrian transgression, which started some 15 000 a BP after the last Pleistocene glaciation.

The confined deltaic aquifer is up to 10 to 15 m thick and lies directly over the Pliocene marls and clays that constitute the impervious base of the aquifer system. The Pleistocene layer outcrops landward in the lower river valley, where it is part of the highly permeable (100 to 800 m d^{-1}), lower valley alluvial aquifer. Along the coastline the aquifer is at around 70 m depth and extends seawards, reaching the sea bed at around 100 m depth and 3–4 km offshore from the central part of the coast. The sediments are highly permeable and display a strong lateral heterogeneity related to sedimentary features like the existence of palaeochannels. The aquitard disappears and becomes sandy at the S end of the lower alluvial valley and at the deltaic margins. The maximum thickness (40 m) of the prodeltaic wedge is in the centre of the delta coastline. In this area vertical permeability is around 2×10^{-5} m d^{-1}. The upper Holocene layer is 10–20 m thick. In the left and right margins of the delta, and also northward to the river valley, the water table aquifer overlies directly the Pleistocene gravels, thus forming a single water table aquifer.

During the sea level rise the Pleistocene alluvial layer was filled with sea water and the Holocene prodeltaic clayey wedge trapped sea water while settling. But as explained below, due to groundwater flow during the Holocene old marine water remains only on the upper half of the central part of the layer, while in the rest it has been replaced by more recent fresh groundwater.

Recharge to the lower valley aquifer and to the deltaic aquifers comes mainly through river water infiltration either through the actual river bed and from irrigated fields. Recharge is artificially enhanced by ploughing of the river bed at the end of the river valley and also, under favourable circumstances, by injection of plant-treated river water through wells.

Currently, the discharge of the lower valley aquifer occurs through pumping and as underground transference to the deltaic deep aquifer. The discharge of the deep confined deltaic aquifer takes place through pumping in the centre of the delta and at the margins. Before intensive development the discharge was through its submarine outcrop, and to the margins of the delta, when the aquitard is rather permeable and allows some vertical flow to the water table aquifer, or disappears.

Before the intensive development of the groundwater the river drained the alluvial aquifer in the lower valley and the water head at the end of it enabled fresh water discharge to the sea to be maintained through the con-

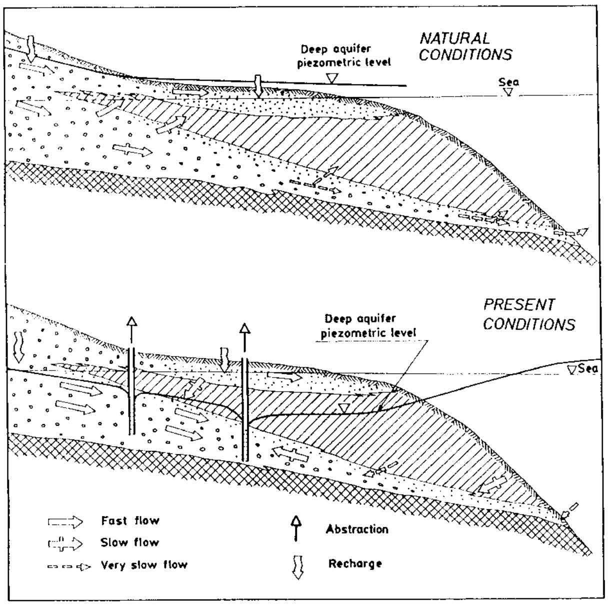


Figure 7.2. Conceptual model of the aquifer system. Under natural conditions the water head between the two deltaic aquifers allowed groundwater to start upward flow through the intermediate aquitard. The head at the inner boundary was high enough to allow discharge to the sea through the submarine outlet of the confined aquifer. Under the present conditions groundwater flows downwards through the aquitard and the discharge to the sea is replaced by sea water intrusion (after Custodio *et al.*, 1992).

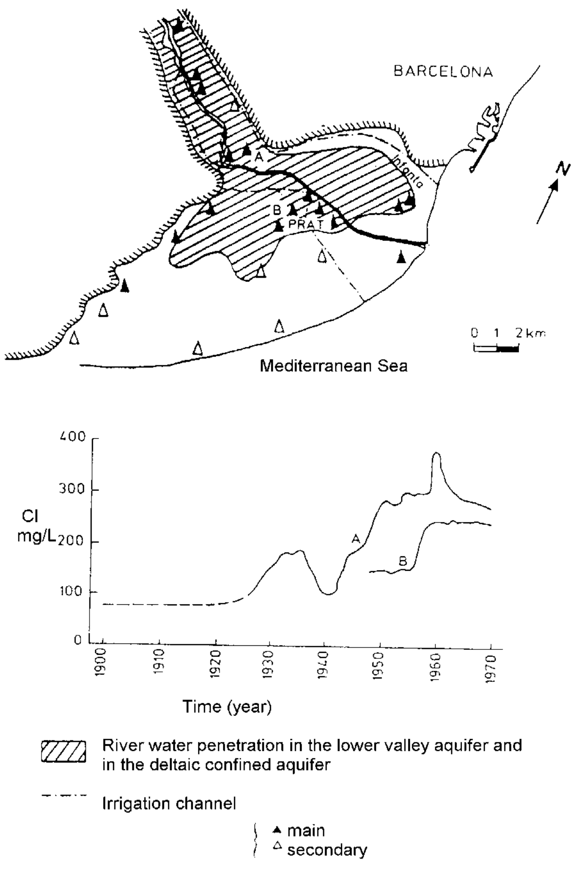


Figure 7.3. Saline groundwater in the deltaic confined aquifer and in the lower valley aquifer in 1970 as a consequence of river water contamination from potassium chloride mining and processing activities in the middle river basin. The plumes extend to the main pumping sites, corresponding to a minimum of water head. Wells in the plume front abstract an admixture of young chloride contaminated and old uncontaminated water. The time evolution graph shows the breakthrough curve of contaminated water in a well placed in the head of the confined aquifer (A) and another placed 4 km downgradient (B) (after Custodio *et al.*, 1992). From the curves a transit time of 10 a can be deduced around the 1950s. Later on this time shortens due to increased head differences.

fined deltaic aquifer outcrop in the well confined central part of the delta (Fig. 7.2a). In the delta itself, the water head difference between the two aquifers allowed upward flow of fresh water into the aquitard. This situation resulted in the flushing out of the original marine water of the deep aquifer during a few thousand years, and produced a dilution of connate marine porewater in the lower part of the aquitard.

The recent, intense groundwater exploitation, mainly concentrated at the south end of the river valley and in the centre of the delta produced a widespread piezometric drawdown in the confined aquifer. Since late in the 1960s the water table in the river valley has been permanently under the river bed (except during exceptional flooding episodes) while the piezometric head of the deltaic confined aquifer is below the sea level all along the coast line (Fig. 7.2b), which allows groundwater to move landward instead of seawards.

7.2.2 Hydrochemistry

By 1965 the sea water encroachment in the deltaic confined aquifer was already showing up in some sections of he coastline (Custodio, 1967), while river water salinity, about 700 mg L^{-1}, had already reached the pumping wells in the centre of the delta, at the lowest point of the drawdown cone. Before 1925 the river had less than 100 mg L^{-1} of Cl^-. Salinity changes in the river water took 10 years to arrive at these pumping wells at that time (Fig. 7.3). Now the travel time is shorter due to higher water head differences. Fresh water in the confined aquifer between this recent river recharged water and the intruding saline water is pre-1925 water recharged in the lower river valley, which was moving towards the offshore outflow area and now moves landwards until replaced by sea water. In 1965 a wide strip of this pre-1925 water was seen but currently it has been depleted except in some low permeability areas.

Groundwater chemistry in the deep confined deltaic aquifer is dominated by seawater intrusion in the delta coastal area and by the reducing conditions created by organic–rich sediments at the upper boundary. Since the beginning of the process two plumes showed up in the NE of the delta (Fig. 7.4) in response to the drawdown cone created by abstractions (Custodio *et al.*, 1986; Iribar, 1992; Iribar and Custodio, 1992). The one to the NE corner follows the coarse sediments at the boundary and the other, close to the current position of the river, follows a main palaeochannel of the Pleistocene river. Between the two plumes there is a shrinking area of low permeability which indicates some pre–1925 water, and which is progressively depleted. The progression of these plumes is currently more or less arrested since some saline water is being abstracted for cooling in some factories, and as brackish water for salination, thus establishing an equilibrium between salinity inflow and salinity outflow. Small

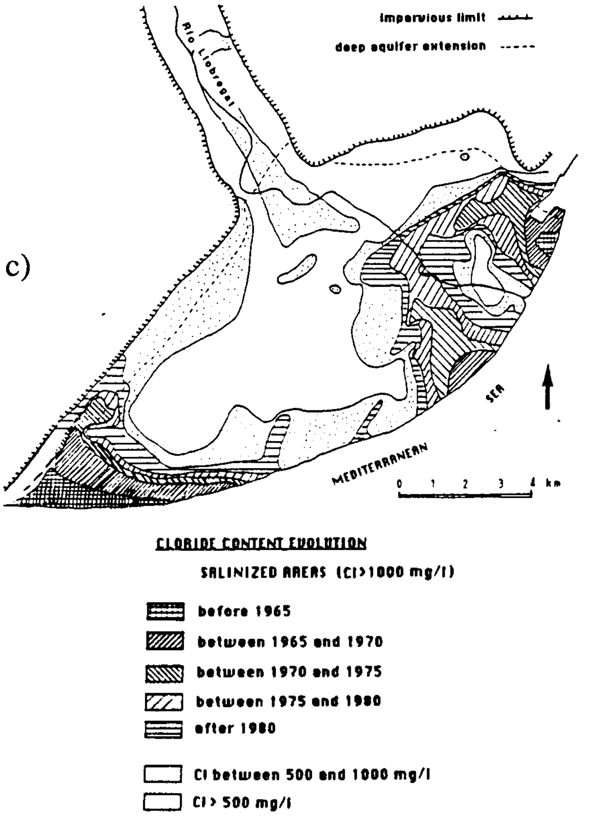


Figure 7.4. Progression of the marine water intrusion into the deltaic confined aquifer between 1965 and 1990. Saline water moves faster through areas of higher permeability, like a palaeochannel placed to the right of the river mouth or along the side areas of the delta, where the intermediate silty wedge is thinner or absent and coarse sediments dominate (after Iribar *et al.*, 1991).

changes in abstraction quantities and pattern produce conspicuous shifts of salinity.

The SW saline groundwater is in reality unflushed connate marine water, although currently it is also moving landwards. In this area local alluvial fan sediments coalesce with the Pleistocene deep gravel layer and the sandy Holocene deposits, forming a roughly single water table aquifer, with a rather low water head which prevents seawater flushing from deep layers.

Between the NE and the SW saline areas pre-1925 groundwater is still found since there the gravel layer is thin or absent, but a new saline plume is developing following the more permeable features.

Saline water and its mixing in different proportion with fresh groundwater in the deep aquifer have brought about additional hydrochemical changes, mainly derived from cation exchange and redox reactions. The resulting most significant changes are local hardening (where marine encroachment is recent) or softening (in areas where connate marine water was being flushed out), and HCO_3^- content increase due to carbonate dissolution due to SO_4^{2-} reduction. No clear chromatographic pattern is found. The convective dominated flow in the seawater intrusion areas prevent a clear salinity stratification in the relatively thin aquifer.

Saline pore water in the aquitard was detected in the late 1960s during the hydrogeological surveys. To ascertain the origin of this water, pore water samples were obtained during the 1970s by dilution from aquitard cores (Custodio *et al.*, 1971; Peláez, 1983). The aquitard was found to contain marine connate water from its top down to a variable depth, where dilution starts to reach values characteristic of the deep aquifer fresh water at the bottom of the aquitard. Integrating this data with the conceptual historical flow model the dilution was interpreted as the result of a fresh water upward flow from the deep aquifer to the upper one during a maximum of 6000-8000 a BP when natural flow conditions operated in the aquifer system. During this time only a small part of the saline water in the aquitard had been displaced.

Hydrochemical studies were made in order to explain the observed pore water composition and to determine the hydrochemical processes that have modified the composition of the conservative mixed water. From the vertical Cl^- and Na^+ curves found in the central coastal area of the aquitard, a longitudinal dispersivity (mainly due to molecular diffusion) of 1 to 2×10^{-5} $m^2 d^{-1}$ was calculated for this area. The Na/Cl ratio indicated a progressive vertical cation exchange between Na^+ in the water and Ca^{2+} in the sediments as the flushing of seawater decreased upwards. These waters were tritium free.

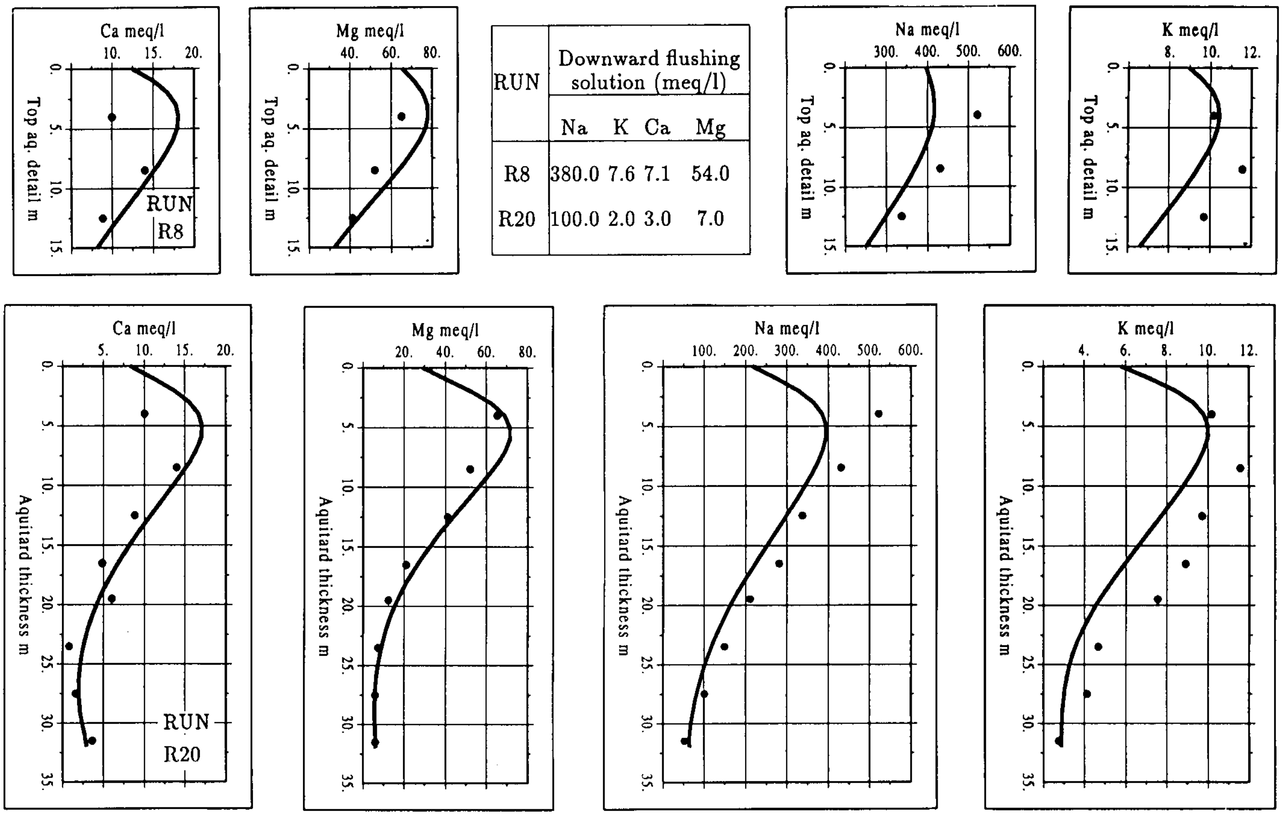
Later in the 1980s new pore water samples were obtained by squeezing (Manzano and Custodio, 1987). Cl^- and $\delta^{18}O$ and δ^2H values responded to an almost perfect conservative mixing curves. However, the vertical distribution of cations in the aquitard column showed an almost perfect chromatographic distribution. The deduced main controlling chemical reactions were cation exchange (Na^+ for Ca^{2+} and Mg^{2+}), calcite dissolution at the bottom of the aquitard and precipitation upwards, and SO_4^{2-} reduction (Manzano, 1993; Manzano *et al.*, 1990; Manzano and Custodio, 1998). The conceptual model was simulated with a reactive multicomponent transport model and very reasonable results were obtained (Fig. 7.5). The model for cation distribution at the base of the aquitard has been improved by adding redox changes (Xu *et al.*, 1999).

7.2.3 *Environmental isotopes*

Environmental isotope studies carried out in the area since late in the 1960s helped to confirm the origin of the water and the conceptual model of the flow system.

River water has a higher tritium content than local rainfall due to its allochthonous (more continental) origin. This shows up in the aquifer. Tritium content and distribution in the lower valley, referred to samples taken from wells tapping the full aquifer thickness, follows what can be expected from an exponential mixing model. However, careful interpretations have to be made when comparing samples from different dates and places along the aquifer because of the variable aquifer storage, besides tritium evolution with time. Transit time through the unsaturated zone is between a few days under the river bed and one to two years under the irrigated fields. Average groundwater turnover time for wells in the lower valley varies between 1 and 4 years. Groundwater spends about 10 years moving from the recharge area to the wells in the confined aquifer in the centre of the delta, as found in the 1960s. All this in the aquifer is coherent with transit times deduced in Fig. 7.3.

Tritium data in the deltaic confined aquifer have been interpreted as the result of well mixed groundwater recharged in the lower valley which moves afterwards along the deep aquifer according to a piston flow model. Trit-



RUN	Downward flushing solution (meq/l)			
	Na	K	Ca	Mg
R8	380.0	7.6	7.1	54.0
R20	100.0	2.0	3.0	7.0

Figure 7.5. Saline pore water in the aquitard (dots) as a result of diluting connate marine water by upward flow of fresh water from the confined aquifer during the period of natural hydraulic conditions in the system (6–8 ka BP). The cation experimental curves show a perfect chromatographic sequence where cation exchange plays the main role. Continuous lines have been simulated with a multi-component reactive transport model using experimental values for the initial concentrations of pore water and fresh water in the underlying aquifer. Longitudinal dispersivity was calculated by inverse calibration of the Cl curve; values for the exchange reactions selectivity coefficients were calculated from the experimental pore water chemistry and cations adsorbed in the sediments (after Manzano *et al.*, 1993).

ium distribution in the aquifer between 1972 and 1976 showed high contents (>10 TU) for young waters close to the recharge area, while near the coast both fresh and saline water were almost tritium free. The limit between both zones roughly agreed with the position of the main pumping wells defining the minimum of the drawdown cone. This also agreed with the hypothesis that sea water intrusion started lately in the 1950s or early in the 1960s through the submarine outlet of the deep aquifer, which is 100 m depth and 3–4 km offshore. However, late in the 1970s the most saline coastal groundwater showed measurable tritium contents (1–3 TU), which means that the intruded marine water already had some thermonuclear influence (Fig. 7.6). Calculations based on data from the 1982–1987 period means that the marine water had moved 4 km in some 30 years. This means an average permeability of around 40 m$\cdot$d^{-1} for this part of the deep aquifer (Custodio *et al.*, 1992; Iribar *et al.*, 1991).

Mean water isotope values for rain water in Barcelona are $\delta^{18}O \cong -6.5\pm2.6‰$ and $\delta^{2}H \cong -41.6\pm25‰$ SMOW (Iribar, 1992). Averaged river water composition is $\delta^{18}O \cong -6.8\pm0.1‰$ and $\delta^{2}H \cong -51.5\pm3.97‰$ SMOW (Iribar, 1992), which is lighter than local rainfall, as could be expected considering that the Llobregat river basin includes heights up to 2000 m in the Pyrenees. But the river is regulated by two dams where some isotopic evaporation fractionation occurs, and along the middle valley the industrial and energy uses of the river produces evaporation as well. This means a decrease of the deuterium excess. Recharge water in the lower valley has an average composition of $\delta^{18}O \cong -6.5$ to $-7.0‰$ and $\delta^{2}H \cong -47$ to $-50‰$ SMOW, in agreement with the river water infiltration origin. Some local differences correlate perfectly with chemical changes that indicate some lateral groundwater contribution, as well as an additional fractionation process due to ponding in the irrigated fields, which further decreases the deuterium excess. This is especially clear towards the lower part of the valley.

Groundwaters in the deltaic confined aquifer show very small and non-discriminative differences: fresh and young groundwater (with measurable tritium) found between the recharge area and the centre of the delta has isotopic values similar to the lower valley ones. Older fresh groundwater (without tritium) still present in the central coastal area between the two saline plumes seems to be a little bit lighter. The fresh water component of saline groundwater in the deep aquifer has a composition similar to the fresh old groundwater. The fresh groundwater in the W and E deltaic single aquifers is a little bit heavier, suggesting the influence of the isotopically heavier local recharge.

Pore water in the aquitard has $\delta^{18}O$ and $\delta^{2}H$ values that correspond to a conservative mixing of fresh water from the deep aquifer and marine water (Fig. 7.7) during the period of natural (undisturbed) hydraulic conditions in the system. Small deviations from the conservative mixing

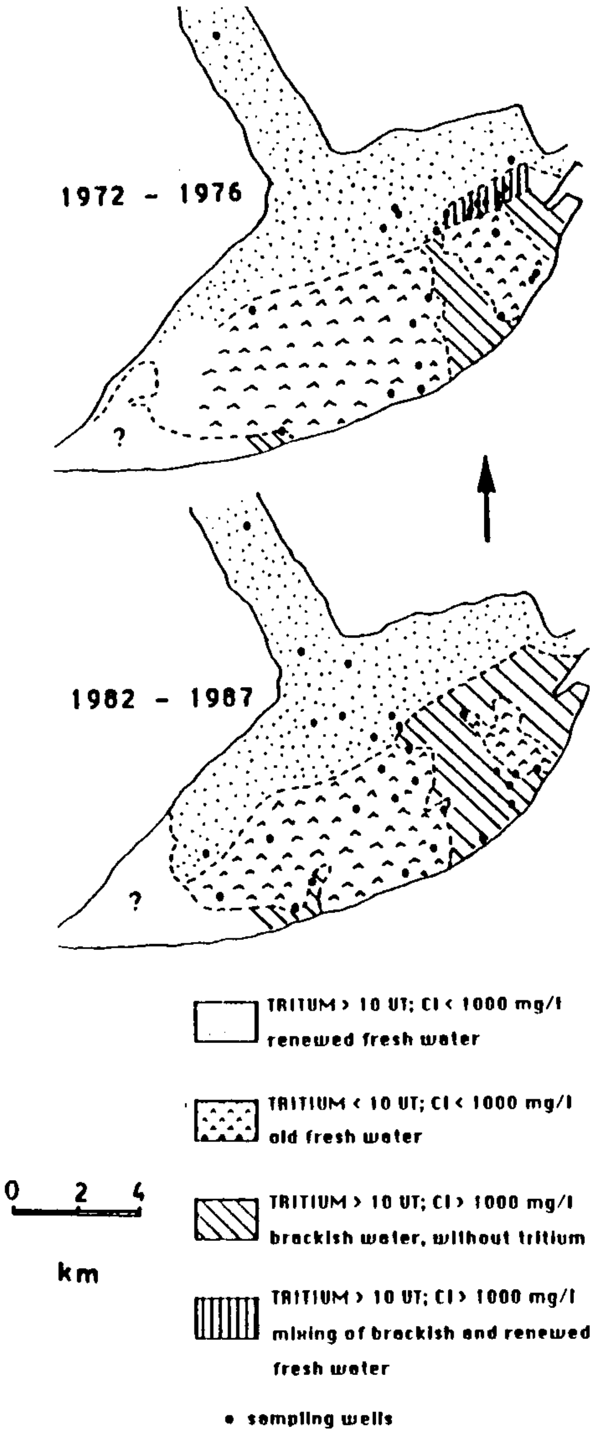


Figure 7.6. Tritium content in water from wells in the deltaic confined aquifer (derived from Iribar, 1992; Custodio *et al.*, 1992).

can be explained by fractionation during the water extraction from the cores (by squeezing). An exception is the uppermost sample, which corresponds to a mixing with groundwater of the upper water table aquifer in a rather sandy layer.

Groundwater in the lower valley has $\delta^{13}C$ values between −12.9 and −14.9‰ PDB, which are typical of groundwater in carbonates with recharge following a reaction path open to soil CO_2. CO_2 input only takes place during recharge, especially in the irrigation fields, where it comes from the soil and the degradation of water contributed (dissolved or particulate) organic matter. This is in agreement with the observed increase of HCO_3^- content in waters resulting from recharge of irrigation excess water. This suggests initial ^{14}C activities of 0.54 to 0.58 pmc if free of thermonuclear ^{14}C. Some samples measured in 1972 showed ^{14}C activities > 200 pmc, which could indicate recharge through the river bed without incorporation of C in the soil (Custodio *et al.*, 1992).

$\delta^{13}C$ data available in the deltaic confined aquifer are somewhat heavier than in the valley. The cause is not well known, but it can be due to an additional dissolution of calcite in the aquifer driven by different chemical processes such as NO_3^- and SO_4^{2-} reduction the mixing of salt and fresh water.

Figure 7.8 shows the incorporation of water containing tritium in samples lying to the right of the conservative mixing line between biogenic C ($\delta^{13}C \cong -25‰$ PDB and $^{14}C \cong 100$ pmc) and C from carbonate minerals (assuming $\delta^{13}C \cong 0‰$ PDB and $^{14}C \cong 0$ pmc) in a system closed to soil CO_2 or in a system open to CO_2 with an equilibrium fractionation constant of $\varepsilon = -8‰$. Most of these waters have measurable tritium contents. There are only three samples without tritium, but they are very close to the mixing lines. Moreover some of them are from saline zones and show the effect of cation exchange and of SO_4^{2-} reduction, so the lower ^{14}C activity could be due to CO_2 incorporation from carbonate minerals dissolution or to organic matter in the formations ($\delta^{13}C \cong -25‰$ PDB but some 8000 years old). Therefore these samples can be only a few centuries old. Only one sample is clearly somewhat older (probably around 3000 a BP), in agreement with its derivation from a sluggish low, almost stagnant, area in the central coastal zone of the aquifer.

7.2.4 Conclusions

Hydrochemical studies carried out since 1965 have provided a good knowledge of the groundwater flow system of the delta and its behaviour under man's influence. Moreover, environmental isotope data have provided very useful tools to check-out conclusions and calculations, as well as to solve some particular aspects.

River recharge can be identified through the high altitude environmental signature of its headwaters, even when mixed with intruding sea water. Local contribution from nearby gullies and local rainfall can be separated from river recharge.

The study of vertical chemical and isotopical composition of pore water from undisturbed cores from the aquitard allowed values of its vertical permeability to be obtained and to check them by numerical modelling. The chemical reactions deduced to be responsible for the aquitard pore water vertical distribution were also validated by a flow and reactive numerical transport model. The results confirm a mixing of Holocene connate marine water and fresh water flow upwards during a few thousand of years as the origin for the actual pore water. The resulting chromatographic ionic distribution in some 40 m of aquitard thickness can be applied to understand the origin of the chemical variability observed in other coastal aquifers where the hydraulic evolution is not clear. It can also be used to forecast future changes.

Groundwater in the confined deep aquifer is only a few centuries old due to the permanent discharge of this aquifer to the sea through its submarine outcrop since it was formed, and also to an increased renovation rate due to the intensive groundwater development since early in

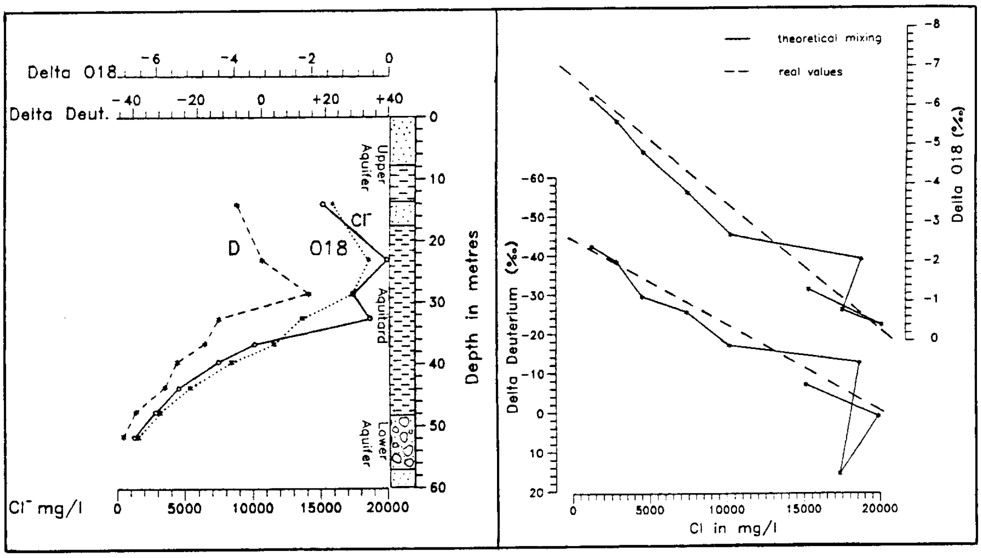


Figure 7.7. Vertical distribution of $\delta^{18}O$, δ^2H and chloride in the aquitard pore water showing an almost perfect conservative mixing between marine water (close to the aquitard top) and fresh water typical of the underlying confined aquifer (after Manzano *et al.*, 1991).

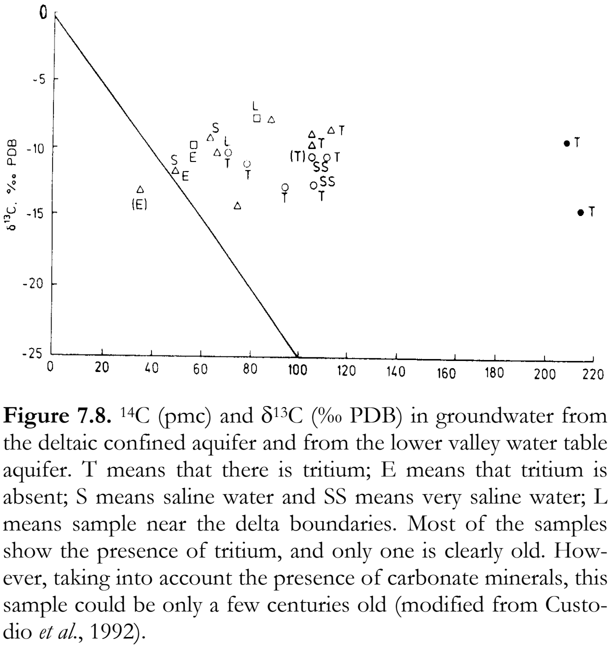


Figure 7.8. ^{14}C (pmc) and $\delta^{13}C$ (‰ PDB) in groundwater from the deltaic confined aquifer and from the lower valley water table aquifer. T means that there is tritium; E means that tritium is absent; S means saline water and SS means very saline water; L means sample near the delta boundaries. Most of the samples show the presence of tritium, and only one is clearly old. However, taking into account the presence of carbonate minerals, this sample could be only a few centuries old (modified from Custodio *et al.*, 1992).

the 1960s. Thus isotopically depleted palaeowater is not present in the delta aquifers, but some pre-1925 water is still there and being depleted.

7.3 Doñana aquifer system, SW Iberian Peninsula

The Doñana natural region and aquifer is situated in the SW Atlantic coast of Spain, partly occupying the ancient estuary of the Guadalquivir river but also extending far to the N and W of it. It is a unique area where the confluence of special geographical and biological factors determine its high ecological value as habitat of a wide fauna and vegetation diversity. Water plays the main role in this richness, both as surface and groundwater. Most of the area is under the highest protection status for natural spaces existing in the Spanish law.

The Doñana National and Natural parks cover together more than 100 000 ha, but the natural region known as Doñana is around 250 000 ha, are shared between the provinces of Huelva, Sevilla and Cádiz. Most of the area is uninhabited except for people in charge of the protection, the occasional developers of some natural resources and the visitors. Some important towns surround the area. The main economical activities are agriculture and tourism, both of them competing for water, as does the maintenance of the protected area.

7.3.1 Geology and Hydrogeology

The aquifer system consists of unconsolidated Plio-Quaternary materials overlapping impervious Miocene marine marls.

At the end of the Miocene the precursor of the Guadalquivir river valley was an elongated SW–NE marine basin filling up with sediments coming from the Iberian Plate, to the N border, and from the African Plate, to the S. In the W sector of this trench fluvio-marine sands settled during the Pliocene. During the Pleistocene and Holocene the east of this area subsided more than the west one, probably driven by tectonics, giving place to the building up of thick gravelly Pleistocene layers, and forming a wide early Holocene estuary. The Flandrian (post-Würm) transgression almost replenished the estuary with clayey, silty and sandy interlayered sediments, but it was still a shallow, semi-closed bay during Roman times (lake Ligur or Ligustinus), with an extensive littoral sand barrier. Nowadays fresh and brackish water marshes exist overlying on the estuarine deposits (FAO, 1970, 1972; IGME, 1982; Vanney, 1970; Salvany and Custodio, 1995).

The aquifer system has a surface area of 3400 km², a variable thickness from a few meters inland to some 150 m at the coastline, and a roughly triangular shape. The aquifer outcrops to the W and N, but to the SE it deepens and becomes confined under some 50 m thick Holocene estuarine clayey layers, with interlayered clays. The confined area is about 1800 km² (Fig. 7.9).

The Pliocene fluvio-marine sands overlapping the impervious Miocene marls have a moderate permeability. The Quaternary consists of permeable fluvial gravel layers and less permeable fluvial and eolian sands. Fig. 7.9 shows

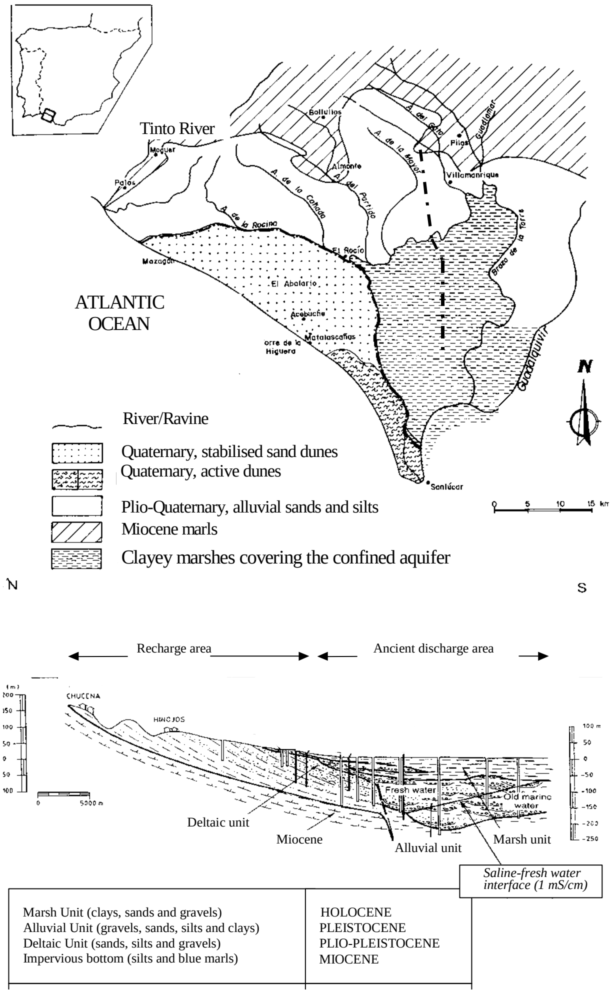


Figure 7.9. Geology of the Doñana aquifer system and cross section along the study area.

a cross section from the northern outcrop to the centre of the marshland through the area studied in the PALAEAUX project. There, the thicker gravel layers are Pleistocene and rest under the Holocene clays in the confined part of the aquifer. The thickness of the gravel layers decrease landward, as they become wedge–shaped (Pleistocene and Holocene) among thick fluvial sand layers of the unconfined area. The Holocene gravels also extend to the S, interlayered among the contemporaneous clays.

The aquifer system is recharged by rainfall in its outcrop area, to the W and N of the marshes. Under undisturbed conditions groundwater flowed southwards to the confined part of the aquifer. Groundwater discharge used to occur near the confined/unconfined boundary and as upward flows through the Holocene clayey sediments. The SE sector of the confined aquifer is filled with saline groundwater, which has not been flushed out due to the low hydraulic gradient existing since the late Holocene sea level stabilization (some 6000 a BP, after Zazo *et al.*, 1997). The natural flow pattern has been modified during the past three decades because of increasing pumping for irrigation in the area just to the N of the marshes, as well as around El Rocío (Trick, 1998). Nowadays, most of the recharged water is probably pumped out from the water table area (IGME, 1982; Llamas, 1991; Custodio and Palancar, 1995), and some local flow reversals may occur.

Head evolution in point boreholes screened at different depths show that under current circumstances vertical downward head gradients exist both in the unconfined and in the confined parts of the aquifer.

Electrical conductivity (EC) and temperature (T) downhole logs in boreholes placed in both areas show the existence of vertical downward groundwater flow (Fig. 7.10). This is the result of decreasing water head downwards, both in the unconfined and the confined areas, due to groundwater abstraction.

Mean annual air temperature is around 18 to 18.5°C. The thermal vertical gradient in the unconfined area is <0.01°C m^{-1}, while in the confined area it is between 0.01 and 0.02°C m^{-1}. A preliminary study can be found in Custodio *et al.*, (1996). EC varies between 0.3 mS cm^{-1} in the unconfined (recharge) area to up to 40 mS cm^{-1} in the saline confined aquifer.

7.3.2 Hydrochemistry

Rain water in the recharge area is of the sodium chloride type, due to the airborne marine influence. Some calcite is the only reactive mineral present in the aquifer northern outcrop, and groundwater here approach the sodium–calcium–chloride–carbonate type. As groundwater flows to the S under the marshes, it becomes increasingly brackish because of mixing with the saline water trapped in the SE sector. A broad mixing zone develops from NW to SE. Maximum salinity in the aquifer is a bit lower than that of sea water. Also, pore water salinity in the Holocene clays increases upwards in the top 30 m, reaching values twice that of sea water in the top 5 m. This is interpreted as the result of repeated evaporation and dissolution proc-

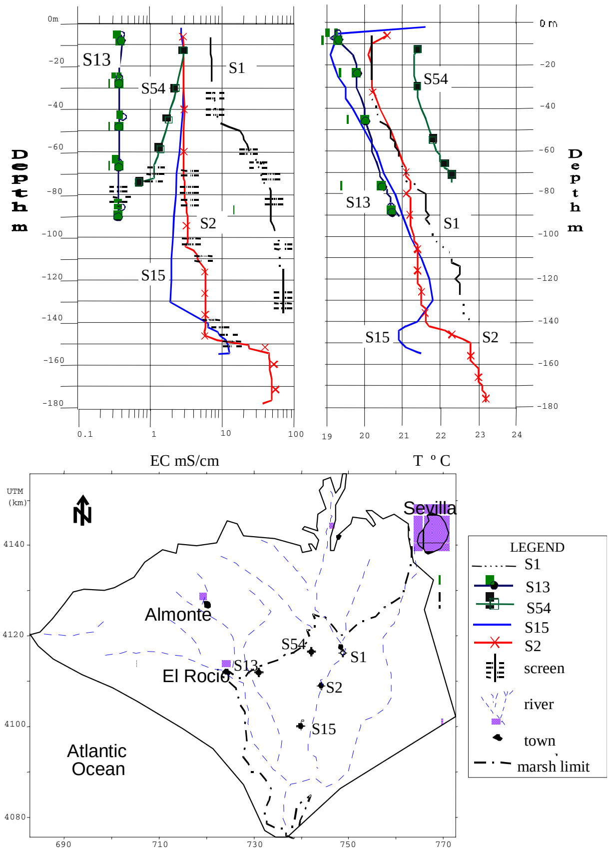


Figure 7.10. Temperature and electrical conductivity logs in boreholes close to the recharge area (S13, S54), and in the confined aquifer (S1, S2, and S15), showing vertical downward groundwater flow.

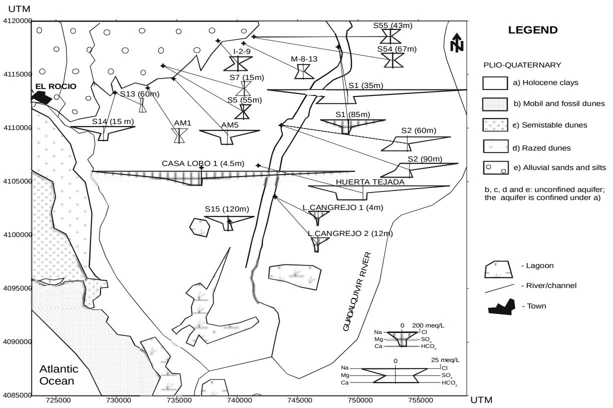


Figure 7.11. Hydrochemistry of groundwater along the contact between the unconfined and the confined areas.

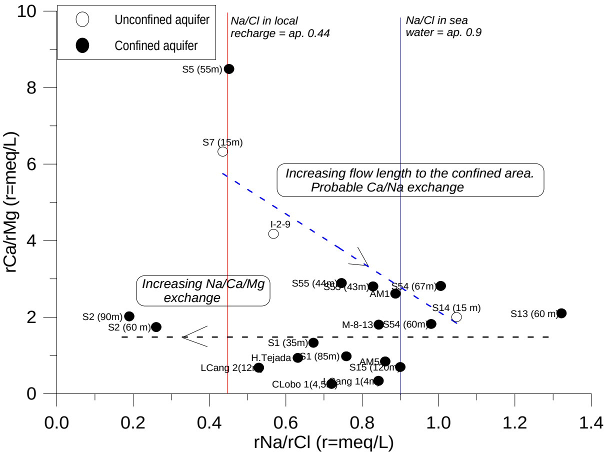


Figure 7.12. Main hydrochemical reactions taking place in the mixing zone between fresh water from the unconfined aquifer and saline water in the confined aquifer (situation of the samples in Fig. 7.11).

esses of water of the uppermost centimetres of the clays, and also in shallow body waters in the marshes (Baonza *et al.*, 1984; Manzano *et al.*, 1991; Rodriguez-Arévalo, 1988; Custodio, 1993).

Information derived from major ions (Fig. 7.11) agrees with what is known from previous studies. Considering downward flow from the water table to the confined area, the main chemical reaction superimposed on the mixing of fresh recent water and saline older water seems to be Na/Ca and Na/Mg exchange (Fig. 7.12). However, a chromatographic spatial distribution has not been found.

In the recharge area some but not all the samples display incorporation of SO_4^{2-} and NO_3^- from agricultural practices, while some of them (S7 and I–2–9 in Fig. 7.13) are depleted in SO_4^{2-} relative to the conservative mixing with sea water, as happens to most of the waters in the confined area. This is interpreted as the result of reduction processes. CH_4 has not been found in four groundwater samples taken in September 1997 for noble gases analyses. The wells reported by Baonza *et al.*, (1984) as giving heavy C have not been resampled and they are further into the marshland. No other major chemical reaction seems to be quantitatively significant.

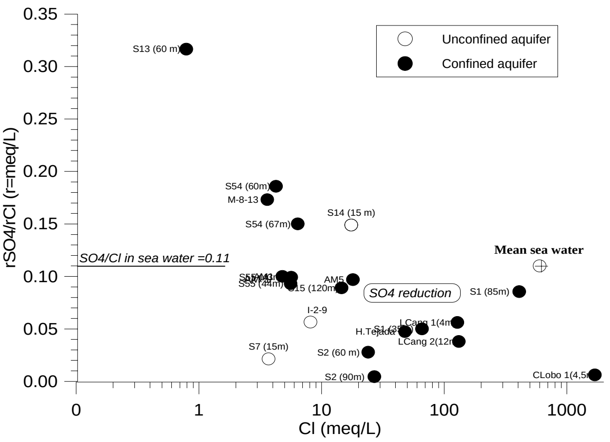


Figure 7.13. Main hydrochemical reactions taking place in the mixing zone between fresh water from the unconfined aquifer and saline water in the confined aquifer (situation of the samples in Fig. 7.11).

7.3.3 Environmental isotopes

From previous work (Baonza *et al.*, 1984; Manzano *et al.*, 1991; Iglesias, 1999) it is known that groundwater in the recharge area has the $\delta^{18}O$ and δ^2H signature of local rain without significant fractionation by evaporation. Residence times based on tritium calculations was estimated between a few and more than 40 years. ^{14}C activity values measured in the 1980s were in the range between almost 100 pmc and about 7 pmc. Following Baonza *et al.*, (1984) groundwater becomes older southward under the marshes, up to 14 ka according to the Fontes and Garnier (1979) model. Baonza *et al.*, (1984) found that some wells in the recharge area showed mean $\delta^{13}C$ values of dissolved organic carbon (DIC) around −16‰, which was explained as the result of isotopic equilibrium of carbonate species and CO_2 in an open system with soil CO_2 coming from the decay of Calvin type plants ($\delta^{13}C \sim -25$‰ PDB), and afterwards changing into a closed system for the dissolution of soil carbonates with average $\delta^{13}C = -4.7$‰ PDB. In the confined area measured $\delta^{13}C$ values seemed to become heavier with increasing salinity. Also, some of the fresh waters under the clays showed very heavy $\delta^{13}C$ values of DIC (–4 to +2‰). This may be due to the input of heavy C from old organic matter (ubiquitous in the clay sediments) which is enriched in $\delta^{13}C$ due to CH_4 formation and separation. The presence of CH_4 was not reported, although one of the authors (Plata personal communication) observed some gas evolution.

In the framework of the PALAEAUX project new environmental isotopes have been measured mainly to determine the age structure of the deep waters and to detect possible admixtures of recent waters.

Age structure of the waters.

Results of isotope determinations are given in Table 7.1. Table 7.2 summarizes the composition of the gases collected for ^{39}Ar activity measurements. The amount of gas is increased by about 30% compared to air-saturated water in samples S54 and M–8–13; this is due to the considerable CO_2 content in the extracted gases. Table 7.3 contains the noble gas concentrations determined mainly to calculate recharge temperatures (RT).

Table 7.1. Isotope data and modelled ^{14}C ages.

Well	^{3}H	^{85}Kr	^{39}Ar	^{14}C	δ^{13}C	^{14}C ages (a BP)			δ^{18}O	δ^{2}H
	TU	dpm/cc	dpm/cc	pmc	‰	Pearson(1)	Pearson(2)	Tamers	‰	‰
I-2-9	0.39±0.26			46.9	−14.3	1624	51	1328	−5.0	−30
M-8-13	0.17±0.26	3±0.3	70±6		−12.0				−4.7	−26
S54	0.23±0.25	0.34±0.05	34±3(3)	51.7	−11.6	−942	−3515	73	−4.6	−26
AM5	0.3±0.24			27.5	−13.5	5579	3763	5385	−4.6	−26
S13	1.15±0.26	0.28±0.04	28±4	20.9	−13.0	7497	5509	7403	−5.0	−32
S2	0.48±0.26	0.7±0.11	<10	7.34	−11.0	14853	11966	46454	−4.3	−25
AM1	0.65±0.26			33.6	−14.0	4224	2564	3955	−4.7	−29

(1) Ages based on Pearson model assuming δ^{13}C of $CaCO_3$ = 0‰

(2) Ages based on Pearson model assuming δ^{13}C of $CaCO_3$ = 4.7‰ (after Baonza *et al.*, 1984)

(3) Results of repeated measurements: 19 ± 4% and 46 ± 6% (preliminar)

Table 7.2. Amount and composition of the extracted gases, and NO_3 content in the water.

Sample	Gas vol	Depth	O_2	N_2	Ar	CO_2	CH_4	N_2/Ar	NO_3
	cc L^{-1}	m bgl	vol %	vol %	vol %	vol %	vol %		mg L^{-1}
S54	18	68	−0.01	66.1	1.29	27.5	−0.01	51	3.0
S13	13	74	1.0	90	1.73	1.75	−0.01	52	1.9
S2	12	72	0.03	92.7	2.0	4.85	<0.01	46.4	0.0
M-8-13	17	55	1.75	65.0	1.5	30.45	0.05	43.3	3.0

Table 7.3. Noble gas contents and recharge temperatures (RT)

Sample	He×10^{8}	^{3}He/^{4}He	Ne×10^{7}	Ne	Ar×10^{4}	Kr×10^{8}	Xe×10^{8}	RT
	cm^{3}STP g^{-1}	×10^{7}	cm^{3}STP g^{-1}	excess %	cm^{3}STP g^{-1}	cm^{3}STP g^{-1}	cm^{3}STP g^{-1}	°C
S13	8.13	10.31	2.38	29	3.73	7.95	1.06	19.7±3.4
M-8-13	10.71	8.10	2.43	31	3.72	8.04	1.053.4	19.8±1.8
S54	8.96	10.27	2.69	45	4.01	8.73	1.1819.8	15.1±1.2
S2	27.78	3.34	2.29	24	3.65	7.92	1.071.8	17.8±1.7
errors	±0.5%	±0.5%	±1%	0	±1%	±1%	±1.8%	

An initial interpretation of the data shows that recent water components in all wells are smaller than about 10%, even for M–8–13, I–2–9 and S54, which show the highest ^{39}Ar and ^{14}C values. The I–2–9 well is in the water table aquifer area, while the other two are nearby but tap several layers of the confined aquifer. This limit of 10% for a recent admixture can be estimated from the ^{3}H content, if 10 TU is assumed for present day precipitation. An even lower limit of about 1% is estimated for S54, S13 and S2 from the low ^{85}Kr activity values (Table 7.1). These low values also demonstrate that the sampling intervals of 50–70 m below surface are deep enough to prevent gas exchange between this water and the atmosphere thus preventing the increase of ^{39}Ar activity from external sources.

A close look at ^{3}H, ^{85}Kr, O_2 and NO_3 data allows more detailed conclusions:

- the water of M–8–13 may contain about 5% of recent water, as estimated from its ^{85}Kr activity of 3 dpm mL^{-1} and the amount of 1.75% O_2 found in the extracted gases;
- the measured data of S13 are more complex: its ^{85}Kr content is really low excluding more than about 1% of recent water. This however seems to be in contradiction to the measured ^{3}H, NO_3 and O_2 contents. A possible explanation of all data assumes the admixture of a water component with an age of several decades. The ^{3}H/^{85}Kr ratio in the atmosphere was then much higher (Loosli *et al.*, 1999). There is the suspicion that the terrain in the surroundings of the borehole screen still has drilling water, which was probably taken from one of the nearby agricultural wells;
- the NO_3 content in S54 may also indicate some influence of fertilization, which may have happened up to 30 a ago, when agriculture became intensive in the area.

From the above it can be concluded that most of the water of the wells investigated in the PALAEAUX project is older than about 40 years. This is important because all wells except S2 are close to the supposed recharge area.

The combination of ^{39}Ar and ^{14}C allows the age of these deep waters to be indicated more precisely:

- the low ^{39}Ar value in water from S2 allows the estimation that the underground production of ^{39}Ar is below about 10%. Therefore the measured ^{39}Ar activities in M–8–13, S54 and S13 may be converted into ages: if for M–8–13 a uniform age is assumed, a value of about 170 years can be calculated, taking into account the above mentioned addition of 5% recent water;

- with the same assumption of piston flow a value of about 400 years can be estimated for S54 and S13;
- the water of S2 is older than the above mentioned three waters, based on its low ^{39}Ar activity and indicated by its ^{4}He content (Table 7.3). The ^{39}Ar activity converts in a lower age limit of about 900 years for S2.

This age structure from ^{39}Ar activities may now be compared with the interpretation of ^{14}C and δ^{13}C measurements. Some of the samples measured for PALAEAUX had been analysed previously in the 1984 study. The new ^{14}C and δ^{13}C determinations in or close to the recharge area generally confirm previous results as can be seen in Figs. 7.14 and 7.15. No clear indication of a change of the flow pattern is therefore given. Heavy δ^{13}C values found by Baonza *et al.*, (1984) have not been found during the PALAEAUX study, in which samples were collected somewhat closer to the infiltration area (Fig. 7.14). As in the 1984 study, the highest ^{14}C values (around 50 pmc) show up in the NE, decreasing along the infiltration boundary to about 20 pmc to the W. The lowest ^{14}C value here found, about 7 pmc, is from the new drilling S2, which is screened in the deep layers (down to 200 m depth) of the multilayered aquifer in the confined area (Fig. 7.15).

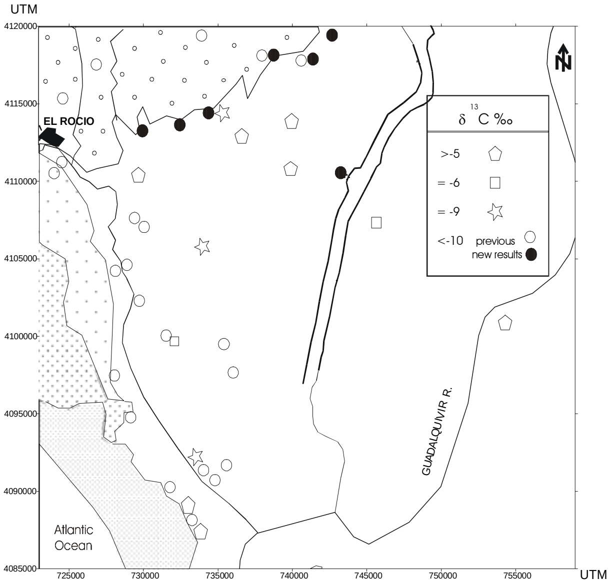


Figure 7.14. δ^{13}C distribution in groundwater after Baonza *et al.*, (1984) data, and after the PALAEAUX results.

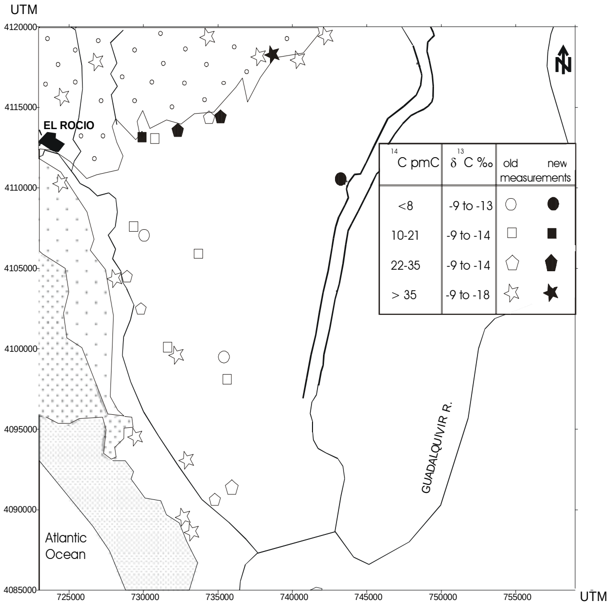


Figure 7.15. ^{14}C and δ^{13}C distribution after Baonza *et al.*, (1984) data, and after the PALAEAUX results.

There is no relationship between δ^{13}C or ^{14}C and total DIC or salinity content (Fig. 7.16 and 7.17). Samples in the confined area with low ^{14}C contents have DIC ≈ 2 mmol L^{-1}, lower than in the unconfined area (DIC ≈ 6 mmol L^{-1}; data from several samples). So neither calcite dissolution from the marine clays nor incorporation of C from the organic matter in the sediments seems to be a quantitatively significant processes, although they probably have taken place. The δ^{13}C–^{14}C relationship agree with this hypothesis: δ^{13}C values characteristic of the recharge area are also found in the confined aquifer as groundwater is being depleted in ^{14}C, mainly because of radioactive decay (Fig. 7.17). Vertical mixing of groundwater with different ages is probably the major process, especially in the unconfined area, where most of the sampling wells are multiscreened. All the measured values seem to fit a system closed to CO_2. In the confined area this is in agreement with the existence of thick clay layers on top and in between the sand and gravel permeable layers. In the water table area it can be explained because of the aquifer configuration of alternated layers of different permeabilities (mainly of sand, but also of gravels and some silts).

Age information from ^{14}C data (in addition to the conclusions form ^{39}Ar) is given as model ages in Table 7.1:

- a strong argument in favour of Pearson's model ages (Ingerson and Pearson, 1964) comes from the results

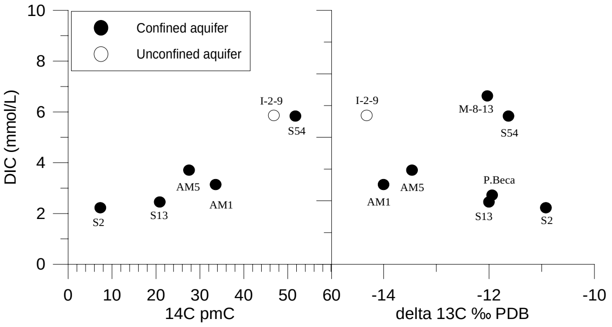


Figure 7.16. ^{14}C and δ^{13}C versus DIC content in groundwater.

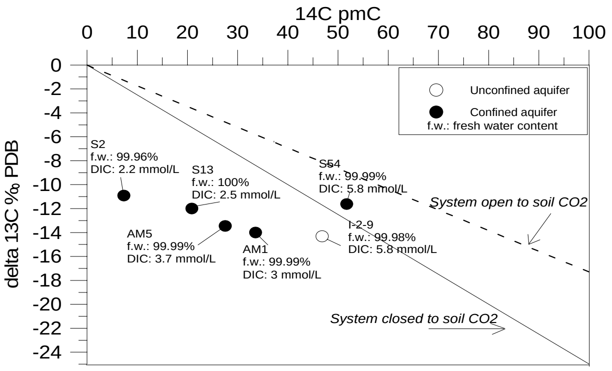


Figure 7.17. ^{14}C versus δ^{13}C in samples analysed in the PALAEAUX project.

of M–8–13: the ^{39}Ar age is about 170 a (see above); a nearby and comparable well investigated in 1984 showed a ^{14}C activity of about 55 pmc with a δ^{13}C value very similar to that measured now at M–8–13;

- therefore it can be concluded that the corrected ^{14}C ages of M–8–13, I–2–9 and S54, all situated close to the recharge area in the NE, should be younger than a few hundred years, as given in Table 7.1;
- it also can be concluded that a model age around 12–15 ka seems appropriate for S2, mainly because no change in δ^{13}C compared to young waters has been observed;
- an alternative to the average ^{14}C model age of S13 is concluded from the ^{39}Ar–^{14}C comparison: it cannot be excluded that this water gets its ^{3}H, ^{85}Kr, ^{39}Ar and ^{14}C activity from an admixture which is several decades old. Then, the main component could be water much older than about 1 ka.

Stable isotopes

δ^{18}O and δ^{2}H values agree with previous studies and correspond to mean annual values in local recharge, which is originated by rainfall (δ^{18}O = −4.7 to −5.0‰; δ^{2}H = −28 to −30‰ SMOW). No palaeoclimatic signature has been found in the freshwater component of groundwater of the confined aquifer, after correction of δ^{18}O and δ^{2}H values for marine water contribution. However a pollen record described in the coastal area of Doñana which covers the last 18 000 a suggests no major climatic changes during this period, and that during the last glacial maximum the weather in the SW of the Iberian Peninsula was humid and warm, not very different to the present one (Zazo *et al.*, 1996).

Noble gas recharge temperatures (RT)

Excess air can in principle be determined from each noble gas concentration; neon however is most sensitive. Therefore Ne excess values are given in Table 7.3. Excess air of about 20–45% agrees with the N_2/Ar ratios given in Table 7.3. The excess air correction has been used to calculate the recharge temperatures from the other noble gas concentrations. The basis for this calculation is the solubilities at 18°C and at an elevation of 50 m above sea level. Most reliable, with corresponding lower errors, are the results for S54 and S2. All RT are within the present day mean annual air temperature.

Radiogenic ^{4}He is present in all samples (Fig. 7.18 and Table 7.3). S2 contains the highest radiogenic ^{4}He content and its ^{3}He/^{4}He ratio is closer to the end member value for this ratio than the other three samples. If the ^{3}He/^{4}He ratio is plotted against 1/^{4}He an extrapolation of this end member value is possible. This shows that all measured ratios correspond to a mixing between air saturated water (ratio $=1.35\times10^{-6}$) and an end member with ratio 7×10^{-8}. This points to ^{3}He production by a Li rich rock or possibly to an admixture of He from deeper crustal layers. This correlation furthermore allows the conclusion that the tritiogenic ^{3}He content is very low. Therefore ^{3}He/^{3}H dating is not possible.

7.3.4 *Discussion*

The situation observed in the Doñana aquifer suggests that approximately half of the confined Pleistocene aquifer has been freshened by fresh groundwater flowing to the SE from the unconfined area, and probably discharging during some 6000 a inside the marshland as upward flow through the Holocene clays. The upward head gradient was still visible a few decades ago as flowing wells. Nowadays, the piezometric level of the confined aquifer is 1 to 2 m beneath the land surface due to the drawdown occasioned by agricultural pumping in the water table aquifer close to the marshes. Fresh groundwater head prevailing since the sea level stabilization 6000 a BP has not been high enough to flush out all the saline water in the Pleistocene gravels. Salt water probably remains in the southeast- most extreme of the aquifer, but there are not observation points there. In the saline waters studied palaeoclimatic signatures are not present.

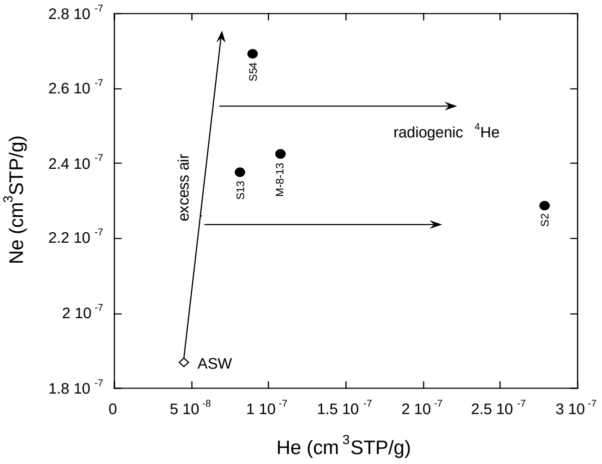


Figure 7.18. Relationship between noble gases He and Ne in the 4 measured samples.

From the point of view of the PALAEAUX objectives, this is an aquifer where old saline water still exists extensively due to the aquifer structure and prevailing hydraulic heads, and only a more or less wide strip contains freshwater. This situation means that no large reserves of old fresh groundwater are available, but the case can be applied to forecast the probable groundwater quality changes in areas with moderate average recharge and low topographic slopes, under a hypothetical future sea level rise.

7.4 Inca-Sa Pobla aquifer, Mallorca island

S'Albufera area is the extreme NE of the Inca-Sa Pobla aquifer system, in the NE corner of the Mallorca island (Eastern Mediterranean Sea). S'Albufera means "the lagoon", which still exists as the remains of the Flandrian marine transgression during the first half of the Holocene period.

7.4.1 *Geology and hydrogeology*

The aquifer materials consist of a more than 300 m thick sequence of marine carbonates (mostly limestones) and calcarenites ranging from the Upper Miocene (Tortonian) to the present (Gelabert, 1998). They settled in a SW-NE subsiding trench some 35 km long and 7 to 15 km wide (Fig. 7.19). To the N and NW the trench is limited by overthrusted Triassic, Jurassic and Cretaceous dolomites and limestones with marls and gypsum, forming the Serra de Tramuntana range, up to 1400 m high. To the S and

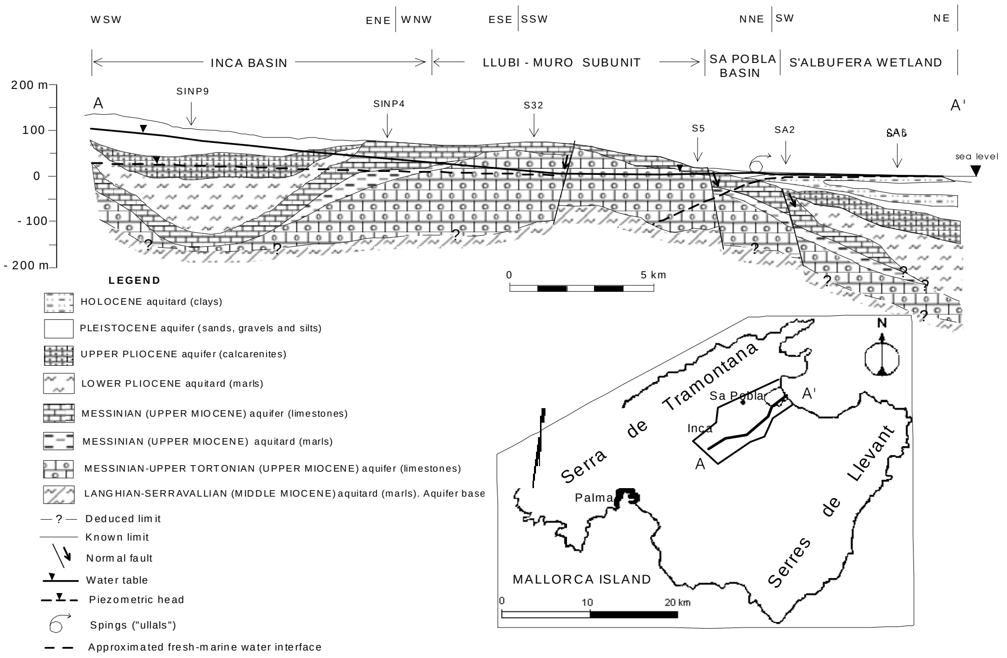


Figure 7.19. Hydrogeological cross section of the Inca–Sa Pobla aquifer system.

SE the trench is limited by Tortonian and Pliocene calcarenites and by Plio-Quaternary molasses, forming smooth hills up to 100 m high. To the NE the aquifer is limited by the Mediterranean Sea.

From the hydrogeological point of view, the aquifer is a multilayered system. In some areas two super-imposed aquifers appear, an upper unconfined and a deep confined one, but in most of the area only a water table aquifer exists. The system is recharged mainly by local precipitation and probably to a minor extent by lateral groundwater flow from the Serra de Tramuntana and from the southern hills. There are not significant permanent rivers and surface flows exist only after intense rainfall episodes. Groundwater flows north-eastward to the sea, and discharges through pumping wells for agricultural and urban use all along the aquifer, and as springs and diffuse upward outflow in the landward boundary of the S'Albufera wetland clay infilling.

To the W and NW of S'Albufera wetland high vertical temperature gradients develop. The dominant hypothesis before the PALAEAUX studies was that saline waters were stagnant, and existed due to mixing with deeper salt water moving upwards as a result of groundwater abstraction. This hypothesis has now been modified. Very low vertical temperature gradients were found in the rest of the area (Custodio *et al.*, 1992; Barón *et al.*, 1994).

Detailed downhole electrical conductivity (EC) and temperature (T) logs in point and multiscreened boreholes in the Pleistocene-Holocene sediments and in the underlying Miocene-Pliocene have been recently carried out as part of the PALAEAUX project. Vertical and spatial distribution of EC, T and thermal gradients show a spatial pattern of what seems to be a dominantly convective flow network of saline water in the coastal sector of the aquifer. This pattern appears under and in the surroundings of S'Albufera wetland, down to >200 m depth. Fresh and saline water flow downwards along the central axis of the basin. Close to the NNW and SSE boundaries of the basin upward flow of saline groundwater exists. Here, thermal gradients are close to 0.03–0.035ºC m^{-1}, but values up to 0.05ºC m^{-1} have been measured locally, as in borehole S20 (Fig. 7.20). Upward flows seem to concentrate through highly fractured (and probably karstified) areas, but this has to be confirmed. Due to the lack of adequate observation points the relationship between these flows and the hydraulic gradients remains unknown. The small size of some geological bodies and the unclear existence of effective confining materials does not favour the existence of residual high potentiometric values (inherited from higher sea stages in the past) for the saline groundwater in deep formations.

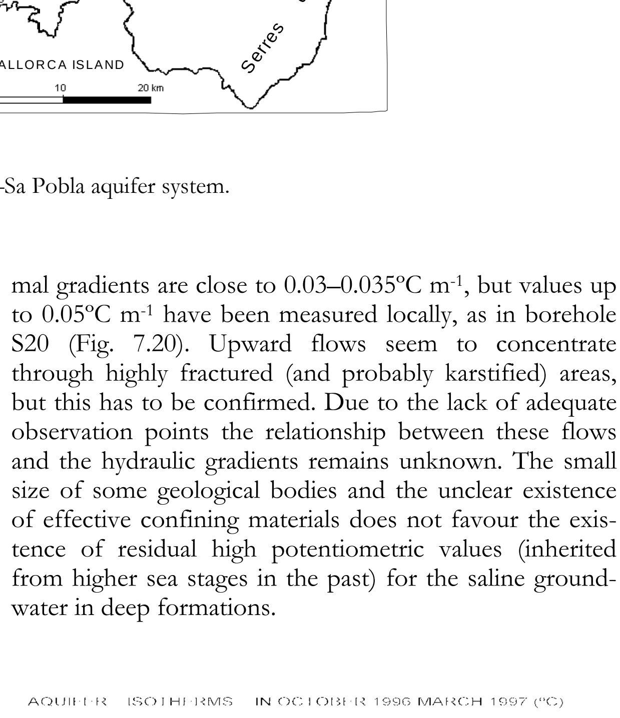


Figure 7.20. Electrical conductivity and temperature cross–section (October 1996–March 1997) of the coastal area of the Inca–Sa Pobla aquifer system (S'Albufera area).

7.4.2 Hydrochemistry

Despite the multilayer configuration of the aquifer, all the carbonate layers are hydraulically connected. The Upper Miocene deep limestone layer is the most transmissive unit (Fig. 7.19). Although most of the pumping wells penetrate the full set of layers, they collect water mainly from this thick Miocene layer. This enables samples placed along a flow line but taken from the deepest part of the aquifer to be compared.

Away from the coastal fringe groundwater in the Inca-Sa Pobla aquifer is of calcium-carbonate type as the result of rock dissolution by infiltrated rainfall. Beneath and in the surroundings of S'Albufera wetland groundwater is brackish and saline due to mixing with marine water of until now unknown age. A thin freshwater layer exists around the N and S boundary of S'Albufera wetland, but to the W and NW a wide step-wise transition zone develops, which is characteristic of fissured and karstified rocks (Custodio and Bruggeman, 1987).

Groundwater from the Serra de Tramuntana, to the N of the studied aquifer, is also of the calcium carbonate type.

Groundwater salinity in the Inca-Sa Pobla system increases slightly downflow (to the NE) in the first 25 km of the unit, but 10–12 km to the coast the mixing with saline water starts. In most of the aquifer system groundwater flow in the uppermost tens of metres is mostly vertical downward, allowing rain and irrigation excess water to penetrate. But through the deepest part of the unit, and from SW to NE, horizontal flow seems to dominate as a general pattern until the coastal area, where the mentioned convective flows dominate.

Although most of the fresh water is of calcium-carbonate type, some spatial differences are observed. Groundwater with the lowest salinity is found in the SW part of the system, where the recharge area begins. Only a few samples in the central part of the unit are of the sulphate calcium or sulphate magnesium type. Since dolomite is rare in the aquifer, these waters are probably due to the influence of the Miocene marls that constitute the impervious base of the aquifer, which is elevated in this central area (see Fig, 7.19). In the coastal area (S'Albufera) groundwater is of the sodium-calcium-chloride-carbonate type, and closer to the sea is of the sodium-chloride type.

As a result of convective flows, the interpretation of the spatial water chemistry changes in S'Albufera area has to be referred to the sampling depth and the hydraulic characteristics of each point. However, a look to the downflow evolution of some ionic ratios (Fig. 7.21) shows two different mixing trends between freshwater recharged along the unit and saline water encroached in the coast.

(xviii) Brackish and saline groundwater under and to the SE of S'Albufera wetland appears as the result of a non-conservative mixing between current recharge water and Mediterranean sea water.

(xix) Brackish groundwater to the N and NW of S'Albufera, along the boundary with the Serra de Tramuntana range, seems to correspond to a non-conservative mixing of present recharge water and a brackish groundwater with more than twice the Ca content and a rCa/rMg ratio (r=meq/L) ≈ 1 four times that of the former area (rCa/rMg ≈ 0.25, similar to that of sea water).

Besides, in several boreholes close to the boundary with the Serra de Tramuntana range upward flows of saline groundwater have been measured. This suggests the existence of deep lateral groundwater flows in the area coming from water recharged in the nearby heights of the Serra. This hypothesis is supported by isotopic data, as is shown below.

7.4.3 Environmental isotopes

Tritium content in groundwater sampled in November 1997 decreases progressively down gradient, from 6–8 TU in the SW of the unit down to <1 TU in saline waters of the coastal area (Fig. 7.22). In the SW half of the aquifer tritium seems to decrease just by decay, although a piston flow model does not fully describes the expected evolution due to some inflow of locally recharged recent water along the flow path. Neither doesa well-mixed model fit the measured data. The high-and-low-content peaks appearing downflow in the SE half of the aquifer has to be explained considering the local sampling depth and the particular configuration of the vertical flow in each point. Spring waters correspond to several sampling surveys during the last 8 years. They show different percentages of admixture between freshwater of different ages and older than 45 years saline water in the coastal area.

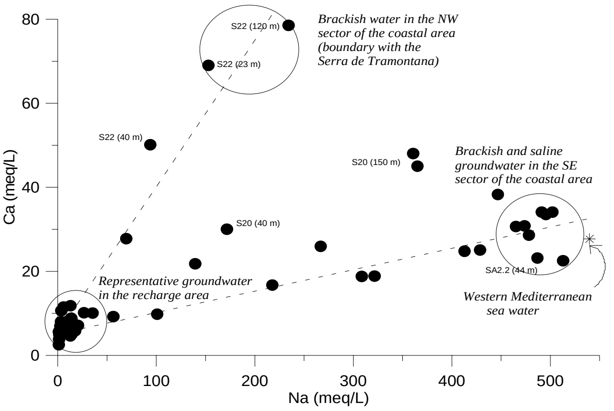


Figure 7.21. Mixing trends between present day recharge water and saline and brackish groundwater in the coastal area of the aquifer, as shown by Na–Ca relationship.

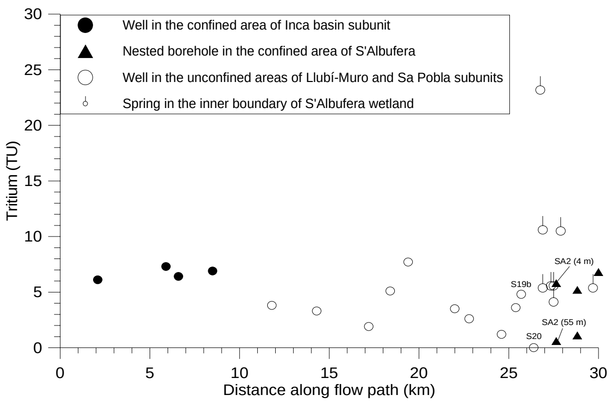


Figure 7.22. Tritium content along a flow path through the deepest part of the Inca–Sa Pobla aquifer, and at different depths in the coastal area.

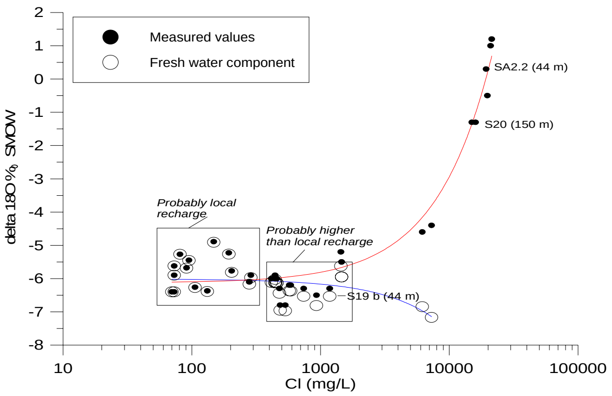


Figure 7.23. $\delta^{18}O$ signature of the fresh groundwater in the aquifer, and of the fresh water component in saline groundwater of the coastal area after correction for saline contribution.

$\delta^{18}O$ and $\delta^{2}H$ in groundwater's fit well with the present local meteoric line (excess ^{2}H = +13 to +15‰). Recently recharged groundwater has the signature of average present local rain water ($\delta^{18}O \cong -6$‰; $\delta^{2}H \cong -36$‰ SMOW). In spite of the apparent homogeneous origin for all the samples, two groups seems to show up (Fig. 7.23): a locally recharged groundwater, and a second one which is 0.5 to 1‰ lighter in $\delta^{18}O$, and 8–10‰ lighter in $\delta^{2}H$ that local recharge. On the other hand, the freshwater component of the brackish samples from the coastal area is even lighter than the second group. This suggests again recharge at higher altitude than that of the local area although, as discussed later looking to C isotopes, the possibility of a remnant groundwater recharged in a colder period in the past can not be discarded.

Attempts to know the age of this light freshwater component and also of the marine water has been made through ^{14}C dating. ^{14}C activity of DIC and tritium content in 4 groundwater samples in the coast decrease as freshwater content increases, apparently showing an ageing as freshwater content increases (Fig. 7.24 and Table 7.4). Assuming a conservative fresh-salt water mixing, and the $\delta^{13}C$ content of sample S19b representative of recently recharged groundwater, the calculated mixing fractions for samples SA2.2, S20 and S22 provide $\delta^{13}C$ values heavier than the measured ones (Fig. 7.24).

DIC content of samples S20 and S22 is higher than expected from a fresh-salt water conservative mixing (Fig. 7.25), while sample SA2.2 (97% of sea water) has the expected DIC content, but a lower than expected ^{14}C activity. This suggests the incorporation of light C with a very low or null ^{14}C activity for samples S22 and S20, so the simple incorporation of young water is discarded. These samples are from boreholes where upward flow of saline water has been measured, and belong to the set of waters having a saline component different to the western Mediterranean sea water (see Fig. 7.26) and assumed to proceed either from the Serra de Tramuntana recharge or to be a remnant of groundwater recharged in older times.

The sample SA2.2 almost pure marine water, is not very old (2000–3000 a).

Groundwater ages have been calculated under very simple assumptions (Table 7.4), without considering the possible contribution of lateral groundwater inflow from the nearby Serra de Tramuntana range, because informa-

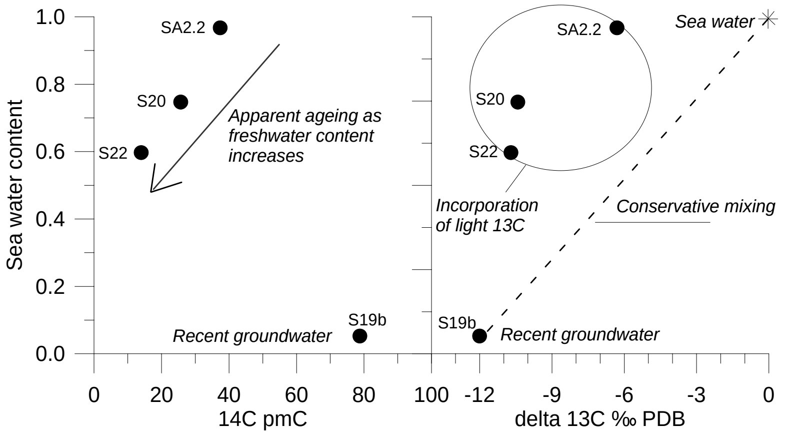


Figure 7.24. ^{14}C and $\delta^{13}C$ versus sea water content in groundwater from the coastal area.

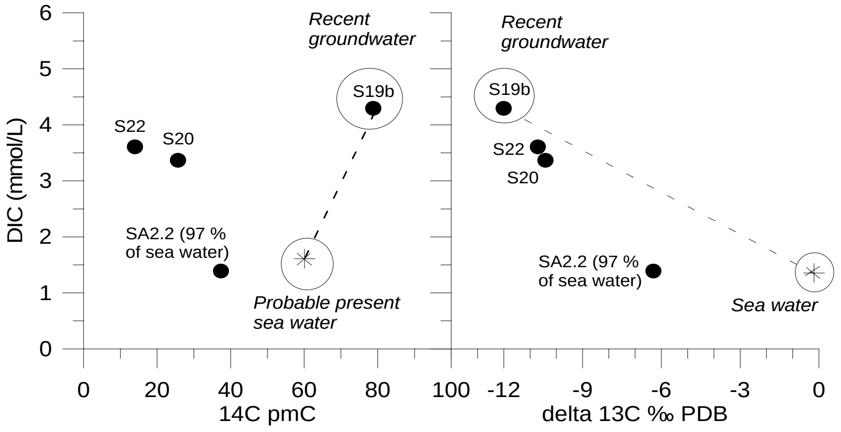


Figure 7.25. ^{14}C and $\delta^{13}C$ versus DIC content in groundwater from the coastal area.

Table 7.4. Calculated ages on the basis of ^{14}C and δ^{13}C data.

Sample	**^{14}C**	**δ^{13}C**	**seawater**	**^{14}C ages (a BP)**		**^{3}H**	**δ^{18}O**	**δ^{2}H**
	pmc	**‰**	**%**	**Pearson**	**Tamers**	**TU**	**‰**	**‰**
S19b (44 m)	78.8	–12.0	5	–4099	–2674	4.8±0.5	–6.5	–38.5
SA2.2 (55 m)	37.4	–6.3	97	¬3265	3336	0.6±0.4	0.3	0.0
S20 (150 m)	25.7	–10.4	74	3990	7771	0.0±0.4	–7.1	–35.3
S22 (120 m)	14.0	–10.7	60	9240	13307			

Pearson: Ages based on Pearson model assuming δ^{13}C of $CaCO_3$ = 0‰
Tamers: Ages based on Tamers model

tion on original end member waters, mixing percentages and a quantification of the mass transfer involved in the subsequent chemical reactions still remain unknown. δ^{13}C values in the limestones and in the local soil CO_2 are not available, so the standard 0‰ and –25‰ PDB respective values have been used for δ^{13}C. Results indicate that the most diluted water (S19b) is very recent. The ages of the other three samples range between recent water and 9000 a BP if Pearson (Ingerson and Pearson, 1964) correction applies, and between 3000 and 13 000 a BP if Tamers (1975) correction applies. Calculations have been made on the basis of a closed system to soil CO_2, although taking into account the flow configuration in borehole S19b this sample should probably be interpreted under the assumption of an open system.

7.4.4 Discussion

Electrical conductivity downhole logs show that in the coastal area of the Inca-Sa Pobla aquifer the whole aquifer thickness (the Holocene clays, the underlying Pliocene calcarenites and marls, and the Miocene limestones that constitute the lowermost transmissive layer) contain brackish and saline water. This suggests that during the Holocene the only natural discharge mechanism of the aquifer system was upward flow of fresh water along the fresh-salt water interface in the surroundings of S'Albufera wetland, together with upward flow of saline water along the NW and SE boundaries of the wetland. Nowadays discharge takes also place through pumping, but still these upward flows are the source of the conspicuous springs and the diffuse outflow occurring along the inner (SW) boundary of S'Albufera wetland.

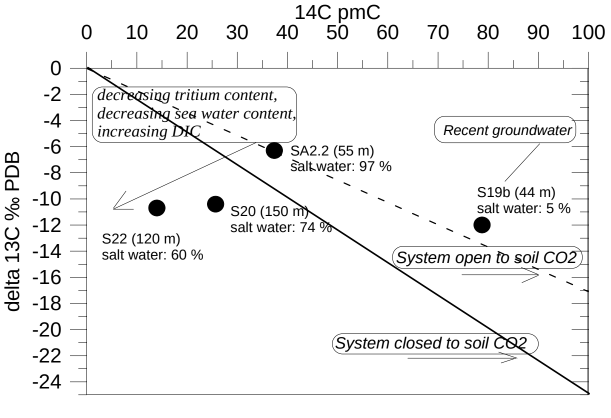


Figure 7.26. ^{14}C versus δ^{13}C in groundwater from the coastal area of the Inca–Sa Pobla aquifer; δ^{13}C values are not corrected for marine water contribution. The graph shows the theoretical evolution of both isotopes in a system closed to CO_2. Borehole SA2.2 is confined by about 50 m of clays. Thus a closed system to CO_2 can be assumed, what means than some thermonuclear ^{14}C is present.

Fresh groundwater has a composition very similar to that of local recharge water, with slightly increasing total salinity, mainly due to calcite dissolution/precipitation processes. Local recharge around the Sa Pobla basin incorporates agricultural SO_4^{2-} and NO_3^- to groundwater.

δ^{18}O and δ^{2}H values are very similar to current local average rain water, but ^{3}H contents decrease downflow reaching values less than 1 TU some 5 km away from the coast. The freshwater component of saline groundwater in the NW sector of the coastal area has the δ^{18}O and δ^{2}H signature of a water recharged either at higher altitude than the aquifer recharge area, or in a colder environment than at present time. The last hypothesis seems to be supported by the fact that these waters have the oldest ^{14}C ages determined in the area.

In three of the most saline waters the ^{14}C activity decreases as freshwater content increases, and as DIC and Ca content increase. This could indicate the presence of a freshwater component older than the present recharge. Also, the saline component of some of the samples has a different origin than the rest of the coastal saline groundwater. So, at least for some of the samples (S22 and S20) a ternary mixing should probably be considered, being the end members: 1) a saline groundwater of unknown age, 2) a recently and locally recharged fresh groundwater, and 3) an older fresh component recharged either outside the aquifer system or in older (and colder) times. For sample SA2.2, components 1) and 2) can provide the measured values. Then, some palaeoclimate signature in saline groundwater of the coastal area of the aquifer is not discarded, although further isotopic and geochemical studies have to be carried out to confirm this.

The convective flows found in S'Albufera area makes the interpretation of water quality changes a function of the sampling depth and on the particular hydraulic configuration of each sampling point. But it is has been clearly seen that both the Pleistocene aquifer, which is rather thin in this area, and the thick carbonate Miocene-Pliocene aquifer underlying the Pleistocene sediments, contain salt water. Hydraulic gradients favour the vertical mixing of salt water of different ages and young fresh water, although the mechanism is not yet fully understood. From the point of view of the PALAEAUX objectives the main interest of this aquifer lies, as in the case of Doñana, in the chemical changes affecting recharge water as well as in the quantification of the time needed for the mixing processes to take place.

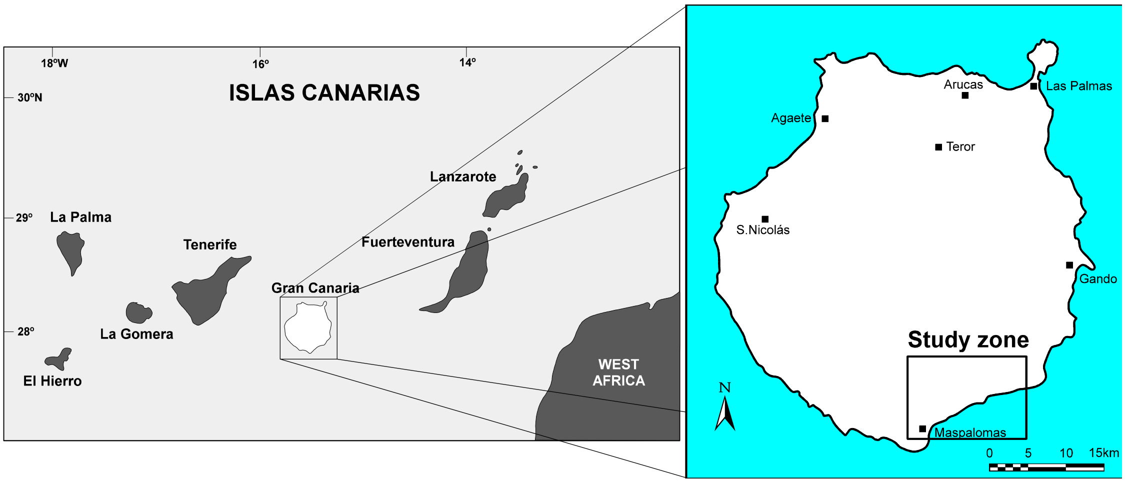


Figure 7.27. Location of the Amurga massif study area.

7.5 Amurga Massif, Gran Canaria

In the wedge–shaped, thick sequence of phonolite lavas of the Amurga Massif, in SE Gran Canaria, Canary Islands, brackish water is found in the deep water table aquifer. Its origin is due to the arid environment in which episodic recharge events incorporate relatively high airborne salinity. No direct seawater intrusion or trapped old marine water is found exceptfor one well close to the coast after several years of continuous exploitation. Water isotope contents reflect the fractionation previous to recharge due to the lack of a continuous vegetation canopy. The trend line points to a mean content of rainfall which cannot be distinguished from present values. Abstracted water has no measurable tritium. Radiocarbon concentration in dissolved total inorganic carbon is well below modern organic carbon. The ^{13}C content shows some dilution with heavier carbon, which cannot be resolved uniquely. A mean age of about 11 000 years is a reasonable possibility. This is compatible with the small mean recharge, the very thick unsaturated zone and the turnover time of water in the unsaturated zone, but other interpretations cannot be ruled out. If the hypothesis of late Pleistocene age for abstracted water is admitted, this means that there is not a clear isotopic climate signal.

7.5.1 Geology and hydrogeology

The Amurga Massif is a wedge–shaped phonolite formation of ca. 5 Ma resting on rhyolitic ignimbrites and Miocene basalts (ca. 10 Ma) of the Gran Canaria Island volcanic complex (ITGE, 1992), in the archipelago of the Canaries (Fig. 7.27).

The total surface area is about 125 km^2. The highest point is 1191 m above sea level, at the apex of the wedge, and dips towards the coast with a mean slope of 0.086.

The massif is dissected by deep gullies, which produces a rough surface, with scarce interbasin flats and almost vertically walled canyons. The wedge is limited at the sides by two deeply incised main gullies (barrancos), Fataga and Tirajana (Fig. 7.27). The old basement only outcrops in the Tirajana barranco outcrops. The coast line presents cliffs and intermediate torrential alluvial fans.

The island of Gran Canaria is in the Saharan dry belt. Mean rainfall at sea level is below 200 mm a^{-1}, but increases up to 1000 mm a^{-1} on the highlands due to orographic effects on the dominating NE trade winds and occasional SW Atlantic wet winds. Amurga is in the downwind dry part of the island with mean rainfall of about 100 mm a^{-1} at the coast and less than 250 mm a^{-1} in the small surface at the top. But occasional intense and short downpours may happen some years. High net sun radiation produces high potential evaporation, over 1500 mm a^{-1}. Only dispersed vegetation of mostly euphorbiae is present, which leaves a large part of the land surface open to direct sun radiation most of the time. A large part of the land is bare rock or rock debris.

Most of the massif consists of phonolite lava flows running from close to the island centre to the coast, some metres to some tens of metres thick, in a well defined sequence containing well developed interflow brecciae, and some interbedded ash flow formations, which frequency increase downwards.

Exploitation by means of deep boreholes (down to 250 m) started in the 1980s. Groundwater is brackish and thus unsuitable for human supply and agriculture. This prevented its use until late in the 1980s, when an electrodialysis desalination plant started operation to convert this water (plus groundwater from the Tirajana delta area and the Barranco of Fataga) from about 4 g L^{-1} salinity into potable water for the large touristic complex of Maspalomas–El Inglés. Studies were carried out to know the resources, origin of water and evolution of salinity to ensure the plant could operate as foreseen during the 25 years of economic life.

The regional water table is very deep, from tens to some hundred metres below the interfluves and is not intersected by the intramassif barrancos. There are no springs except for a few, small perched ones, outflowing from some interflow brecciae or at the foot of large landslide masses along the two major barrancos. Total discharge is about 0.2 L s^{-1}, but the Barranco de Fataga may collect up to 15 L s^{-1} of diffuse discharge in favourable years. Along the coastal cliffs there were some water seeps at some altitude above the beach and wet patches in the barranco mouths. They disappeared after landscape changes produced by intensive urbanization and gardening.

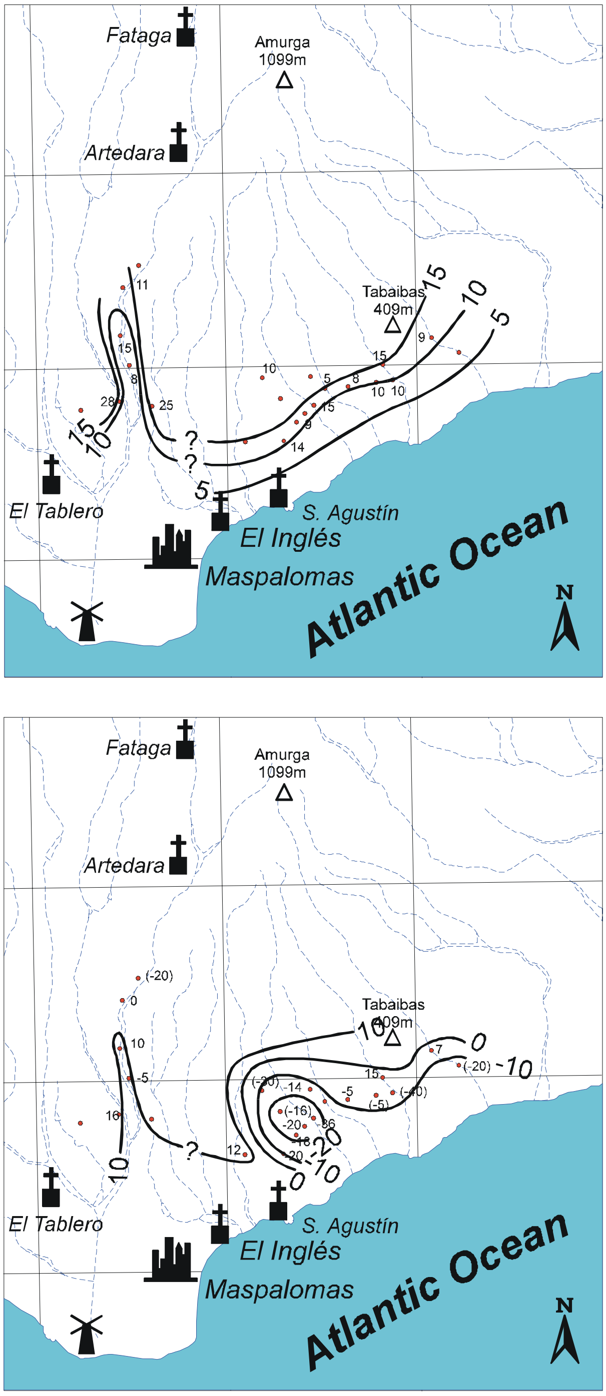


Figure 7.28. Representation of the water table in the Amurga massif, showing the situation both without (above) and with (below) the influences of exploration and exploitation boreholes.

Exploration and exploitation boreholes show a regional water table as shown in Fig. 7.28. They do not cover the whole area due to the difficulty of emplacing drilling machinery in the rough land and the thick unsaturated zone.

Pumping tests in the boreholes and exploitation data of the wells show transmissivity values in the range 50 to 800 m^2 day^{-1}, although there is a bias due to only considering the productive ones; the mean regional transmissivity may be an order of magnitude less.

The only source of recharge is rainfall infiltration. Most of precipitation remains close to the surface where it evaporates. The discontinuous vegetal cover transpires a part and the remaining water returns to the atmosphere directly from bare land. Only a small fraction of precipitation escapes evaporation and produces recharge, which varies widely from year to year, and is only significant in wet years. The long term mean value is estimated between 2 and 4 mm a^{-1} (Custodio, 1992a).

Recharge moves downward through the rock matrix. Even rain water penetrating through fissures, directly or at the bottom of the barrancos, is probably entrained through the fissure walls and incorporated into the matrix as the unsaturated zone is very thick and there are frequent horizontal interlayers of breccia, ash flows and ash falls. Then input to the saturated zone is smoothed and time scales to reach the water table are considerable. Piston flow seems a reasonable model for recharge transfer description.

In the unsaturated zone the combination of horizontal brecciae and scoriae with vertical fissures produces a three-dimensional (3-D) water flow whose thickness is unknown but likely to be up to some hundred meters thick.

Current groundwater abstraction from Amurga and the Barranco de Fataga valley is about 60 L s^{-1} (up to 80 L s^{-1}). This represents about 10 mm a^{-1} for the whole Amurga massif and up to 500 mm a^{-1} for the 2–3 km wide strip parallel to the coast where most of the wells are placed. Thus groundwater reserves are depleted and there is a continuous water table drawdown. Estimated drainable (effective) porosity is 0.03 to 0.07, which is in the range admitted for other lava dominated formations (Custodio, 1978).

Temperature and electrical conductivity logs carried out in some of the currently uncased, dismantled boreholes show homogeneous salinity along the penetrated saturated thickness but variable vertical thermal gradient (Fig. 7.29), from nil to about a normal value 0.03°C m^{-1}. No residual volcanic heat is seen, in agreement with the age of the rock and the lack of recent effusions. Some boreholes in the bottom of deep barrancos show anomalous high temperatures of the air in the borehole but normal thermal gradients; this is assumed the result of the topographic position in the canyon, well below the interfluve, and the intense sun action due to the N–S orientation. Some boreholes show no vertical temperature gradient in all or part of their length. This is due to significant vertical flow of water inside the borehole, downwards or upwards, depending on the 3-D flow pattern induced by groundwater abstraction.

7.5.2 Hydrochemistry

Numerous water analyses from the pumping wells are available since 1985. Most waters are of the sodium–chloride type and cluster around some main poles. Most of the boreholes in the Amurga massif yield quite similar brackish water (electrical conductivity in the range of 4.5 to 6.3 mS cm^{-1}) which has not changed significantly with time but for one case in which there is a clear evolution towards marine composition. This is the only well to show the possible effects of sea water intrusion after the conspicuous sustained local water table drawdown due to groundwater development.

Water from boreholes along the Barranco de Fataga are also brackish but with lower salinity than in Amurga (electrical conductivity around 1.7 mS cm^{-1}) and chemically enriched in sodium. This is interpreted as the effect

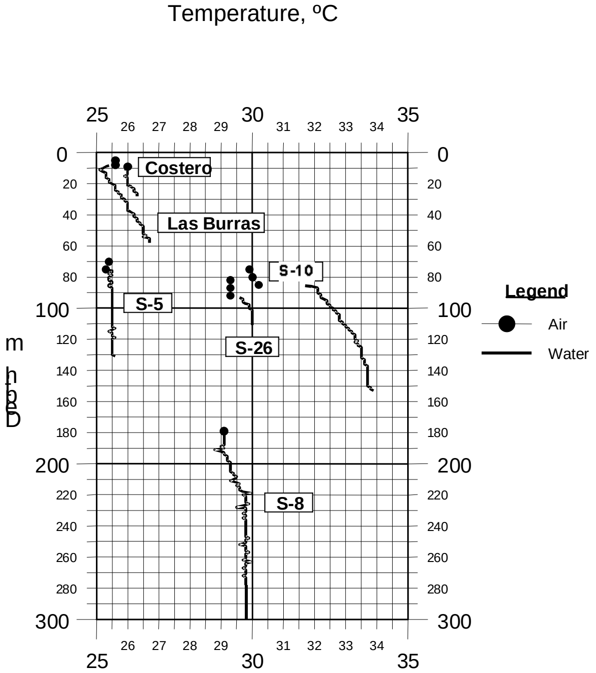


Figure 7.29. Temperature logs measured in some boreholes in the Amurga massif.

of the more acidic nature of volcanic formations (rhyolites and thrachytes), different from that of Amurga, but suffering a similar process to become brackish.

Most groundwater is close to saturation with respect to calcite and amorphous silica, and slightly oversaturated with respect to dolomite. Equilibrium CO_2 pressure is between 0.003 and 0.001 atm, or an order of magnitude higher than in the atmosphere.

Salinity is assumed to be the effect of the arid environment (low precipitation which is evaporated almost completely) and relatively high airborne salinity due to the closeness to the coast and relatively rough sea. A precipitation–recharge chloride balance in the areally variable input wedge land is in agreement with this hypothesis (Custodio, 1992, a,b). The rCl/rBr (r = meq L^{-1}) ratio (800 to 900) shows that chloride may be of marine origin (ratio of 660) with some fractionation and not from evaporites or residual evaporation brines, but further research is needed. The rSO_4/rCl ratio (around 0.11) is typically marine. Total dissolved inorganic carbon (DIC) is 0.5 to 2 (mean 1.2) meq L^{-1} for the springs and about 3.3 meq L^{-1} for the wells.

7.5.3 Environmental isotopes

Water isotopes in rainfall in Gran Canaria show a clear altitudinal effect and similar pattern in the northern and southern halves. The meteoric line shows a slight deuterium excess (d = $\delta^2H - 8\delta^{18}O$‰ SMOW) assumed to be the result of the regional relatively dry environment which enhances kinetic evaporation of sea water. See Gasparini, 1989, and Gasparini *et al.*, 1990, for more details.

Groundwater clusters around a δ^2H vs. $\delta^{18}O$ line of slope 4, which indicates fractionation of rainfall before converting into recharge. This is in agreement with the aridity of the area and the lack of a continuous vegetation canopy. The intersection of this line with the local meteoric line corresponds to a weighted rainfall of $\delta^{18}O$ = –5.5‰ and δ^2H = –32‰ SMOW. But considering the range of altitudes a range of possible mean isotope compositions of rainfall can be expected for evaporation slopes less than 4, which corresponds to intense fractionation of soil humidity when vapour transport in dry soil is important. In any case this shows a recharge in agreement with the rainfall at mid altitudes. No clear palaeoclimatic effect appears and if it exists it is obscured by the wide range of possible values.

All sampled groundwaters from the boreholes have no measurable tritium (less than 1 TU and even less than 0.2 TU), which means that there is no significant direct input of rainfall through fissures or through the boreholes from perched levels discharging into the unsealed borehole. One of the sample sets is close to the end of an extraordinary wet period. Even direct recharge from the bottom of the barrancos seems dispersed when moving downwards.

Radiocarbon analyses from two surveys separated by ten years consistently show contents much lower than modern organic carbon (MOC), (Table 7.5), and pumped water seems really old. Total dissolved inorganic carbon (DIC) is high for almost bare soils in non–carbonate rocks. With the help of $\delta^{13}C$ data (see Fig. 7.30), three possible origins of DIC can be proposed, or some combination of them:

(xx) only soil CO_2 is incorporated, in an open system in which recharge is in equilibrium with the CO_2 rich unsaturated zone air; original organic matter derived CO_2 is close to $\delta^{13}C$ = –25‰ PDB, after a few analyses of the vegetation, but it is not known how $\delta^{13}C$ of CO_2 in soil air changes with depth and effect of air CO_2 in bare areas.

(xxi) There is some volcanic CO_2 input, which slowly diffuses from deep-seated magma chambers. This is not expected due to the lack of volcanic activity for a long time in this area, but is not impossible since other areas of the island some km away show subhistorical activity and there are well producing CO_2 rich water. The composition of this CO_2 is not known but can be assumed close to $\delta^{13}C$ = –8‰.

(xxii) Soil and/or volcanic CO_2, weathering silicate minerals, dissolve the carbonate encrustations in the rock fissures and voids that can be seen in the cores of some deep boreholes. The $\delta^{13}C$ of these carbonates is not known but may be assumed in equilibrium with volcanic CO_2, or $\delta^{13}C \approx 0$‰ if formed at low temperature, but may be as light as $\delta^{13}C \approx -8$‰ if formed at high temperature, after the fractionation factors (Friedman and O'Neil,

Table 7.5. $\delta^{13}C$ and $\delta^{14}C$ data on Amurga and Fataga areas.

Well	Year	$\delta^{13}C$ ‰ PDB	$\delta^{14}C$ pmc	TDIC mmol/L
Fataga 1	1986	–8.47	6.5±0.9	5.6
Fataga 1	1997	–8.56	6.7±0.2	5.0
Fataga 7	1986	–12.15	58.9±0.9	2.0
Fataga 7	1997	–11.80	57.9±0.4	2.0
Amurga 11	1986	–12.71	24.6±1.0	2.2
Amurga 12	1986	–12.13	27.3±0.7	2.3
Amurga 17	1997	–12.34	17.2±0.4	3.0
Amurga 18	1997	–12.07	25.8±0.5	2.4
Amurga 21	1986	–12.62	29.5±0.7	3.7
Amurga 21	1997	–10.04	34.8±0.3	4.9
Amurga 25	1997	–11.86	26.4±0.3	2.2

TDIC = total dissolved inorganic carbon

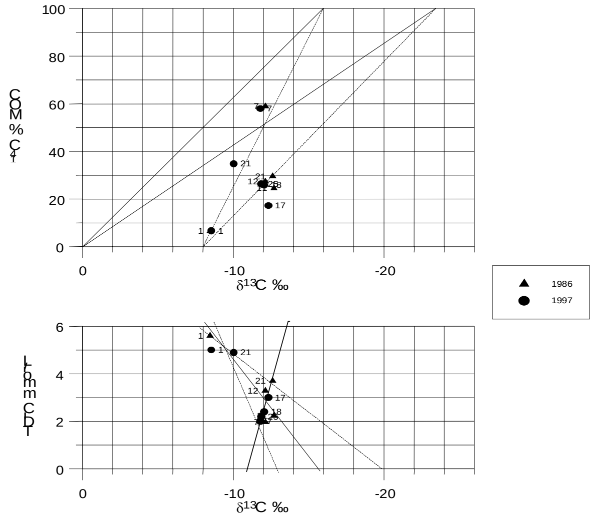


Figure 7.30. ^{14}C and TDIC content vs. $\delta^{13}C$ and possible relationships.

1977).

The work carried out by Gasparini (1989) shows that $\delta^{13}C$ content of soil CO_2 is highly variable, without a clear relationship with site, depth, lithology or vegetal cover. Values close to –15‰ seem common (effect of CAM dominated vegetation?) but in the study area ranges between –11‰ (base soil) and –22‰.

The age correction yield values from recent to about 11 000 years. This last value seems the most consistent. If it is accepted this means that abstracted water from the Amurga Massif is mostly late Pleistocene palaeowater. This is in agreement with the thick unsaturated zone and the small recharge values if piston flow or a dispersive mixing model with a dispersion parameter less than the unsaturated thickness is assumed (Custodio, 1992b).

7.5.4 Conclusions

Salinity of groundwater is due to environmental aridity and relatively high airborne salinity. No direct seawater intrusion or trapped marine water existed under natural conditions.

Abstracted water age is uncertain but a value about 11 000 years seems a reasonable compromise which is compatible with the small mean recharge, the thick unsaturated zone and the turnover time in the unsaturated zone.

Groundwater was recharged probably under similar environmental conditions as those existing today. If a late Pleistocene age is admitted for groundwater this means that no significant isotopic shift appears due to climatic change at these latitudes (27ºN).

The thick unsaturated zone is the responsible for the existence of what appears as palaeowater in the aquifer.

7.6 Concluding remarks

The situation observed in the Doñana aquifer suggests that approximately half of the confined Pleistocene aquifer has been freshened by fresh groundwater flowing during a period of some 6 ka BP.

This situation applies to several other aquifers along the Spanish coast such as the Ebre delta (Bayó *et al.*, 1997). In these areas there are not large reserves of old fresh water, but the known geological and water head evolution during the Late Pleistocene–Holocene period can be used to forecast what may happen during a possible future elevation of the sea level in areas with moderate average groundwater recharge and low topographic slopes. The characterization of the quality changes in the recharge water due to mixing with trapped old salt water is then the main question to be addressed in these areas.

A different situation is that of the Llobregat delta deep aquifer and other small deltas in the Mediterranean coast (Custodio and Bruggeman, 1987) where salt water was flushed out to the sea, but later sea water encroached easily under intensive development.

In the coastal area of the Inca-Sa Pobla aquifer the whole aquifer thickness (Miocene to Holocene carbonate rocks and detritic sediments) has brackish and saline water. This suggests that during the Holocene the only natural discharge mechanism of the aquifer was upward flow of fresh water along the fresh-salt water interface in the surroundings of the S'Albufera wetland, together with upward flow of saline water along the NW and SE boundaries of the wetland. Some palaeoclimate signature in saline groundwater of the coastal area of the aquifer is not discarded, although further isotopic and geochemical studies have to be carried out to confirm this.

The convective flows found in S'Albufera area makes the interpretation of water chemistry to depend on the particular hydraulic configuration of each sampling point. Hydraulic gradients favour the vertical mixing of salt water of different ages and young fresh water, although the mechanism is not yet fully understood. From the point of view of the PALAEAUX objectives the main interest of this aquifer lies, as in the case of Doñana, in the chemical changes affecting recharge water as well as in the quantification of the time needed for the mixing processes to take place.

In the Amurga Massif groundwater salinity is due to environmental aridity and relatively high airborne salinity. No direct seawater intrusion or trapped marine water existed under natural conditions. Abstracted water age is uncertain but a value about 11 000 years seems a reasonable compromise which is compatible with the small mean recharge, the thick unsaturated zone and the turnover time in the unsaturated zone. Groundwater was recharged probably under similar environmental conditions as those existing today. If a late Pleistocene age is admitted for groundwater this means that no significant isotopic shift appears due to climatic change at these latitudes (27ºN).

8 Geochemistry and flow modelling of the Aveiro multilayer Cretaceous aquifer, Portugal

8.1 Introduction

The Aveiro Cretaceous coastal aquifer is located in northwestern Portugal, covering an area of 600 km^2 in the Portuguese Western Meso-Cenozoic sedimentary basin. The region has a warm humid climate with wet and dry seasons. Mean annual rainfall varies between 1000 and 1400 mm a^{-1}. This region is one of the most industrialized areas in Portugal with a high population density, and since the 1960s relies on groundwater for most of the urban and industrial water supply.

In recent years a continuous fall in the water table has been observed due to intensive groundwater abstraction, leading in some areas to values of 25 m below m.s.l. Because it occurs in a coastal aquifer, partially confined and with limited natural recharge it can lead to gradual deterioration of the water quality either because of salt-water intrusion or due to mixing with very high-mineralized waters from deeper aquifer levels, nowadays with higher water potentials.

Previous detailed studies of the aquifer include the works done by Marques da Silva (1990), Carreira *et al.*, (1996) and Carreira (1999). During the PALAEAUX project it was expanded the work done by these authors to the southern and eastern part of the study area. The new geochemistry data obtained is considered to be important for the characterization of the interface between modern and old water, and to evaluate the extent of mixing with waters from adjacent aquifers.

From the point of view of the PALAEAUX project the Aveiro Creataceous aquifer is quite unique in Europe and very important as an archive of past climate conditions in temperate regions of Europe. In contrast to what is observed in northern Europe aquifers, enrichment in $\delta^{18}O$ (Δ= 0.8-1.0‰) and $\delta^{2}H$ (Δ= 5-7‰) is found in the late Pleistocene recharge waters of the Aveiro aquifer. This is considered to reflect the enrichment in the Pleistocene ocean water as well as the constancy in the source of moisture.

The aquifer groundwater contain a smooth record of radiocarbon ages indicating continuity of recharge through the LGM and noble gas recharge temperatures indicate that atmospheric cooling of 5-6°C occurred before and during the LGM (Carreira, 1999).

Being a unique aquifer in Europe from the geochemistry point of view and a vital resource for the region, the Aveiro aquifer is of significant economic importance, which makes important the adequate evaluation, exploitation, management and conservation of its resources.

Detailed hydrochemical studies, including the analysis of major, minor and trace elements, and groundwater modelling are used to gain better understanding of aquifer behaviour and as a scientific tool for groundwater management.

8.2 Hydrogeology

Cretaceous sediments in the region are mainly siliciclastic and generally of transitional and continental depositional environments. The only exception to this continental sequence was the deposition of carbonate sediments of platform facies during the Cenomanian transgression

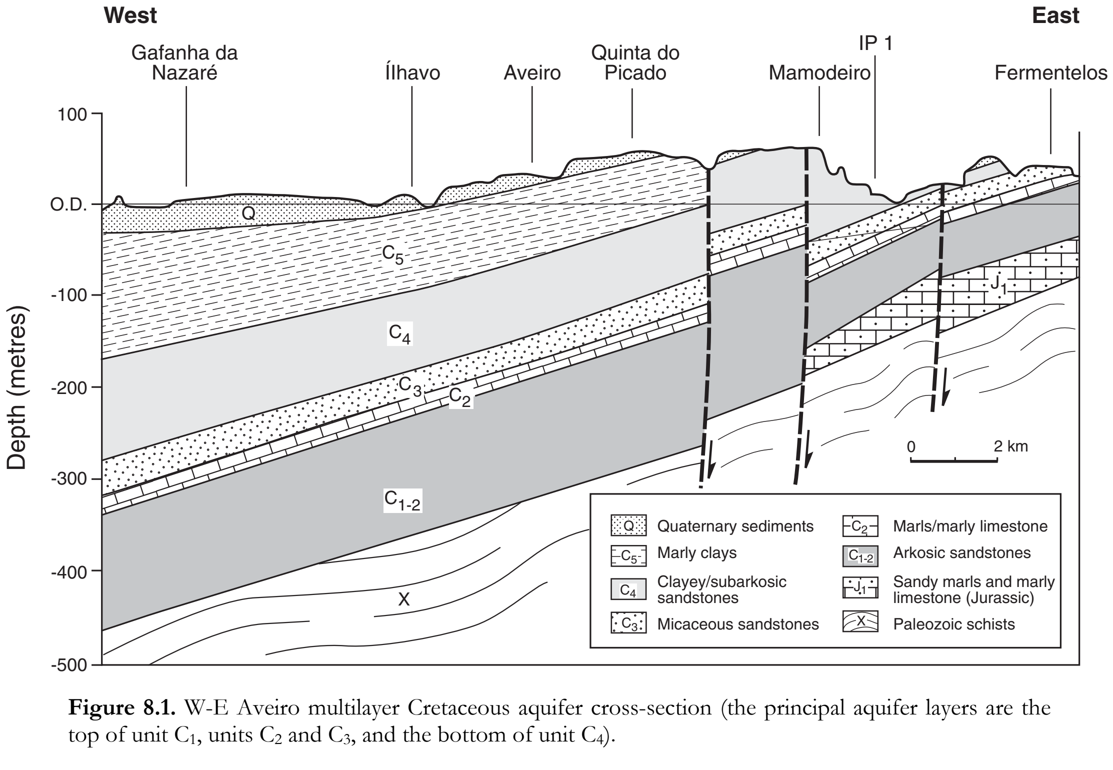


Figure 8.1. W-E Aveiro multilayer Cretaceous aquifer cross-section (the principal aquifer layers are the top of unit C_1, units C_2 and C_3, and the bottom of unit C_4).

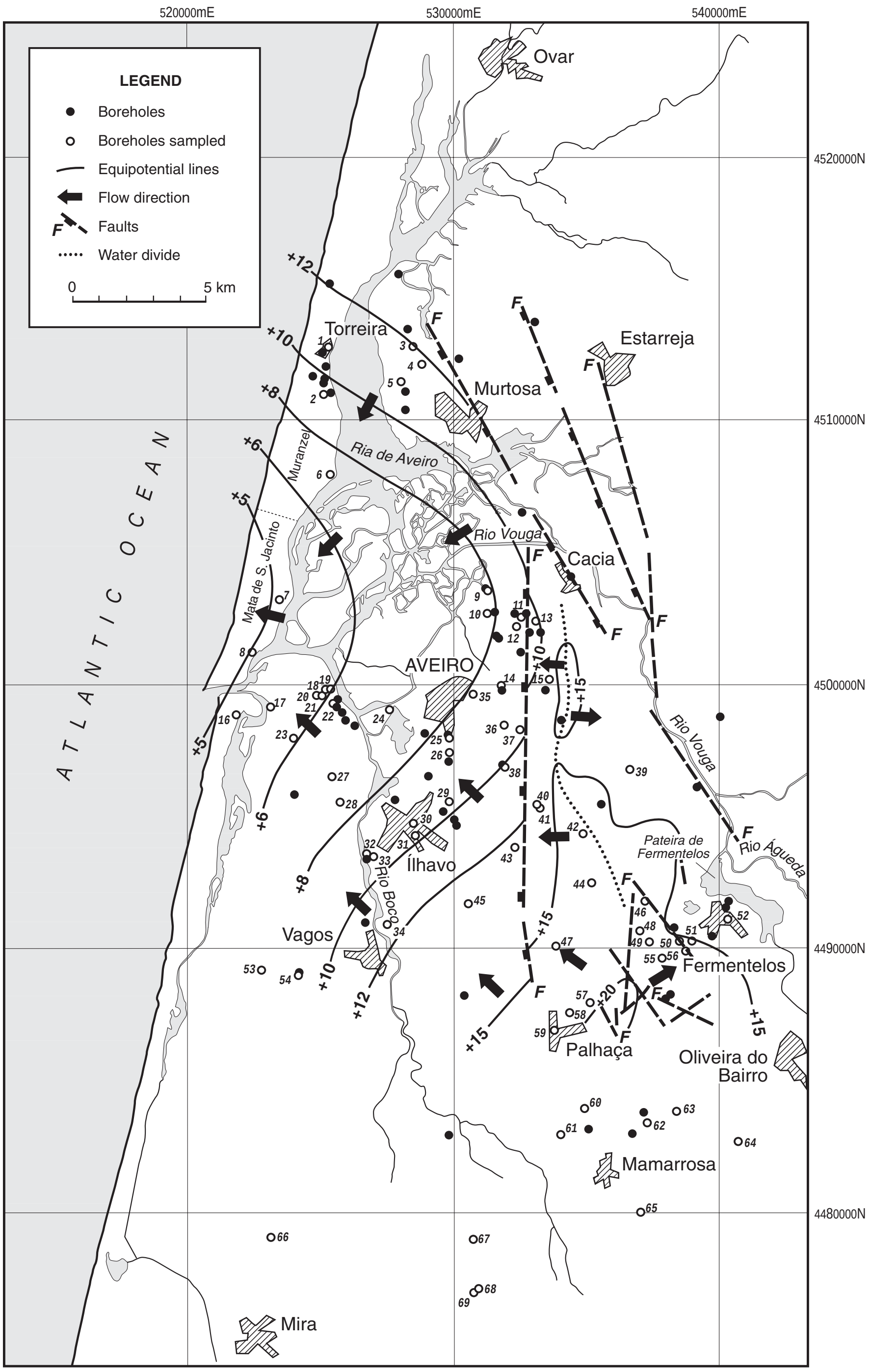


Figure 8.2. Location of groundwater sampling sites (natural flow pattern according to Marques da Silva, 1990)

(Teixeira and Zbyszewski, 1976; Barbosa, 1981).

Five lithostratigraphic units can be defined in the region: C_1 – Lower Sandstone Formation ('Palhaça Sandstone'), C_2 – Carbonate Formation, C_3 – Micaceous Sandstone, C_4 – Upper Sandstone Formation (at the bottom, 'Oiã Sandstone' and, on top, 'Verba Sandstone') and C_5 – Marly Clays ('Aveiro Clays'), represented here in the W-E cross section illustrated in Fig. 8.1.

These units have different grain sizes and mineralogical compositions, forming a multilayer aquifer system with different hydrogeological properties. From a hydrogeological point of view, the most productive units and with the lowest salinity levels correspond to the top of unit C_1, the entire unit C_3, and the bottom of unit C_4.

Although the carbonate layer (unit C_2) is not significant in terms of thickness (less than 8% of the total aquifer thickness), it presents hydrogeologic characteristics in the majority of the study area that permit its exploitation. The top of the unit C_4 and the bottom of unit C_1, due to their low permeabilities are usually considered as aquitards.

The Cretaceous strata dip gently to NW beneath the present coastline. Faults of approximately N-S orientation affect the complete sequence of Cretaceous sediments. The confining marly clay unit (C_5) is not present in the eastern part of the study area where the aquifer is unconfined.

Recharge to the aquifer by rainwater infiltration has been calculated to vary between 100 mm a^{-1} (calculated from the chloride balance) and 130 mm a^{-1} (calculated from the unsaturated zone studies).

The groundwater flow direction under natural conditions is from the recharge area in the east towards the sea, with a natural gradient around 0.002. Large groundwater abstraction during the last ten years in the area of Gafanhas and between Aveiro and Cacia has resulted in a large depression of the piezometric surface and in a reversal of the natural flow direction.

8.3 Analytical Methods

Water samples for laboratory analysis were collected from 62 public supply and private boreholes (over 160 m deep) during two field campaigns carried out in October 1996 and September 1997 (Fig. 8.2).

As it is common in the region all the boreholes are multiscreen, pumping water from the different aquifer layers. The water samples obtained correspond to a mixture of waters of the different aquifer layers with different chemical characteristics, making the interpretation of the chemical results more difficult. Two water samples were collected simultaneously from each borehole and filtered through 0.45 μm membrane filters, once stabilization of the principal field parameters – pH, conductivity, temperature, dissolved oxygen and redox potential on anaerobic conditions was observed.

An acidified sample (1% v/v AristaR HNO_3) was used for analysis by ICP-OES and ICP-MS, while the other unacidified sample was analysed for Cl^-, F^- and total oxidized nitrogen (TON) by automated colorimetry, and HCO_3^- by automated titrimetry.

During the second field campaign water samples were also collected in glass bottles for isotope analysis of $\delta^{18}O$, δ^2H, $\delta^{13}C$ and ^{14}C in order to extend to the southern part of the study area the previous isotopic study of the aquifer by Carreira *et al.*, (1996).

8.4 Hydrogeochemistry

The natural hydrogeochemical evolution trends from Ca-HCO_3 type waters near the recharge area to Na-HCO_3-Cl type waters in the areas close to the coast. These groundwaters have their origin in part associated with the infiltration of rainwater of Atlantic origin and the flushing of older sea water.

The trend towards Na-HCO_3 indicates that ion exchange was a dominant geochemical process in the aquifer, probably reflecting cation exchange processes that occurred in the initial phases of the aquifer leaching by dilution of the original saline water from clay minerals

Br/Cl ratios of the groundwater samples plot on a mixing line between the rainwater and seawater ($[Br^-]/[Cl^-]=0.0016$) which is consistent with Cl^- being mainly of marine (aerosol) origin (Fig. 8.3).

Na/Ca molar ratio increases along the aquifer towards the coast confirming that cation exchange is an important process in the aquifer. Cation exchangers in the aquifer have mostly Na^+ adsorbed on the surfaces. In the areas closer to the coast Ca^{2+} is being taken up from water, in return for Na^+, which is being released in solution (Fig. 8.4).

The increase of the anion HCO_3^- in the waters close to the coast saturated with respect to calcite is an indirect consequence of the processes of cation exchange, because the reduction of the amount of Ca^{2+} in solution resulting from cation exchange leads to further calcite dissolution.

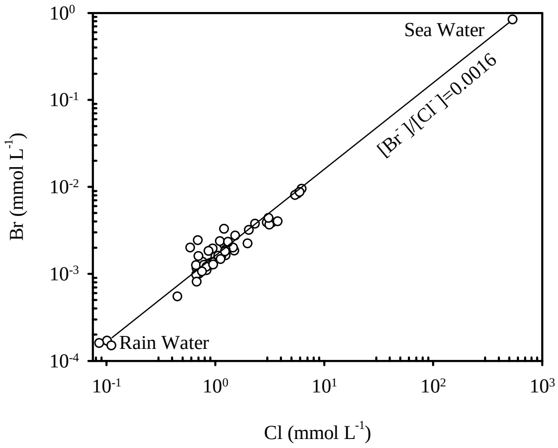


Figure 8.3. Relation between Br^- and Cl^- content in the groundwater samples.

Fresh groundwater in the Aveiro Cretaceous aquifer is of remarkably low salinity (below 100 mg L^{-1}≈2.8 mmol L^{-1} Cl^-), corresponding to less than 1% of the fraction of seawater in the groundwater composition (based on conservative mixing of sea water and fresh water) (Fig. 8.4).

The dilute nature of the Aveiro groundwaters indicates previous freshening of the coastal aquifer. Higher hydraulic gradients (~0.004) during the Last Glacial Maximum (LGM) imposed by a sea level lowered by approximately 100m compared to present day must have contributed to the complete refreshening of the aquifer, with fresh water flushing the original salt water to the sea. However, the hypothesis of the aquifer being flushed even before LGM should be also considered.

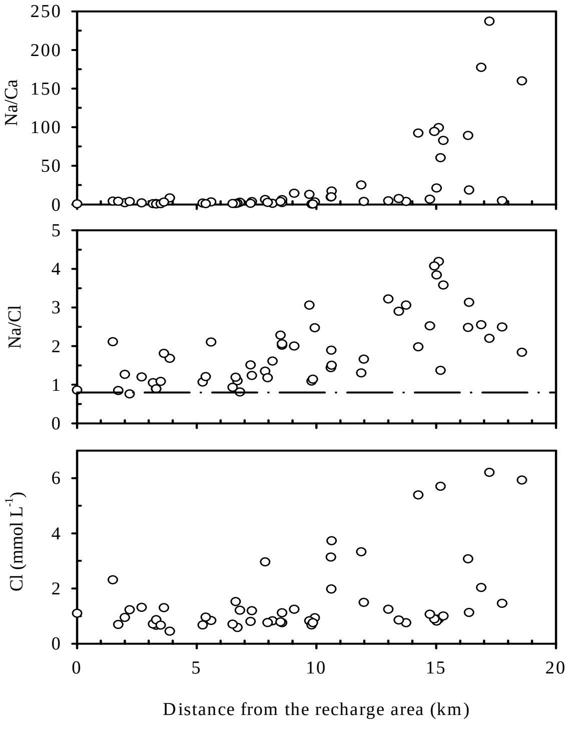


Figure 8.4. Evolution of the Na/Ca, Na/Cl molar ratios and Cl^- content along the flowpath.

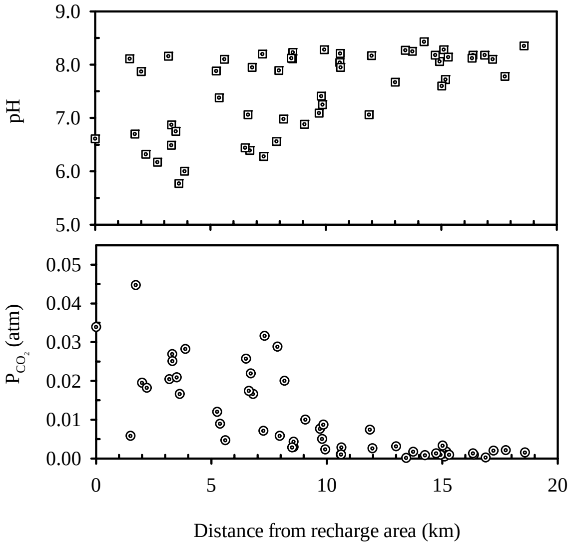


Figure 8.5. Groundwater pH and P_{CO_2} evolution along the flow path.

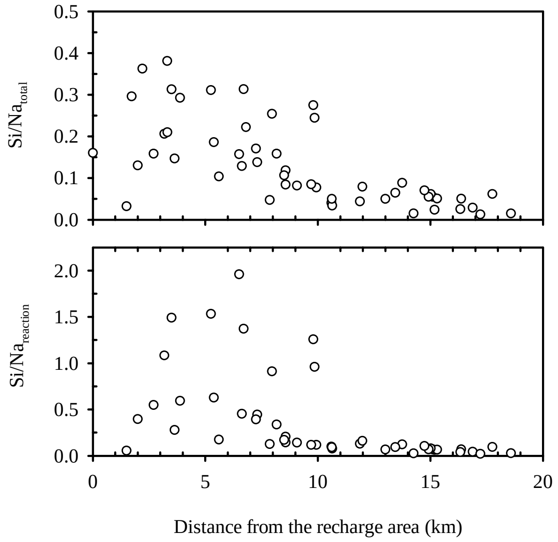


Figure 8.6. Evolution of $Si/Na_{reaction}$ and Si/Na_{total} content along the flowpath.

Sodium is the dominant cation, but the Na/Cl ratio is not consistent with a simple fresh/seawater mixing process. Some other geochemical process such as silicate weathering must be liberating solutes to solution. Aquifer silicate minerals can be a source of solutes through dissolution and a sink via the processes of adsorption and precipitation.

The decrease of the P_{CO_2} along the flowpath confirms that mineral reaction is taking place (Fig. 8.5).

The dissolution of silicate minerals is generally a very slow process that may not produce significant variations of the water chemistry. This was clearly observed in the studied area where the groundwater silica concentrations are remarkably uniform for all aquifer, providing evidence of a coastal aquifer formed of predominantly siliceous material with very slow dissolution kinetics.

Sodium feldspar dissolution might be responsible for the Na/Cl ratios higher than one, or for the high ratio of Na^+ to Ca^{2+}. Local rainwater has annual averaged Na/Cl ratios of 1.21 (Table 8.1), close to the characteristic value for the seawater (0.85) and reflecting the marine aerosol.

In this region only the recently recharged groundwaters have Na/Cl ratios close to 0.85–1.2. These groundwaters are the result of rainwater infiltration, reflecting just the chemical composition of local precipitation, and the residence times have not been long enough to show any chemical evolution due to water-rock interaction.

The ratio of Si to Na is a reflection of the dominant weathering processes. Figure 8.6 shows the evolution of this ratio along the flow path. Si/Na ratio decreases along the flow path, from values around 0.40 in the recharge area to values of 0.02 in the deeper part of the aquifer.

Table 8.1. Annual averaged local rainwater composition (data in mmol L^{-1})

Na^+	K^+	Ca^{2+}	Mg^{2+}	Na/Ca	δ^2H (‰)
0.109	0.007	0.043	0.028	2.55	-4.7
Cl^-	SO_4^{2-}	HCO_3^-	Br^-	Na/Cl	$\delta^{18}O$ (‰)
0.090	0.055	0.096	0.000	1.21	-25.7

Considering just the sodium due to silicate reaction and discarding mixing with sea water, a ratio of Si to Na lower than two is derived. That value cannot be formed by the weathering of common rocks to kaolinite or gibbsite therefore; a 2:1 silicate such as smectite must be forming (Drever, 1997).

The results obtained to date confirm the division of the aquifer into two parts with different hydrogeochemical characteristics. Decreasing Eh, NO_3 and U indicate the presence of a redox boundary close to the unconfined-confined boundary (Melo *et al.*, 1998).

In the unconfined part of the aquifer, corresponding to the recharge area, oxidizing groundwaters with low pH (~5.5) and temperature (~18°C) were found. These parameters increase gradually along the aquifer cross-section towards the coastline. Increase in groundwater temperature is an indicator of the increasing depth of abstraction, while the increase in pH is the result of CO_2 consumption during silicate dissolution. Calcite dissolution leads to a higher pH of around 8.3 in the boreholes closer to the coast.

Although the carbonate layer (unit C_2) makes up less than 8% of the aquifer, calcite is still a dominant source of solutes during weathering. Minerals do not contribute to the solutes in groundwater in proportion to their abundance in the bedrock.

The stability of these minerals in the groundwater system was evaluated by calculating the saturation state for different minerals using PHREEQC (Parkhurst, 1995) (Fig. 8.7).

The groundwaters are saturated with respect to quartz. Subsaturation persists for plagioclases and other felsdspar minerals. Calcite dissolution is still taking place increasing the degree of saturation along the aquifer and the waters from the areas closer to the coast achieve saturation with calcite.

Most silicate minerals dissolve incongruently with the formation of iron oxides and clay minerals. The formation of secondary minerals complicates the interpretation of solute concentrations, and it seems questionable whether true equilibrium with these secondary phases is ever attained (Appelo and Postma, 1996).

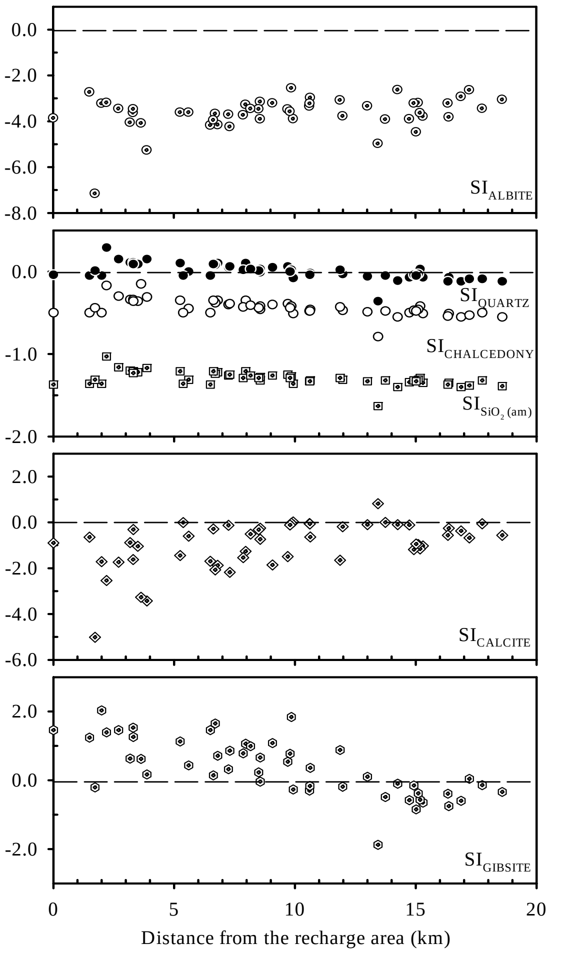


Figure 8.7. Evolution of groundwater saturation indexes for albite, silica polymorphs, calcite, and gibsite along the flowpath.

The validity of the results obtained for the saturation indices of the different minerals relies on the accuracy of the analytical data. When calculating the saturation of silicate minerals, dissolved aluminium (<0.45 μm) concentrations are taken into account. However considering that the concentration of total dissolved aluminium in most groundwater samples was less than 0.006 mg L^{-1} (2σ detection limit is 0.32 μg L^{-1}), the potential importance of the analytical error should be emphasized.

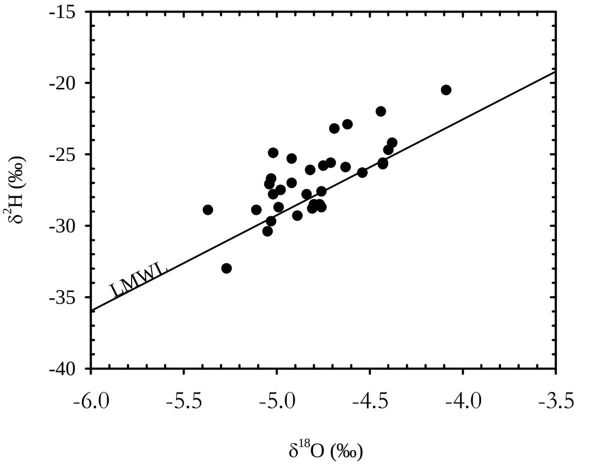


Figure 8.8. The $\delta^{18}O$ and $\delta^{2}H$ composition of groundwaters.

8.5 Modern-old water interface

Temperate latitude climates have experienced significant changes in temperature since late Pleistocene time that are shown by a shift in the stable isotope content of precipitation, and in deuterium excess. According to Clark and Fritz (1997) this palaeoclimatic effect is one of the most important tools in identifying palaeogroundwaters.

The isotopic database for the Aveiro aquifer was expanded during PALAEAUX project to areas further south and eastern within the study area. All the new isotopic data, including the ^{14}C determinations, are summarized in Table 8.2.

The new isotopic results confirm the existence of late Pleistocene groundwaters in the confined part of the aquifer but also show that mixing with modern waters is occurring in the areas close to the recharge area.

Late Pleistocene groundwaters are characterized by a slight enrichment in ^{18}O and ^{2}H with respect to modern waters reflecting the probable heavy isotope enrichment of the ocean during glacial times as it was justified by Carreira *et al.*, (1996) (Fig. 8.8).

The associated use of hydrochemical data (NO_3, Cl content) with the isotopic results has let us define approximately the interface between modern and old water in the aquifer. This limit may coincide with faults N-S that affect the whole thickness of the aquifer and seem to be acting as low permeability regions, restricting the modern water recharge (Fig. 8.9).

Table 8.2. Summary of the new isotopic data for the study area.

MapRef	National Grid Ref.	$\delta^{18}O$	$\delta^{2}H$	$\delta^{13}C$	^{14}C
		‰	‰	‰	pmc
2	162A/007	–4.43	–25.7	–12.5	2.74
3	163/005	–4.43	–25.6	–14.6	3.50
6	173/003	–4.09	–20.5	–10.6	1.93
10	174/012	–4.69	–23.2	–12.3	3.68
11	174/014	–4.71	–25.6	–16.2	
13	174/019	–5.05	–30.4	–14.2	
17	184/007	–4.92	–27.0	–11.6	
18	184/002	–5.04	–27.1	–12.6	
19	185/016	–5.02	–27.8	–12.0	
27	184/006	–4.63	–25.9	–12.9	
34	196/001	–4.82	–26.1	–12.7	
35	185/054	–4.44	–22.0	–12.6	
39	185/039	–4.92	–25.3	–22.2	
43	185/011	–5.03	–26.7	–12.2	
46	185/032	–4.99	–28.7	–17.6	52.21
48	196/020	–4.98	–27.5	–16.2	
52	185/042	–4.38	–24.2	–19.8	
53	195/003	–4.84	–27.8	–12.4	7.28
54	195/001	–4.40	–24.7	–13.1	1.92
55	196/024	–4.81	–28.8	–18.7	
57	196/022	–4.75	–25.8	–11.6	28.15
59	196/009	–5.37	–28.9	–19.2	
60	196/005	–4.89	–29.3	–13.2	
61	196/025	–4.62	–22.9	–17.6	
62	196/015	–5.11	–28.9	–14.4	
63	196/019	–5.02	–24.9	–22.1	64.87
64	196/021	–5.27	–33.0	–13.9	
65	196/023	–4.76	–27.6	–14.3	
65	207/004	–4.76	–28.7	–26.8	
66	206/001	–4.54	–26.3	–16.7	
67	207/002	–4.80	–28.5	–14.1	
68	207/003	–4.77	–28.5	–12.5	34.23

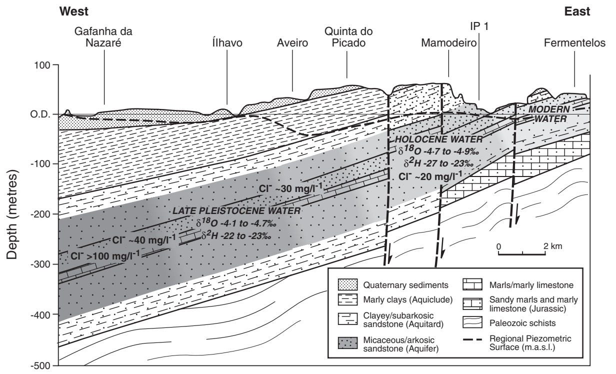


Figure 8.9. Modern-old water interface in Aveiro Cretaceous aquifer.

8.6 Flow modelling

In addition to detailed hydrogeochemical studies, flow modelling of the Aveiro Cretaceous aquifer is being used to study the groundwater flow system, and gain a better understanding of the areal distribution of the hydraulic properties in the aquifer.

For the model exercise the same cross-section as for the previously described hydrochemical studies was considered (Fig. 8.1). This way geochemical data was used whenever possible to strengthen the conceptual model, defined with the physical hydrologic data.

The modelled cross-section is 22 km in length, and the thickness varies between 60 m in the eastern part of the aquifer to over 400 m in the areas close to the coast. The database consists of information from more than 120 wells and test borings with water level data available for over 60 wells.

Groundwater flow was simulated using a profile finite-difference model MODFLOW (McDonald and Harbaugh, 1988). The interest of using a cross-sectional model at this stage was to test the validity of the conceptual model of the system, prior to designing a full three-dimensional model, and also to confirm the regional patterns of the flow system.

The main aquifer cross-section was discretized into 220 columns and 13 layers, 8 layers more than defined in the conceptual model (Fig. 8.10). This allows simulation of the vertical changes in permeability caused by regional faulting.

As a first approximation flow was considered to be at steady state. Horizontal hydraulic conductivity was considered to be 100 and 10 times higher than vertical values for the aquifer and aquitard layers, respectively, varying with depth and also spatially, with distance to the coast. The deposits closer to the coast were considered less permeable than their equivalents in the central part of the aquifer.

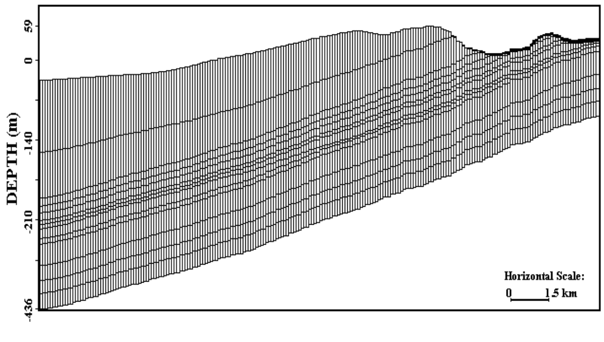


Figure 8.10. Finite difference grid used in the simulation (220 columns × 13 layers)

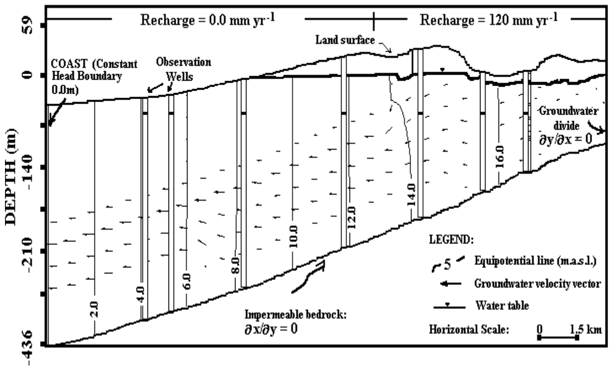


Figure 8.11. Head-distribution for steady-state simulation.

Aquifer transmissivities and storage coefficient values were determined from the interpretation of pumping test data. Table 8.3 summarizes the main values used in the simulation.

The upper boundary of the model was simulated as a flux boundary as recharge was assigned to the top layer of the aquifer. In the eastern part of the aquifer, where the permeable layers crop out providing a preferential route to groundwater recharge, recharge rates were estimated to be around 120 mm a^{-1}, about 10% of the annual mean rainfall. In the confined part of the aquifer recharge was considered to be equal to zero.

The bottom boundary represented the depth at which impermeable rock was encountered and was simulated as a no flow boundary. A constant head boundary was used to simulate saltwater interface.

Discharge from the aquifer was considered to be due to groundwater pumping, and just 4% were attributed to flow to surface water bodies and across the aquifer boundaries.

Flow modelling preliminary results for steady-state simulation are represented in Fig. 8.11, and confirm the reduced natural hydraulic gradient for the aquifer.

Table 8.3. Aquifer properties and hydraulic parameters

Major Aquifer	Cretaceous Sandstone, C3
Aquifer Type	Matrix porosity Confined
Transmissivity	$2.3\times10^{-3} - 4.6\times10^{-3}$ m^2 s^{-1}
Storage Coefficient	5×10^{-4}
Porosity	20%
Upper Confining Layer	Cretaceous marly clays, C5
Hydraulic Conductivity	1.2×10^{-8} m s^{-1}
Porosity	40%
Lower Layer	Cretaceous clayey sandstone
Hydraulic Conductivity	1.2×10^{-7} m s^{-1}
Porosity	20–30%
Basement	Pre-Paleozoic and Paleozoic Schist
Mineralogy (Rocha, 1993)	Quartz, Phylosilicates, K-Feldspar Plagioclase, Kaolinite, Illite, Smectite

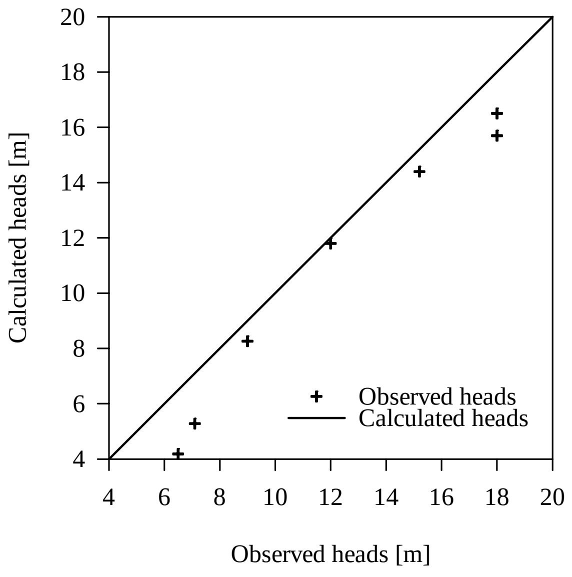


Figure 8.12. Calculated heads versus observed heads.

The head distribution obtained for steady-state simulation was compared with water level data for the reagion before any groundwater exploration started, as it was suggested by Marques da Silva (1990). The results are plotted in Fig. 8.12.

The simulated heads agree well with observed heads for the region, corroborating in principal the validity of the conceptual model considered and confirming the aquifer limited groundwater recharge.

8.7 Conclusions

From the hydrochemical point of view the results obtained show an aquifer with a very slow chemical kinetics for the water-rock interactions resultant from the mainly siliciclastic composition of the aquifer sediments. Calcite dissolution and cation exchange are the other processes responsible for the groundwater chemical composition.

Geochemistry data confirm the existence in the confined part of the aquifer of late Pleistocene and Holocene fresh waters, having a slightly enriched isotopic signature.

There is evidence of fresh water circulation to depths over 250 m OD in areas about 500 m from the present day coastline.

Flow modelling was important to check the validity of the conceptual model suggested for the aquifer, and contributed to confirm the reduced natural hydraulic gradient and the limited aquifer natural recharge.

9 Evidence for palaeowater in theLower Tagus and Lower Sado aquifers, Portugal

9.1 Introduction

The Lower Tagus and Lower Sado aquifer is located in the Setúbal-Lisbon region and represents an important water resource for a vast region. The highly populated urban and industrialized areas of Setúbal and Lisbon are supplied by this system, which has been extensively exploited over the recent decades.

A hydrogeological study using chemical analysis and environmental isotope techniques was performed from 1987 to 1991, on a small group of wells located near the Sado estuary. In order to better understand the present flow pattern and groundwater evolution and dynamic changes from 1991 to 1998, fieldwork was initiated near Setúbal and developed approximately along a N-S line from the Sado river (Troia Peninsula) to the Tagus river southern margin. This cross-section was selected to examine the hydrochemistry and isotopic evolution of the groundwater from the recharge area in the north of the basin down-gradient. The work was performed with the collaboration of the Portuguese National Water Institute, who are responsible for the water management in Portugal and who have been reporting an increase in the groundwater mineralization all over the Setúbal peninsula (south of Lisbon).

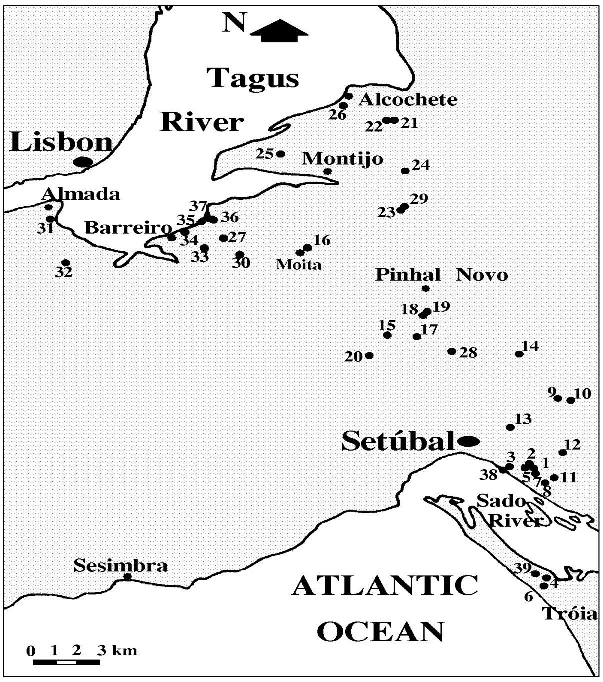


Figure 9.1. Location of the sampled wells in the Lisbon-Setúbal region.

In order to find out the source of salinization in the Miocene and Pliocene aquifers chemical (Cl^-, HCO_3^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+, and K^+) and isotope analyses (^2H, ^{18}O, ^3H and ^{14}C) were performed on groundwater samples collected in 39 boreholes as part of the PALAEAUX project (Fig. 9.1). There is a growing concern in the region that further exploitation may be threatened by pollution due to a mixing with shallow aquifer, or due to seawater intrusion or brine dissolution.

9.2 Hydrogeological setting

The Lower Tagus and Lower Sado aquifers lie within a synclinal structure and are composed of Tertiary sediments, mainly marine deposits. In the region, three main groundwater systems have been identified: a shallow Quaternary aquifer composed of alluvial sediments showing high transmissivity values, followed by the Pliocene and Miocene aquifers. The Miocene sediments show an average thickness that ranges from 200 to 300 m, although in the central part of Setúbal peninsula (SE of Lisbon), these values increase to 800 m (Fig. 9.2).

The Miocene deposits, made up of sandstones and limestones of marine origin, are related to different marine transgression and regression events. Overlying the schist

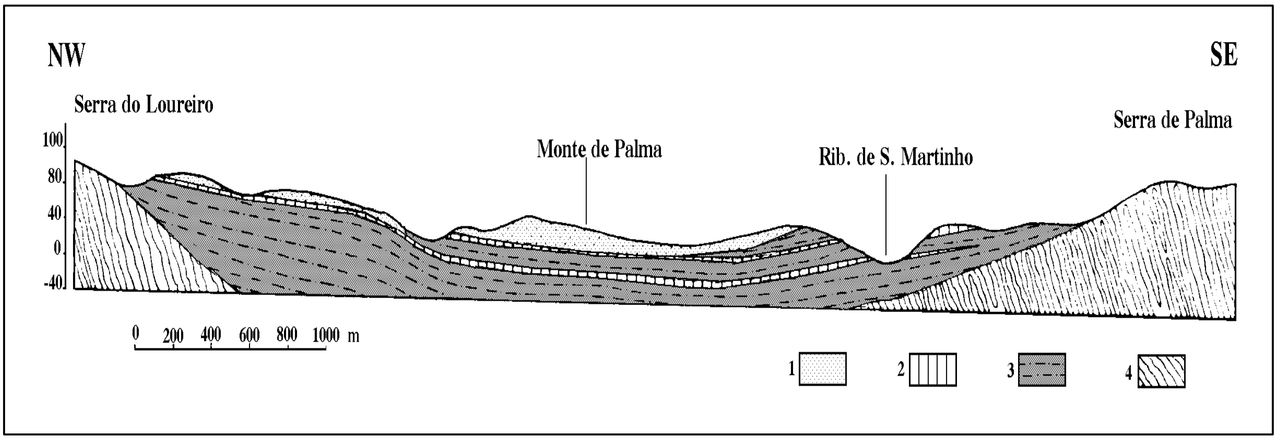


Figure 9.2. Cross-section between Serra do Loureiro and Serra de Palma. 1– Silt-sandstone formation. 2– Carbonate layers, marine Miocene. 3– Sedimentary sequence of clay and sandstones (Miocene). 4– Schist and greywacke from the upper Devonian.

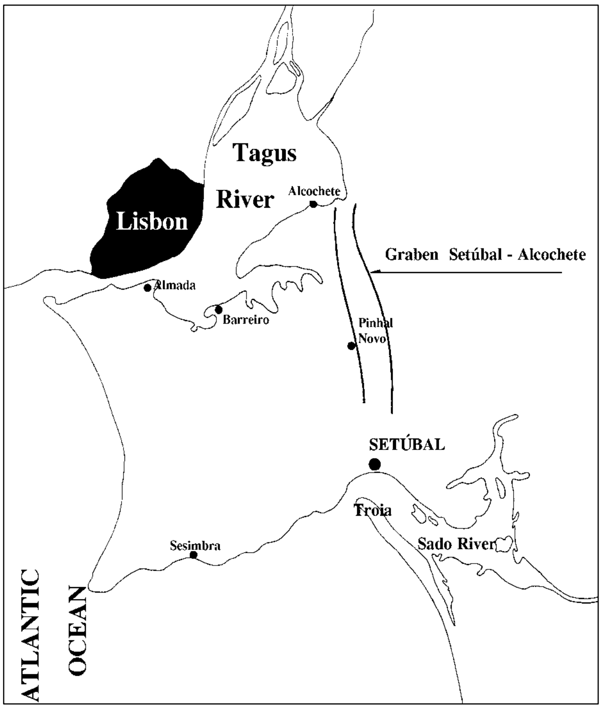


Figure 9.3. Location of the graben Setubal-Alcochete structure, detected in depth trough geophysical studies.

and greywacke formations of the upper Devonian, the Miocene deposits underlie clays and sand layers from the upper Miocene and Pliocene. The Pliocene sediments are mainly composed of fluvial terraces (sands and clays). The Quaternary alluvial deposits (shallow aquifer) represent the top of the sedimentary sequence.

The geophysical studies performed in the basin, show that the Miocene sediments are crossed by two important faults. The first is located in the lower Tagus valley with a N30°E direction, while the other one, the so-called Setúbal-Pinhal Novo fault, also detected at depth runs N-S forming a graben structure (Fig. 9.3). This fault is considered to allow a brine or ancient seawater trapped in the sediments during the formation of the Lower Sado basin to rise to shallow depths in the basin.

The lithological information based on boreholes reveals a complex sedimentary sequence of sands and clays, with different transmissivity values (T) and hydraulic conductivity (K). A variety of values ranging from T=15 up to 2000 $m^2 d^{-1}$ and K=1 to 100 $m d^{-1}$ were obtained in the region (Gonçalves & Andrade Afonso, 1998). These mean values of transmissivity and hydraulic conductivity variations are the result of the different lithologies observed in the sedimentary basin (sand and clay formations) and the lateral spatial inhomogeneities related to the formation of the sedimentary basin (Table 9.1).

Table 9.1 Hydrogeological and geophysical parameters at Setúbal peninsula

Map reference	Transmissivity $(m^2 d^{-1})$	Hyd. Conductivity $(m d^{-1})$	H_2O(1) (Ωm)	Sand(2) (Ωm)	Porosity(3) (%)
432	650	29	34	140	24
434	420	16	67	140	38
443	700	39	50	195	24
444	830	34	72	250	21
445	320	10	39	170	25
454	254	17	33	140	15
455	530	33	65	210	14

(1) H_2O – Electrical resistivity of water
(2) Sand – Electrical resistivity of the permeable layer
(3) Porosity of the permeable layer

From the hydrogeological point of view these sediments with different permeabilities occur throughout the basin creating a multi-layer aquifer. The presence of a continuous clay layer throughout the basin separates this multi-layer system into two main aquifers: the deeper aquifer (Miocene) and the shallow aquifer (Pliocene). The Miocene aquifer acts as semi-confined aquifer since the impermeable clay layer tends to act as an aquitard allowing some cross flow between the two main units.

The intensive exploitation of the Miocene aquifer in the coastal areas can lead to seawater intrusion problems in wells located near the coast or along the Tagus and Sado rivers.

The mean annual temperature in the region is around 16°C, and the mean annual precipitation range between 500 up to 700 mm (Fernandes & Silva, 1998).

9.3 Results and discussion

9.3.1 Hydrochemistry

The hydrochemical evolution of the groundwater is characterized by a progressive increase in the total dissolved solids, ranging from 80 mg L^{-1} up to 2565 mg L^{-1} in the Pliocene aquifer, while in the Miocene the mineralization varies from 200 mg L^{-1} up to 7800 mg L^{-1} (Fig. 9.4). The general hydrogeochemical evolution of the deeper aquifer is characterized by a gradual change, from an HCO_3-Ca

Figure 9.4. Electrical conductivity (mS cm^{-1}) variation of the groundwater samples.

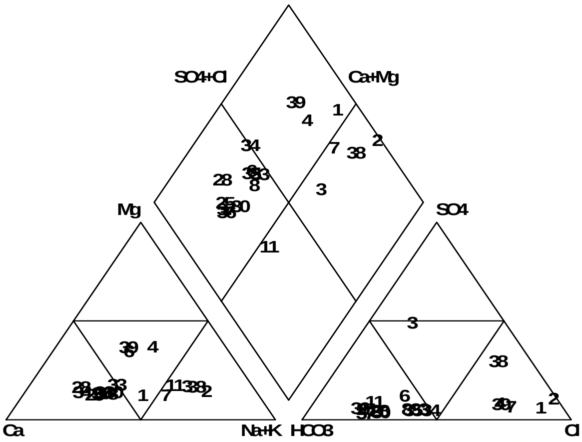


Figure 9.5. Hydrochemical evolution of the groundwater samples.

type to a Cl-Na type of water in the southern part of the basin, near the Sado estuary (Fig. 9.5). Cl contents (Fig. 9.6) show an increase of salinization in the central part of the basin, near Pinhal Novo, where Cl-Na water is been exploited for agriculture and public supply from Mio-Pliocene units. This occurrence is most probably related to the graben structure responsible for the rising to shallow depths of a brine or ancient seawater within the sediments.

Changes in the calcium content and in Ca/Na ratio along the general direction of the groundwater have been detected. When plotted in a diagram (Fig. 9.7) two different evolution lines can be identified along the basin: one reflecting seawater mixing in the northern part of the basin near Almada, and the other with higher sodium content reflecting, most probably, the brine dilution (Setúbal region).

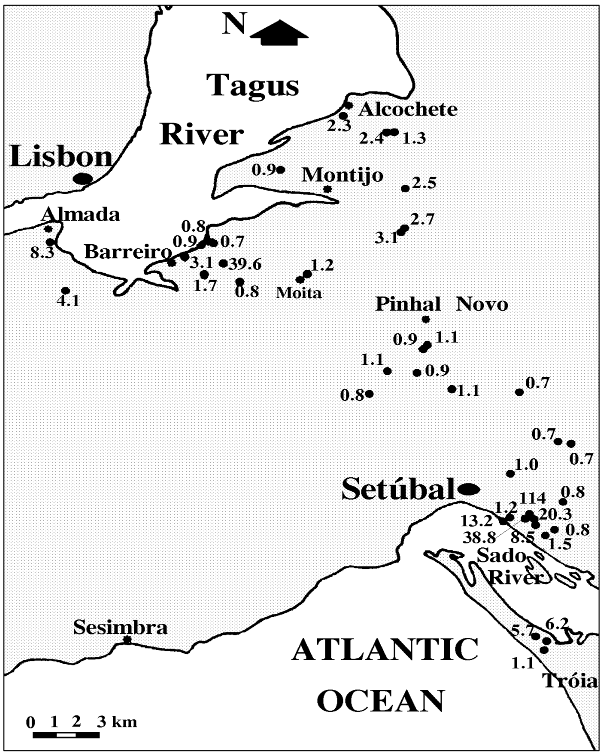


Figure 9.6. Variation of the Cl^{-} content (meq L^{-1}) of the groundwater samples

Table 9.2 Apparent carbon-14 groundwater age

Reference	Aquifer	EC	δ^{13}C	^{14}C±σ	Apparent age
		µS/cm	‰	pmc	ka
3	Miocene	1636	–10.0	2.9±0.3	25.4±3.3
4	“	986	–12.1	5.9±0.5	20.8±2.9
31	“	1860^{S}	–10.5	45.8±0.6^{S}	2.9±2.6^{S}
38	“	2281	–10.0	10.8±0.7	14.4±2.9
39	“	919	–7.3	6.7±0.6	16.1±3.4
JK1 EDP	“	7650^{B}	–9.2	8.4±0.8^{B}	15.9±3.2
AC1 EDP	“	8010^{B}	–8.1	5.6±1.2^{B}	18.3±4.6
FRISADO	“	3000^{B}	–10.4	12.9±0.9^{B}	13.3±2.9
5	Pliocene	4631^{S}	–17.9	88.1±0.8^{S}	Modern
21	“	342	–17.6	71.9±0.7	3.1±2.3
27	“	2507^{S}	–10.0	85.6±3.3^{S}	Modern
32	Mio-Pliocene	1112	–12.9	32.8±0.5	7.2±2.5

S - Sea water intrusion
B - Brine dilution

The nitrate content was an important tool in the characterization of the two main aquifers and in the identification of mixing between these units. No nitrate was detected in the deeper aquifer although in the Pliocene the NO_3 content varying from 7 mg L^{-1} up to 93 mg L^{-1}, due to agricultural activities.

9.3.2 Isotopes

Tritium contents in the upper aquifer showed a ^{3}H content range from 1 TU up to 3 TU. No tritium was measured in the Miocene water samples.

Radiocarbon was measured on the total dissolved inorganic carbon in samples from 12 wells (Table 9.2). The values obtained range between 71.9±0.7 pmc up to 88.1±0.8 pmc in the Pliocene aquifer, and between 2.9±0.3 pmc up to 45.6±0.9 pmc in the Miocene aquifer (well 31). The high ^{14}C content measured in well 31 together with the raised TDS observed in this sample, point to seawater intrusion occurring in this area (Almada region).

The apparent carbon-14 age of the groundwater was calculated using the “Gonfiantini equation”, using the δ^{13}C values as a correction factor. The application of this model to estimate the apparent ^{14}C ages was chosen be-

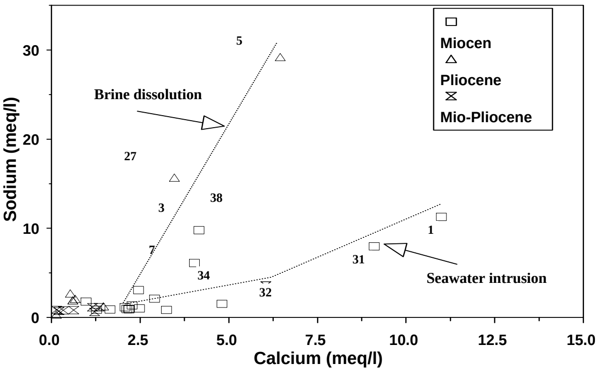


Figure 9.7. Sodium content as a function of calcium concentration

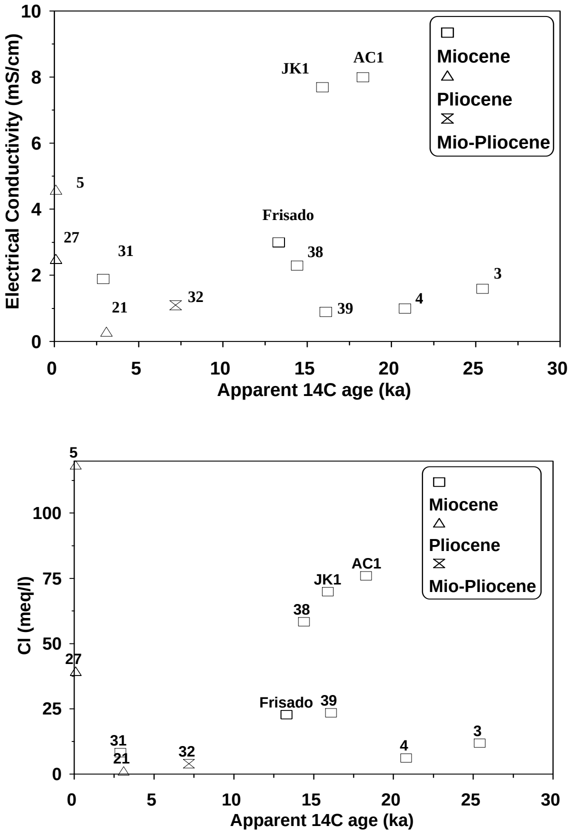


Figure 9.8. Electrical conductivity (mS cm⁻¹) and Cl^- content as a function of the apparent ^{14}C age of the groundwater samples

cause all the analysed samples are undersaturated in calcite (the saturation index, $SI_{calcite}$, ranges from –4.01 to –1.69 in the Pliocene and between –2.52 up to 0.46 in the Miocene). Also, $\delta^{13}C$ values in the Miocene samples remain almost constant ($\delta^{13}C$ around –10‰). The apparent ^{14}C ages of the groundwater in the deeper aquifer range from modern (well 31 – seawater intrusion) to 25.4±3.3 ka in the Miocene aquifer (well 3).

The relation between the ^{14}C apparent groundwater age in the sampled wells and the electrical conductivity or with the Cl^- content reveals an interesting pattern (Fig 9.8). The lack of relationship between the increase of salinization and the ^{14}C content in the southern part of the basin appears to confirm the brine dilution mechanism.

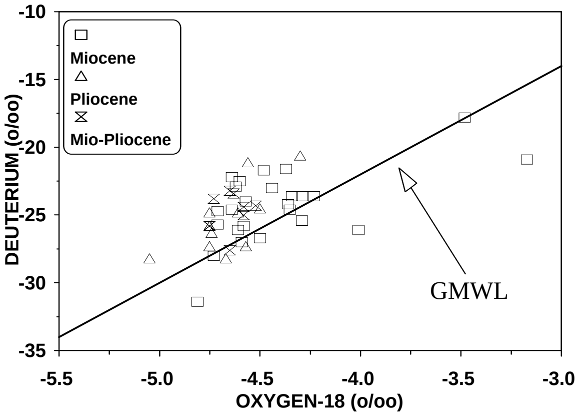


Figure 9.9. δ^2H as a function of $\delta^{18}O$ values.

The opposite pattern was found in the Almada region (northern part of the basin) where a strong relation between ^{14}C and Cl content is observed, pointing to recent seawater intrusion in this area.

A small difference of about 2‰ in deuterium and 0.2‰ in oxygen-18 was found in the mean isotopic composition between the two main aquifers (Fig. 9.9). The small enrichment in heavy isotopes observed in the Miocene groundwater samples, when compared with values obtained in the Pliocene system, may be related to the isotopically heavier ocean during late glacial time.

9.4 Conclusions

Although the study is not yet been concluded, some important results have already been obtained:

- The Miocene aquifer is isolated from the shallow groundwater system based in the absence of tritium and nitrates.
- The baseline hydrochemical evolution of the groundwater in the aquifer is the result of continuous interaction of infiltrating waters with the rock matrix. Changes of Ca and Ca/Na ratio along the general direction of the groundwater were identified.
- In the northern part of the basin near Almada there is evidence of recent seawater intrusion related to the intense pumping in the area.
- In the southern part of the basin the lack of relation between the increase of salinization and the ^{14}C content, suggests that a brine dilution mechanism is responsible for the deterioration of the water quality.

10 Palaeowaters from the Glatt Valley, Switzerland

10.1 Introduction

Continental climate records from mid-latitude regions that experienced ice cover during the last glacial period are scarce. Groundwaters have been used as palaeoclimate archives in permanently ice-free regions (Rudolph *et al.*, 1984; Stute *et al.*, 1995a; Stute *et al.*, 1995b; Stute and Sonntag, 1992). Here we present groundwater data from the Glatt Valley, Switzerland, which was ice-covered after a glacial advance during the last glacial maximum (Schlüchter *et al.*, 1987). The impact of glaciation on groundwater recharge and dynamics is not well known, but numerical models have shown that glaciers can dramatically change groundwater flow (Boulton *et al.*, 1995; Piotrowski, 1997). In groundwater, past values of climate variables can be derived from the stable isotopic composition of water molecules (Münnich and Vogel, 1962) and the concentrations of dissolved atmospheric noble gases (Mazor, 1972). Besides the local air temperature, many factors control the isotopic composition of groundwater. In contrast, the concentrations of atmospheric noble gases dissolved in groundwater are determined mainly by the solubility equilibrium during infiltration, given by the mean local atmospheric pressure (specified by the altitude of the recharge area), and by the water temperature prevailing during recharge. The so-called noble gas temperature (NGT) is therefore a measure of the temperature at which groundwater equilibrated with the atmosphere during infiltration and commonly corresponds to the mean annual air temperature (Stute and Schlosser, 1993). Consequently, information on stable isotopes and noble gases taken together allows one to evaluate the δ^{18}O-temperature relation over long time scales.

This continental area is used within PALAEAUX a) to illustrate comparable groundwater development to coastal regions b) the evolution of groundwater beneath another ice-covered region.

10.2 Hydrogeological basis

The area of investigations, the Glatt Valley, is situated south east of Zurich in the alpine foreland of Switzerland (Fig. 10.1). Because of the vicinity to the Alps the area was repeatedly ice covered during ice ages (Schlüchter *et al.*, 1987). The subterranean valley containing the aquifer was formed by glacial erosion during the next to last glacial

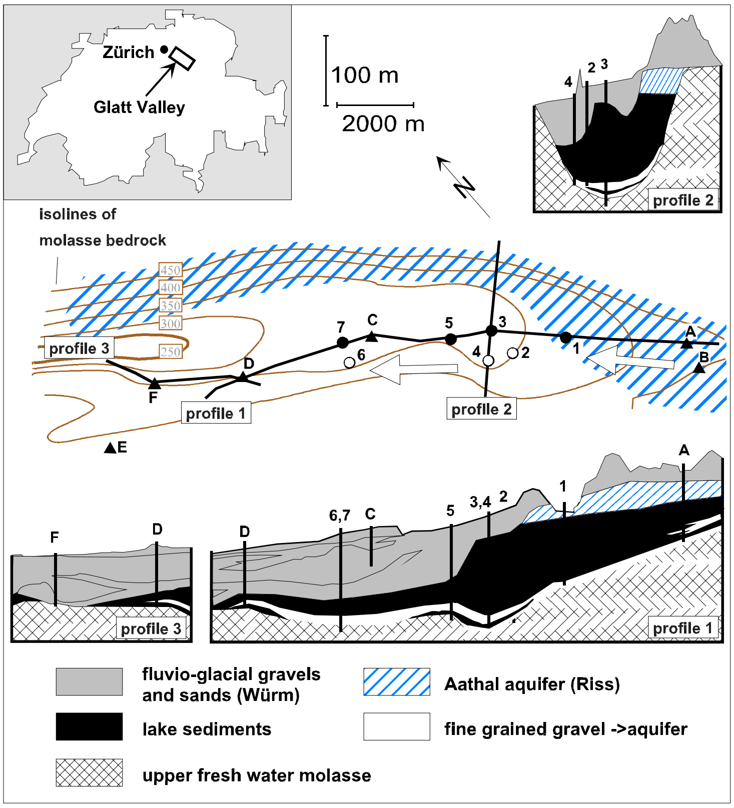


Figure 10.1. Hydrogeological profiles and the locations of sampling wells) (Wyssling, 1988). Samples A to F contain some ^{3}H and therefore some admixture of recent water. Wells containing no recent water components (^{3}H free) are labelled with numbers. Open symbols represent wells with an admixture of a younger but ^{3}H free component identified by ^{39}Ar. The deep Glatt Valley aquifer (GVA) is underlain by the molasse bedrock. Highly impermeable Pleistocene lake sediment separate the GVA from the shallow Aathal aquifer. The presumed recharge are lies south-east of site A, where the confining sediments outcrop. Arrows indicate the general direction of groundwater flow. Contour lines of the molasse bedrock are shown at 50 m intervals. The shaded area indicates the extension of the shallow Aathal aquifer.

period (Riss) (Wyssling, 1988; Wyssling and Wyssling, 1978). Deposits of the retrieving glaciers form the actual deep aquifer (GVA). Afterwards the valley was filled with poorly permeable lake sediments (max. 140 m thick) which separate the deep aquifer from shallower groundwater systems, e.g. the Aathal aquifer (Fig. 10.1). The GVA is about 15 km long, 3 km wide and has an average thickness of 10 m. The hydraulic conductivity of the gravel and sand of the aquifer is about 10^{-5} m/s. The mean flow velocity derived from recent conditions (porosity: 15%; mean hydraulic gradient: 5%) is in the range of 1 to 10 m a^{-1} which correspond to water ages up to 15 ka. The locations of the boreholes are shown in Fig. 10.1. Waters containing no ^{3}H are indicated with numbers. Borehole C accesses only a shallow aquifer. The presumed recharge area of the GVA is located near site A at an elevation of about 540 m asl Some wells in the south western part are artesian (sites 1, 4, 6).

10.3 Sample collection, measurements and calculations

Water and gas samples were collected from a total of 13 wells during the summers 1995 and 1996. In order to avoid degassing during sampling all samples were taken using a submersed electrical pump. Hydrochemistry, noble gases, radionuclides (^{3}H, ^{85}Kr, ^{37}Ar, ^{39}Ar, ^{14}C) and stable isotopes (δ^{13}C, δ^{2}H, δ^{18}O) were measured. The samples for noble gas measurements were stored in pinched-off copper tubes and measured using a Sector Mass Spectrometer (Beyerle *et al.*, in preparation).

For ^{37}Ar and ^{39}Ar measurement about 5000 L water were degassed and gases were compressed into evacuated cylinders. A ^{85}Kr analysis requires a water sample of about 200 L. Argon and krypton were separated from extracted gases and activities were determined in high pressure gas proportional counters as described in (Loosli, 1983).

^{14}C samples were obtained by direct precipitation, as $BaCO_3$, of the total carbonate (TIC) dissolved in several tens of litres of water. For ^{14}C analysis the $BaCO_3$ was converted to CO_2 by acidification and CH_4 was synthesized for low level gas counting (Oeschger *et al.*, 1976). Separate samples (1 L) were collected for ^{13}C analysis and measured by mass spectrometry.

Noble gas temperatures (NGTs) are calculated from noble gas concentrations by accounting for their temperature-dependent solubilities and for the common excess air component found in groundwater. However, the processes responsible for this excess of atmospheric gases are not fully understood.

Groundwater ages were determined from the ^{14}C activities of the TIC. Conventional correction models (Eichinger, 1983; Fontes and Garnier, 1979; Ingerson and Pearson, 1964; Tamers, 1967) using chemical and isotopic balances were applied to convert activity values into ^{14}C ages. Conversion into calibrated years BP is based on (Linick *et al.*, 1986; Pearson *et al.*, 1993; Pearson and Stuiver, 1993; Stuiver and Pearson, 1992; Stuiver and Pearson, 1993).

Numerical results are summarized in (Beyerle *et al.*, 1998) and discussed in details in (Purtschert *et al.*, in preparation). Different water components can be identified by their chemical composition and by the isotopes ^{3}H, ^{85}Kr, ^{39}Ar, and ^{14}C. In Fig. 10.1 different symbols and labels indicate different components. In the following we only concentrate on the climate signals trapped in the groundwater of the Glatt Valley. We therefore refer in Figs 10.3 and 10.4 only to the parameters of the oldest component; the calibrated ^{14}C ages, the NGTs and the stable isotopes values given below are corrected for the influence of possible young components.

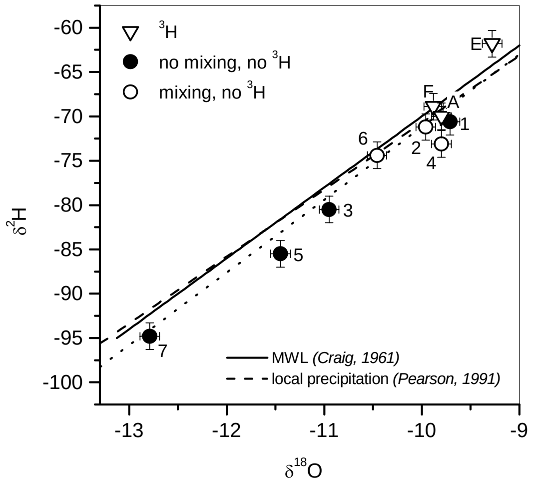


Figure 10.2. Plot of δ^{18}O versus δ^{2}H composition in the GVA.

10.4 Palaeoclimatic information

The isotopic composition of modern groundwaters in GVA (containing significant tritium concentrations) range between −10.1 and −9.3‰ for δ^{18}O and −70 and −61.9‰ for ^{2}H (Fig. 10.2) which are typical modern values for the Swiss Plain (Pearson Jr *et al.*, 1991). All of the groundwaters have isotopic compositions which lie slightly below the global meteoric water line (MWL) (Craig, 1661). The small aberration can be explained either by a smaller deuterium excess d ($d = \delta^{2}H - 8\times\delta^{18}O$) caused by an enhanced relative humidity over the moisture source (Merlivat and Jouzel, 1979) or by a strong surface evaporation in the infiltration area. From the constant deuterium excess for Holocene and Pleistocene samples one can conclude that the relative humidity over source areas for the vapour bringing precipitation to Europe was constant during the past 30 ka. Therefore a climatic origin for the observed isotopic shift is unlikely and more plausible is a small δ^{18}O enrichment of about +0.5‰ due to isotope exchange with carbonates and silicates in the aquifer. Samples with ^{14}C activities below 10 pmc (Samples 3, 5, 6, 7) are depleted in δ^{2}H and δ^{18}O (Fig. 10.2) indicating consistently the Pleistocene origin of these waters. Moreover, infiltration conditions cooler than today are indicated from noble gas recharge temperatures (NGT). The relatively large difference of isotopic composition between the neighbouring wells 6 and 7 cannot be explained with mixing alone. The good hydraulic connectivity (Wyssling, 1988) as well as the identical chemical compositions suggest a similar evolution of these waters. The relatively low δ^{18}O value and high amount of excess air (50%) at site 7 can be explained by an enhanced portion of meltwater from ice with trapped air bubbles.

Recharge temperatures calculated from dissolved noble gas concentrations (Fig. 10.3) range between 9.7°C (sample c) and 3.2°C (sample 7) (Beyerle *et al.*, 1998). NGT of the modern waters scatter around the recent mean annual air temperature in the recharge area of about

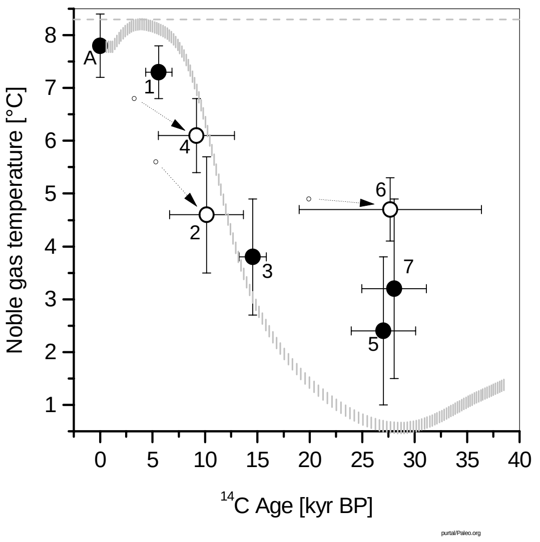


Figure 10.4. NGT versus corrected ^{14}C ages (old component). For samples influenced by two-component mixing (open symbols) the values refer to the old component alone. Arrows indicate the effect of the separation of the young component. The difference between the modern mean annual air temperature (8.3°C; dashed line) and the NGT increases between 6 ka BP and 15 ka BP from 0°C to 4°C (site 3). Site 5 indicates a Holocene/Pleistocene temperature difference of at least 5°C. No data points were found in the time period between 17 ka BP and 25 ka BP. This fact is interpreted as a complete interruption of recharge due to overlying glaciers.

The curve is derived from a model that shows how a temperature evolution similar to that recorded in the oxygen isotope profiles of Greenland ice cores would be transferred through a dispersive flow system with a mean dispersivity of 100 m. The model assumes a constant recharge rate except between 25 and 17 ka BP when no recharge is assumed. The larger distance between the bars of the curve in the age range of the recharge gap reflects the reduced probability of finding, nevertheless, a water sample with a mean residence time between 17 and 25 ka. There is good agreement between the model and the data points with an age younger than 17 ka. For groundwater samples older than 25 ka BP the model predicts lower NGTs than those observed. Preferential infiltration during warmer time periods of the Denekamp Interstadial possibly gave rise to NGTs higher than the long term mean air temperature.

8.3°C (Schüepp, 1981) and demonstrate the validity of the noble gas thermometer. With increasing distance from the recharge area and therefore with increasing age NGTs change significantly. Figure 10.4 shows the relation between NGT and ^{14}C ages of the old water component. The composition of the old component was calculated under the assumption that the water represent a binary mixture with a young component with the same composition as the sample from borehole A and Pleistocene waters. Original data are indicated with small circles and arrows show the effect of the mixing correction.

The NGTs with ^{14}C-ages between 15 and 28 ka BP reflect climate conditions that were at least 5°C colder than today. During the last glacial maximum (around 18 ka BP) the temperature drop may have been even greater than 5°C, but no samples with ages between 25 and 17 ka BP were found. It is unlikely that insufficient spatial resolution of the sampling boreholes is responsible for the observed age gap. Borehole 5 (25 ka BP) and borehole 3 (17 ka BP) are separated by less than 1 km along the direction of the flow. Adopting the mean observed flow velocity of 0.4 m a^{-1} between boreholes A and 3, then 1 km corresponds to an age increase of only 2.5 ka. The gap is therefore interpreted to be the result of an almost complete interruption of groundwater recharge between 25 ka BP and 17 ka BP. Beside the glacio-hydrological relevance the observed age gap represent a time marker and supports likewise the radiocarbon ages. The intermediate NGTs are most likely the results of dispersive mixing within the aquifer under a climatic transition to present-day conditions.

The curve in Fig. 10.4 is the result of a model (Beyerle *et al.*, 1998), that assumes dispersive flow in the aquifer with an interruption of recharge in the period between 25 and 17 ka BP and a similar temperature evolution as recorded in Greenland ice cores. The good agreement between the corrected data younger than 15 ka and the model supports the adopted mixing corrections and gives again confidence in the ^{14}C dating. For the older groundwaters around 28 ka BP the observed NGTs exceed the model predictions. NGTs reflect the mean soil temperature near the groundwater table during time periods when groundwater infiltration occurs. Hence, if groundwater recharge was partly interrupted because of permafrost during the coldest periods (28-33 ka BP) only temperature signals of the warmest periods are recorded within the palaeogroundwater (Beyerle *et al.*, 1998).

For the reconstruction of past climate change, the knowledge of the long term δ^{18}O/T-relationship is of great importance. Data for palaeogroundwaters like the Glatt Valley aquifer provide an opportunity to reconstruct directly the δ^{18}O/T-relationship in the past. In order to derive only climatic contributions to δ^{18}O/T, all other influences on the stable isotope composition than temperature have to be corrected. The temporal change of the δ^{18}O content of the groundwater can be expressed as:

$$^{18}\mathrm{O}(t)_{meas} \qquad ^{18}\mathrm{O}(T(t)) \qquad ^{18}\mathrm{O}(t)_{rock} \qquad ^{18}\mathrm{O}(t)_{ice}$$

To exclude a possible small enrichment of the δ^{18}O content due to rock water interaction we calculated δ^{18}O values from δ^{2}H under the assumption that the composition of the infiltrating precipitation correspond to water on the MWL. Additionally we assumed a δ^{18}O enrichment of the Pleistocene ocean due to the volumetric increase of isotopically depleted ice in polar regions (Δδ^{18}O$_{ice}$) as recorded in (Sowers *et al.*, 1993) (Fig. 10.3). The resulting δ^{18}O/T relationship valid for the area of investigations is plotted in Fig. 10.3.

With the exception of samples 2 and 7 NGT and δ^{18}O correlate reasonably well. The slope of the linear regression line is 0.49±0.05‰/°C (sample 7 was disregarded, see above). This value lies between the recent spatial (0.56‰/°C; Pearson Jr *et al.*, 1991; Siegenthaler and Oeschger, 1980) and seasonal (0.46‰/°C; Siegenthaler and Oeschger, 1980) δ^{18}O/T-slope. The presented data indicate that in the study area short-term δ^{18}O/T-relations are a good approximation for the reconstruction of palaeoclimates. However, there is a tendency that the spatial relationship overestimates the long-term temporal temperature dependency of the δ^{18}O content of precipitation. Holocene-Pleistocene temperature difference estimated from internal borehole temperatures are twice the value inferred from oxygen isotopic composition of the ice calibrated from the modern spatial δ^{18}O/T-relationship (Boyle, 1997). A smaller temporal δ^{18}O/T-slope compared to the modern spatial slope would therefore reduce this discrepancy.

10.5 Conclusions

Several methods indicate the existence of palaeowaters in the Glatt Valley area. This identification is mainly based on:

(xxiii) a 5°C difference between Pleistocene and Holocene waters, as deduced from noble gas recharge temperatures

(xxiv) the time of the Pleistocene-Holocene transition as expected at about 15 ka BP, deduced from corrected ^{14}C ages

(xxv) a gap of detected ^{14}C ages between about 25 and 17 ka BP attributed to an interrupted recharge during the time when the infiltration area was ice covered and

(xxvi) measured low $\delta^{2}H$ and $\delta^{18}O$ values of old waters.

The time information needed for the above given identification of Palo-waters is only obtained after a separation of different water components was possible. The presented study demonstrates that a combination of isotopes with different half lives allows such a separation of components. Recent waters are detected by combining ^{3}H and ^{85}Kr; a component younger than about 1000 years can be identified by comparing ^{39}Ar and ^{14}C. ^{4}He may add qualitative time information. The above mentioned identification of palaeowaters in the Glatt Valley area is valid for the oldest component.

The determined NGTs further allow the conclusion that at around 28 ka BP warmer periods compared to earlier and later periods occurred, during which infiltration was possible. The determination of NGTs corrected e.g. for excess air is demonstrated to be correct as deduced from the present day infiltration temperatures calculated for recent waters.

The linear correlation between NGTs and $\delta^{18}O$ was only obtained considering the time dependent $\delta^{18}O$ values of the world ocean in the last 30 ka. It further was necessary to calculate the $\delta^{18}O$ values from the measured $\delta^{2}H$ values, which corrects for the effects of water-rock interaction. After these two corrections a linear correlation between $\delta^{18}O$ and the temperatures was obtained which allowed to calculate a $\delta^{18}O/T$-slope for the Pleistocene-Holocene times. The derived value for this slope agrees within errors with the present time spatial and seasonal slopes observed in central Europe.

11 Weichselian palaeoclimate and palaeoenvironment in Europe: background for palaeogroundwater formation

11.1 Introduction

The evolution of groundwater both at the local and at the European scale has been controlled by climate and environmental changes during the Late Pleistocene and the Holocene. The effects of glaciation and sea-level changes have played the most important role in reorganizing the groundwater systems in coastal regions. Permafrost and periglacial processes over large areas in central and northern Europe also had a significant influence on a groundwater recharge. Atmospheric circulation in Europe during the Late Pleistocene patterns may have had an effect on the isotopic and chemical signal in groundwater that nowadays forms the basis of geochemical interpretation of palaeowaters.

The influence of these various palaeoclimatic and palaeoenvironmental factors has been different for the different aquifers of the PALAEAUX transect across Europe. The dynamics of the Fennoscandian ice sheet and permafrost processes significantly modified aquifers in the northern part of the transect (Estonia, Denmark, northern United Kingdom, the Netherlands, Belgium). In central and southern part of the transect (southern United Kingdom, France, Spain) sea level changes probably had the strongest influence on groundwater evolution during the Late Pleistocene. A different pattern of atmospheric circulation could have left its signal in the form of different chemical and isotopic compositions in groundwater of those areas.

In order to have a common base for investigation and interpretation of the Late Glacial and Holocene evolution of palaeowaters on the transect across Europe a palaeoenvironmental scenario for this time interval has to be agreed. For the same purpose the commonly accepted stratigraphic terminology has to be used. The internationally accepted terminology for the classification of the Quaternary stratigraphic record of the Nordic countries and adjacent areas of north-west Europe was formally set out in classical paper by Mangerud *et al.*, (1974). The Quaternary was subdivided into Pleistocene and Holocene series and the Pleistocene was further subdivided into provisional stages based on the sequence of glacials and interglacials. The Late Weichselian/Devensian and the Holocene were subdivided into chronozones, with the boundaries defined in radiocarbon years before present (AD 1950). Under this scheme, the Middle Weichselian Substage ended at 13 000 ^{14}C years BP and the Late Weichselian Substage lasted from 13 000 to 10 000 ^{14}C years BP, containing the Bølling (13 000 to 12 000 ^{14}C years BP), Older Dryas (12 000 to 11 800 ^{14}C years BP), Allerød (11 800 to 11 000 ^{14}C years BP) and Younger Dryas (11 000 to 10 000 ^{14}C years BP) chronozones. This chronostratigraphic framework has been widely adopted and the terminology has been applied also to records from other parts of Europe and from other areas of the world.

While this provides a useful general chronostratigraphic framework for the last glacial/interglacial transition, various difficulties have arisen recent years in practice, discussed in detail by Walker (1995) and by Björck *et al.*, (1998). One of the major problems relates to the uncertainties of the radiocarbon time-scale, caused mainly by temporal variations in ^{14}C production which have resulted in radiocarbon "plateaux" of constant age at certain times within the period of the last glacial/interglacial transition. Comparisons between radiocarbon-dated wood samples and dendrochronological records (Kromer & Becker, 1993) on one hand, and paired measurements of U-series and radiocarbon dates from fossil corals (Bard *et al.*, 1990) on the other, suggest an increasing divergence between radiocarbon and calendar years of 2500 by 16 000 ^{14}C years BP. As a result, certain time intervals during the last termination cannot be dated precisely using the radiocarbon method alone.

In order to overcome the difficulties, the INTIMATE (INTegration of Ice-core, MArine and TErrestrial records – a core programme of the INQUA Palaeoclimate Commission) group has recently proposed use of the high-resolution oxygen isotope record from the GRIP ice-core as a basis for an event stratigraphy for the last termination that is applicable to the entire North Atlantic region (Björck *et al.*, 1998). The proposal is based on the fact that the isotopic profile of the GRIP ice-core is, to date, the most detailed and its timescale has been developed by counting annual ice layers down from the surface back to 14.5 ka. Comparison between the GRIP record, north-west European lake sediments records and the recently revised German oak-pine dendrochronology (Björck *et al.*, 1996) suggests that synchronization between GRIP ice years and tree-ring years is within the stated uncertainty of ±30 a for the GRIP record (Björck *et al.*, 1998). The recommendation of the INTIMATE group, therefore, has been that the chronology for the last termination should be expressed in GRIP Ice-core Years Before Present (AD 1950), preferably shortened to GRIP a BP.

However, in spite of convincing arguments for application this new event stratigraphy for the time period of the last termination (ca. 22 to 11.5 ka GRIP BP), a radiocarbon timescale for the last glacial/interglacial transition is retained here and the dates are expressed in ^{14}C years BP, unless otherwise stated. We do that for the purposes of simplicity and comparability, as the paper is based on earlier data on palaeoclimate and palaeoenvironment in Europe, which are almost entirely underpinned by conventional or AMS ^{14}C dates. Our approach is also based on the assumption that the resolution of the Pleistocene records needed for the groundwater studies is much lower than the high resolutions currently available for the various other archives (ice-cores, marine sediments etc.) where decadal scale information is attainable. Therefore the problems connected with the above mentioned uncertainties of the detailed radiocarbon time-scale for the last termination period are not critical for this study.

The main concern of the PALAEAUX project has been the evolution of European coastal aquifers since Late Glacial Maximum (LGM), corresponding to the lowest sea levels around 18 ka BP (21 ka calendar years).

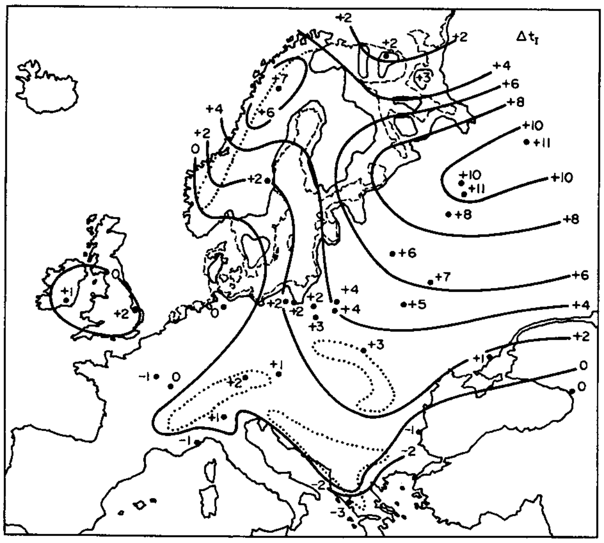


Figure 11.1. The rise of the Eemian January temperatures over the present ones (after Gerasimov & Velichko, 1982 from Raukas, 1991).

However, major changes in global sea-level and changes in glacial condition prior to LGM has to be considered in order to understand the dynamics of the environment and aquifers. Therefore the palaeoenvironmental scenario for whole last glacial cycle beginning from the end of Eemian/Ipswichian interglacial about 110 ka BP, when sea levels were comparable to those of the present day, is considered.

11.2 Weichselian climate and glaciation in Europe

11.2.1 Climate

During the last interglacial about 140–110 ka BP (the Eemian/Ipswichian) the climate in Europe was slightly warmer than during the Holocene and even alpine-type glaciers were probably absent in Scandinavia (Mangerud *et al.*, 1996). According to A.Velitchko (Gerasimov & Velichko, 1982), during the Eemian climatic maximum the climate was more humid, with the mean annual precipitation over the southern part of the Eemian Sea 200-500 mm and over the northern part approximately 100 mm higher than at present. The increase of Eemian winter temperatures over present values was greatest in northern and north-eastern Europe: up to +7°C in Scandinavia and +11°C in the north-east and east of East European Plain (Fig. 11.1). The mean July temperature over the Baltic area was much the same as at present. However, in January the mean temperature was 4–8°C higher. Greenland ice core data also shows that the Eemian interval was about 2°C warmer than present (GRIP Members, 1993). However, GRIP ice core data also suggest that temperatures plunged from 2°C warmer than today to 5°C colder over a few decades during two major intervals within the Eemian (GRIP Members, 1993).

Vegetation changes recorded in a pollen-analysed bog section at Grand Pile, northern France (Guiot *et al.*, 1989, Guiot, 1990) show that the warm Eemian interglacial was followed by cooling at the beginning of marine isotope stage 5d about 115 ka BP, which marks the beginning of Weichselian/Devensian glaciation. The Grand Pile section (Fig. 11.2) shows two very warm interstadials (St. German I and St. German II) and two cool stadials during the early Weichselian(isotope stages 5a-5d). The corresponding interstadials (Amersfoort-Brörup and Odderade) and stadials in northern Europe were considerably colder, and there is evidence of good-sized glaciers in Scandinavia during those stadials (Andersen & Borns, 1994).

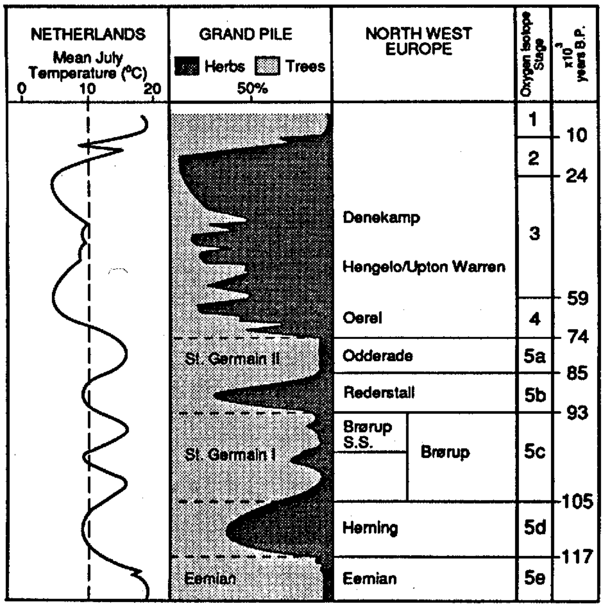


Figure 11.2. Mean July temperatures in the Netherlands, Grand Pile pollen record, chronostratigraphy for northern Europe and oxygen isotope stratigraphy (after Dawson, 1992).

According to the Grand Pile record the climate cooling which followed isotope stage 5a was rapid, and it marked the start of a very long cold period. In addition to the early existing ice sheets in Antarctica and in Greenland, new ice domes developed gradually over northern America, northern Europe and the Barents Sea, whereas mountain glaciers thickened. During the major cold peak of isotope stage 4, tundra and/or prairie covered central and northern Europe. The Oceanic Polar Front moved south to the latitude of southern France and to the north of this latitude most of the North Atlantic Ocean was covered with pack-ice during winters. In spite of some fluctuations, the climate remained cold during most of isotope stage 3. However, the Grand Pile data indicate that there were at least five slightly warmer interstadials, but they were in general also cool (Andersen & Borns, 1994).

The Greenland ice core data, the vegetation records, the fossil fauna, and the fossil permafrost features all indicate that the LGM climate was very cold in Europe from 21 ka to at least 16 ka ago. A number of studies have concentrated on the reconstruction of climate of the LGM and on the following transition toward the Holocene (CLIMAP, 1981, COHMAP, 1988, Lowe & NASP Members, 1995, Webb & Kutzbach, 1998). According to those reconstructions at 18 ka BP, when ice sheets were at their maximum, strong anticyclonic air circulation around the North American ice sheet was bringing cold conditions to the North Atlantic. Along the southern flank of the ice sheets, strong easterly winds and a sharp temperature gradient were associated with a strengthened jet stream aloft, which extended across North America and east to Eurasia. The most substantial change was a drop of global sea-level to about 100–130 m below the present. This regres-

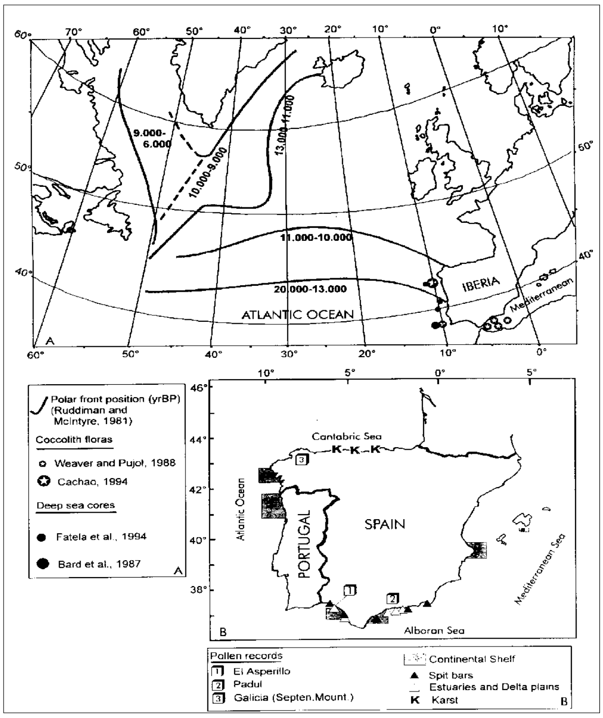


Figure 11.3. The Polar Front position during the last 20 ka; location of the main deep-sea cores and location of the areas with available information about the climatic changes in the Iberian continental margins (after Zazo *et al.*, 1996).

sion was combined with a general decline of precipitation and the expansion of the ice sheets which stored between 60×10^6 and 100×10^6 km^3 of water (Starkel, 1995). According to latest model simulations the presence of ice sheets and lowered atmospheric CO_2 concentration at 18 ka BP made the northern continents very cold with winter temperatures less than –20°C for most areas north of 30°N over land and with annual precipitation rate only 1–2 mm/day (Kutzbach *et al.*, 1998). The biome simulation by the same model shows most of the ice-free area in the northern high latitudes covered by polar desert. According to Frenzel (1992) the annual rainfall in western Europe during the LGM was 500 mm lower, than at present. Spruce and oak forests were absent from Europe because of cold, dryness and permafrost. Even the Mediterranean lowlands were treeless (COHMAP, 1988).

The data from deep-sea piston cores in the Portuguese margin and littoral data from the north-western Iberian littoral (Zazo *et al.*, 1996) clearly shows (Fig. 11.3) that during LGM the limit between the Polar Front and the Gulf Stream was located around the Spanish-Portuguese northern border, that is by 42°N. Bard *et al.* (1994) state that because of the strong thermal gradient separating the Gulf Stream from the polar water mass, the sea surface temperatures in the West Iberian continental margin during the LGM were probably as warm as today. Only at the end of the glaciation the temperatures of surface waters fell from 12°C to 4°C (Fatela *et al.*, 1994), related with the injection of glacial meltwater.

The exact age of the end of the LGM cold period is still under discussion, however, in most parts of the world the coldest glacial period seems to have ended about 14 ka BP and a marked climate warming started shortly thereafter. A comprehensive summary of the palaeoclimate of northern and north-western Europe during the last glacial-interglacial transition (Fig. 11.4) has been presented in the reports of the North Atlantic Seaboard Programme (NASP) (Lowe, & NASP Members, 1995, Walker, 1995).

According to these results the earliest evidence for sustained warming around 15 ka BP is found in pollen

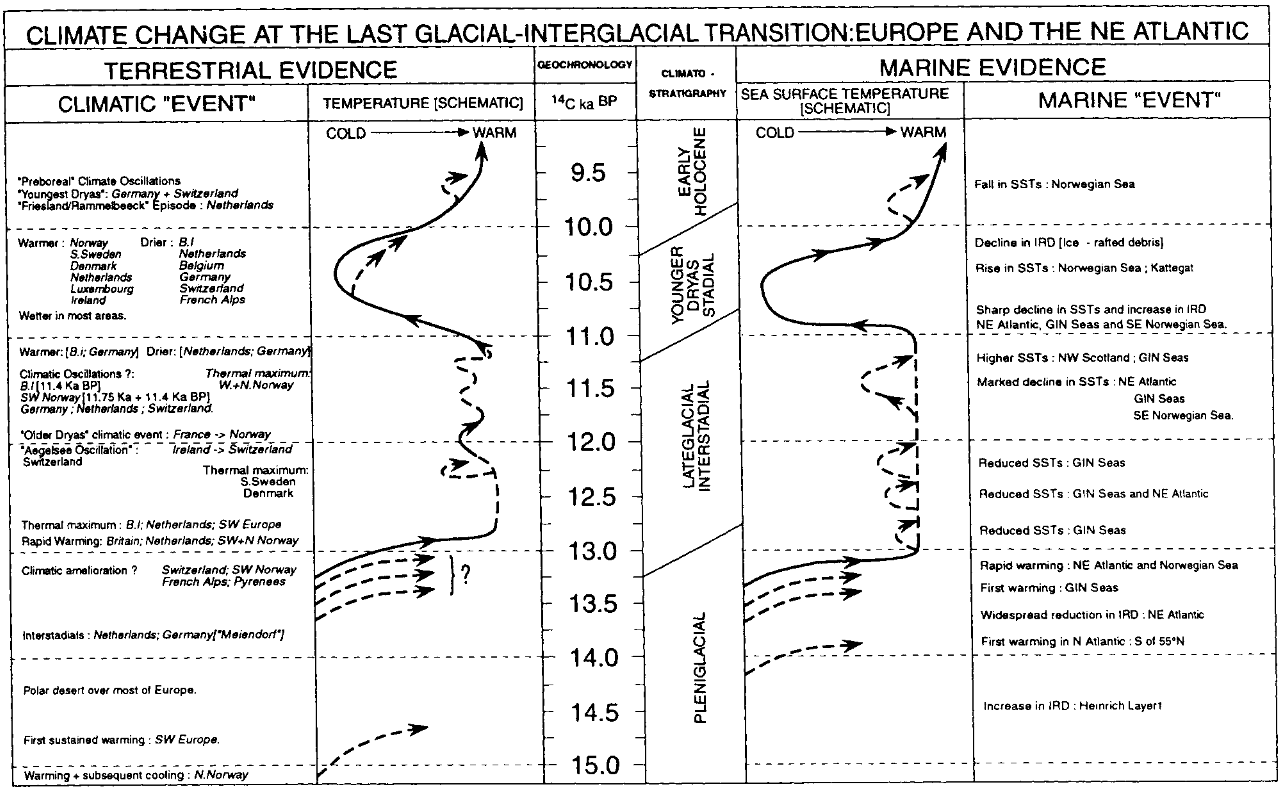


Figure 11.4. Summary of climate changes in Europe at the last glacial transition reflected in marine and terrestrial records (from Walker, 1995).

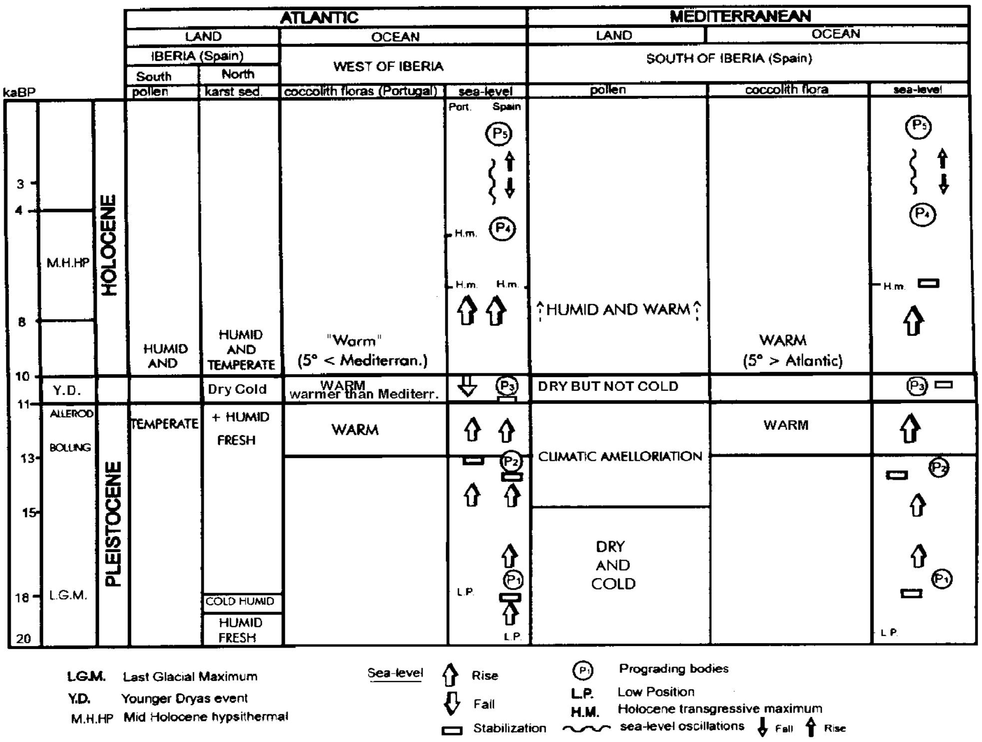


Figure 11.5. Schematic diagram showing the most relevant climatic changes and related sea level oscillations in the Iberian Peninsula during the last 20 ka (after Zazo *et al.*, 1996).

diagrams from south-west Europe. Throughout much of northern and western Europe, however, the first remarkable evidence for widespread climatic amelioration dates from about 13 ka BP (Fig. 11.4).The rapid change to warmer climatic conditions, particularly in north-west Europe is most clearly shown by fossil Coleoptera (Atkinson *et al.*, 1987), but also by the increased representation of aquatic plant taxa in some profiles. The timing and rapid nature of this climate change is reflected also in the Greenland ice core records, which shows, that climate amelioration at the last glacial-interglacial transition was not only abrupt and intense, but was also time-parallel throughout the northern and eastern Atlantic region (Walker, 1995). According to NASP records the thermal maximum of the last glacial-interglacial transition occurred in south-west Europe, lowland Switzerland, the British Isles and The Netherlands between 13 and 12.5 ka BP (during the Bölling) whereas in southern Scandinavia and Germany it was delayed until 12.5 to 12 ka BP (Walker *et al.*, 1994). Marked climatic gradients developed at this time period over north-west Europe, with temperature differences of as much as 6–7°C within a few hundred kilometres (Lowe *et al.*, 1994). These spatial and temporal contrasts reflect, on the one hand, changing patterns of surface and deepwater circulation in the North Atlantic, and on the other, the cooling effects of the wasting Fennoscandian ice sheet (Walker, 1995). In Estonia the pre-Allerød deposits which have been studied palynologically suggest the existence of severe climatic conditions up to at least 11.8 ka BP (Raukas, 1982). During the Allerød , the whole Baltic area experienced considerable warming, which contributed significantly to the rapid ice retreat (Kabailiene & Raukas, 1987).

The Younger Dryas cooling with a temperature drop to full glacial conditions was, without doubt, the most important climatic event during the last glacial-interglacial transition that affected all areas of Europe from northern Norway to the Mediterranean within the time interval of 11 to 10 ka BP (Rind *et al.*, 1986). According to different evidence mean July temperatures in western Norway, Southern Sweden, Poland, Denmark and Switzerland fell by 5-6°C from the preceding thermal maximum, while in the British Isles and The Netherlands the decline in July temperatures from the interstadial maximum was even higher, of the order of 7–8°C (Walker, 1995). In Estonia the Younger Dryas cooling gave rise to the development of tundra vegetation once again and promoted activation of the southern part of the Fennoscandian ice sheet close to Estonia (Karukäpp & Raukas, 1997). Dry but not cold climatic conditions governed the Mediterranean sector of southern Iberia, whilst in the adjacent Atlantic sector climatic conditions remained humid and temperate (Zazo *et al.*, 1996). According to these different climatic conditions, the surface sea-water temperatures were warmer in the Atlantic than in the Mediterranean during this same period. By contrast, in northern Iberia (Cantabria littoral) a moist and cool climate is recorded during the Younger Dryas cold event, displaying afterwards a sudden change to humid-temperate conditions at the beginning of the Holocene (Fig. 11.5).

According to data from the Greenland ice cores GRIP and GISP2, the end of the Younger Dryas is characterized by a very rapid transition towards the current Holocene climate with the temperature rise of about 7°C in Greenland within about only 50 years. In addition to temperature, even more rapid changes affected the precipitation rate and the atmospheric circulation, reflected in doubled snow accumulation in Greenland, possibly in only 1 to 3 years (Alley *et al.*, 1993). The Younger Dryas short cool event is an exception to a pattern of a longer warming period which characterized the transition from glacial to interglacial conditions. There were also other short cool events during the transition, although the rate and extent of Younger Dryas cooling was exceptional. According to Broecker & Denton (1989) this rapid cooling was related to the substantial decrease of the strength of the North Atlantic conveyer at the Allerød-Younger Dryas boundary. This signature could have been caused by a sudden freshwater flux compared with more gradual freshwater build-ups at the other oscillations, and it implies that the cause of Younger Dryas may be related to the draining of huge glacial lakes. Both, Lake Agassiz in North America and the Baltic Ice Lake (Björck, 1995) evidently drained at the time of the Allerød-Younger Dryas transition and created brief but huge meltwater pulses on both sides of the North Atlantic. These meltwater inputs caused a temporary but substantial waning of the conveyer, and may explain why only one Younger Dryas occurred after the onset of deglacial warming (Björck *et al.*, 1996).

The early Holocene amelioration of climate, which led to temperatures comparable with those of the present day being established over much of Europe by 9.5-9 ka BP is shown most clearly in botanical records (Lowe *et al.*, 1995). In Britain and The Netherlands, mean July temperatures of 15-17°C+ were re-established by 9.8 ka BP (Atkinson *et al.*, 1987). In the Iberian Peninsula climatic reconstructions using pollen data suggest a rapid increase in mean July temperatures of about 10°C to values ca.2°C above those of the present (Walker, 1995). In Estonia the early Holocene climate was determined by degradation of the Fennoscandian ice sheet and the complicated history of the hydrological regime in the Baltic Sea basin. At the beginning of the Holocene a relatively quick warming took place and at about 9 ka BP the mean annual temperature could be compared with that at present. At the end of Boreal the temperature was even higher (Kessel & Raukas, 1979).

11.2.2 Glaciation

The most characteristic feature of the Weichselian is the growing and vanishing of the ice sheets and glaciers. Information on the rate and timing of early and middle Weichselian glaciation in Scandinavia and northern Europe is limited due to the erosion of pre-existing sediments by Late Weichselian ice. However, some information still available, points to the occurrence of several periods of glaciation since the Eemian interglacial and prior to the LGM (Lundqvist, 1997).

The Weichselian glacial started with global cooling at about 115 ka BP and the last remnants of the Fennoscandian ice sheet finally disappeared about 8.5 ka BP. In Europe three or four different glaciations, separated by interglacials, are identified usually within this time period. Each of the glaciations has been divided into cooler stadials and warmer and essentially ice-free interstadials (Fig. 11.6). The three till formations in northern Germany indicate that the Fennoscandian ice sheets reached this far south at least three times during Weichselian (Ehlers, 1994). However, the ice sheet certainly covered most of Scandinavia many more times.

The first ice advance in Scandinavia is known as Gulstein Stadial which is related to isotope substage 5d. The second period of ice advance during Bønes stadial is thought to have taken place during isotope substage 5b (Larsen & Sejrup, 1990). The most extensive period of glaciation took place in Middle Weichselian during the long interval between isotope stages 4 and 2 (Fig. 11.6), when all of the Scandinavia and Finland were probably ice-covered (Mangerud, 1991) and the tundra/prairie covered central and northern Europe. According to the model proposed by Lundqvist (1992), the ice margin was fairly stationary along the western coasts of Scandinavia from isotope stage 4 until stage 2, but showed minor oscillations corresponding to series of cool interstadials (Hengelo, Denekamp and others).

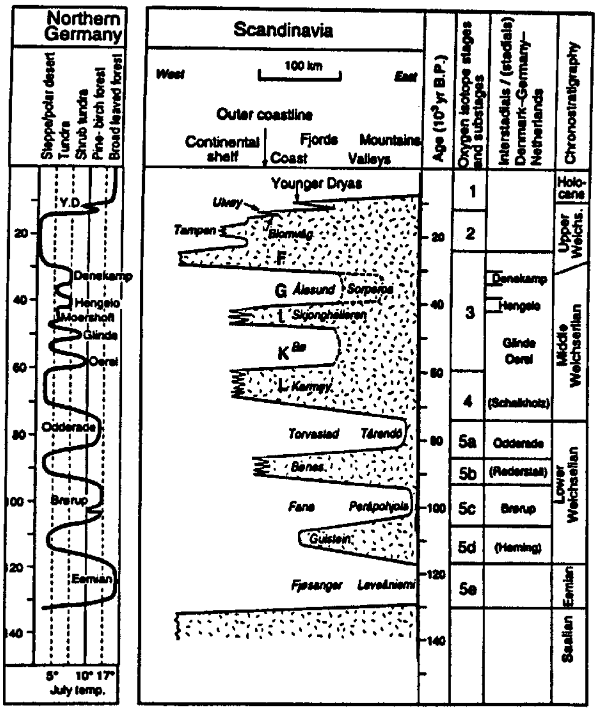


Figure 11.6. Glacial fluctuations and vegetational changes in Europe after the last interglacial, the Eemian. Vertical scale is age, given in ka (thousands of years before present) with calibrated radiocarbon years. The left panel shows the vegetational changes in northern Germany. The right panel shows ice front fluctuations in western Scandinavia; the mountains are plotted to the right and the continental shelf to the left. The dotted area shows the extent of the ice sheet in the time and distance from the mountains. (after Mangerud *et al.*, 1996).

The Weichselian maximum ice advance in Europe began sometime after 25 ka BP and culminated between 20 and 18 ka BP with the LGM (Lundqvist, 1992). The extension of the last Weichselian ice on the European continent (Fig. 11.7) is well marked by extensive end moraines in Denmark, northern Germany, Poland, the Baltic countries and Russia. In Poland, as in Germany, the southern ice margin is marked by moraines and by very large marginal drainage channels (pradolinas, Urstromtäler) towards the west. The entire drainage that now flows into the Baltic and the North Sea was deflected to traverse the exposed bed of the North Sea and deposited extensive deltaic sediments (Lundqvist, 1997).

The extension of the ice margin west from Denmark is controversial. Some authors assume that the Weichselian ice, like the pre-Weichselian ice, covered the North Sea, and that the Fennoscandian ice sheet and small Devensian ice sheet, covering the British Isles and Ireland, were confluent (Denton & Huges, 1981). However, Sejrup *et al.*, (1994) postulated coalescence between Fennoscandian and Devensian ice sheets only in a period between 29.4 and 22 ka BP. When the ice reached its maximum limit on the European continent, the confluence in North

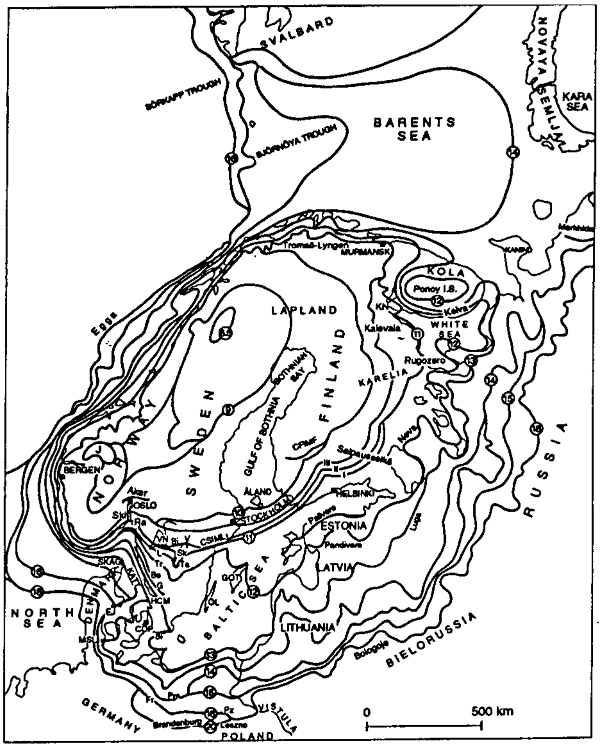


Figure 11.7. Location map of the Fennoscandian ice Sheet. Numbers in circles show radiocarbon years (ka BP). Geographical names are in capital letters, names of moraines in lower case letters. (from Lundqvist, 1997).

Sea area was broken to leave an ice-free corridor between Scandinavia and Scotland - Shetland Isles (Sejrup *et al.*, 1987). Because of eustatically lowered sea level, the main part of the North Sea floor was dry land, dissected by large drainage systems from the European continent (Lundqvist, 1997).

The main retreat of the Fennoscandian ice sheet began about 18 to 17 ka BP, although at slightly different times in different areas. Recent radiocarbon dates from the North Sea area indicate that the retreat of the ice sheet there probably started as early as 21 ka BP. The size of the ice sheet over the British Isles also diminished considerably between 18 and 13 ka BP. At the end of this period the shores in southern Britain and southern Europe were 60-80 m below the present shores. A broad zone of the north European plain, including most of Denmark and the south-west coast of Sweden, was deglaciated during the period 18 to 13 ka BP (Andersen & Borns, 1994). As a result of the difference in deglaciation rate in this area a broad ice lobe formed in the southern part of the Baltic, turning north over eastern Denmark. This ice lobe was very active and its alternating retreats and readvances in Denmark were recorded by widespread glaciotectonic structures (Berthelsen, 1979).

The North European ice sheets retreated considerably during the warm Bølling/Allerød interstadial (Fig. 11.4) which lasted from about 13 to 11 ka BP. In Britain the Devensian ice sheet disappeared, probably completely, by about 13 ka BP and a limited amount of relatively warm Gulf Stream water had begun to enter the North Atlantic and North Sea area (Andersen & Borns, 1994). As a result of rapid retreat of the south-eastern part of the Fennoscandian ice sheet the ice dammed Baltic Ice Lake started to develop in the southern part of the Baltic Sea basin about 13.5 ka BP (Björck, 1995). During the Younger Dryas cooling, the ice sheet retreat almost stopped and in some areas (e.g. western Norway) local re-advances took place. Due to eustatic lowering of sea level, the sounds between Scandinavia and Denmark were dry. South from Mount Billingen in south central Sweden the Baltic Basin was isolated from the ocean in the west by the South Swedish highland (Lundqvist, 1997). Further ice sheet retreat in Baltic area is closely related to the development of Baltic Sea and subsequent sea level changes and this will be discussed later in this chapter.

11.2.3 Subglacial hydrology

Glacial cycles have had the strongest impacts on groundwater dynamics in Europe. Overpressure in subglacial aquifers and aquitards and subglacial meltwater drainage may have led in many places to complete reorganization of groundwater flow as compared with interglacial conditions. This is a controversial topic but of great relevance to the present PALEAUX studies.

Ice sheets and glaciers melt on their surfaces and, due to frictional, strain and geothermal heating, most of them also melt at their base. Rates of basal melting are expected to be within the range of 1-100 mm/year over long periods, whereas surface melting rates in the ablation areas are typically up to four orders of magnitude greater (Boulton *et al.*, 1995). The amount of surface meltwater, which finds its way to the bed is uncertain. However, in the case of ice sheets the water penetration to the bed is restricted because of their great thickness and therefore basal melting is the main source of meltwater. There are three principal mechanisms for meltwater discharge at the base of an ice sheet (Boulton *et al.*, 1995):

(i) flow in a thin layer at the ice/bed interface;
(ii) flow in tunnels, canals and other conduits;
(iii) flow as groundwater.

Shoemaker (1986) has argued that the main mechanism for meltwater discharge beneath the ice sheets is water flow in a thin layer and in conduits at the ice/ bed interface, and that groundwater flow can play only an insignificant role because of the limited transmissivity of subglacial rocks in comparison with the magnitude of subglacial water discharges. Boulton *et al.* (1993) have suggested that most of the aquifers fringing the core area of the Fennoscandian ice sheet during the recent glacial periods had sufficient transmissivity to discharge most of subglacial meltwater. According to their reconstruction, as the ice sheet terminus expanded over shield rocks of low transmissivity, groundwater flow was unable to discharge all the meltwater, so that the groundwater head rose to the value of ice pressure and excess melt was drained from the bed by some form of conduit system. As the ice sheet advanced beyond the shield and across the zone of sedimentary basins, bed transmissivity became sufficiently large to drain all the basal melt through groundwater flow alone (Boulton *et al.*, 1995). Of great importance in controlling the hydraulic behaviour in the terminal and proglacial zone was the presence or absence of proglacial permafrost, which can cause the increase of water pressures in the ice sheet margin zone and determine the groundwater fluxes and heads far from the ice sheet margin (Boulton *et al.*, 1995).

Piotrowski (1994, 1997) has shown that for marginal portions of the Fennoscandian ice sheet in north-western Germany, due to generally low hydraulic transmissivity of the substratum, only about 25% of subglacially produced meltwater could have been evacuated through the aquifers. The rest of the meltwater was evacuated through tunnel valleys in spontaneous outburst events, that were likely to be asynchronous during the ice sheet maximum and shortly thereafter and preceded probably by water ponding in subglacial lakes (Piotrowski, 1997). Tunnel valleys are abundant not only in north-western Germany (Piotrowski, 1994) but also in other areas within the Fennoscandian ice sheet limits. Bjerkéus (1998) has described the valley system in the Hanö Bay, southern Baltic Sea. Together with similar valley systems in the south-eastern and south-western Baltic Sea and on land in Baltic coastal regions, it belongs to a distinct belt of periglacial erosional valleys, formed by meltwater erosion at, or inside the ice front (Bjerkéus, 1998). Ehlers & Wingfield (1991) have also found deep valleys cut into sedimentary bedrock in the North Sea. Deep valley structures are also present offshore Britain (Wingfield, 1989). According to Bjerkéus (1998) in most cases the valleys are of three generations, formed during three different glaciations (Elsterian, Saalian and Weichselian). An abundance of erosional tunnel valleys in different areas within the Fennoscandian ice sheet limits indicate, that evacuation of meltwater through the tunnel valleys has probably played an important role in subglacial meltwater discharge.

11.2.4 Permafrost

A permafrost region is defined as an area in which the temperature of some or all of the ground below the seasonally freezing and thawing layer remains continuously at or below 0°C for at least two consecutive years (van Everdingen, 1998). In practice, however, there is a common understanding that continuous permafrost occurs at mean annual air temperatures from −6 to −8°C and lower, discontinuous permafrost at −4 to −8°C and sporadic permafrost at temperatures from −1 to −4°C (Brown *et al.*, 1997). At present, permafrost environments occur over 20% of the Earth's land surface and during the LGM an additional 20% may have been affected (French, 1976).

For reconstruction of former permafrost and periglacial environments specific indicators are used which represent relict features developed above or within the permafrost. However, from the numerous periglacial feature only a very limited number really testify to former permafrost (Washburn, 1980). Pseudomorphs of ice wedges, sand-wedge casts, remnants of pingos and palsas are among those features, having better preservation chances and therefore also having palaeoclimatic relevance. Polygonal cracks associated with the casts of former ice wedges may be indicative of former mean annual ground temperatures between –2°C and –10°C (Washburn, 1980). According to Romanovsky (1985), ice wedges can form in fine-grained sediments when the mean annual ground temperature is below –2.7°C. To convert the estimated ground temperatures to air temperatures the general rule is that in average, the mean annual ground temperature is about 2 to 6°C warmer than the mean annual air temperature (Pewe, 1975).

As a proxy indicator for the existence of cold conditions which are favourable for permafrost development, Gordon *et al.* (1989) have used the growth frequency of speleothems, which is dependent on the occurrence of significant diffuse groundwater recharge as well as on the biogenic production of CO_2 in the soil. Both of these parameters are dependent on temperature and water availability. Therefore, under cold conditions, where permafrost develops, diffuse groundwater recharge will be greatly reduced and speleothem deposition will be very slow or cease entirely.

Climate in Europe during the Early Weichselian (marine substages 5d–5a) was generally mild (Fig. 11.6) and therefore periglacial phenomena from this time are rather scarce. Small-scale cryoturbations and frost fissures related to the cold intervals between the Eemian and Brørup (substage 5d) as well as between Brørup and Odderade (substage 5b) are reported by a number of researchers (e.g. Zagwijn & Paepe, 1968, Vandenberghe & Pissart, 1993). These features indicate periglacial conditions with deep seasonal frost, however, without the necessity of permafrost. It means that the mean annual temperature was at least below −1.5°C (Maarleveld, 1976).

The entire Middle Weichselian interval (substages 4 and 3) between about 73 to 28 ka BP has been recognized as a relatively mild period except a cold period just at the beginning (substage 4) up to 61 ka BP, when continuous permafrost existed in western and central Europe. In the sandy regions of western Europe the whole Middle Weichselian sediment sequence has been characterized by the occurrence of frost cracks and small-sized cryoturbations, which point at least to deep seasonal frost. Ice wedge casts and associated large cryoturbations in sediments related to the cold episode between 41 and 35 ka BP have been discovered in the northern Netherlands (Vandenberghe & Pissard, 1993) This has been the period with sporadic or discontinuous permafrost in Europe. Using several different criteria, Vandenberghe & Pissard (1993) argued, that a mean annual temperature of −4.5°C was probably the lowest value and −1.5°C the highest one reached during the Middle Weichselian at sea level in north-western Europe. Based on speleothem growth frequency peaks Gordon *et al.* (1989, p.21, Fig. 6) have identified six warmer periods within the Middle Weichselian for U.K. with increased growth of vegetation, when evidently no permafrost existed.

The coldest period of the Weichselian appears to have occurred between about 28 ka BP to LGM at about 18 ka BP. The major factor responsible for the formation of periglacial conditions in Europe within this time interval was the increased atmospheric circulation with cold north-easterly anticyclonic winds adjacent to the south-eastern sector of the North European ice sheet, and strong, cold north-westerly cyclonic winds from a predominantly ice covered North Atlantic (Andersen & Borns, 1994). The cyclonic and anticyclonic circulation in combination with the strong cold and dry catabatic winds created the special Arctic periglacial conditions in Europe. Most of the France, Germany, Poland, Belgium, The Netherlands and southern Britain were characterized by permafrost (Washburn, 1979, see also Fig. 1.5). Traces of periglacial structures from this period are widespread and generally well preserved (Vandenberghe & Pissart, 1993). According to Karte (1983) the thickness of permafrost ranged from 10 m in the west and south-west to more than 100 m in the east and north-east. In the Berlin area frost wedges were formed in the tills of morainic plateaus, and as most of them are sand- wedge casts with primary infilling, they indicate a dry and cold climate (Böse, 1995). Similar conditions with the formation of permafrost sand-wedge casts in till and stone pavements with ventifacts are described in Poland (Kozarski, 1974). According to Vandenberghe &

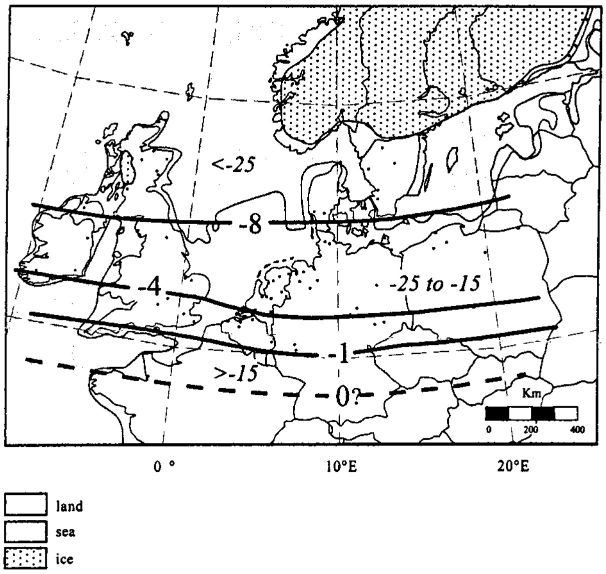


Figure 11.8. Reconstructed mean annual air temperatures (normal font) and mean temperatures of the coldest month (italic) at sea level during the Younger Dryas (from Isarin, 1997).

Pissart (1993) the frequent occurrence of ice wedge polygons and associated large-amplitude cryoturbations, the presence of closed-system pingos and the absence of speleothems in Belgium point to existence of continuous permafrost. At the maximum of this cold period the ice wedges developed in all kinds of subsoils. This allows the conclusion that, in accordance with modern analogues, mean annual temperatures dropped below –8°C at that time.(Vandenberghe & Pissart, 1993).

The climate amelioration during the Bølling/Allerød warming was characterized by warmer summers, but winters remained fairly cold (Andersen & Borns, 1994), so that seasonal cracks developed and the overall dissipation of permafrost was rather slow. Climate cooling during the Younger Dryas also activated the periglacial processes. Most detailed study on distribution of permafrost in north-western Europe during the Younger Dryas has been performed by Isarin (1997a). According to his results during the coldest part of the Younger Dryas continuous permafrost existed north of ~54°N (i.e. in Fennoscandia and the northern part of the British Isles and Ireland). Mean annual air temperatures at sea-level near or below -8°C and mean temperatures of the coldest month well below -20°C are deduced for this zone (Fig. 11.8).

Discontinuous permafrost was present between 54 and 50°N (i.e. in central and southern England and Ireland, The Netherlands, upland Belgium, northern Germany and Poland). It is suggested that in this zone mean annual air temperatures were between –8 and –1°C, with mean temperatures of the coldest month not lower than -20°C (Isarin, 1997b).

The data on distribution of relict periglacial features in the southern Scandinavia and in the Baltic area are rather sporadic. Relict wedge structures and polygon patterns are observed most frequently in deglaciated areas of south-western Scandinavia and they are related mainly to the younger Dryas cooling period (Svensson, 1988, 1992).

For the eastern Baltic area there are very few convincing data concerning the distribution of permafrost during the last glacial. Some findings of ice-wedge casts and cryoturbations in the north-east Estonia, related to the Younger Dryas cooling period, are reported by Miidel (1974). However, stagnant ice landforms indicate the existence of stagnant ice fields in the area, after the Fennoscandian ice sheet retreated. According to Raukas & Karukäpp (1994) some of stagnant ice fields in Estonia could have exceeded 10–20 km in width and were up to several hundred meters thick. In some places buried stagnant ice bodies in Estonia melted only during the early Holocene. This is showing relatively good conditions for preservation of ice, which is indirect evidence of possible existing of permafrost in the area.

The existence of permafrost in Europe several times during the Weichselian may have had strong influence on groundwater systems. The break in the supply to the groundwater reservoirs during the last expansion of permafrost is proved by the radiocarbon ages of groundwater in Europe older than 20 to 25 ka BP and younger than 10 ka BP (Andres & Geyh, 1970, Bath *et al.*, 1979, Stute & Deak, 1989), as well as by the entire cessation or very slow speleothem deposition (Gordon *et al.*, 1989).

The retreat of permafrost in the early Holocene allowed deep percolation of water into the ground, establishing the common groundwater table and regulating the runoff by groundwater supply and vegetation.

11.3 Growth and decay of the permafrost layer during the glacial maximum

The occurrence of a permafrost layer near the surface can have a strong influence on the groundwater flow cycles in the aquifer system below it. At first the recharge of the water table is inhibited, causing severe lowering of piezometric levels after some time, and secondly while the permafrost layer is growing, due to the transformation of water to ice, fluid is extracted from the top of the aquifer system. This can at least temporarily cause an upward flow of groundwater. Much depends on the thickness of the permafrost layer and its growth rate, determining the discharge rate from the water table. Therefore calculations have been done trying to simulate the evolution of the thickness of the permafrost layer under different temperature conditions at the surface. The northern part of Belgium has been modelled, as a representative example of the PALAEAUX study. The surface conditions used are only rough estimates for the possible meteorological environment in the region, assuming average annual temperatures were restricted to a few degrees below zero.

11.3.1 Analytical model

Principles

First an analytical model was used to estimate the permafrost thickness for rather simple uniform temperature conditions at the surface. Analytic formulas for such simple cases can be derived (Lunardini, 1995) by dividing the underground in three distinct layers:

(iv) a top layer which contains the permafrost layer;

(v) an intermediate layer in which the temperature distribution is influenced by the overlying permafrost;

(vi) a bottom layer in which a normal geothermal gradient occurs.

The following boundary conditions can be derived:

- the temperature on the top of the permafrost is predefined and constant;

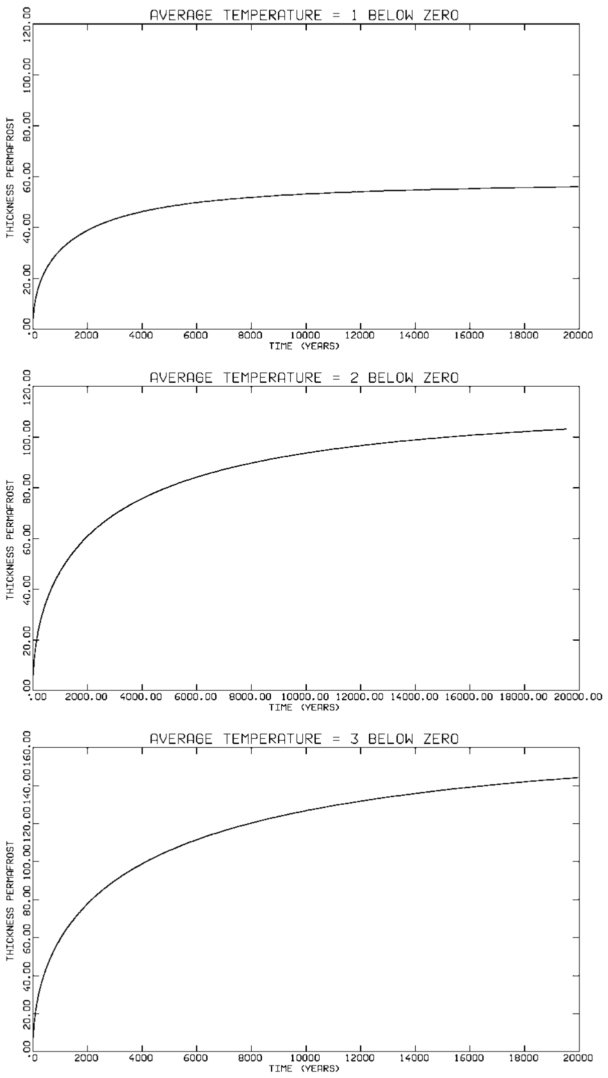


Figure 11.9. Calculated permafrost thickness with the analytical model.

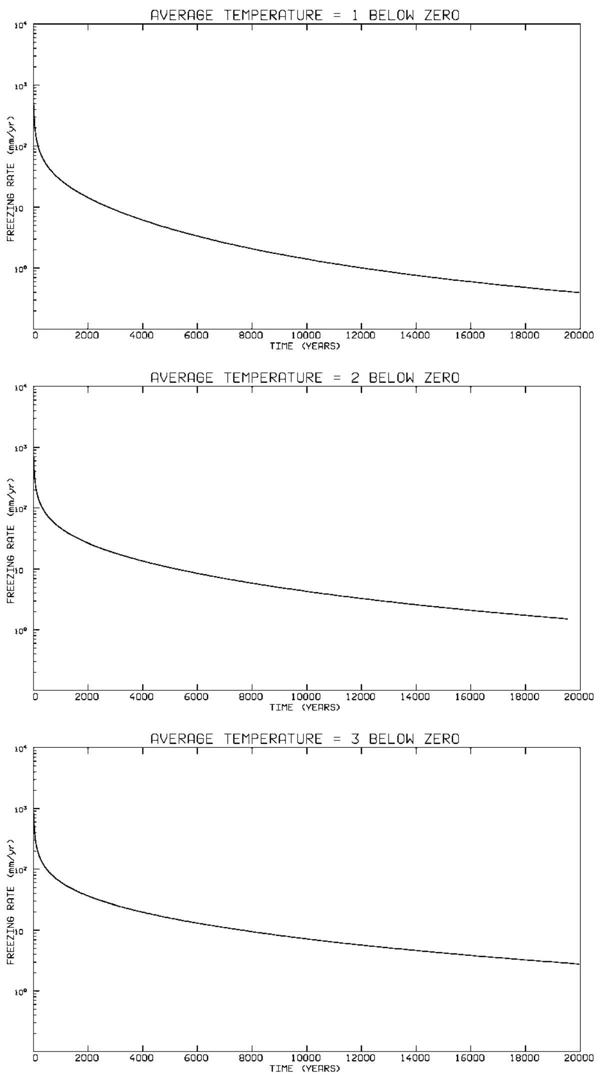


Figure 11.10. Calculated growth race of permafrost with the analytical model.

- the temperature at the bottom of the permafrost layer is zero;
- the gradient in the lowest layer is the geothermal gradient (0.0286°C m^{-1})

The applied formulas are based on the heterogenetic freeze relations (Lunardini, 1995).

Input data

The following thermal properties must be quantified:

- thermal conductance and specific heat for water;
- thermal conductance and specific heat for ice;
- thermal conductance and specific heat for matrix material;
- latent heat for water;

The values used for the calculations are the same as in Lunardini (1995). Thermal properties are well known and are therefore applicable over a wide range of geographic sites. The model calculates the position of the freezing front as a function of time, giving the evolution of permafrost thickness.

Results

Calculations are done for three different average surface temperatures (–1, –2 and –3°C) during a period of 20 000 a. The calculated thickness is presented graphically as a function of time. The main characteristics of the curves are (Fig. 11.9. and Fig. 11.10):

- after infinite time an equilibrium thickness will be reached;
- the increase in thickness is fast in the early time of freezing conditions but slows down after a few thousands of years;
- as surface temperatures are lower it will take more time to approach the equilibrium thickness.

The main results are summarized in Table 11.1. The equilibrium thickness can be viewed as the maximum permafrost thickness that can be expected under the given surface conditions. More important than the equilibrium thickness is perhaps the thickness that can be reached after a limited time period, e.g. during the last glacial maximum. Therefore the calculated thickness after two periods of time (5000 and 10 000 years) is given. Also the time required to freeze 50% of the equilibrium thickness is indicated. These values show that it requires only a

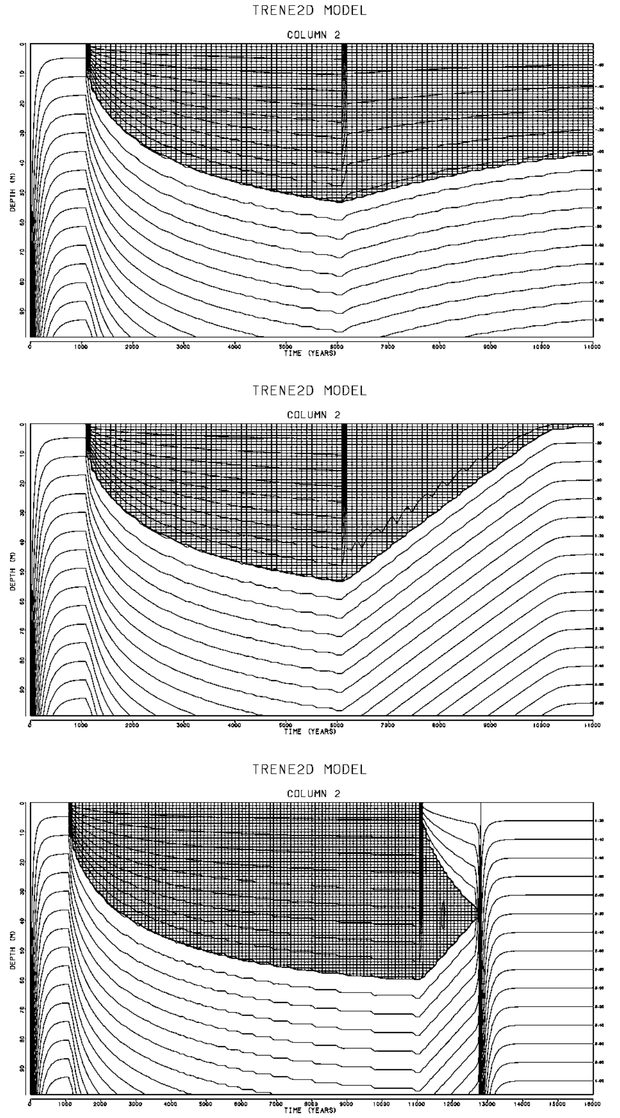


Figure 11.11. Calculated permafrost evolution with the numerical model: (from the top) a) scenario 1; b) scenario 2; c) scenario 3.

Table 11.1. Calculated permafrost thickness with the analytical model

Surface temperature	Thickness			Time to 50% equilibrium
	Equilibrium	5000 a	10 000 a	
°C	m	m	m	a
-1	60	48	53	1000
-2	120	80	94	2000
-3	180	106	127	3000

rather short period (compared to the length of a glacial period) to reach half of the maximum permafrost thickness.

The results suggest that when continuing freezing conditions occur, even if they are only a few degrees below zero, within the time limits of the last glacial maximum, a permafrost layer of between 50 and 100 m could have developed. Recent investigations of the Younger Dryas period (Isarin, 1997), during which near-(peri)glacial conditions reoccurred between 11–10 ka BP, were based on both in situ observations of periglacial phenomena (e.g. ice wedges) and simulations with an atmospheric global circulation model (AGCM). The results show that in this period in North Belgium average annual temperatures between −1° and −4° can have existed. The temperature conditions during the last glacial maximum can be estimated to be at least equal or lower that the values obtained for the Young Dryas.

11.3.2 Numerical model

Principles

More complex scenarios can be simulated using a numerical model. Therefore the TRENE-model which simulates the transport of energy through porous media was developed. The main characteristics of this model are:

(vii) 2-dimensional model: can be used for simulating cross-sections or columns;

(viii) it uses a finite difference approach based on a rectangular grid;

(ix) the energy flow transport equation is solved iteratively using an ADI scheme;

(x) incorporates the energy release/consumed by phase transitions between water and ice;

(xi) boundary conditions can be defined as constant energy flux (inflow or outflow) and constant temperature.

The model calculates the temperature and ice content for each cell of the model grid. Because of the spatial discretization the movement of the permafrost front through a grid-cell is calculated as the fraction of the cell that is frozen (or melted). Cells belonging to the permafrost layer have an ice content of 100%, non-frozen cells 0%. When the permafrost front is located somewhere in a cell the ice content is between 0 and 100%.

Input data

Calculations have been performed simulating a 1-dimensional column of 100 m thickness, which shows the temperature and ice distribution as a function of depth. The following boundary conditions are chosen:

(i) top of column: constant temperature: defined average annual surface temperature;
(ii) bottom of column: constant energy flux: geothermal flux estimated at 50 mW/m^2.

Results

The results are presented (Fig. 11.11) in the form of two-dimensional plots on which the X-axis is the time and the Y-axis is the depth below the surface. The calculated temperatures are presented with isothermal lines (with interval of 0.2°C). The extension of the permafrost layer is indicated by hatching.

The numerical model was mainly used to simulate the melting of the permafrost layer. Three different scenarios have been followed after an initial period of 10 000 years during which a permafrost layer develops under an average annual temperature of –2°C:

(i) SCENARIO 1: warming up to –1°C; at the surface freezing conditions continue;
(ii) SCENARIO 2: warming up to near 0°C; in this case the surface remains marginally freezing;

(iii) SCENARIO 3: warming up to +1 C; ice near the surface can melt.

During each simulation the first 1000 years were used to generate the normal geothermal gradient in the system. After the end of this short interval the isothermal lines are nearly horizontal, indicating the system is in (geo)thermal equilibrium.

The results of scenario 1 (Fig. 11.11a) show that because surface temperatures are getting higher, the equilibrium thickness will be less. Freezing at the surface continues, so the change in thickness will be caused by bottom melting by the earth's heat flux. The pattern of isothermal lines indicates that the temperature distribution in the permafrost layer adapts quite fast to the new surface conditions, but the bottom melting of the ice takes a much larger time. When surface temperature is at freezing point the equilibrium permafrost thickness is, theoretically, infinitely small. Thus following scenario 2 the permafrost layer will melt almost completely, but because surface temperatures stay marginally under zero, the melting will occur exclusively at the bottom. The results show (Fig. 11.11b) that it takes nearly 4000 years to melt the permafrost layer completely.

The third scenario (Fig. 11.11c) shows what happens when the warming up is enough to start melting the top of the permafrost layer. In the case of a surface temperature of +1°C, the top melting is already more important than the bottom melting. Above the permafrost layer an active layer develops, increasing in thickness with time. At this time the aquifer system is subdivided in two aquifers separated by the not-yet-melted part of the permafrost.

For the simulated example the thickness of the upper aquifer can reach a few tens of meters. In realistic situations local flow cycles can develop to discharge the meltwater. Under the given temperature conditions normal recharge of the water table by precipitation can take place. The lower aquifer under the ice is only recharged by the meltwater which originates from the bottom melting of the permafrost. Finally around 1800 a in the simulated column the ice is completely melted and the two aquifers make hydraulic contact. From this moment on the whole aquifer will heat up very fast. As long as there exist any ice somewhere in the aquifer, the temperature distribution in the aquifer above it will decrease from surface temperature to zero at the top of the ice layer. Under the ice, the temperature will increase from zero at the bottom of the ice layer conforming to the geothermal gradient. After the last ice has melted a new temperature profile will commence with temperature linearly increasing with depth.

11.3.3 Discussion

Simulations with both an analytical and a numerical model show that average annual temperatures of even a few degrees below zero can generate permafrost layers of 50 to 100 m thick in less than 10 000 years. Especially in the early stages of freezing the growing rate will be fast, slowing down after a few thousands of years. An equilibrium with constant thickness will be reached, but only after infinite time. The equilibrium thickness increases with lowering surface temperatures, and half-equilibrium thickness will be reached after longer times for lower surface temperatures.

During the growth of the permafrost layer a discharge from the water table occurs. The average discharge rates can have been at least a few mm/year in longer marginally freezing periods (e.g. –1°C), and may be tens of mm/years during shorter, colder periods (e.g. –3°C). These rates are high enough to induce an upward flow in the system when no recharge takes place.

Following cold periods a permafrost layer of 50 to 100 m may melt down in a few thousands of years. When temperature rises but stays around freezing point (0°C), melting will occur mainly at the bottom of the layer, caused by the earth heat flux (estimated at 50 mW m^{-2}). When surface warming is enough to reach temperatures above zero, top melting will occur and at +1 C, the top melting will be more important than bottom melting. In this case the aquifer system will be divided in two independent systems, separated by the last remnants of the permafrost layer. The top system can reach a thickness of at least a few tens of meters if the original permafrost thickness was between 50 and 100 m. In this top aquifer system the normal recharge of the water table is restarted and local flow cycle systems may develop. The aquifer system under the remaining permafrost is recharged by the melting at the bottom. This recharge is likely to be much smaller than recharge rates under normal non-periglacial conditions. During the melting of the permafrost layer complicated flow situations can occur, especially when the last parts of the permafrost are melting and the two systems are making hydraulic contact. These complex flow systems can have influenced the emplacement and distribution of the palaeowaters and are consistent with the lags in recharge implied by the hiatus in radiocarbon ages observed in some aquifers studied in PALAEAUX.

11.4 Sea level changes

11.4.1 General features

The major fluctuations in global sea levels during the late-Quaternary were glacio-eustatic in origin, being the result of changes in global ice volume (Dawson, 1992). By far the most detailed record of past sea level changes (Fig. 11.12) has come from the oxygen isotope record of benthic fauna and this is significant since it is calculated independently of emerged or submerged shoreline data and is directly proportional to the contemporaneous global volumes of sea water and ice (Shackleton, 1987). The radiometric ages derived from corals also closely match the data from Late Pleistocene sea levels derived from benthic fauna (Chappell and Shackleton, 1986).

Global sea level reached its highest level up to 6 m above present one during the marine isotope substage 5e about 125 ka BP (Shackleton, 1987). Much of the con-

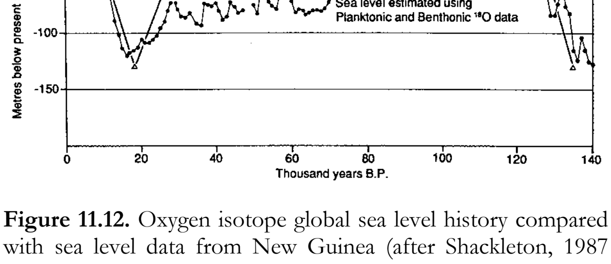


Figure 11.12. Oxygen isotope global sea level history compared with sea level data from New Guinea (after Shackleton, 1987 from Dawson, 1992).

temporary shoreline in north and north-west Europe as well in the lowlands of the south-west and south-east coasts of the Iberian Peninsula (Guadalquivir mouth, Mar Menor, Albufera de Valencia, Ebro and Llobregat deltas) was submerged (Garcin, 1994). The Baltic Sea was then connected with the North Sea in the west via the Skagerrak, Kattegat and Danish Sounds through the present lake system of Vänern and Mälar in central Sweden and with the White Sea in the north-east through the system of shallow sounds and the lakes Onega and Ladoga (Raukas, 1991).

According to Shackleton's curve sea levels as high as the present have only persisted for some 10% of the past l00 ka, including 5 ka of the present interglacial. During isotope substages 5d to 3 along the changes in global ice-volume sea-level was lowering stepwise down to its minimum about -120m at LGM around 18 ka BP (Dawson, 1992; Pirazzoli, 1998). Peltier (1994) has shown that sea level at LGM was only 105.2 m lower than present However, the southern part of the North Sea Basin, the Baltic and much of the English Channel were land mass during this period with Britain joined to the European continent. The Atlantic coasts of Iberia and the Mediterranean coasts of Spain and France were also significantly affected by the sea level lowering. The extended period of emergence provided opportunities for reactivation of groundwater flowing in the coastal unconfined aquifers due to lowering of the hydrostatic head and similar activation of flow in deeper (confined) aquifers near coastlines where outlets such as faults or relatively impermeable confined strata are present. Whilst groundwater circulation should have been enhanced over much of the late Pleistocene in southern and western Europe there is still controversy as to whether net groundwater recharge and circulation was inhibited in northern Europe during the same period due to permafrost and /or ice cover.

11.4.2 North west Europe

According to Lambeck (1997), sea-level change along the English Channel and French Atlantic coast after the LGM was not uniform because of the response of the crust to the changing ice and water loads during Late Pleistocene and Holocene time. The pattern of the spatial variability is a north to south trend of decreasing sea levels at any time. This was a combined effect of isostatic response to the melting of the Fennoscandian ice sheet superimposed upon the isostatic response of the crust to the addition of the meltwater into the Atlantic ocean. As a result, at any time sea levels vary spatially along this coastline by amounts that are predicted to rich 20 m from the time of LGM to about 11.5 ka BP and about 15 m at 8.5 ka BP. Therefore not a single sea level curve but regional curves for relatively short sections of the coastline, such as Pas-de Calais and Picardie, Normandie, Côtes-du-Nord, Finistère, or the Vendée and Charente-Maritime region, should be used for this area (Lambeck, 1997).

The area of the southern North Sea was land for much of the Pleistocene and was drained by the 'Loburg River', originating in Kent and leading to the extended Rhine/Meuse river system (Bridgland & d'Olier, 1995). The river Thames was a tributary of this river system and contained several valleys which intersect the present coastline (Fig. 11.13). The maximum present day channel depth of the Thames estuary is 40–50 m. However, buried channels may have incised further into the underlying sediments.

To stick

Figure 11.13. Courses of river drainage into the North Sea and late Pleistocene channels/deposits (after Bridgland & d`Olier, 1995).

Palaeobathymetry and palaeoshoreline reconstructions for the Irish Sea indicate that a tenuous land bridge between Britain and Ireland developed only across the Celtic Sea, between about 18 and 14 ka BP. No land connection is predicted further north, although the Isle of Man is connected to north-west England briefly from about 14 to 11 ka BP (Lambeck, 1996).

At the time of LGM the English Channel was aerially exposed as far west as 6°W as was the broad shelf offshore from the present south-west coastline of France (Lambeck, 1997). The effect of sea level lowering was to create a drainage system centred on the English Channel which was fed by extensions of the river systems from England (e.g. the Solent River) and France (e.g. the Somme) (Bellamy, 1995). This river system extended to form the Hurd Deep (–100 to –130 m datum) lying some 70 km off the Cherbourg peninsula (Smith, 1985) (Fig. 11.14).

The effective base level controlling groundwater circulation in the eastern English Channel (for example reactivating flow in the Chalk aquifers in the area of Brighton) is more likely to have been controlled by the depth to the main channel lying some 20–25 km off the English coast at a depth of ca 70 m (max.). The Chalk crops out at or near the surface over much of the Eastern English Channel and is gently folded; the synclinal areas are infilled with Tertiary confining strata (BGS 1:250 000 Sheet Wight). There is good evidence from seismic profiles and cores of the typical configuration of the valley systems (Fig. 11.15)

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Figure 11.14. The palaeovalley system of the English Channel and its relationship with the deeps, the depressions in the southern North Sea, and the "pits" of the central North Sea (after Smith, 1985).

and the development of superficial sub-aerial sedimentation including peat during the late Pleistocene (Bellamy, 1995).

By 11.5 ka BP the English Channel was partly open to the sea in the west, but while the exposed shelf area has contracted substantially in most localities, the shorelines would still be offshore from their present location and no brackish- or salt-water deposits would be expected of this age and older anywhere along the present coastline (Lambeck, 1997).

Some relative sea-level curves from western Europe (Fig. 11.16) have been summarized by Pirazzoli (1998). Among the others, curve B by Mörner (1980), deduced from about 40 shoreline sectors from the Kattegatt region (west coast of Sweden) and checked and confirmed against other north-western European records, has often been used as a reference especially for north-western Europe/north-eastern Atlantic regions. According to that eustatic sea level in north-west Europe during the LGM was between –85 and –90 m and it subsequently rose to -60 m by about 15 ka BP. Thereafter, eustatic sea-level lowering took place until after 13 ka BP when there was a rapid rise until about 11 ka BP when sea-level reached –45 m (Mörner, 1980). During the Younger Dryas between 11 and 10 ka BP sea-level fluctuated slightly (Fig. 11.9) and thereafter it began to rise with the most rapid rise having occurred between 9 and 7 ka BP.

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Figure 11.15. Cross-section of infilled valley beneath the English Channel near Worthing, UK (after Bellamy, 1995).

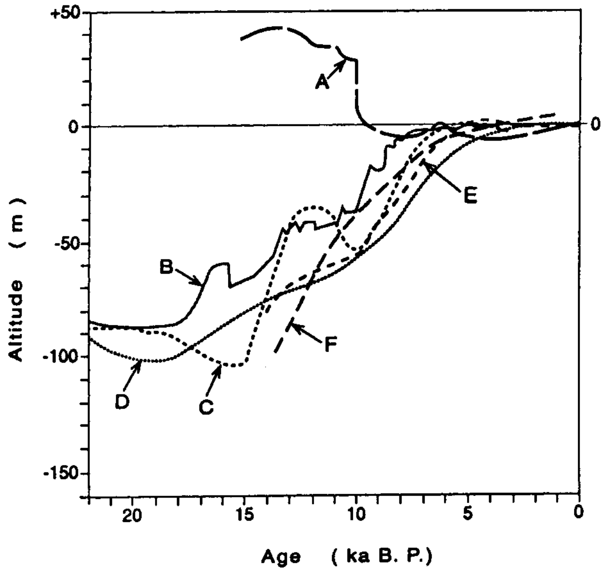


Figure 11.16. Deglacial relative sea-level changes in Europe (from Pirazzoli, 1998). Curve A: Spitsbergen (after Forman *et al.*, 1987); B: NW Europe (after Mörner, 1980); C: W of Belle Ile, France (after Pinot, 1968); D: Roussillon, France (after Labeyrie *et al.*, 1976); E: SW France (after Aloïsi *et al.*, 1978); F: French Riviera (after Dubar & Anthony, 1995).

11.4.3 Baltic area

Sea-level changes in Baltic area have been directly dependent on evolution of Baltic Sea. The final ice recession from the south-western Baltic basin occurred 13.5 to 13 ka BP (Berglund, 1979). As the deglaciation appears to have been very rapid until at least 12 ka BP, large parts of the southern Baltic became ice free relatively quickly (Björck, 1995). The rapid deglaciation produced huge volumes of meltwater and icebergs and this ice free region might be termed the first proper Baltic Ice Lake (*i.e.* the first stage of Baltic Sea).

The Estonian territory became ice free during a time span between 13 and 11 ka BP (Raukas, 1996). During the last stages of ice sheet retreat (the Pandivere (Fig. 11.17) and the Palivere stages) practically the whole area in front of the ice margin was covered with vast ice-dammed lakes which, starting at least from the Palivere stage formed the eastern part of Baltic Ice Lake.

Due to the stadial-oscillatory character of deglaciation, the level of Baltic Ice Lake changed several times rapidly. Thereby, the level of the lake was mainly controlled by the presence or absence of glacial ice in the area of Mount Billigen in Central Sweden (Fig. 11.18). The Mt Billigen is a key point in the history of the deglaciation as well as the Baltic basin. East of Mt Billigen, in the southern part of the basin, the Baltic Ice Lake was ponded up by the receding ice margin in the north, the southern Swedish highland in the west and the European continent to the south and east. The drainage from the lake passed through the Danish Straits, at that time dry because of the eustatically low North Sea level. The level of the Baltic Ice Lake at Mt Billigen was about 150 m, while the corresponding sea-level in that area was 125 m (Lundqvist, 1987). This pond-

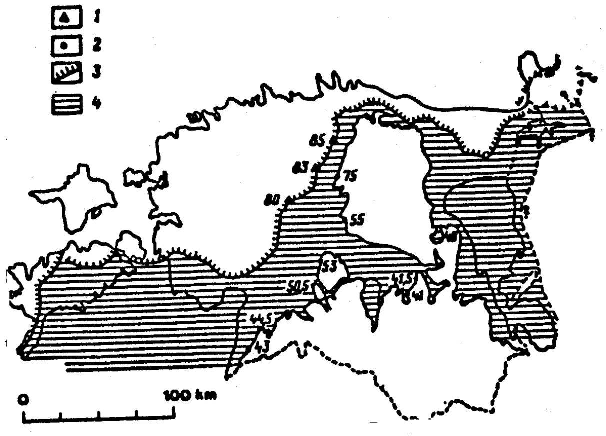


Figure 11.17. The initial point of the formation of the Baltic Sea after the retreat of the Fennoscandian ice sheet from the Pandivere Upland. Legend: 1 - elevation of aqueoglacial forms above the present sea level, m; 2 - elevation of coastal forms asl; 3 - ice margin; 4 - area occupied by ice-dammed lakes. *Compiled by J. Vassiljev on the basis of data published by H. Kessel, E. Lõoke, K. Markov, K. Pärna, A. Raukas & E. Rähni.*

ing persisted as long as the ice margin was stationary at the Younger Dryas line.

At the end of the Younger Dryas cold stage the rapid amelioration of the climate caused rapid retreat of the ice margin, and the Baltic Ice Lake drained catastrophically into the North Sea via the Öresund Strait. Its surface was lowered by 26-28 m within only a few years (Björck, 1995). An open sound north of Billingen provided direct connection between the Baltic basin and the North Sea (Strömberg, 1989). Recent investigations (Björck& Digerfeldt, 1986) have indicated that the catastrophic draining of the Baltic Ice Lake was repeated once. According to them a first drainage took place about 11.2 ka BP during the Alleröd retreat of the ice margin. This was followed by a significant readvance between 11 and 10.5 ka BP, that is, the main part of the cold Younger Dryas event. The final drainage according to S. Björck & G. Digerfeldt (1986) is dated at 10.5 to 10.4 ka BP. However, by several more datings (Wohlfarth *et al.*, 1993) the age of the event has been adjusted slightly to ca 10.3 ka BP (Björck, 1995). A marine incursion into the Baltic, identified by marine fauna, occurred briefly, from about 10.3 to 9.5 ka BP, forming Yoldia Sea. According to those data, the development of the Baltic Sea between 13 and 8 ka BP can be divided into three main stages: the Baltic Ice Lake stage, 13 to 10.3 ka BP; the Yoldia Sea stage, 10.3 to 9.5 ka BP and the Ancylus Lake stage, 9.5 to 8 ka BP.

During this very dynamic time period of the Baltic Sea history the water level of the Baltic was dammed above sea level during three periods, 12 to 11.2 ka BP, 10.8 to 10.3 ka BP and 9 to 8 ka BP (Björck, 1995). This updamming was caused by the damming of the ice sheet and the isostatic uplift of the functioning threshold. The complex threshold history combined with the fact that the uplift centre of the Late Weichselian Fennoscandian Ice Sheet is situated in the northern part of the Baltic basin and the southernmost region of the Baltic is regarded as a submergence region, means that the early Baltic Sea history was characterized by both regressions and transgressions, often occurring at the same time in different parts of the basin (Björck, 1995, Raukas, 1996).

In the context of the PALAEAUX project it is important to stress that, in spite of several drastic changes in the Baltic Sea level (Fig. 11.19) and the high glacioisostatic uplift rate in north Estonia during and after the last deglaciation (13 mm a^{-1} in preboreal time and 2-3 mm a^{-1} at the present time in the north-west Estonia (Raukas & Miidel, 1995)), the main discharge area of the coastal aquifer into the Gulf of Finland has been submerged during all stages of the Baltic Sea.

For northern part of Denmark a sedimentologically based revision of the classical relative sea-level curve has

To stick

Figure 11.18. A. The Baltic Ice Lake showing uplift isobases (in meters) and the location of the lake drainage outlet near Mt. Billingen. B. The extent of the Yoldia Sea at cà 10 ka BP showing the shorelines isobases (after Eronen, 1983).

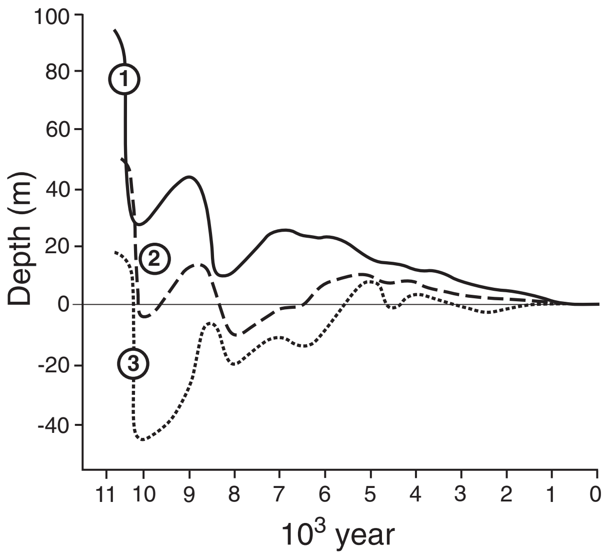


Figure 11.19. Water level changes of the Baltic Sea at Kõpu, Island Of Hiiumaa in NW Estonia (1), W Latvia (2) and W Lithuania (3) with two clear rapid regressions of the Baltic Ice Lake, and of the Ancylus Lake (from Raukas, 1996).

been presented lately by N.Richardt (1996). According to that, the highest Late Weichselian shorelines in northern Jylland are found c. 60 m above the present sea level. The high relative sea level persisted with possible minor fluctuation until about 13.3 ka BP, and was followed by rapid fall down to about 25 m asl at c. 12.5 ka BP (Richardt, 1996, p. 269, Fig. 10). From about 12.5 to 12 ka BP there was a break in relative sea-level fall in this area and from 12 ka BP started a gradual but slow fall leading to about the present sea level in early Holocene (Richard, 1996).

11.4.4 Iberian Peninsula

As the slopes of the continental shelve of the Iberian Peninsula are in general steep and narrow, the eustatic movements have not had much influence on the peninsulas coast-line. As a consequence, even the Eemian high sea level stand (+ 6 m asl) caused clear marine transgressions only on the lowlands of the south-west and south-east coasts of the peninsula (Guadalquivir mouth, Mar Menor, Albufera de Valencia, Ebro and Llobregat deltas), while in other coastal areas the invasion of the land by the sea had a reduced extension.

During LGM the sea level lowered about 120 m. In the north-east of the Iberian Peninsula the Mediterranean deltas emerged, and the coastline migrated to the south-east for 20 to 70 km. In the south-west of the peninsula, the Gibraltar Strait became narrower, decreasing the water exchange between the Atlantic Ocean and the Mediterranean Sea. The Balearic Islands Mallorca and Menorca, as well as Eivissa and Fomentera were united landmasses (Mateu *et al.*, 1984). However, the change of the coastline doe to the glacio-eustatic oscillations was in general small, which caused also small effect of induced continentality of a climate. On the other hand, due to the great vertical variations and to the steep slopes of the continental shelve, the erosive action of the rivers was strongly increased.

The most complete record of sea level oscillations between the LGM low stand and the Holocene maximum for the Spanish peninsular margin presents five major progressing units (Hernández- Molina, 1993, Zazo, 1994). Three of them are submerged along the south-west and south coast (P1 between –140 m and –120 m; P2 between -110 m and –100 m and P3 between –60 m and –45 m). The remaining two are emerged in south and south-east. The chronology of the P1, P2 and P3 units has been inferred relative to the climatic changes recorded in Europe, whilst the P4 and P5 units have been dated by means of ^{14}C (Zazo *et al.*, 1994). The P3 has been interpreted as developed during the Younger Dryas event, and it is recorded both in the Atlantic margin, above 40ºN, and in the Mediterranean margin below this same latitude (Hernández-Molina *et al.*, 1994). Regarding the sea level fluctuations, all these coastal-progressing P units are interpreted roughly as stillstands.

The study of sea-level cycles defined by P units allowed Hernández-Molina *et al.*, (1994) to elaborate the set

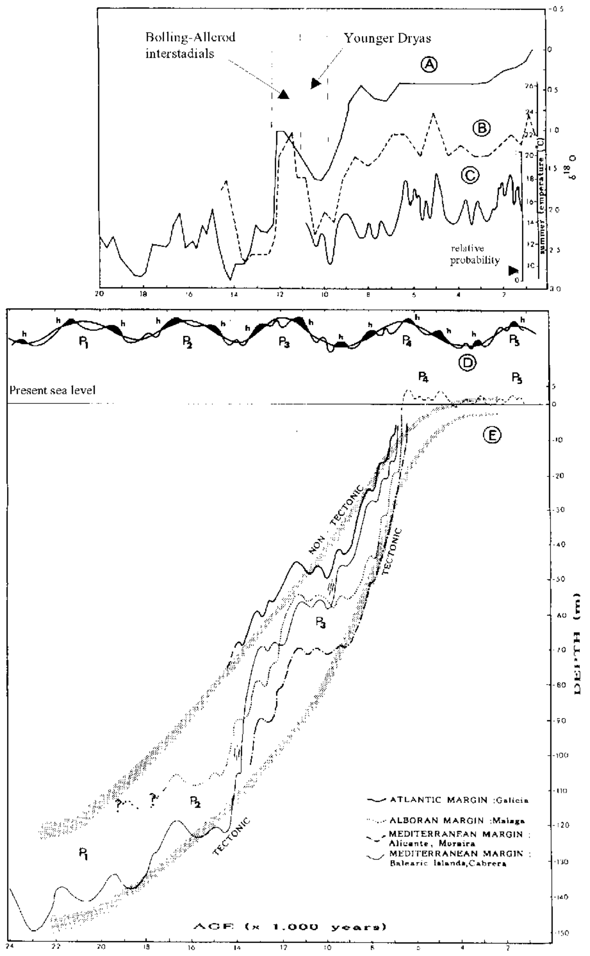


Figure 11.20. E: curves of relative sea level changes during the last 20 ka derived from the positions and morphologies of the associated sedimentary bodies. These can be compared with the curves A and B which show sea temperature changes based on oxygen isotope data over the same time span (Duplessy, 1990). Curve C is a histogram showing summer temperatures over the last 10 ka based on ^{14}C data from an ancient beach crest in the Almerìa area, southern Spain (Somoza *et al.*, 1991). Curve D shows the different orders of shorter cycles which modulate the main curve. Some labelled sectors of the curves are known to have been modified by tectonic subsidence (after Hernàndez-Molina *et al.*, 1994).

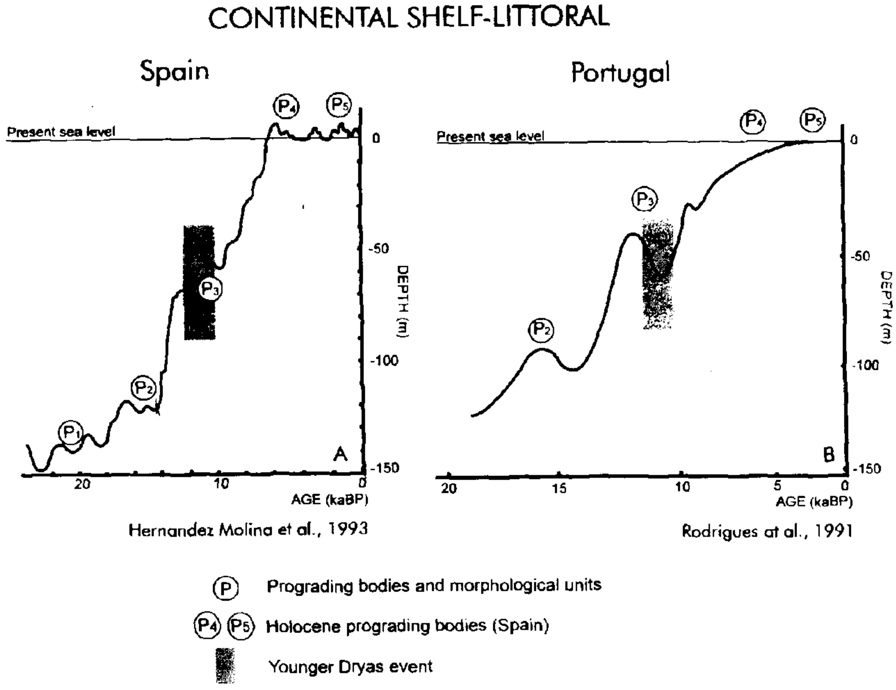


Figure 11.21. Sea level curves for the last 20 ka inferred from data regarding the Spanish and Portuguese continental margins (including information from all the study sites shown in Fig. 11.3) (After Zazo *et al.*, 1996).

of sea level curves (Fig. 11.20). The P units are positioned at their present depths and are chronologically correlated with water-temperature variations over the last 20 ka in the North Atlantic area (Duplessy, 1990), as well as with a ^{14}C histogram of the last 10 ka on the south-west Spanish coast.

One of the most important control of sea level changes in the south-eastern and eastern Iberian coasts has been the so-called "Surficial Atlantic Water" (SAW), because the rate of shorelines displacement is partly governed by the input of SAW into the Mediterranean Sea (Zazo *et al.*, 1994). At present, input of SAW dominates in summer, under warm and very dry climatic conditions, but it diminishes drastically during the winter (Garret *et al.*, 1990). The SAW stream is accompanied by a Deep Mediterranean Water (DMW) stream going from east to west. According to the sedimentary records in the Gulf of Cádiz, the DMW stream was more intense during the LGM than during the Holocene or than nowadays (Melieres, 1974). On the contrary, the SAW decreased during the pleniglacial.

Studies performed on the north-western margin of the Portuguese continental shelf indicate that sea-level during the LGM was lowered by about -130 to -140 m, rising to -100 m during the first stage of deglaciation between 16 and 13 ka BP. The following period from 13 to 11 ka BP is characterized by a fast raising of the sea-level to values around -40 m. During the Younger Dryas the sea-level was lowered to -60 m followed, at the beginning of the Holocene, by a fast rise (in average about 2 cm/a) until the present sea level which was reached at about 5 to 3 ka BP (Dias, 1985, Rodrigues *et al.*, 1991).

The change on the sea-level during glacial times must have imposed a much higher hydraulic gradient on the coastal aquifers, leading to substantially higher flow velocities of the groundwater, when compared to Holocene conditions. The total length of the Aveiro Createceus aquifer is not known, although studies performed at the continental shelf have found the Cretaceous layers spreading out under the sea (Vanney & Mougnot, 1981). Up to now it is not known if the permeable layer crops out at the bottom of the ocean or if, on the contrary, they are protected by the aquitard and impermeable clay layer. Mineralogical studies carried out on Pleistocene sediments allow the identification of a transition from a margino-littoral environment to a more continental one (Rocha & Gomes, 1993/94). The data also indicates a climatic evolution from a temperate climate with strong and irregular periods of pluviosity to a warmer climate with an almost year-round uniform pluviosity

Five morphologic units, generally of erosional character, have been recorded in the Portuguese north-western margin between –140 and 9 m. These units are associated with still-stands or with gentle regressive periods, reflecting the different steps of the retreating polar front.

Comparing the curves of the relative sea level changes during the last 20 ka. for the Spanish and Portuguese littorals (Fig. 11.21), very high degree of similarity can be observed. However, the Younger Dryas sea level drop observed in the Portuguese curve has not been recorded in any studied coastal sites in Spain.

On the basis of the study of the evolution of spit bars systems, estuaries, and deltas, two periods of coastline progression have been identified in southern Iberia after the Holocene maximum (ca. 7 ka BP). The first period took place between 6.9 and 2.7 ka BP, and the second one between 2.4 ka BP and the present. These two periods of progression suggest that once the Holocene Maximum was reached, sea level underwent at least two different oscillations, a slight fall followed by a slight rise (resulting in a sea transgression), but sea level was never higher than its highest position reached ca. 7 ka BP.

11.4.5 Atlantic coasts

In the case of the Canary Islands, a few data from the easternmost islands Fuerteventura and Lanzarote record sea level oscillations during the last 250 ka (Zazo *et al.*, 1997). Records of sedimentary and faunal studies show several sea level oscillations, both during the last interglacial period (135–75 ka BP) and during the previous one (240–180 ka BP). In both cases marine terraces formed which are under the present sea level, but there are clear evidences of volcano-tectonic activity affecting the islands in the last 250 ka. The Holocene transgressive maximum is recorded in Lanzarote coasts at around 6 ka BP.

In the Balearic islands there are only a few studies and data available regarding sea level and climate changes during the Holocene. In Mallorca the transgressive maximum of the present interglacial took place around 7 ka BP (Goy *et al.*, 1997). Climate conditions were more humid than present ones from 7.1 ka BP to 6 ka BP (Holocene optimum). At this moment a regressive trend started which is recorded as a littoral spit formation in S'Albufera, ^{14}C dated as 5.5 ka BP. This general regressive tendency reverts in some periods, as shown by the existence of two littoral spit systems in S'Albufera and the remains of marine terraces in other places of the island. These highstands on the generally regressive trend of sea level within the last 6 ka reflect short periods of more humid climate conditions and a relative sea level rise. The two littoral spit systems reflect periods of coastline progression, which means more arid climatic conditions and a stable or lowering sea level (Goy *et al.*, 1997).

11.5 Isotopic composition of past precipitation

Isotopic composition and noble gas content in groundwater are the main tools for to investigate the extent to which groundwater retains the signature of past recharge conditions (Rozanski *et al.*, 1997, Stute & Schlosser, 1993). However, the conversion from isotopic and noble gas proxies into climate parameters requires certain assumptions. For example, in order to convert a glacial/interglacial change in ^{18}O values, derived from an aquifer, into a temperature change, transfer function relating isotope values and temperatures should be established. Preservation rate of climate signals in groundwater systems over a time scale in order at least 10 ka has to be estimated.

The isotopic composition of groundwater generally reflects the weighted mean isotopic composition of precipitation in the recharge area. Today's temporal and spatial relationship between isotopic composition of precipitation and temperature for global and regional scales have been established on the base of data, gathered over the last more than three decades mainly through the IAEA/WMO Global Network "Isotopes in Precipitation" (Rozanski *et al.*, 1992, 1993). As a first approximation, those data suggest that the temperature controls the isotopic composition of precipitation over high and mid-latitudes, whereas the amount of precipitation is a dominant factor for tropical regions. However, atmospheric circulation patterns, linking the vapour source regions with precipitation sites, are of importance in all cases (Rozanski *et al.*, 1992, 1997).

According to those data the long-term ^{18}O/T relationship for mid- and high latitudes varies in a relatively wide range from 0.5 to 0.9‰ per °C (Rozanski *et al.*, 1997). As the isotopic composition of precipitation has been monitored only for the past tens of years, consequently, the long-term climatic sensitivity of the isotopic signature of precipitation is known with a relatively high uncertainty. For independent estimation of this parameter, archives where both the isotopic composition of precipitation and temperature are independently recorded, might be used. By far the best archive for that kind of information seems to be the Greenland ice sheet. Johnsen *et al.* (1989) have established today's relationship between mean annual ^{18}O of snow on Greenland and mean annual surface temperature to be about 0.67‰ per °C. Long-term ^{18}O data from deep ice cores and corresponding borehole temperature calibrations obtained from GRIP (Johnsen *et al.*, 1995) and GISP 2 (Cuffey *et al.*, 1995) establish that for the deglaciation period about 20 to 10 ka BP the apparent ^{18}O/T relationship was around 0.33‰ per °C, i.e. very different from today's relationship (Rozanski *et al.*, 1997).

As another independent archive, the aquifer of Great Hungarian Plain was extensively investigated for both its stable isotope composition and its noble gas content of groundwater. The apparent increase of ^{18}O in groundwater of the region during the deglaciation period amounts to about 2.5‰ whereas a change of surface air temperature at the same time interval, derived from the noble gas content of these waters was about 7°C (Stute & Deak, 1989). The resulting apparent ^{18}O/T value for deglaciation period is about 0.36‰ per °C. This value, if corrected for the change of ^{18}O of the ocean during the LGM-Holocene transition (approximately 1.3‰, according to Shackleton (1987)) is close to the long-term ^{18}O/T coefficient derived from the instrumental record of ^{18}O in precipitation and surface air temperature in Europe, available for the last three decades (Rozanski *et al.*, 1992).

In order to estimate the preservation rate of isotope signal of palaeorecharge in groundwater system, Stute & Schlosser (1993) simulated the smoothing of high-frequency climate signal through mixing processes and leakage between aquifers. Their calculation show that smoothing of the climate derived isotopic signal in an aquifer increases with age. According to that, high-frequency isotopic fluctuations occurring on a time scale of less than about 1000 years have already completely disappeared at the very beginning of the record, while the main features of glacial/interglacial transitions are still preserved. Based on these results, Stute & Schlosser (1993) expected that for the last 30 ka (the time scale accessible by ^{14}C dating) climate features related to the LGM and the preceding interstadial may be resolved on the base of isotopic composition of groundwater.

12 Isotopic methods and their hydrogeochemical context in the investigation of palaeowaters

12.1 Introduction

Isotopic and geochemical methods are used in the PALAEAUX work to

- determine the origin and the former recharge conditions of groundwaters;
- determine the flow paths, the evolution of the water and to understand the effects of water-rock interaction;
- determine mixing components and their age structure;
- validate flow models.

Two aims can be realized by the combination of hydrogeological and isotopic methods in the investigations of palaeowaters. The first is mainly scientific: information about climate signals can be found stored in palaeowaters. The other aim is a practical application: how to exploit reservoirs of old groundwater in a sustainable way. Such conclusions are possible, for example, from the observation of how fast anthropogenic influences are penetrating into the reservoir (see Chapter 16) or how fast the interface between palaeowater and Holocene water is moving (see Fig 1.1, Introduction).

In general, groundwater systems are complex. Palaeowaters, however, are even more complicated because, for example, permafrost and ice cover may have changed infiltration conditions. It is also necessary to consider that atmospheric circulation and atmospheric composition (especially pCO_2) and therefore infiltration parameters may have been different from present day conditions. The weight of glaciers may have changed subsurface flow parameters, such as permeability and flow direction.

For all these reasons it is necessary wherever possible to use a combination of techniques. Isotopic, geochemical, hydraulic and modelling data where these exist should be interpreted together. They interact with each other; for example, for conversion of isotope results into time information, the understanding of the geochemical system and its evolution is necessary. Furthermore, isotopic ages need to be compared with time information from hydraulic modelling. It is often the case that isotopic and geochemical data are the primary information available and the palaeohydrological indications pose further questions for the hydraulic interpretation.

In this chapter, the present-day knowledge about isotopic and geochemical methods relevant to the investigation of old waters is presented. Most emphasis is placed on those aquifers investigated and conclusions obtained during the PALAEAUX programme.

12.2 Isotopes as residence time indicators

Time information is important in order to describe flow systems in a quantitative way. In the PALAEAUX project, for example, it is necessary to know how fast the two main fronts are moving: (a) the interface separating waters with man-made signals from older water, and (b) the interface between palaeowater (of Pleistocene or early Holocene age) and younger water. The dating techniques for the first front are described in the chapter discussing modern and pristine groundwater interfaces (Chapter 16); recent applications of dating methods to young waters are described also in Loosli *et al.* (1999). This chapter concentrates on dating methods for waters older than about 100 years, essentially prior to human intervention. In Fig. 12.1 the dating ranges of different isotope methods are schematically shown.

From this figure it is clear that overlapping methods exist for young waters. However, although it is highly desirable always to combine methods (see below), for older waters sometimes only a single method is available to cover a dating range. The species ^{4}He and ^{40}Ar/^{36}Ar can at present only be used in a qualitative supporting way; therefore their range is shown by an interrupted line.

12.2.1 ^{39}Ar- and ^{14}C-methods

The frequently-used ^{14}C method is practically the only 'clock' available for the transition from ice age to postglacial times. The range of ^{14}C-dating is limited to about 25 ka because water-rock interaction effects may predominate over simple ^{14}C decay in very old samples.

Since the problems of converting the measured ^{14}C-activity of the total dissolved inorganic carbon (TDIC) into time information are well known and extensively described (e. g. Fontes, 1992, Pearson *et al.*, 1991), only some selected aspects are considered here, and mainly in connection will the PALAEAUX studies. All models currently in use require an estimate of A_0, an initial ^{14}C-activity for each sample to be used as basis for applying the radioactive decay. Otherwise the models differ in their approaches: for example the Tamers model is mainly based on mass balances, the Pearson model on δ^{13}C-balance, while others combine mass- and isotope balance (the Fontes-Garnier and Eichinger models). It must be realized that only model-ages can be calculated, and the reliability of these depends on how well the carbon system in individual aquifers is understood. For example, whenever measured δ^{13}C values are more enriched than about −6‰, an extensive evolution of the system has to be assumed.

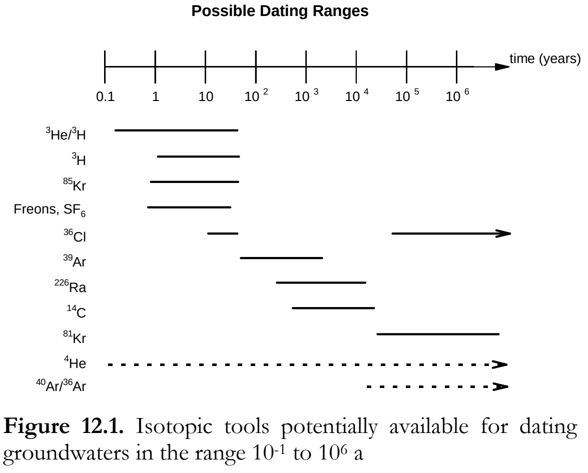


Figure 12.1. Isotopic tools potentially available for dating of groundwaters in the range 10^{-1} to 10^6 a

Table 12.1. Isotope data of PALAEAUX waters used to estimate initial ^{14}C values

Name	Lowest ^{39}Ar$_{meas}$ %	^{39}Ar$_{meas}$ in young water %	^{14}C$_{meas}$ in young water pmc	δ^{13}C$_{meas}$ in young water ‰	A$_0$, calc young water pmc	^{14}C$_{meas}$ old water pmc	δ^{13}C$_{meas}$ old water ‰
Switzerland							
Glattal 1	9 ± 5						
Glattal 3	12 ± 3					9.2 ± 0.5	–11.0
Glattal 7	< 18					1.9 ± 0.2	–10.3
Glattal A		109 ± 8	79 ± 1	–15.1	58–61		
Glattal D		92 ± 12	56 ± 0.5	–12.8	48–51		
Spain							
Donana S2	< 10					7.3	–11.0
Donana M-8-13		70 ± 6	54.6 ±1.3	–11.5	46–54		
England (Triassic)							
Grove I	< 4.6					18.7	–12.3
Rampton	< 3.3					< 0.8	–10.2
Newton I	<3.2					1.9	–10.6
Far Baulker 2		94 ± 4	58.9	–13.5	59–76		
Ompton 3		57 ± 3	40.6	–13.3	49–76		
Halam 3		55 ± 3	30.9	–10.3	31–54		

The isotope exchange reactions between liquid and solid phase may still affect the ^{14}C activity, but will not greatly alter δ^{13}C. The reliability of ages calculated for such samples will be low. A more effective approach could be to use the Sr/Ca ratio of samples to determine chemical evolution (Moulin *et al.*, 1989). It is also highly desirable to combine the ^{14}C-method with another isotopic indicator with a different geochemical behaviour to understand better the effects of water-rock interaction (e.g. ^{226}Ra – see next section).

The PALAEAUX project has made some progress in the verification of A$_0$ values for young water samples. Table 12.1 gives isotope results from some of the aquifers investigated in PALAEAUX projects. In each aquifer some samples have low ^{39}Ar activities, showing that underground production is low or negligible (cf. Loosli *et al.*, 1999). The almost modern ^{39}Ar contents of other samples must therefore be due to atmospheric equilibrium activity, showing that these second sets of samples are young (up to a few decades old). Therefore in these samples the measured ^{14}C activities must reflect A$_0$ values (except in the sample Glattal A, in which some thermonuclear ^{14}C is included). These measured A$_0$ values can be compared to model-calculated A$_0$ values (Fontes-Garnier, Pearson, Eichinger). This comparison shows a general agreement in ^{14}C activity values. However, it also shows that precise conversions of ^{14}C-activities into young water ages is an over-interpretation: for example, an attempted conversion for Doñana M-8-13 (^{85}Kr and ^{3}H free) of 54.6 pmc based on a calculated A$_0$ of 46 pmc into a negative age shows clearly the limit of ^{14}C-model ages. Such a comparison may also indicate a young (possibly ^{3}H-free) admixture, which yields A$_0$ measured values larger than A$_{0,calc}$ values. The main conclusion from Table 12.1 however relates to the ^{14}C-dating of old waters in the same aquifers, which generally have a low ^{39}Ar-activity. If the δ^{13}C values of these old samples are similar to the δ^{13}C values of the young waters (with reliable calculated A$_0$ values), then a conversion of the low ^{14}C-activity value into old ages seems reliable. This is for example the case for the Glattal and English Triassic aquifers, and one of the Doñana samples.

In dual porosity aquifers, such as the Chalk aquifer of the UK and France, groundwater dating is made difficult because of the mixing between the two components (matrix and fissures) with water of different ages. Incongruent reactions between the incoming water and the reactive chalk sediment also lead to near-surface reactions such that the A$_0$ values are low, around 70% modern (Kloppmann, 1998; Edmunds *et al.*, 1992)

12.2.2 *Radium 226*

A method based on ^{226}Ra can assist with the validation of ^{14}C ages. Recent developments in thermal ionization mass spectrometry (TIMS) and in the chemical separation of Ra and Ba through cation exchange chromatography now permit the analysis of ^{226}Ra and U-isotopes (^{234}U, ^{238}U) in smaller quantities than those required for conventional counting techniques. Routine measurements can be obtained with picogram (pg) (U) to sub-pg (Ra) quantities of these elements (i.e. in water samples of a few mL for U-isotopes, and ≤ 200 ml for ^{226}Ra). Owing to a half-life (1620 years) intermediate between those of short-lived isotopes (e.g. ^{3}H) and of ^{14}C or ^{36}Cl, the use of ^{226}Ra in hydrogeological studies holds great promise.

The method focuses on early mineralization processes and overall chemical and isotopic properties of surface and sub-surface water. In carbonate-rich soils most U is co-dissolved with the carbonate matrix, and therefore there is no significant enrichment in ^{234}U of the dissolved fraction, since it could only have been produced by recoil effects. The evidence for co-precipitation of U are ^{230}Th/^{234}U ratios below the secular equilibrium value, and a slight excess of ^{234}U over ^{238}U.

The variation of concentration of radium is derived from the three sources: 1 – dissolution; 2 – recoil effect; 3 – production from absorbed ^{230}Th; and can be summa-

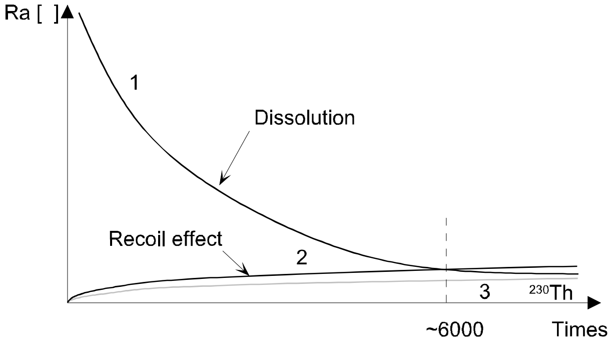


Figure 12.2. Time dependence of processes (Dissolution, recoil effect and absorbed ^{230}Th).

rized as illustrated in Fig. 12.2. Nevertheless, the early Ra-loading of natural waters, either in the unsaturated zone, or in the saturated aquifer, correlates respectively with total conductivity or Sr content. Through time, the decay of this "initial" Ra will be progressively compensated by the Ra "recoiled" from ^{230}Th in the lattice of the outer matrix grains, or produced by the ^{230}Th adsorbed at grain surfaces and produced by the uranium dissolved in pore water.

The Ra production through processes (i) and (ii) can be modelled using Sr concentration and in particular using the Sr/Ca ratio which indicates the occurrence of calcite dissolution or reprecipitation. The U contents in the solid phase and the evolution of the ^{234}U/^{238}U radio are necessary to monitor the production of Ra through process (ii). In both cases the models assume:

- that the steady state between the solid and liquid phases is not complete; and
- that the reaction rate is linear along the flow path.

The use of ^{226}Ra as a time tracer must be compared with the results of ^{14}C analysis, the purpose being to validate the radiocarbon ages by using an isotopic tracer with a different geochemistry to carbon.

During PALAEAUX two types of aquifer have been studied with ^{226}Ra and ^{14}C. These, both in France, are the Astien sandstone and the Chalk of the Paris Basin. The agreement between radium and radiocarbon ages is better for the calcareous sandstone than for the carbonate aquifer. In the sandstone aquifer, the dissolution process is three orders of magnitude more important than the other sources. The ^{226}Ra ages can be then obtained through a "strontium model". For the carbonate aquifer, Ra coming from dissolution and recoil effects must be taken in account. In such a case the redox conditions in the aquifer are very important with respect to the uranium solubility and in reducing groundwaters there may be limits to the application of the ^{226}Ra approach.

For ^{226}Ra the measurement techniques give a theoretical range of use from 0.5 to 10 ka, but more frequently the range of good agreement between radiocarbon and radium ages is from 0.5 to 6 ka, particularly in aquifers where recoil effects and ^{230}Th production cannot be neglected.

12.2.3 Krypton-81

For dating very old groundwater (>5×10^4 years), ^{81}Kr is an ideal isotope in terms of half-life and certain other properties. Like ^{39}Ar it is produced by cosmic rays and is available in the atmosphere at its equilibrium activity. This was initially determined by counting (Loosli and Oeschger, 1969) and recently confirmed by cyclotron measurements (Collon *et al.*, 1999a) to be about 1.3x10^{-6} Bq/cc Kr. It can be assumed that bomb production in the atmosphere is negligible and also that subsurface production does not contribute to the activity of this isotope, shielded as it is by ^{81}Br (Collon *et al.*, 1999b). For ^{81}Kr it is also unnecessary to consider the effects of water-rock interaction. However, the fundamental disadvantage of this method is the low activity of ^{81}Kr; with only about 1 atom decaying every 300 years in one litre of recent water. Therefore measurement by instrumental counting of disintegrations is impossible, especially since any small admixture of recent Kr would introduce a much higher ^{85}Kr activity. The only feasible way of detecting ^{81}Kr is therefore to count the numbers of ^{81}Kr atoms available in a sample, i.e. to measure the atomic ratio ^{81} Kr/Kr. Accelerator mass spectrometry (AMS) is however not possible because a noble gas does not form negative ions. The recent attempt to measure ^{81}Kr contents was performed using a cyclotron (Collon *et al.*, 1999, b). An amount of about 0.5 cm^3 of pure krypton was needed for individual measurements, which was obtained in a lengthy process from about 16 m^3 of water for each sample. The aquifer selected was part of the Great Artesian Basin (GAB) in Australia, because there it was hoped to find for the first time ^{81}Kr concentrations below the atmospheric level. Such low concentrations were indeed determined, yielding ^{81}Kr-ages between about 220 and 400 ka (Collon *et al.*, 1999b). At present the interpretation of these results is in progress, especially the comparisons with ^{4}He-, ^{36}Cl, noble gas- and other data.

12.2.4 Chlorine-36

The ^{36}Cl method covers a dating range similar to that of ^{81}Kr. Its main disadvantage is the difficulty in distinguishing cosmic ray-produced from underground-produced ^{36}Cl-activity. If for example a small fraction of interstitial fluids is admixed in a deep groundwater, the measured ^{36}Cl content has little connection with the bulk age of the groundwater, because the introduced Cl may contain a ^{36}Cl/Cl ratio which has evolved by *in situ* production during a very long period of residence in the matrix.

The main areas of application of ^{36}Cl have been the aquifers of Milk River, Canada, the GAB, Australia and the Triassic sandstone in the East Midlands, England. The latter area is the only one where data is available in the PALAEAUX study. The present state of knowledge has given rise to some controversy. For the Milk River aquifer a very high ^{36}Cl concentration in the water near the recharge zone is not easy to explain (Andrews *et al.*, 1991). However in some of the older waters, ^{36}Cl/Cl ratios which agree with the calculated *in situ* production were measured (Hendry and Schwartz, 1988; Nolte *et al.*, 1991). These waters therefore may represent high ages in which the equilibrium ratio may be approached and conserved. For the East Midlands Triassic aquifer the ^{36}Cl 'clock' seems not to be applicable (Andrews *et al.*, 1994) whereas the situation for the GAB remains uncertain (e.g. Bentley *et al.*, 1986; Torgersen *et al.*, 1991 and Andrews and Fontes, 1993). However the ^{36}Cl/Cl ratios may be used to examine the recharge conditions during the late Pleistocene/Holocene (Andrews *et al.*, 1994).

12.2.5 Helium 4

In principle ^{4}He contents should increase linearly with time as a result of the U- and Th-decay series. The production rate in the rock therefore can easily be determined. It is also well known that the major part of ^{4}He produced in minerals has escaped from the rock (e.g. Tolstikhin *et al.*, 1996) and should be found in the liquid phase. However, if measured ^{4}He concentrations in moving water are compared with 'known' (e.g. ^{14}C-model) ages, a higher increase than that estimated from the in situ production is usually observed. The ^{4}He accumulation rate may also show large variations for different water components (e.g. Purtschert *et al.*, 1999). For the UK East Midlands Trias aquifer an increase of about 10^{-11} cc/cc water per year has been measured compared with an estimated in situ production rate of only half of this value (Lehmann and Purtschert, 1997). In the GAB the measured rate is about 6×10^{-11} cc/cc per year and in the Milk River aquifer about 1×10^{-10} cc/cc per year, both higher than the estimated *in situ* production rates (Lehmann *et al.*, 1996). It has to be assumed that ^{4}He is admixed with that derived from aquicludes above and especially below. Therefore at present a ^{4}He-increase, e.g. with distance from the recharge area, can only be used as a relative and qualitative time indicator. It is however an important tracer for understanding rock water interaction and underground processes. Recently, lower age limits of the order of 10^6 years were calculated (together with assumed diffusion parameters and scale lengths involved) from ^{4}He-measurements in porewater (Lippmann *et al.*, 1998).

Lehmann *et al.* (1996) have pointed to an averaged linear relation between He-accumulation and Cl^--increase observed for a wide range of groundwaters. Increasing Cl^-, derived from internal sources, such as residual saline fluids within the aquifer and diffusion from more stagnant zones, seems to be accompanied by He-accumulation, as a result of in-situ production. The authors have indicated a difference for Cl^-/He ratios between groundwaters derived from sedimentary and crystalline rocks; this could be due to the fact that Cl^- is more readily leached from sediments than from crystalline rocks. They have found that it is possible to explain the observed He and Cl^- concentrations as being derived from local sources, under the assumption that neither He nor Cl^- was lost from the system and that the water, therefore, was more or less stagnant over millions of years.

12.3 Stable isotopes and noble gases as indicators of recharge conditions

The stable isotopic and noble gas contents of groundwaters are fundamentally controlled by the ambient temperature at the time of recharge. In addition to providing important information about palaeoclimatic conditions, they can also function as qualitative indicators of age where climatic conditions in the past were sufficiently different from those of the present day. The noble gases are absolute indicators of temperature while stable isotopes, though easier to sample and measure, give relative information requiring local calibration for maximum benefit.

12.3.1 Stable isotopes

All natural waters contain a proportion of the heavy stable isotopes ^{18}O and ^{2}H as well as the majority isotopes ^{16}O and ^{1}H. The $^{18}O/^{16}O$ and $^2H/^1H$ ratios are commonly expressed in terms of delta notation, where $\delta^{18}O$ and δ^2H denote the difference in parts per thousand (‰) between a particular water and the seawater reference, Vienna Standard Mean Ocean Water (VSMOW), according to the expression:

$$\delta = [(R_{sample}/R_{ref})-1] \times 10^3$$

where R is the $^{18}O/^{16}O$ or $^2H/^1H$ ratio of the sample or reference water.

The $\delta^{18}O$ and δ^2H compositions of groundwaters are governed by a variety of physical processes acting mainly during the evaporation-precipitation part of the hydrological cycle. Changes in climatic conditions have tended to modify the stable isotope signatures of recharge waters, thereby providing an important qualitative tool for the identification of palaeowaters. However, the magnitude of any ratio change with time is affected by essentially local factors, and therefore isotopic "shifts" in waters of the same age may not be identical from area to area. This will be demonstrated below (1.3.3) by consideration of examples from the European continent.

Stable isotopic composition of rainfall

Recharge to aquifers occurs predominantly via the infiltration of rainfall. Most rainfall is ultimately derived from evaporation of seawater, mainly from subtropical ocean areas. Evaporation and subsequent condensation of the water vapour thus formed takes place under a variety of temperature and humidity conditions (i.e. changing weather patterns), and therefore even though any marine source area will have a basically similar composition (around 0‰ for both $\delta^{18}O$ and δ^2H) there may be changes in rainfall isotopic ratios at any particular location from event to event. Large changes can be seen on a daily and even monthly basis for many collection stations, but tend to even out between years providing rainfall does not occur in a few strongly seasonal events (see data in IAEA, 1992). As a rain-bearing system moves away from its source area, preferential rainout of the minor heavy isotopes causes the δ-values of the remaining moisture to become progressively more negative, i.e. 'depleted' in the heavy isotopes. Since these systems tend to move from their subtropical source areas towards higher latitudes, a basic latitude effect is noted for rainfall whereby tropical values of $\delta^{18}O$ in the range 0 to –2‰ change to values more depleted than –50‰ in the Antarctic. These changes tend to be most pronounced over the oceans at higher latitudes (e.g. Clark and Fritz, 1997).

Latitude effects, however, may be considerably distorted by physiographic factors. The main effect is a depletion in both $\delta^{18}O$ and δ^2H caused by rainout as air masses move over high ground. This generally gives rise to progressively more negative δ-values with change in altitude, typically from -0.1 to -0.5‰ $\delta^{18}O$ per 100 m increase in altitude (data from sources attributed in Clark and Fritz, 1997). However, rain-shadow or seasonal changes in air mass movements may distort this pattern in certain cases.

A further isotope-related property of rainfall is the so-called 'deuterium excess' or d-factor (Dansgaard, 1964). The definition of this is:

$$d = \delta^2H - 8\delta^{18}O$$

Deuterium excess has a worldwide average of about 10‰, but can vary quite considerably areally and temporally because of changes in humidity, sea temperature and other factors in the rainfall source areas. Variations in d-factor are less easy to interpret on a local level than many of the other parameters measured during PALAEAUX studies, and therefore have received relatively little attention.

Effects of air temperature on rainfall isotopic composition

When long-term weighted averages are considered, there is a reasonable degree of correlation between air temperature and the isotopic composition of rainfall for different sites, first identified by Dansgaard (1964). With the acquisition of further data, it has been possible to produce different temperature-isotope correlations for different groups of stations, i.e. marine, continental-coastal, continental interior and polar regions. For $\delta^{18}O$, temperature effects range from 0.17‰ per °C for marine stations to 0.90‰ per °C for the Antarctic Peninsula (Clark and Fritz, 1997). For the continental category, which would apply at present to much of Europe, an average of 0.58‰ per °C was noted by these authors.

Identifying palaeo-groundwaters from stable isotopic content

In principle it should be easy to identify palaeowaters. For example, various lines of proxy evidence (floral and faunal) point to decreases in average annual temperature of several degrees in periglacial areas of the Northern Hemisphere. Using the data analysed by Clark and Fritz (1997) mentioned above, this would translate into an easily-identifiable depletion in $\delta^{18}O$ of the order of 2 to 3‰ (measurement precision is around ± 0.1‰). However, even on the assumption that palaeowaters remain unmixed with modern waters, assessment of the period when recharge occurred on the basis of stable isotopes is not necessarily straightforward for the following reasons:

(xii) the temperature-isotope relationship appropriate for the present day may not apply: a modern coastal area may have been situated some distance inland during periods when sea levels were much lower owing to extensive glaciation.

(xiii) changes in ocean circulation may have had profound effects on the circulation of air masses.

(xiv) ice-cover or permafrost may have distorted the isotopic composition of recharge or prevented it altogether.

(xv) tectonic processes (principally mountain uplift) can have profound effects on isotopic contents for a variety of reasons, although they are unlikely to have been of great importance in the late Pleistocene and Holocene in Europe.

Because of these factors, waters with the same recharge age may have different stable isotope shifts in different geographical areas. To a considerable extent these problems can be overcome by measuring noble gas concentrations, which yield a temperature for recharge within certain limits (see next section). Once this has been done for a local area, a noble gas – stable isotope calibration can be used to interpret further isotopic data.

12.3.2 Noble gases

In most parts of the world, temperatures in the unsaturated zone below a few metres from ground surface reflect the average air temperature for the region concerned. When meteoric waters percolate through the unsaturated zone and enter a body of groundwater, they bring gases into solution. The actual amounts depend on individual gas partial pressures and partitioning behaviour at the temperature of solution, which is presumed to be equivalent to average air temperature. Partial pressures of the 'reactive' gases (O_2, N_2, CO_2 and CH_4) in the unsaturated zone are modified from their atmospheric values by processes such as oxidation and reduction. Additionally, once in solution further changes can take place. The reactive gases therefore cannot be used to infer recharge temperatures. Noble gases on the other hand are unreactive and should (at least in theory) maintain concentrations related to their temperature of solution all the way from recharge to discharge, irrespective of their residence time in groundwater.

Like most other gases, the aqueous solubilities of argon (Ar), krypton (Kr) and xenon (Xe) change with temperature (Mazor, 1977), with the result that a particular set of concentrations of Ar, Kr and Xe can be interpreted to give a recharge temperature (RT) with a precision of (ideally) about ± 2°C. However, in certain circumstances 'excess' ^{40}Ar may be produced by radioelement decay. If the ratio $^{40}Ar/^{36}Ar$ is measured, any increase over the atmospheric ratio of 296 can be used to correct back to obtain the 'true' Ar recharge temperature.

Other complicating factors exist in addition to subsurface ^{40}Ar production. The phenomenon of 'excess air' is commonly encountered. This can result from the entrapment of gas bubbles at the point of solution, which may then be carried down to a point in the aquifer where hydrostatic pressure causes them to dissolve. Under similar climatic conditions, the magnitude of the problem appears to increase going from granites via sandstones to limestones. In addition or alternatively, air may enter at the sampling stage due to faulty borehole wellhead construction or spring sampling conditions, etc. This excess air can have a profound effect on calculated RT values, and must therefore be corrected for, usually by subtracting theoretical increments of air from the analysed compositions until the best agreement between the Ar, Kr and Xe temperatures is obtained. In some cases, however, further correction based on the 'neon index' (Stute *et al.*, 1995) is required. Since the solubility of neon is not so much temperature-dependent, excess Ne can be used to estimate excess air. Another factor is groundwater mineralization, because high salinities can have a significant 'salting out' effect on the noble gases which will perturb the original concentrations present at recharge. Such effects can be corrected for by use of curves based on salinity-solubility data tables. A further complication is introduced if the elevation of the recharge area is significantly higher than that of the discharge area: unless the former is accurately known it is difficult to know what the concentrations at recharge would have been (though the *ratios* between Ar, Kr and Xe should remain the same).

12.3.3 Chemical indicators of groundwater age

Sequential hydrogeochemical changes may occur in confined groundwater flow systems which may be interpreted in terms of residence time, or to give an indication of former climatic or environmental conditions. This information may provide additional insight into relationships that have been established using isotopic methods described above, since a chemical model is usually required in order to interpret ^{14}C and other indicators. The integration of geochemical and isotopic indicators is needed to verify numerical hydrogeological models and in turn can provide challenges to their interpretation. At the very least the sequential processes that are observed in many aquifers can be used to provide relative age estimates.

Two types of chemical evolution are illustrated in the PALAEAUX studies:

- evolution as freshening of a formerly saline aquifer takes place, and
- downgradient changes in a freshwater system,

Freshening aquifers are those in which a marine-derived water (whether truly connate or not) is being replaced by freshwater. This situation applies to many of the aquifers studied during PALAEAUX. In the typical case of a freshening aquifer, two end members are concerned: a saline NaCl-type marine water initially filling the aquifer, and a fresh $CaHCO_3$-type recharge water resulting from rainfall in which $CaCO_3$ has been dissolved.

After the fresh recharge water has started to infiltrate into the aquifer, the first process consists of the gradual dilution of the original marine porewater. This will result in the development of a salt/fresh-water interface, which will be more or less sharp according to the extent of hydrodynamic dispersion. The interface will move in the direction of groundwater flow. Downgradient from it, the initial seawater will persist. Upgradient of the salt/fresh-water interface, evidence appears of the different stages of cation exchange, resulting in a chromatographic pattern, when a sequence of Na^+-, K^+-, Mg^{2+}- and finally Ca^{2+}-rich waters is developed. Cation exchange processes take place after the marine porewater has been replaced by fresh recharge water, causing a disequilibrium between the new porewater and the marine cations that are still adsorbed on the exchange sites of (mainly) the clay minerals. The marine cations Na^+, K^+ and Mg^{2+} will be desorbed and exchanged for Ca^{2+} of the new porewater, in the order as mentioned, according to the affinity sequence. This leads sequentially to an increase in Na^+, followed by a K^+-peak, and finally a Mg^{2+}-peak, in the upflow direction. The Na^+-increase is not distinguished as a separate peak, because Na^+ continues to increase toward the salt/fresh-water interface. In addition, immediately upflow of the salt/fresh-water interface, the first exchange reaction consists of Na^+-release in exchange for Mg^{2+}-uptake by the clay, as a result of charge effects (Appelo, 1994).

Downgradient changes. In this case (in the absence of pollution) the geochemical changes observed in the groundwater result either from atmospheric inputs or, from water-rock interaction. An example is given below (see Fig. 12.6) where the chemical evolution is calibrated using radiocarbon ages obtained in just a few samples. This relationship has then been applied to new chemical data alone and may be used to extend the timescale given by the radiocarbon (Edmunds and Smedley, in press).

In the freshwater aquifer, where it can be demonstrated that inert tracers are derived predominantly from atmospheric inputs, it may be possible to infer palaeoclimatic information and therefore independently another indicator of age. This approach has been used in the East Midlands aquifer (Andrews *et al.*, 1995; Edmunds and Smedley in press) where the Cl concentrations are atmospherically derived and the Br/Cl ratio and the $^{36}Cl/Cl$ atomic ratios can possibly provide information on past recharge rates and the changes in source areas of precipitation.

12.4 Applications of stable isotopes and noble gases at the European scale

12.4.1 Stable isotopes

Because of a wide diversity in climate, relief and geology, the European continent has a variety of groundwater environments/habitats. Many of these have received close attention over the past 30 years in terms of their stable isotope systematics, and provide a good illustration of the ways of interpreting isotopes in terms of change (or in some areas lack of change) during the transition from past to present climates.

Consideration of published data from the main groundwater supply aquifers of England provides an example of the amount of information that stable isotopes are able to provide by themselves or in conjunction with other data. Figure 12.3 shows plots of $\delta^{18}O$ vs ^{14}C activity, from which several points emerge:

(i) There is less of a stable isotope offset between present and past conditions in the waters of the carbonate aquifers (Lincolnshire Limestone and Chalk) than in the sandstone aquifers (East Midlands Trias and Lower Greensand). This is presumed to be largely due to the greater opportunity for mixing between modern and palaeowaters provided by the extensive fissuring in the carbonates. The implication is that in carbonate aquifers any signal of palaeo-conditions is likely to have been smoothed out. However, both kinds of aquifer show evidence of the hiatus in recharge ('infiltration gap') that seems to have occurred in Europe at around the end of the Pleistocene.

(ii) In the sandstone aquifers, $\delta^{18}O$ in the palaeowaters is shifted by a maximum of –2‰. Using the 'continental' precipitation relationship of 0.58‰ per °C (in fact, likely to be somewhat lower for a maritime area such as England), this would indicate a drop in annual average temperature of perhaps 3.5°C, but other 'absolute' indicators such as noble gases and fauna indicate a drop of 5°C or more over the same period. The apparent discrepancy is to a large extent resolved by changes in oceanic $\delta^{18}O$ over the interval: owing to a greater amount of isotopically-light water sequestered in the ice-caps of the late Pleistocene, the $\delta^{18}O$ of ocean water is likely to have been raised by around 1‰ above present-day values (Schrag *et al.*, 1996). Thus the 'real' shift would have been around double that observed, with the implication of a correspondingly greater temperature drop.

(iii) There is an offset in $\delta^{18}O$ between the two sandstone aquifers. This is presumed to be a latitude effect; the recharge area for the East Midlands Trias lies to the north of the recharge area of the Lower Greensand, and therefore receives a somewhat more isotopically-depleted rainfall as a result of rainout from the predominantly southwesterly source of moisture. The ^{14}C data show that this offset is maintained into the past, implying that there was no fundamental change in air-mass movement.

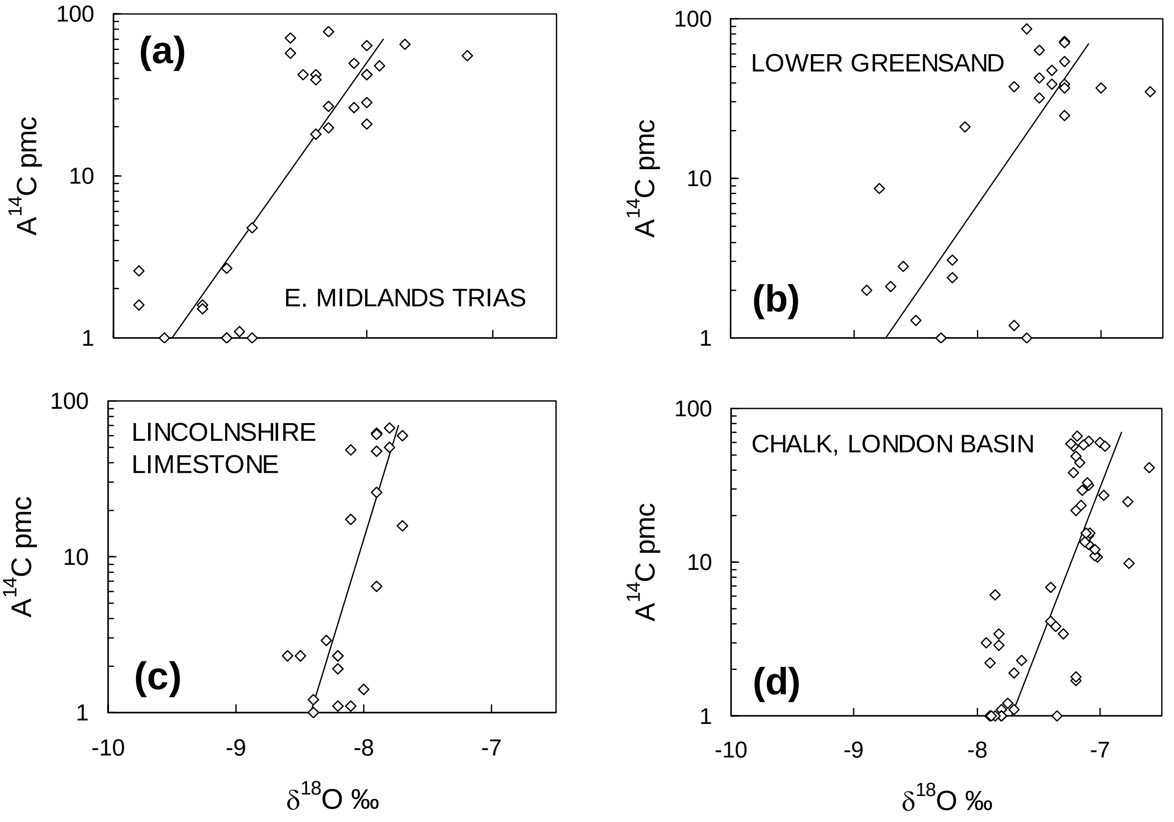


Figure 12.3. Plots of ^{14}C activity versus $\delta^{18}O$ for groundwaters in the four main sedimentary aquifers of England (from data summarized in Darling *et al.*, 1997). Aquifers (a) and (b) are sandstones, while (c) and (d) are carbonates. There is evidence of an 'infiltration gap' between older and younger groundwaters in each aquifer, although this is better developed in the sandstones.

The $\delta^{18}O$ data thus reflect a lower annual average rainfall temperature, possibly supplemented by an element of latitude effect resulting from a somewhat greater distance between the recharge areas and the ocean due to the fall in sea level that accompanied the growth of the ice-caps. While the above gives an indication of the amount of information that stable isotopes can provide about individual areas, a Europe-wide perspective requires the comparison of data from different areas. Fig 12.4 shows the way in which the $\delta^{18}O$ of groundwaters has changed between the present and late Pleistocene across Europe, based on data from the PALAEAUX investigations and other studies. The figure represents a transect from SW (Portugal) to NE (Estonia), using data projected from coastal or near-coastal aquifers in which the maximum $\delta^{18}O$ shifts for the given area appear to have been preserved. Data from more continentally-influenced aquifers from Switzerland to Hungary are also shown on a separate transect. For the coastal aquifers, it is clear that at the present day there is a progressive depletion from SW to NE, related to continental effects acting on a south-westerly source of moisture. It is equally apparent that in the late Pleistocene, a SW-NE depletion was also occurring. However, this seems to have had three separate elements:

(i) an isotopic *enrichment* in Portugal. This is likely to have been the result of a relatively small temperature drop at this latitude(owing to ocean buffering) coupled with the raising of oceanic $\delta^{18}O$ value (owing to the sequestration of isotopically-depleted waters in the ice caps). Additionally there was little change in the Portuguese coastline during the late Pleistocene, so that depletion effects related to rainout over the 'extra' land would not have occurred. Thus it would have been possible for $\delta^{18}O$ to increase slightly.

(ii) a western-to-eastern European trend, terminating in Lithuania, that gives a depletion gradient similar to today's, confirming the interpretation of the data from England (see above) that there have been no large-scale changes in air mass circulation between the late Pleistocene and the present.

(iii) a considerably greater change in Estonia than can be explained by continental effects alone. It is considered that late-Pleistocene recharge in this area was the result of the recharge of isotopically-depleted glacial meltwater, either in the outwash plain of the ice cap, or as the result of sub-glacial melting. Recharge of this depleted water may have affected other parts of the present Baltic littoral: for example, waters with $\delta^{18}O$ values some 3‰ lighter than the palaeowaters generally encountered in northern Poland (see Fig 12.4) were sampled from the Hel peninsula in the extreme north-east of the country (Zuber *et al.*, 1990). However Estonia is the only location where such isotopically light water has so far been encountered.

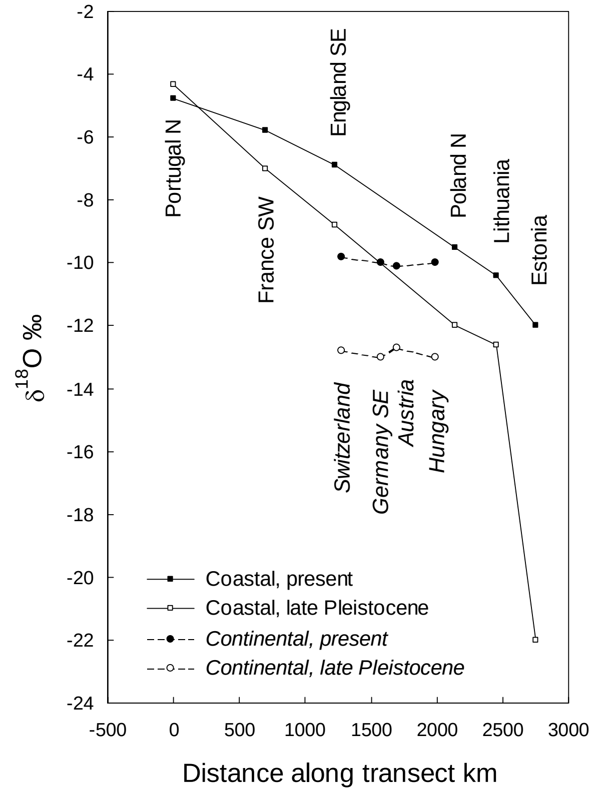


Figure 12.4. Differences in European groundwater $\delta^{18}O$ values between the present day and the late Pleistocene, following an approximately SW-NE transect from Portugal to Estonia. Data from: Portugal - Carreira *et al.*, (1996); France - Le Gal La Salle (1996); England - Darling *et al.*, (1997); Poland - Rozanski (1985); Lithuania - Mazeika and Petrosius (1998); Estonia - Punning *et al.*, (1987); Switzerland – Beyerle *et al.*, (1998); Germany – Bertleff *et al.*, (1993); Austria – Andrews *et al.*, (1985); Hungary – Stute and Deak (1989).

By contrast, the continental transect in Fig 12.4 is almost flat. It might perhaps have been expected that the mountainous centre of Europe would have had a more profound effect on isotopic compositions between Switzerland and Hungary, particularly in late-Pleistocene times, but clearly air-mass trajectories were, and remain, such that latitudinal effects are minimized.

12.4.2 Noble gases

The measurement of noble gases to derive RT values is a relatively specialized technique and comparatively few data exist for Europe. One of the main aims of the PALAEAUX project has been to extend knowledge of noble gas-derived RTs to Estonia, Belgium and the Iberian Peninsula, in order to gain a wider perspective on conditions of recharge for Europe as a whole.

The importance of obtaining RT data from these areas is illustrated by the plot in Fig 12.5, which shows gradients of RT versus $\delta^{18}O$ for some European aquifers. While countries from Belgium to Hungary have gradients with sub-parallel trends showing roughly similar amounts of isotopic depletion for a given drop in RT between the present and late-Pleistocene, those from Portugal and Estonia are completely different, from both the general trend and each other. As before, three elements emerge:

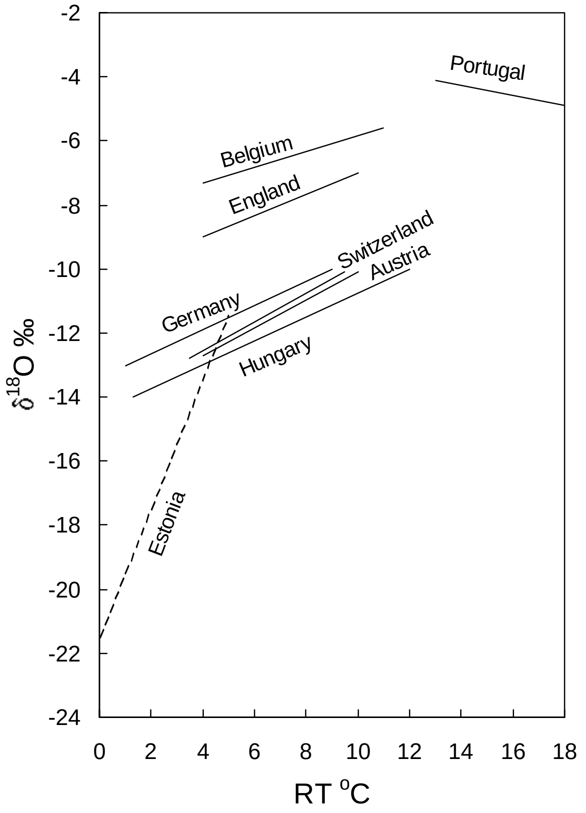


Figure 12.5. Plot of $\delta^{18}O$ versus RT (recharge temperature) showing the gradients between the present day and the late Pleistocene for various European countries. Data sources as for Fig 12.4 plus Chapters 2, 4 and 8 of this report. The trend for Estonia is subject to some uncertainty (see text).

(i) the negative gradient in Portugal shows that despite the small positive palaeo-shift in $\delta^{18}O$, conditions were actually cooler in the late Pleistocene, in line with other parts of Europe although smaller in magnitude.

(ii) the generally similar (RT) temperature gradients in north-western and central Europe lead to averaged out shifts in stable isotopes of about -0.35‰ per °C drop in temperature, less than the –0.58‰ figure for present-day rainfall mainly because of the rise in oceanic $\delta^{18}O$. However since the errors of the determined $\delta^{18}O$/RT-slopes are still rather large, this difference is not yet established.

(iii) the extreme gradient in Estonia is very preliminary at present. Whereas the data points for present day recharge are reliable (around –12‰ in $\delta^{18}O$ and about +4°C in RT), the RT values for the Pleistocene points are very uncertain. The reasons for this are the extreme oversaturation of the water with gas and the uncontrolled degassing during sampling (Chapter 2). Therefore preliminary values for RT show variations between –7°C and +7°C. Assumed subglacial recharge in the late Pleistocene would explain the large amounts of excess air; the negative $\delta^{18}O$ values would correspond to the conditions during snowfall in the north and at high altitudes of the glacier. Three explanations of temperature would then be possible: (a) if the recharge under a melting glacier happened under closed conditions, the noble gas concentrations in the water would be dominated by the amount of trapped air in snow and ice. “Recharge temperatures” from measured noble gas contents could only be calculated after large corrections for excess air and negative values would be expected for the remaining gas component; (b) if before infiltration some gas exchange took place, e.g. through fissures in the tongue of the glacier or through the unsaturated zone, temperatures of around 0°C would be expected; and (c) time and space variations of infiltration may have contributed and a combination of solutions a) and b) seem possible.

In none of the above cases can the gradient for Estonia be directly compared to the slopes for the other areas, because the measured points of the Pleistocene waters do not reflect an undisturbed climate signal: in case (a) $\delta^{18}O$ and temperature reflect conditions during snow accumulation and in case (b) the temperature has nothing to do with a climate signal.

It is apparent from the various points considered in this section that stable O and H isotopes are only qualitative indicators of palaeowater recharge temperature, and it is therefore important that they are calibrated locally by measurements of noble gas recharge temperatures. However, it is also clear that the stable isotopes have a major role to play in establishing the climatic context of past recharge, as has been amply demonstrated by the cases of Portugal and Estonia.

12.5 Identification of palaeowaters using isotopic methods: examples from PALAEAUX

In this section a *palaeowater* is defined as a groundwater that infiltrated during the Pleistocene or early Holocene. Therefore the identification contains both a time and a climate component. The tools to be combined for these two components of the identification are summarized in Table 12.2 in a systematic way. Short-lived isotopes like ^{3}H, ^{85}Kr and ^{39}Ar are omitted as age indicators, since for the following we assume that admixtures of young water components are determined by these isotopes and taken into account. The question whether a water is a ‘palaeowater’ or not should be only decided for the components older than about 1 ka.

In an ideal situation several age indicators are combined with several climate indicators. As discussed below this ideal situation is reached in only a few cases of the aquifers studied during the PALAEAUX programme. This is primarily due to the fact that for age determination usually only (corrected) ^{14}C-ages are available. All other dating methods (except ^{81}Kr in Australia) cannot be used (at present) as quantitative tools. In many cases even the corrected ^{14}C ages are questionable. For example, radiocarbon “ages” are doubtful when the $\delta^{13}C$ value is more positive than about −6‰, because an extensive evolution of the carbonate system has to be assumed to have occurred. Radiocarbon ages have to be interpreted carefully when considerable amounts of CH_4 are dissolved in the water, because methanogenesis may have shifted $\delta^{13}C$ in DIC to more positive values, or if large amounts of CO_2 with unknown origin are admixed.

In the case of the climate indicators a combination of different signals is desirable but not necessarily straightforward; for example, the detection of the typical late Pleistocene– early Holocene temperature jump of about 5°C or more requires a high frequency of sampling and the infiltration gap naturally is restricted to areas of ice cover or permafrost. However the argument is very convincing, if the temperature jump and/or infiltration gap are detected at the expected ^{14}C ages. In general, agreement between an age signal and a climate signal is required; a ^{14}C-RT-plot or a ^{14}C - $\delta^{18}O$-plot demonstrates obviously how reliable the identification of a palaeowater is (see e.g. Fig. 12.3). Naturally the influence of the distance from the ocean on the $\delta^{18}O$ shift has to be taken into account (see 12.3.1 above).

In 12.3.2 it was mentioned that the recharge temperatures (RT) calculated from noble gas contents allows a more straightforward calculation of a temperature than by using $\delta^{18}O$ and δD. The values of the stable isotopes are determined by the temperature during precipitation and other factors (e. g. continental and altitude effects, circulation of air masses). The shift to more positive values of the water of the oceans during Pleistocene however should be taken into account. Here again a combination of methods seems favourable: most convincing is a consistent correlation between RTs and (adjusted) stable isotope data.

An assessment follows of palaeowater identification during the PALAEAUX studies, based on a traverse from Estonia through the coastal regions of Europe as far as the South of France, and terminating with the Glattal aquifer of Switzerland. The most convincing cases are based on the results obtained for the Cambro-Vendian aquifer (Estonia), the Ledo-Paniselian aquifer (Belgium), East Midlands Triassic aquifer (England), the Aveiro aquifer (Portugal) and the Glatt Valley aquifer (Switzerland). More difficult to interpret are results which indicate only an admixed (and possibly small) old water component, because then only diluted and mixed age and climate signals are available. For some aquifers investigated in the project PALEAUX we summarize the methods which have been used (ŏ) and by a symbol ☺😐☹ the reliability for identification of a palaeowater. The observations made below are based on the references cited and the individual PALAEAUX partners’ reports (see Chapters 2-10).

12.5.1 Cambrian-Vendian aquifer, N Estonia

Palaeowaters are identified by their extremely negative $\delta^{18}O$ values (around −20‰). Some RTs are reliable and are around 0°C. Radiocarbon values are difficult to convert into ages because the $\delta^{13}C$ values below −9‰ are hard to understand if infiltration happened below a glacier. This sub-glacial recharge mechanism appears to have been involved from the evidence of measured high gas oversaturation (up to a factor of about 4 compared to air saturated water).

12.5.2 Ribe Formation aquifer, Denmark

Very old groundwaters are suggested by low radiocarbon activities (≤1 pmc) and $\delta^{13}C$ values similar to young waters (around −13‰), which imply that the low ^{14}C is due to long residence time rather than exchange with ‘dead’ rock carbonate. However, the $\delta^{18}O$ shift is only small.

12.5.3 Ledo-Paniselian aquifer, Belgium

Samples show an increasing ^{4}He content in the direction of flow; the corresponding noble gas recharge temperatures decrease from present day infiltration values (about 9°C) to cooler climatic values of about 2°C. However the $\delta^{18}O$ values decrease only from about −6.5‰ to −7.1‰

Table 12.2 Indicators of recharge conditions and residence time used in the different PALAEAUX studies, with overall 'palaeowater' rating.

Aquifer	Noble gas RT	$\delta^{18}O$ $\delta^{2}H$	$\Delta T=$ 5°C	$\delta^{13}C$	^{14}C	^{39}Ar	^{36}Cl	^{4}He	$\delta^{34}S$	U series	Chem evol	Palaeowater
	❆	❆	❆	🕓	🕓	🕓	🕓	🕓	?	🕓	❆🕓	?
Estonia												
Cambro-Vendian	ŏ	ŏ		ŏ	ŏ	ŏ		ŏ				☺
Denmark												
Ribe	ŏ	ŏ		ŏ	ŏ							😐
Belgium												
Ledo-Paniselian	ŏ	ŏ	ŏ	ŏ	ŏ			ŏ			ŏ	☺
England												
S Chalk		ŏ		ŏ	ŏ						ŏ	☺
EM Triassic	ŏ	ŏ	ŏ	ŏ	ŏ	ŏ	ŏ	ŏ	ŏ	ŏ	ŏ	☺
France												
Dogger		ŏ		ŏ	ŏ					ŏ	ŏ	☹
Astian		ŏ		ŏ	ŏ					ŏ	ŏ	☹
Portugal												
Aveiro	ŏ	ŏ	ŏ	ŏ	ŏ						ŏ	☺
Sado-Tagus		ŏ		ŏ	ŏ						ŏ	😐
Spain												
Donana	ŏ	ŏ		ŏ	ŏ	ŏ					ŏ	☹
Switzerland												
Glatt Valley	ŏ	ŏ	ŏ	ŏ	ŏ	ŏ		ŏ				☺

Paleaowater rating:				
	☺	Strong indications	❆	Climate indicator
	😐	Some indications	🕓	Residence time indicator
	☹	Few indications		

(Walraevens, 1990). Some ^{14}C values are difficult to convert into age information because of elevated $\delta^{13}C$ values (−4‰ to +2‰); but several convertible low ^{14}C-values exist (e. g. 0.5 pmc and −9.2‰) and demonstrate a Pleistocene age for these waters. An infiltration gap is observed based on ^{14}C ages with I_0= 70 pmc (Walraevens, 1990).

12.5.4 East Midlands Trias aquifer, E England

The identification of palaeowaters is mainly based on an infiltration gap between 10 and 20 ka BP (corrected ^{14}C ages) and on the corresponding step in $\delta^{18}O$ and noble gas temperature (Bath *et al.*, 1979, Andrews *et al.*, 1984). Qualitative support of palaeoclimatic conditions is given by chemical components and S- and Sr- isotopes (Andrews *et al.*, 1994 and Edmunds *et al.*, 1996). While ^{4}He increases along the flow direction, *in-situ* production cannot account for the total amount measured; the inferred addition of ^{4}He from the adjacent strata prevents its use as dating tool (Andrews *et al.*, 1984).

12.5.5 Dogger aquifers, N and W France

Groundwater in the highly fissured carbonate aquifer in the Caen area is slightly saline and has so far given a maximum corrected age of about 7.5 ka, i.e. Holocene. A $\delta^{18}O$-shift of approximately −0.7‰ has been noted compared to modern waters in the vicinity. Despite the salinity, the groundwaters have no apparent connection with the sea, and ^{14}C activities are independent of salinity. Therefore this aquifer is not currently undergoing a freshening process.

In the Dogger of the Marais Poitevin, a less-fissured but still calcareous aquifer, chemistry suggests a simple mixing series between fresh groundwater and seawater, but isotopic evidence is less clear. The minimum observed ^{14}C activity is 12.1 pmc and therefore a Holocene age is indicated.

12.5.6 Aveiro aquifer, N Portugal

Palaeowaters are identified by their apparent ^{14}C ages in combination with their recharge temperatures. A 5°C drop from the present day infiltration temperatures was observed for waters with modelled ^{14}C-ages of around 18 ka BP. Stable isotopes show more positive values for old waters than for shallow recent waters. This is likely to be reflecting the isotopic enrichment of the world oceans during glacial times.

12.5.7 Miocene Lower Tagus-Sado aquifer, SW Portugal

Modelled radiocarbon ages of up to 25 ka were noted for the more saline waters. No $\delta^{18}O$ shifting was observed

12.5.8 Doñana aquifer, SW Spain

Few indications of palaeowater were found although such a component cannot be excluded . The lowest ^{14}C activities are around 7 pmc, converted by Pearson's model (Pearson *et al.*, 1991) to 11–15 ka. However, one recharge temperature determined for such an old water does not show any difference to present day precipitation. This is in agreement with a pollen record for the Doñana area covering the last 18 ka, suggesting no major climatic changes since the last glacial maximum (Zazo *et al.*, 1996).

12.5.9 Astian aquifer, South of France

The Astian in this area is a micaceous sand. Mean residence times based on ^{14}C range from modern in the recharge zone to 6 ka (earlier Holocene) near the coast. In the eastern part of the aquifer the effects of contamination by 'dead' volcanic CO_2 have been corrected for by the use of ^{226}Ra. A small (0.15‰) depletion in $\delta^{18}O$ is shown by the oldest waters.

12.5.10Glatt Valley aquifer, Switzerland

Admixtures of younger but tritium-free water components were detected by ^{39}Ar. The old component is identified as a palaeowater by corrected ^{14}C ages, a corresponding temperature shift of 5°C determined from noble gas contents, a corresponding $\delta^{18}O$ shift and by an infiltration gap between about 28 and 15 ka BP (Beyerle *et al.*, 1998).

12.6 Hydrochemical examples from PALAEAUX

Illustrations of the hydrogeochemical approach are considered here: one from a freshwater aquifer (The East Midlands) and one from a 'freshening' aquifer where old marine waters is being replaced by freshwater (Ledo-Paniselian), for both of which ^{14}C calibration is available. The other examples are then briefly reviewed

12.6.1 East Midlands Aquifer, UK

The East Midlands Triassic aquifer of England consists of a typical red-bed sandstone thought to be mainly of fluviatile origin (Edmunds & Smedley, in press). The groundwater chemistry tends to be strongly influenced by the presence of two carbonate cements: an early post-depositional dolomite, and secondary calcites, resulting from dedolomitization by successive groundwater fluxes. Decalcification of the sandstones may have taken place near to outcrop (Edmunds *et al.*, 1982; Bath *et al.*, 1987).

For this aquifer, a number of potential residence time indicators have been proposed (Edmunds & Smedley, in press). Conservative indicators comprise noble gas ratios, chloride and the other halides. They have been shown to be entirely atmospherically derived for this aquifer, and can thus provide information on climatic and palaeogeographic (e.g. continentality, urban pollution) conditions. The second group are reactive indicators of time-dependent hydrogeochemical reactions. Within this group of reactive tracers are several trace elements (Li, Rb, Cs, Mn, Mo, Sr as well as ^{13}C), which show near-linear increase with increasing groundwater temperature (as proxy for distance) across the flow length of the aquifer (Edmunds & Smedley, in press). Examples for Li, Sr and $\delta^{13}C$ are shown in Fig. 12.6. The increase in Li results from weathering of silicates, the Sr and $\delta^{13}C$ increases result from progressive reaction of dolomite. Once calibrated with the available radiocarbon data, selected results have been used to construct a separate timescale (see Fig. 5.12), enabling dating to be extended beyond the limits of the ^{14}C timescale.

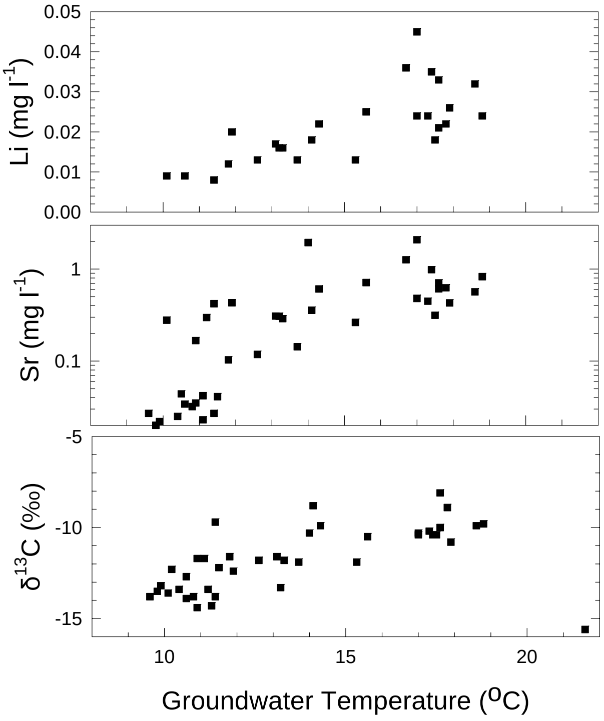


Figure 12.6. Downgradient plots of Li, Sr and $\delta^{13}C$ from the East Midlands Triassic sandstone aquifer (groundwater temperature serves as a proxy for distance). These linear increases have been calibrated in terms of age, e.g. as shown in Fig. 5.12.

12.6.2 Ledo Paniselian Aquifer Belgium

In Fig. 12.6 the modelled concentrations of Cl^-, Na^+, K^+, Mg^{2+} and Ca^{2+} are shown for the Ledo-Paniselian aquifer, as a function of increasing distance from the recharge area (a proxy for groundwater age). Also shown, for the same cross section are the ^{13}C and ^{14}C data taken form Walraevens (1990). The full lines correspond to the piston-flow model, according to which flow velocities are constant throughout the aquifer (Walraevens & Cardenal, in press). In reality, the Bartonian Clay overlying the aquifer is semi-permeable, allowing a gradual escape of groundwater from the aquifer and thereby reducing the flow velocities. When this is neglected, it is seen that the whole modelled section (20 km from recharge area) is completely flushed (the original seawater has disappeared: almost no Cl^- remains, and Na^+-concentrations between 15 and 20 km have only increased owing to cation exchange), which is not consistent with observations. Substituting the observed lower flow velocities after 12 km from the recharge area results in keeping the salt/fresh-water interface within the modelled section (of 25 km), corresponding to the observations (dotted continuation of lines in Fig 12.7 - Walraevens & Cardenal, submitted). The fresh/salt-water interface can be clearly observed in Fig. 12.7 by the Cl^--increase, associated by an equivalently strong increase in Na^+. Upflow from the interface, a smaller Na^+-increase is caused by Na^+-desorption (first in exchange for Mg^{2+}, then to a very large extent in exchange for Ca^{2+}). Na^+/Ca^{2+}-exchange is followed by K^+/Ca^{2+}-exchange, expressed by the K^+-peak at around 10 km from the recharge zone, followed by Mg^{2+}/Ca^{2+}-exchange shown by the Mg^{2+}-peak spreading around 5 km from the recharge zone. Towards the recharge zone, Ca^{2+} is gradually increasing with decreasing extent of cation exchange. At the limit of the recharge area, no evidence of cation exchange persists, and Ca^{2+} appears at full concentration, resulting from $CaCO_3$ dissolution at infiltration.

The decrease in ^{14}C activity and the parallel enrichment in $\delta^{13}C$ indicate a degree of water–rock exchange (with carbonate minerals). However this clearly demonstrates an ageing trend in the aquifer and that the exchange reactions sequence provide a relative indication of groundwater age.

The Ledo-Paniselian aquifer comprises several recharge areas in which the time scales of recharge are different, and it is emphasized that the inferred relation only refers to the considered flow path. For a different recharge area, the hydrogeochemical evolution may need to be calibrated separately, by establishing a relation between the chemical parameters and age information obtained in the specific part of the aquifer.

12.6.3 Other examples from PALAEAUX

Being predominantly coastal, most other aquifers studied within the framework of PALAEAUX are freshening aquifers. Several of them are of marine origin, and connate seawater may still be an end member contributing to the groundwater chemistry, e.g. the Chalk of the English South Coast. Other aquifers have a continental origin, but were intruded by salt water as a result of later marine transgression, e.g. the Doñana aquifer in Southern Spain and the Cambro-Vendian aquifer in Estonia. In all of these cases, freshening started after regression of the sea, allowing fresh water, derived from rainfall in the recharge areas, to enter the aquifer.

From the radiocarbon activity and the chloride content in groundwater of the Dogger aquifer in Western France, three end members have been inferred: seawater intruded during the Flandrian transgression, and two fresh waters - a fresh water older than Flandrian, which was recharged into the aquifer before the marine transgression, and a modern fresh water.

The chromatographic pattern may be obscured by flow conditions in the aquifer (e.g. mixing of water of different flow lines: hydrodynamic dispersion). In general, the most important cation exchange process, i.e. Na^+/Ca^{2+}-exchange, will be most readily detected, resulting in the $NaHCO_3$-water type – as in the Aveiro aquifer in Portugal, and the Ribe Formation in Denmark.

In several aquifers studied in PALAEAUX, over-exploitation is locally leading to a salinity increase, mostly due to up-coning of saline groundwater from larger depths, or to direct seawater intrusion. This local salinization is disturbing the regional freshening of the aquifer, e.g. in the Landenian aquifer in Southern France, and the Cambro-Vendian aquifer in Estonia.

12.7 Overall conclusions

It is concluded that isotope methods are most powerful if applied in combination. This is not only the case for the detection of younger water components. For dating of an old component, e.g. ^{14}C should for example be combined more often with ^{226}Ra. The interpretation of isotope data also requires knowledge about the hydrochemical processes and their temporal evolution, e.g. by investigating its Sr/Ca ratios system. Which methods should be combined may depend on the investigated aquifer; a combination is certainly necessary if only a few water samples are available from the flow system. Further development and additional efforts are required to better understand the ^4He contents, the $^3He/^4He$ ratios and the ^{36}Cl and possibly ^{129}I results of an groundwater system.

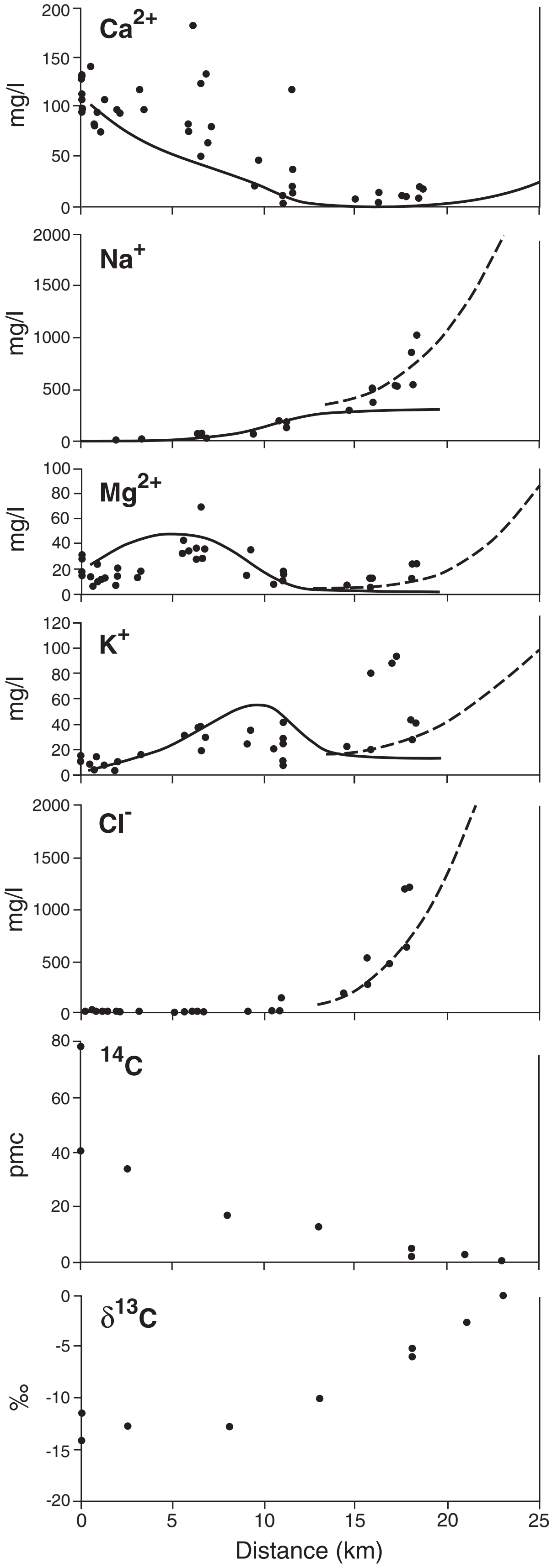


Figure 12.7. Chemical parameters in the groundwater of the Ledo-Paniselian aquifer along the flow path. Symbols are field data; solid lines represent calculated concentrations for a homogeneous flow velocity throughout the aquifer;. for calculation the flow velocity in the downflow part (after 12 km) has been substantially reduced. Carbon isotope data from Walraevens (1990).

The most effective way to confirm a palaeowater of known age is the combination of noble gas recharge temperatures with stable isotope results. The PALAEAUX project has allowed progress on the identification of the front between Palaeowaters and younger components; however the former continental distribution mainly of the stable isotopes needs further work. Climatic effects on continental atmospheric circulation patterns are not yet fully established. Such information is especially important for the calibration of numerical flow models which are useful for sustainable water management.

From the viewpoint of aquifer management it is desirable to have easily accessible indicators of groundwater age, which may be used to extend the interpretation of relatively costly isotopic investigations. In the present investigations it has been possible, with the field examples chosen, to investigate how chemical parameters may be combined with isotopic parameters to provide information on relative groundwater age. This may be possible in both freshwater aquifers where a clear sequence of geochemical reactions is seen, and in marine aquifers being freshened by meteoric waters. Relationships between specific hydrochemical parameters and residence times are valid only for the flow path for which it was derived and require calibration for each aquifer being considered.

The isotope and chemical interpretation should be strengthened where possible using hydrogeochemical modelling of the system, which may then help to validate hydrodynamic models The need to interpret the various data in a consistent way will improve the understanding of aquifer systems, by increasing constraints, avoiding the use of ‘black box’ models, and questioning concepts that have usually been taken for granted. The combined use of isotopic techniques, hydrochemical methods and a knowledge of the overall hydrogeological context forms a powerful tool for applied investigations, which are essential for the good management of aquifers.

13 Modelling scenarios for the emplacement of palaeowaters in aquifer systems

13.1 Introduction

This chapter contains a discussion of the physical processes which affect fluid flow in basins, concentrating on those which have a significant effect on a timescale of 10s of thousands of years. The emphasis is on the use of generic models which give insight into the possible behaviour of typical aquifer systems. This approach provides results that can be applied to many of the aquifers studied in detail in this project as well as others which might be investigated in the future.

The major question that has been considered during this work is: How does changing climate (recharge rates, base level, permafrost and glaciation) affect the distribution of groundwater ages and the location of the fresh/saltwater interface in coastal aquifer systems?

13.1.1 Literature review

Few studies exist that have investigated factors controlling the emplacement of palaeowaters in coastal aquifers systems. Fresh to brackish water has been identified beneath the Atlantic continental shelf of the United States. The age of these waters is not known. Two conceptual models have been proposed for the origin of that freshwater: 1) offshore discharge from mainland aquifers and 2) emplacement of Pleistocene waters during the last glacial maximum and subsequent entrapment in offshore sediments (Hathaway *et al.*, 1979). Meisler, *et al.*, (1984) concluded that the location of the saltwater-freshwater transition zone within the North Atlantic Coastal Plain and Continental Shelf is not consistent with equilibrium conditions given the current sea level, but rather reflects the influence of low eustatic sea levels during the Quaternary. Furthermore, the low sea levels promoted the deep circulation of freshwater offshore and variations in sea level have resulted in the development of a broad transition zone which is moving landward in response to present sea level at a rate of about 0.2 miles per 10 000 years. Coastal systems consisting of low-permeability sediments may take hundreds of thousands of years for groundwater flow and chemical profiles to achieve equilibrium (Konikow and Arevalo, 1993).

13.1.2 Methodology

Analytical and numerical models have been used to simulate the response of groundwater flow systems to historical climatic changes in order to better our understanding of the factors controlling the distribution of palaeowaters in European coastal aquifers.

The distribution of palaeowaters in coastal aquifers largely reflects the hydraulic characteristics of regional groundwater flow systems and the response of these systems to changes in climate. This includes changes in sea level, precipitation and evapotranspiration, glaciation and the presence of permafrost. An understanding of the evolution of the physical flow systems provides a basis for the interpretation of geochemical and isotopic characteristics of aquifers. The chapter is based on the following premises:

- The transient movement of groundwater is controlled by physical characteristics of the aquifer system (geometry and distribution of flow properties) and climate.
- An understanding of contemporary regional flow systems provides the framework for the evaluation of the transient behaviour of groundwater flow paths and fluxes from the late Pleistocene through the Holocene. This is accomplished by changing the boundary conditions or driving forces of flow models of contemporary systems in accordance with conceptual models of historic sea and base levels, recharge rates and extent of glaciers and permafrost.

The response of coastal aquifers to changes in climate was evaluated by:

(xvi) developing conceptual models of representative aquifer types

(xvii) developing conceptual models of driving forces over the past 20 000 years, and

(xviii) applying analytical and numerical models to simulate groundwater flow and residence times

13.2 Conceptual models of aquifer systems

The majority of the coastal aquifer systems studied in the PALAEAUX project consist of a regionally extensive, high permeability zone within a thick sequence of clastic and/or carbonate sediments ranging in age from Paleozoic to Cenozoic. The regional dip of the aquifer systems is typically towards the coast and high-angle faults are present in some of the basins. The aquifers are overlain by low-permeability layers, which are generally thin to absent in the upland recharge areas. The aquifers and overlying low-permeability layers are continuous offshore. The aquifers and semi-confining units generally consist of porous media, however the confining units may also contain significant fracture permeability. Quaternary and Holocene deposits overlie the regional aquifer systems and typically form local- and intermediate-scale groundwater flow systems. In northern Europe, deep Quaternary valleys may locally breach the confining units providing direct hydraulic connection between deep and shallow aquifers.

Conceptual models of two generic coastal aquifer systems were developed based upon a review of the hydraulic properties, flow characteristics and degree of hydraulic connectivity of the individual aquifer systems being studied within the PALAEAUX project. The conceptual models need to represent the major features that control groundwater flow within the majority of the aquifer systems studied. The features considered were the aquifer geometry, hydraulic properties, flow characteristics and degree of hydraulic connectivity between the aquifers and marine waters. The aquifers are shown schematically in Figs 13.1 and 13.2.

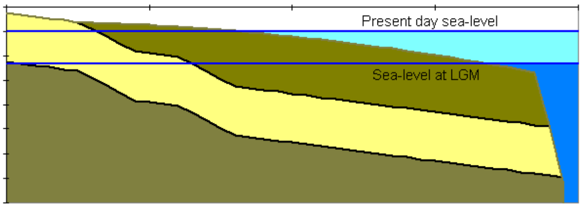


Figure 13.1. ‘Atlantic’ type aquifer system

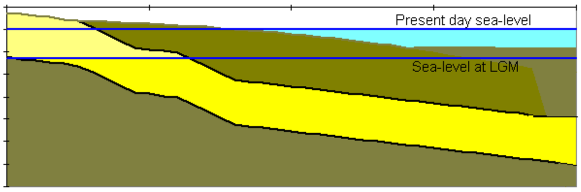


Figure 13.2. ‘North Sea’ type aquifer system

The major difference between the coastal aquifers studied in this project is the degree of hydraulic connectivity between the aquifers and marine waters. This connectivity is important in controlling the base level history, groundwater flow paths and rates, the position of the freshwater-saltwater interface and groundwater age distributions within the coastal aquifers. Ocean bathymetry and the permeability and thickness of sediments overlying the aquifers controls the degree of the hydraulic connectivity. The aquifers are considered to have ‘direct’ hydraulic connectivity where the aquifers are in contact with marine waters and have 'indirect' hydraulic connectivity where low-permeability sediments separate the aquifers and marine waters.

Regional aquifers extending out under the Atlantic Ocean and the Mediterranean Sea have both indirect and direct hydraulic connectivity with marine waters. These aquifers are overlain by low-permeability sediments on the continental shelf and are in direct contact with marine waters where they subcrop along the continental slope. The exchange of freshwater and saltwater between the aquifers and marine waters can occur as leakage through overlying low-permeability layers on the continental shelf and as direct flow where the aquifers subcrop along the continental slope.

In contrast, regional aquifers extending out under the North Sea, the Baltic Sea and the English Channel have only indirect hydraulic connectivity with marine waters. These shallow inland seas are constrained to the continental shelf and lack a continental slope. The exchange of freshwater and saltwater between the aquifers and marine waters can occur only as leakage through the low-permeability layers on the continental shelf.

For much of the work described in this chapter the distinction is made between a ‘North Sea’ type aquifer system and an ‘Atlantic’ type aquifer system. This naming convention is for convenience and it is recognized that these ‘types’ of aquifers exist in many coastal areas.

13.3 Controls on groundwater flow

Groundwater flows through an aquifer system in response to hydraulic gradients and the addition or loss of water through sources and sinks. The driving forces that have affected the hydraulic gradients and source/sink terms in the aquifer systems being studied include recharge, sea level and the extent of glaciation and permafrost. Glaciers and permafrost can also act as barriers to flow and may thus have a profound influence. Variations in controls due to climatic change from the late Pleistocene through to the present day have influenced the transient behaviour of groundwater flow paths and fluxes through coastal aquifer systems. The geochemical characteristics and age distribution of groundwater reflect processes of water/rock interaction and variations in groundwater flow paths and fluxes. Understanding how groundwater flow paths and fluxes were affected by historical variations in controls assists in the interpretation of water/rock interaction and the evolution of the geochemical characteristics and groundwater age distributions.

13.3.1 Recharge

Recharge is defined as the volume of water per unit area that is accreted to the water table and becomes part of the groundwater flow system. Recharge controls the volume of water available to flow through aquifer systems. Recharge to present aquifer systems includes the infiltration of precipitation and surface water. Effective recharge to deep-seated, regional aquifers may be less than the total recharge to the groundwater system because of the presence of shallow flow systems that discharge to streams, lakes and wetlands. For example, recharge rates in western Denmark are estimated to be approximately 250 mm a^{-1}. However, most of this water discharges from shallow, local- and intermediate-scale flow systems in the form of base flow to streams. Recharge rates to the regional, deep-seated flow system are estimated from mass balance and modelling studies to be approximately 50 mm a^{-1} (Harrar *et al.*, 1996). Recharge to the confined sections of regional aquifers included in the PALAEAUX study range from approximately 40 to 100 mm a^{-1}.

Precipitation and evapotranspiration rates have varied significantly during the past 20 000 years. During glacial periods recharge and evapotranspiration rates are both relatively low. Present precipitation in the Netherlands is between 600 to 900 mm a^{-1}, while during glacial periods it has been estimated to be only 200 to 500 mm a^{-1} (Zagwijn *et al.*, 1992). During periods of glaciation, aquifers underlying ice sheets were recharged by meltwater produced at the base of glaciers due to frictional heating and the geothermal heat flux (Boulton *et al.*, 1995). Basal melt rates have been estimated to be between 1 to 100 mm a^{-1} and most likely were between 2 to 50 mm a^{-1} for the Fennoscandian ice sheet (Boulton *et al.*, 1995). These estimates indicate that recharge to flow systems during the last glaciation by melt water production at the base of ice sheets was less than or about the same as present recharge rates to the regional, deep-seated aquifers being studied in this project in Northern Europe.

Glaciers also produce meltwater due to surface melt in the ablation zone. Surface meltwater production is up to four orders of magnitude greater than that of basal melt and is estimated to be between 1000 to 10 000 mm a^{-1} for the Fennoscandian ice sheet (Boulton *et al.*, 1995). Studies have indicated that surface melt water does not penetrate to depth within ice sheets and therefore does not contribute to basal recharge (Echelmayer and Harrison, 1990 and Gow *et al.*, 1979). Surface water melt potentially could have recharged groundwater systems peripheral to the Fennoscandian ice sheet. However, the presence of regionally extensive permafrost would serve to inhibit surface water infiltration. It is assumed that surface water melt from glaciers did not recharge the regional, deep-seated aquifers.

13.3.2 Base Level

Base level represents the ultimate level or elevation that groundwater within a given flow system wants to achieve. This is not the same as the depth to which water might flow on its way to a discharge zone. Rather, base level defines the hydraulic head in the discharge zone and this level controls the length of regional flow paths from recharge to discharge zones. Thus, base level is important with respect to both regional hydraulic gradients and residence times within a flow system.

The present base level for the coastal aquifers being studied is sea level. Base level for coastal aquifers has changed during the past 20 000 years in response to global sea level changes. Global sea levels were at a minimum for the past 100 000 years at time of last glacial maximum (LGM). Low sea levels cause the active freshwater flow system to be deeper and extend further offshore (Meisler *et al.*, 1984).

The coastal aquifers studied in this project have not all responded in the same manner to global sea level change. Atlantic type aquifers which sub-crop along the continental slope have maintained hydraulic contact with marine waters since the last glacial maximum. The base level history of Atlantic type aquifers is defined by the sea level history. In contrast, North Sea type aquifers, which are present under shallow inland seas on the continental shelf and do not extend to the continental slope and as such have not been in constant hydraulic contact with marine waters since the last glacial maximum. At the time of the last glacial maximum, sea level was below the land surface elevation of these basins and base level was defined by the elevation of river and lake systems. The base level history of these aquifers remained fairly constant through the early Holocene. Rising sea levels inundated the river and lake systems about 10 000 to 8000 years BP at which time the base level for the aquifers was defined by the sea level. It was at this time that the aquifers became the coastal aquifers recognized at the present day.

13.3.3 Glaciation and Permafrost

The extent of glaciation and permafrost in the PALAEAUX region has been described in Chapter 11. It is evident that these two features will have a significant impact on groundwater flow patterns within aquifers but it is not immediately clear whether these effects are the same in all affected aquifers.

It is clear that permafrost affects the amount of water able to recharge to aquifers. However it may also affect discharges from aquifers as natural discharge areas become frozen. This effect has been examined for the case of the Ledo-Panesalian aquifer in Belgium.

Permafrost may also have the effect of reducing the bulk transmissivity of the groundwater flow system by reducing its thickness. Also the water which is frozen in permafrost is unable to flow which may lead to disparities in groundwater age within a vertical section of aquifer.

As described in Chapter 11, current literature (Boulton *et al.*, 1995) suggests that glaciers may have the effect of increasing significantly the amount of water which recharges aquifers by imposing very high hydraulic heads on the aquifer under the glacier. The effect of these postulated high heads on three aquifer systems has been investigated by use of numerical models which have given insight into the significance of this effect on a smaller scale than that discussed by Boulton and his co-workers.

13.4 Modelling approaches

Groundwater models are commonly used for prediction and management. In such cases the approach is normally to make the models specific to an aquifer and include as many of the features and properties of the aquifer as are thought to be significant. This leads to numerical computer models of some complexity.

However, modelling serves several other purposes including that of providing insight into probable or possible behaviour. In those circumstances simpler (generic) models tend to be more useful. It is best to keep the number of parameters as small as possible and, where appropriate, work with dimensionless groups of parameters. Often simplifications lead to analytical solutions although the solutions may require computer evaluation. Sometimes it is still necessary to use discretized numerical models (e.g., finite difference models) or even complex models but with simple boundaries and homogeneous aquifer conditions.

In the context of the PALAEAUX project, the types of question that are best attacked with simple generic models are:

- Is the current head distribution in an aquifer essentially in steady-state or are heads still adjusting to long-term changes in sea level or recharge.
- How does the age distribution through an aquifer relate to historical boundary conditions.

Analytical and numerical models were applied to evaluate the response of aquifer systems to changes in sea level, impact of glaciation and presence of permafrost.

13.4.1 Characteristic times

Groundwater flow systems respond to changes in driving forces through changes in hydraulic heads, flow paths and flow rates in an effort to establish equilibrium. The rate at which flow systems respond to changes in driving forces is governed by the hydraulic properties of the flow system and the distance over which the changes propagate.

Flow systems within aquifers can be described by a number of 'characteristic' times. The absolute and, more particularly, the relative values of these times provide an immediate indication of the general flow and/or transport behaviour.

Flow

The characteristic time for flow over distance L in an aquifer of hydraulic conductivity K is given by:

$$T_F = Ln_k / Ki$$

where n_k is the kinematic (or effective) porosity and i is the head gradient. This is the simplest characteristic time for an aquifer but it must be used with caution for aquifer 'systems' (as opposed to a short path through a part of an aquifer. For an aquifer system the hydraulic conductivity should be an average over the entire pathway from recharge zone to the point of interest.

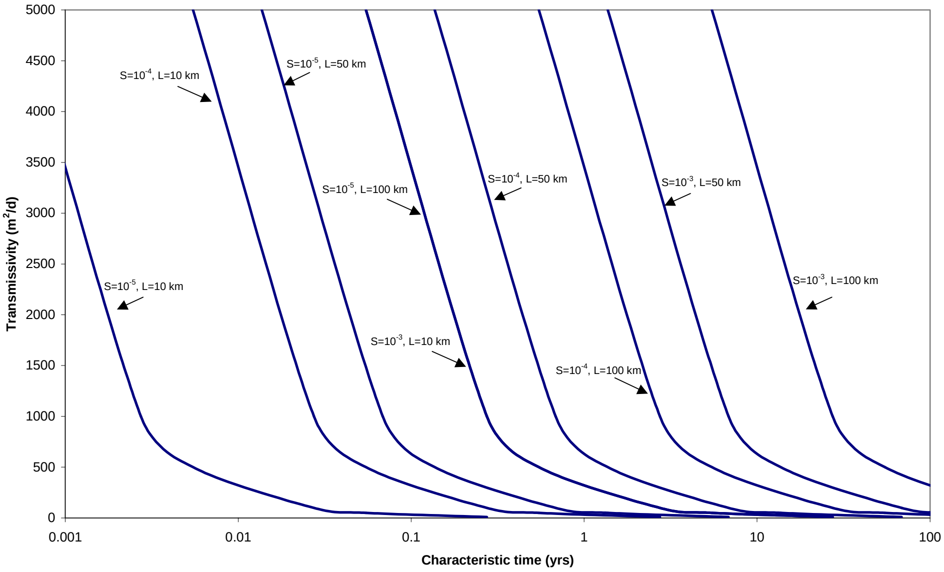


Figure 13.3. Characteristic times for pressure changes to propagate through aquifers of different properties and dimensions.

Pressure change

The characteristic time for pressure changes to propagate a given distance through an aquifer is well described in hydrogeological literature and is known as the aquifer hydraulic diffusion time. (This term relates to the process of chemical diffusion in that both processes are described by the 'diffusion' equation, which is known as Fick's second law within the context of chemical diffusion.)

Hydraulic diffusivity, D_H, is defined in terms of the transmissivity, T, and the storage coefficient, S, of the aquifer through $D_H = T/S$; equivalently, in terms of the hydraulic conductivity, K, and the specific storage, S_s, we have $D_H = K/S_s$. The characteristic time for diffusion over distance L is given by:

$T_D = L^2 / D_H = L^2 S / T = L^2 S_s / K$

Figure 13.3 shows the range of diffusion times for a variety of aquifers. As can be seen the characteristic time for an aquifer with a transmissivity of 500 $m^2 d^{-1}$ a storage coefficient of 10^{-4} and a length of 100 km is about 5 years. This is a very short time in the context of palaeohydrogeology and indicates that pressures in the systems in which we are interested will equilibrate relatively quickly after, for example, a change in sea level or recharge rate.

This analysis does not represent cases where there exist pressure differences due to density variations. Such pressure differences can take much longer to come to equilibrium. Those situations are considered below under the heading of 'interface movement'.

Quasi-steady-state conditions

The relative values of T_F and T_D determine whether the pressure (or head) distribution in a system can be approximated as quasi-steady-state: if T_F is much larger than T_D, pressure transients can be ignored in determining flow times and hence ages. From the above expressions, in terms of hydraulic conductivity, the condition $T_F >> T_D$ becomes

$L S_s i / n_k << 1$

Taking as upper limits the values of $L=10^5$ m, $S_s=10^{-5}$ m^{-1}, $i=10^{-2}$ and as a lower limit $n_k=10^{-2}$ makes the expression on the left of this inequality equal to unity. This strongly suggests that quasi-steady-state conditions can normally be assumed for regional-scale flow and transport in palaeo-aquifers.

Interface movement

Another characteristic time, which is of great relevance to this project, is the time taken for a saline interface to move towards a new steady state position as a result of a change in hydraulic conditions (normally a change in sea level, recharge rate or pumping). Such a time is not evident in the hydrogeological or hydrogeochemical literature and is worthy of some consideration.

The position of the interface is controlled by the hydraulic properties of the aquifer (T and S) and the recharge rate as well as the aquifer geometry. The combination of these parameters defines the head gradients etc in the aquifer which then defines the flow rates etc for the interface position.

Atlantic type aquifer

Lowering of sea-level: The movement of the coastline caused by the reduction in sea-level will drive the interface out towards the sub-crop. As the interface moves, the saline water which is to be replaced by fresh will flow out through the sub-crop area and into the sea. The controlling feature of this flow is the availability of fresh water to drive out the saline water. Thus the time for this to occur will depend on recharge rate and the aquifer porosity and the distance which the interface will move. For a recharge rate of 40 mm a^{-1}, porosity of 0.1 the interface can move at a maximum rate of 0.4 m a^{-1}. The distance that the interface will move can be approximated as the distance that the coastline moves. So for a change in coastline of 10 km the characteristic time for the interface movement is 25 000 years. (Time = distance coastline moves/(recharge rate/porosity)).

Elevation of sea-level: After a rise in sea-level and consequent movement of the coastline the saline interface will move inland, following the coastline. The saline water required for this movement will come from the sea through the sub-crop of the aquifer. For the interface to move the freshwater must be displaced and this water will either go up through the semi-confining layers above or be expelled at the land-side subcrop. The pressure gradient driving this flow is difficult to define but is generated by the density difference between the fresh and saline water and as such is very small (a head difference of <1 m can be envisaged). The flow rate through the semi-confining layer depends on its thickness and hydraulic conductivity. Using representative values for these parameters of 100 m and 10^{-4} m/d and a head difference of 1 m gives a flow rate of 10^{-6} m/d. An aquifer porosity of 0.1 and a thickness of 100 m (as assumed above) will give a rate of interface movement of about 0.004 m a^{-1} which is 100 times slower that the speed at which the interface moves after a lowering of sea-level. It should be emphasized that this rate is calculated using a driving head difference of 1m. As it is unclear whether this value is realistic some numerical modelling of this situation has been carried out. This is described in more detail below.

North-Sea type

Lowering of sea-level: The movement of the interface will be controlled by the rate at which the saline water can be moved. This will have to discharge through the overlying layers and so the rate of movement will be similar to that described above for the Atlantic-type when the sea level rises.

Raising of sea-level: In this case both the saline water and the freshwater must move through the overlying layers. Thus the problems described above are relevant. The rates of movement calculated above are the best that can be done in a simplistic manner and so a numerical model (described below) is used to further understand the relevant timescales.

Summary

Consideration of the timescales involved in different aspects of the groundwater flow systems indicates that:

- The relevant timescale for the equilibration of the heads in the aquifers is the hydraulic diffusion time. This gives timescale of the order of 1–100 years for the aquifers considered in this project.
- The timescale for the movement of the saline interface is more complicated and depends on the aquifer geometry.
- The rate of movement is controlled by the availability of water to replace the existing fresh or saline water.
- The properties of the overlying semi-confining layers are very important.
- The timecales for these processes are often in excess of 10 000 years.
- Numerical modelling is required to understand the head differences generated by density differences.

13.4.2 Saltwater-freshwater interface

Coastal aquifers are characterized by a freshwater flow system that discharges to the sea by upward seepage through overlying semi-confining layers. The freshwater flow system is bounded seaward by saltwater. The two fluids are separated by a mixing or transition zone (Cooper *et al.*, 1964). In this zone saltwater and freshwater mix and move seaward resulting in flow of saltwater towards the transition zone. The shape and position of the transition zone is dependent upon the volume of water discharging from the aquifer and the offshore distance over which the discharge occurs.

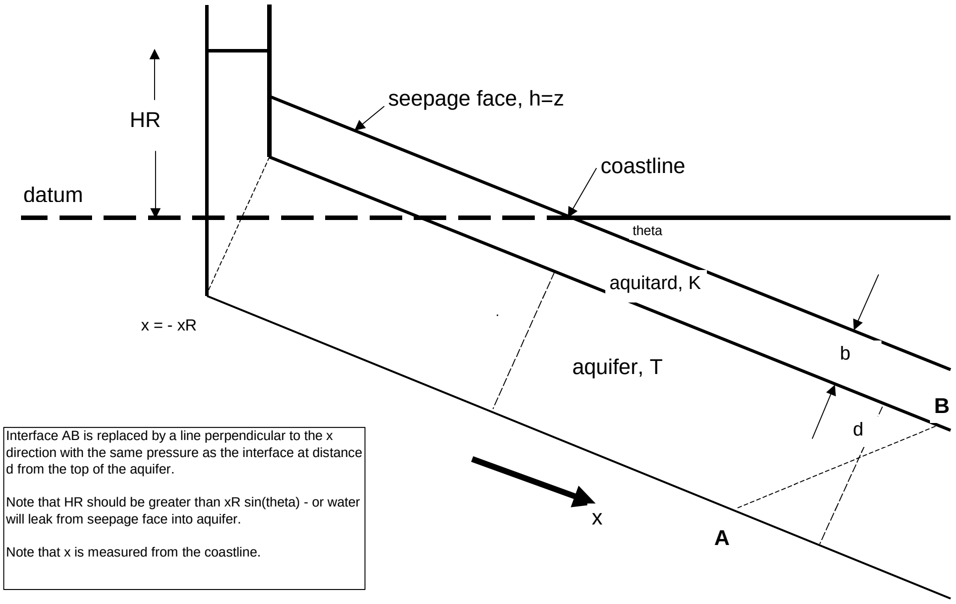
Across the transition zone, the concentration and density of the water varies between that of freshwater and saltwater. If the flow system is in steady-state, the width of the transition zone is controlled by diffusion and the dispersive characteristics of the aquifer system (Freeze and Cherry, 1979, p. 377). The thickness and width of the transition zone may increase in response to variations in recharge and tidal fluctuations (Kohout, 1964, Cooper, 1964 and Henry, 1964). A transition zone that is about 500 metres thick and 16 to 24 kilometres wide is present off of the north-east coast of the United States (Meisler, 1984). The broad width of this zone is attributed to large-scale global sea level fluctuations resulting in the circulation of saltwater due to the transient movement of the shoreline. Connate water in low-permeability sediments deposited under marine conditions can also contaminate offshore freshwater (Das Gupta and Yapa, 1982). The mixing of connate saltwater with offshore freshwater can complicate the delineation of processes controlling the width of the freshwater-saltwater transition zone.

In this study, analytical and numerical simulations were conducted in order to investigate the hydrogeologic and climatic controls on the steady-state and transient location of the saltwater-freshwater transition zone. It is assumed that the freshwater and saltwater do not mix and are separated by a sharp interface. The sharp interface is located where the pressure from a column of freshwater is balanced by the pressure exerted by a column of sea water (Hubbert, 1940). The sharp interface has been shown to coincide with a concentration that is 40% of seawater and thus tends to underestimate the seaward extent of the saltwater-freshwater interface seawater (Henry, 1964). The sharp interface approach is appropriate for use in simulating the position of the freshwater-saltwater interface in regional flow systems dominated by advection (Reilly and Goodman, 1985).

Steady-state location of saltwater-freshwater interface

A simple steady-state model has been developed in the form of an Excel spreadsheet to simulate flow through a semi-confined coastal aquifer. The main objectives of the modelling are to determine the sensitivity of steady-state position of the saltwater-freshwater interface and residence times within the flow system to hydraulic properties of the aquifer system, changes in sea level and onshore hydraulic gradients.

The flow system is conceptualized as consisting of a regionally extensive aquifer overlain by a continuous semi-confining layer (aquitard). The aquifer is exposed at the land surface in the recharge zone and the flow system dips uniformly offshore (Fig 13.4). The aquifer and aquitard are both assigned a constant thickness of 100 metres. This allows the model results to be presented in terms of the ratio of the horizontal permeability of the aquifer to the vertical permeability of the aquitard.



Interface AB is replaced by a line perpendicular to the x direction with the same pressure as the interface at distance d from the top of the aquifer.

Note that HR should be greater than xR sin(theta) - or water will leak from seepage face into aquifer.

Note that x is measured from the coastline.

Figure 13.4. Schematic representation of semi-confined aquifer system used to determine the position of the saline interface.

Assumptions:

(i) Flow is steady-state.
(ii) The aquifer is homogeneous and of uniform thickness.
(iii) The flow is parallel to the base of the aquifer (Dupuit assumption).
(iv) Upward leakage occurs through a homogeneous aquitard (semi-confining layer) of constant thickness in a direction normal to the aquifer.
(v) To the landward side of the coast the upper surface of the aquitard is a seepage face.
(vi) To the seaward side of the coast the upper surface of the aquitard is in direct contact with the sea.
(vii) The aquitard is full of fresh water out to the interface in the aquifer with seawater.
(viii) There is a sharp interface between saltwater and freshwater.
(ix) The saltwater is static, so the Ghyben-Herzberg conditions apply at the interface.

A series of simulations were first performed to determine the sensitivity of the location of the steady-state interface to the vertical hydraulic conductivity of the aquitard. The aquifer hydraulic conductivity was specified as 10^{-4} m s^{-1} and a thickness of 100 m was assigned to the aquifer and the aquitard. A constant head value of 100 m was assigned to the recharge zone at a location of 50 km from the coast. The results are presented in Fig 13.5 and show, for a given regional hydraulic gradient (as defined by the head in the recharge zone and distance to the coast), the sensitivity of the interface location to the ratio of the aquifer (horizontal) to aquitard (vertical) hydraulic conductivity. The interface is located at about the coastline for hydraulic conductivity ratios of 100:1 and moves offshore as the ratio increases and is located 86 km from the coast for hydraulic conductivity ratios of 100 000:1.

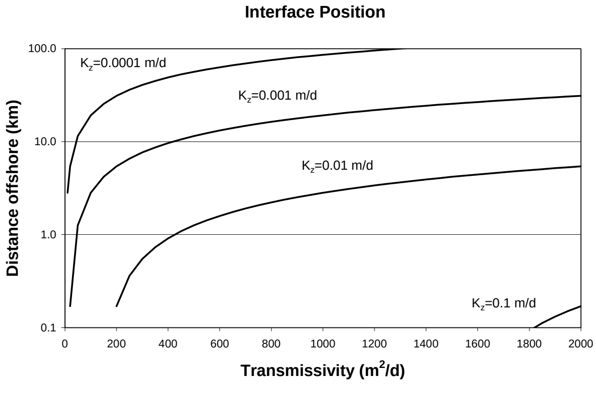


Figure 13.5. Relationship between interface position and aquifer or aquitard permeability.

This result is explained as follows: The volume of groundwater flowing through the aquifer at the coast must discharge to the sea through the semi-confining layer. For a given hydraulic gradient, this volume of water increases as the aquifer transmissivity becomes larger. Thus, for a given semi-confining layer hydraulic conductivity, the offshore distance to the interface must increase because a greater length of the semi-confining layer is needed to discharge the increased volume of water.

A series of simulations were also performed to determine the sensitivity of the location of the steady-state interface to the regional onshore gradient as defined by the head in the recharge zone and the distance from the recharge zone to the coast. Simulations were performed for a range of hydraulic gradients and ratios of aquifer to aquitard hydraulic conductivity. Results are presented in Fig 13.6 and show how the steady-state interface position is sensitive to both the regional hydraulic gradient and the aquitard permeability

Time to reach steady-state interface position

Much modelling of saline interface problems use the steady-state position of the interface as a starting condition. This is done for computational simplicity and also because this is the way that most other groundwater modelling is carried out. A steady state model is first developed to ensure that the boundary conditions etc. are reasonable and consistent and then transients are imposed e.g. increased pumping, changed recharge.

To find out whether this a sensible approach to coastal aquifer modelling and in order to get a feel for how the

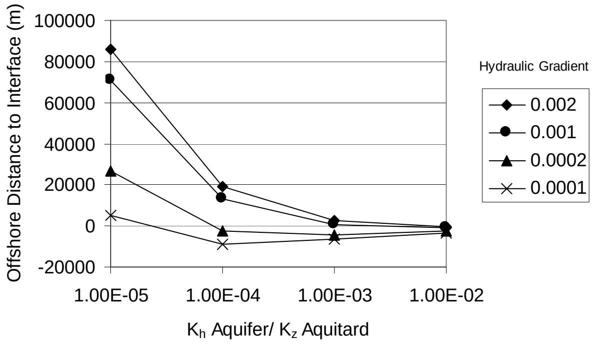


Figure 13.6. Interface position for different regional hydraulic gradients.

saline interface moves when there is a large change in sea-level a numerical model was developed. The model was based on the Aveiro aquifer described in the Portugal section of this report. The modelling package used for this work is the USGS code SHARP (Essaid, 1990) which simulates fresh and saltwater flow in layered aquifers using the sharp-interface assumption. The model accommodates multiple layers but in this case a single aquifer covered by a leaky confining layer was simulated.

The situation modelled is shown in Fig. 13.7. This is a very simplified version of a section through the Aveiro aquifer perpendicular to the coast which extends to the edge of the continental shelf where the aquifer is thought to outcrop. This position is below both the present and historical sea-level. The main features of the model which affect the position and movement of the interface are: the aquifer permeability, the recharge rate and the vertical permeability of the confining aquitard as well as the physical dimensions of the modelled region.

The model was set-up so that it gave a steady-state interface position near the present day coast line. This required the imposition of quite a small recharge rate and a low aquitard permeability. The effect of increasing the aquitard permeability is to make the interface much steeper, which makes the movement more difficult see.

With the sea-level lowered by 130 m, the same recharge and physical properties are used to give a new steady-state head and interface distribution. This resulted in an aquifer which was flushed completely by freshwater, which is as expected as the aquifer outcrop is quite close to the coast.

The head distribution calculated for this steady state condition was used as a starting condition for a transient model run in which the sea-level was returned to its present day position. This simulates an instantaneous rise in sea-level. The position of the interface is plotted in Fig 13.8 for various different times. As can be seen the interface does not move very fast and after 30 000 years has not yet reached the steady-state position. The speed of movement of the interface is affected by the porosity of the aquifer and by the permeability of the aquitard.

Table 13.1. Parameters used for the SHARP model as shown in Figs. 1.7 and 1.8.

Property	Value used
Aquifer permeability	10^{-4} ms^{-1}
Aquitard permeability	10^{-9} ms^{-1}
Aquifer porosity	0.2
Recharge rate	15 mm a^{-1}

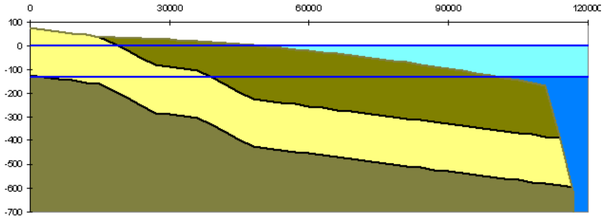


Figure 13.7. Schematic cross-section of modelled Aveiro aquifer showing the position of sea-level and the coast.

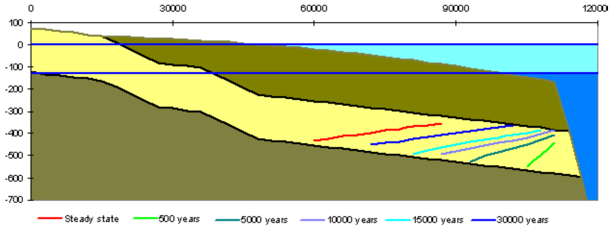


Figure 13.8. Movement of saline interface after instantaneous increase in sea-level

13.4.3 Impact of glaciers on regional groundwater flow systems

The effect of glaciation on three of the aquifers studied in the PALAEAUX project has been examined by using numerical models to consider the effect of the Boulton hypothesis (Boulton, 1995, see also Chapter 11). The three aquifers differ in their geometry in relation to the advancing glacier

North Belgium

Northern Belgium was ice-free during the Weichselian period but during the previous glacial period, the Saalian, the European ice sheet had its southernmost extension, reaching the central part of the Netherlands. Because the Ledo-Paniselian aquifer in North Belgium is located on the south edge of the large sedimentary North Sea basin and dips to the north, it is possible that during the Saalian period the ice sheet changed the groundwater flow in the aquifer system below it, including the Ledo-Paniselian layer. This possibility was investigated with a cross-sectional flow model simulating the impact of a 250 m thick ice cover in the North Netherlands.

The model simulates flow in a long and deep profile, starting from the Central Netherlands in the north and reaching the outcrop of the Ledo-Paniselian in the south. Only groundwater flow is simulated, no changes in the fresh/salt water interface are calculated. Because the layers dip to the north, they occur at large depth near the north side of the profile, where available data are scarce. The depth and thickness of the layers is therefore derived from extrapolating data from the south half of the section. The hydraulic characteristics used are based on values found in the Belgian part of the profile.

Two physical conditions were incorporated in the model, to include the effects of the glacial conditions.

- The boundary conditions under the ice sheet. This is done by imposing a high piezometric level at the bottom of the ice sheet, which is equal to estimated height of the ice cover (Boulton, 1995).

- The occurrence of a permafrost layer at the surface in the rest of the section. This is done by introducing a low-permeability layer under the surface. The land surface is considered at a constant piezometric level a little under the estimated topographic elevation at that time.

The estimated thickness of the ice sheet is up to 250 m (Zagwijn, 1975). Three calculations have been done with 50, 100 and 250 m of ice-sheet thickness. All three gave similar results in terms of direction of groundwater flow, although the velocities of the flows were different. The results indicate that the high pressures under the ice sheet penetrate very deeply in the whole aquifer system. Much water is drained in the upper part of the reservoir from under the ice sheet southwards. Here the groundwater under the permafrost layer was under pressure and could have been drained by cracks in the permafrost layer or where rivers formed 'thermal boundaries' under which the permafrost layer was absent or reduced. In the deep part of the aquifer system the propagation of the high-pressure front caused a pushing up of the deeper waters, towards the south and the upper parts of the layers. Distribution of fresh and salt water in this part of the reservoir may have been influenced by the ice sheet as freshwater is injected into the system from the glacier. However, the flow vectors indicate that the water displacement during a thousand year time interval is small. Significant changes in salinity require a thick ice sheet (at least a few hundreds of metres) during a sufficiently long time (a least several ten thousands of years).

East Midlands aquifer

The sandstone aquifer of the East Midlands is recharged at the outcrop area which is a linear feature running N-S. The aquifer dips in an W-E direction towards the North Sea. To the east of the outcrop area the aquifer is confined under a thick layer of low-permeability Mercia Mudstone. Under present conditions the water which recharges the aquifer flows towards the east into the confined layer. There is no obvious discharge point for this aquifer as it continues to dip eastwards reaching a depth of over 800 m below the coast. The groundwater circulation is therefore controlled by slow seepage up through the confining layers.

During the last Ice Age glaciers spread from the north to cover both the recharge area of the aquifer and the confining layers to the east. The effect of this glaciation on flow in the aquifer was investigated using a numerical flow model by assuming that the Boulton hypothesis is correct. The glacier was modelled as travelling southwards preceded by zone of permafrost which was assumed to behave as a barrier to flow. Basal melting rate from the glacier was applied under the glacier with the head constrained to 80% of the presumed glacier thickness. The movement of water in the aquifer was examined using particle tracking.

The permeability of the confining layer is such that it is not able to transmit all the water melting at the base of the glacier, which leads to a build up of hydrostatic pressure. This pressure is transmitted rapidly (see section on *characteristic times*) through the confining layers to the aquifer where it changes the flow direction. In front of the glacier front the flow direction is now predominantly from north to south. The only variation to this flow direction is under the outcrop area where the permeability allows more water to move. In this area the flow is out of the aquifer.

It can be concluded that the overall effect of the glaciation is to push water from north to south within the aquifer. There is no evidence from the modelling that water will be pushed deeper into the aquifer than the present flow system. This conclusion is specific to the geometry of this aquifer.

Danish coastal aquifer

The geology of south-western Jylland, Denmark consists of 20 to 40 m of Quaternary sediments overlying a westward dipping sequence of Tertiary clastic sediments. Locally, deep valleys filled with Quaternary sediments are present in eastern and western Jylland. Regional groundwater flow patterns are controlled by the hydraulic properties of the Tertiary sediments that are characterized by low-permeability clays in the eastern, high permeability sands in central and a mix of low-permeability clays and high permeability sand in western Jylland. Weischselian glaciers occupied the area underlain by low-permeability Tertiary clays and the maximum extent of glaciation coincides with the eastern extent of the high permeability Tertiary sediments.

Numerical simulations of regional groundwater flow beneath the Weischselian ice margin in western Denmark show that the basal meltwater infiltration rates and the subglacial hydraulic heads are sensitive to the regional aquifer hydraulic conductivity and the vertical hydraulic conductivity of the till underlying the glacier. Base meltwater infiltration rates are low, yet subglacial hydraulic heads are high when the ratio of the aquifer hydraulic conductivity to till vertical hydraulic conductivity is 1000:1 or less. Ratios of 10 000:1 or greater promote increased basal meltwater infiltration and low subglacial pore water pressures. The average hydraulic conductivity of the regional Tertiary aquifer system in western Denmark is 7.0×10^{-4} m/s (Chapter 3) and the vertical hydraulic conductivity of shallow till deposits in western Denmark ranges from 1.0×10^{-8} to 1.0×10^{-9} m s^{-1} (Jørgensen *et al.*, 1998). Modelling results using these values suggest that the hydraulic conductivity of the regional aquifer was high enough to transmit the basal meltwater produced by the Fenno-Scandian ice without the development of high hydraulic heads beneath and peripheral to the glacier. These results contradict those of Boulton *et al.* (1995) where it is concluded that high hydraulic heads beneath Pleistocene ice sheets resulted in the propagation of major pressure pulses through groundwater flow systems beneath and peripheral to the glaciers and that flow systems were completely reorganized.

Summary

This modelling, assuming the Boulton hypothesis (as described in more detail in Chapter 11), has shown that the effect of glaciation is aquifer specific. If the glaciers can provide reasonable recharge rates at high heads then the flow system in underlying aquifers will be affected in a way dependent on the relative geometries of the aquifer and the glacier.

- Belgium: the Saalian ice sheet which reached central part of Netherlands reversed flow patterns in Ledo-

Panesalian aquifer from normal south to north direction to north to south direction.
- UK: During the glaciation little ‘extra’ recharge occurred to the aquifer and the change in groundwater flow directions meant that freshwater was not pushed further into the confined part of the aquifer than would have occurred without the glaciation.
- Denmark: The combination of till and aquifer permeabilities is such that the glaciation did not result in ‘pulses’ of pressure being transmitted through the aquifer.

13.4.4 Impact of permafrost conditions on groundwater flow

As mentioned in Chapter 11, permafrost can have a significant effect on the regional hydrology of affected aquifer systems. Here the Ledo-Paniselain aquifer of Northern Belgium is used as an example. The effect which is of most interest is the reduction in recharge which occurs as the surface is frozen

The Ledo-Paniselian aquifer lies in a region which was never covered by an ice sheet, but which has seen, at least during the Last Glacial Maximum (LGM), periglacial conditions. Surface temperatures must have been low enough for the development of a permafrost layer. The occurrence of the permafrost has severely influenced the flow in the aquifer system, in the first place by reducing or suspending the recharge of the water table. The model described in Section 11.3 gives some indications about the expected thickness of the permafrost layer given certain surface conditions. In this section the impact of this permafrost layer on the piezometric levels in the aquifer system below are considered.

A schematic four layer hydrodynamic model was constructed using the MODFLOW code, to simulate the impact of the suspension of the recharge of the water table and prevention of discharge in a 40 km long north-south profile. The simulation period was restricted to 10 000 years which is roughly the length of the last glacial maximum. This model simulates only groundwater flow and doesn't account for the presence of the permafrost layer itself, which can grow in the 10 000 year interval to a significant thickness, freezing the top of the considered profile and immobilizing the groundwater.

The main characteristics of the model simulations are as follows:
- The simulation first calculates a steady state situation during which the aquifer system is recharged over a 5 km long section (recharge rate 0.1 mm/day) near the south end of the profile (present situation). During the second part of the simulation the recharge and discharge is halted and transient flow in the profile is calculated.
- It is assumed that in the Ledo-Paniselian aquifer the hydraulic head under the sea equals the sea level. During the LGM sea levels were around −150 m, and the shoreline is taken at a distance of 500 km to the north.
- Near the south side where the Ledo-Paniselian layer outcrops, a constant head boundary is imposed during the steady state calculation, representing drainage to surface waters. This constant head boundary is removed as a permafrost layer prevents groundwater flow to the surface.

Table 13.2. Calculated piezometric levels in the simulated profile

TIME (a)	Point 1	Point 2	Point 3	Point 4
before permafrost	28.99	13.44	−0.05	10.00
1	28.66	13.81	1.13	11.07
10	26.17	16.26	1.52	15.77
100	15.50	12.71	3.52	12.93
1000	4.49	4.33	3.09	4.35
10000	−24.89	−25.03	−26.02	−25.00

The results are considered as calculated hydraulic heads in function of time for four selected observation points in the profile
- Point 1 gives the water table in the recharge area
- Point 2 gives the hydraulic level in the Ledo-Paniselian aquifer under the recharge area
- Point 3 gives the hydraulic head in the Ledo-Paniselian aquifer near the north side of the profile
- Point 4 gives the water table elevation in the outcrop area of the Ledo-Paniselian aquifer

The calculated values after 1, 10, 100, 1000 and 10 000 years are given in Table 13.2.

The main conclusions that can be drawn from the simulations are:
- The water table in the recharge area (Point 1) starts lowering from the moment that recharge is suspended.
- In the Ledo-Paniselian aquifer the piezometric levels increase initially (Point 2). This is due to the fact that the permafrost layer in the outcrop area prevents groundwater drainage to surface waters.
- In the outcrop area water levels will also rise initially and the water under the permafrost layer is overpressured.
- After more than 10 years the piezometric levels in the Ledo-Paniselian become higher in the outcrop area than under the recharge area.
- As the water levels in the Ledo-Paniselian are lowering, the horizontal flow velocity decreases. After around 300 years the difference in water level between the recharge area and at the downstream side of the profile (Points 2 and 3) is small and hence the hydraulic gradient becomes small and so goundwater flow becomes less significant. Further lowering of the heads under influence of the low sea levels will slow down the flow even more.
- After around 100 years the piezometric levels in the Ledo-Paniselian aquifer near the north end of the profile start increasing. This continues for several centuries until they finally drop to much lower values.
- After 10 000 years the piezometric levels in the whole profile are between −20 and −30 m, which is between 30 and 40 m lower than today. By that time, the permafrost layer may have grown so thick that the upper section of the simulated profile (or even maybe the whole profile) was completely frozen and water movement nearly impossible.

As a main conclusion it can be stated that at least for the Ledo-Paniselian aquifer in North Belgium a permafrost layer can have caused a severe lowering of piezometric levels and a consequently slowing down of the groundwater flow in the northward direction. It required a few thousands of years to reach levels which were much lower than today.

13.5 Conclusions

Saltwater Interface

The steady-state position of the saltwater-freshwater interface is sensitive to the ratio of the aquifer to aquitard hydraulic conductivity (regional anisotropy), the hydraulic gradient from the recharge zone to the coast and the hydraulic head at the coast. The steady-state interface moves further offshore for increasing values of the regional anisotropy, onshore hydraulic gradients and hydraulic head in the aquifer at the coast. A critical value of 1000:1 for the ratio of aquifer to aquitard hydraulic conductivity exists for the range of aquifer hydraulic conductivity and onshore hydraulic gradients evaluated. The interface was located offshore for ratios of the aquifer to aquitard hydraulic conductivity greater than 1000:1

Atlantic-type aquifer

- Direct hydraulic connectivity to sea where aquifer subcrops along continental slope.
- Base level history defined by sea level history.
- Changes in sea level propagate through system at rates dominated by aquifer hydraulic conductivity and storage, hydraulic heads stabilize relatively quickly, characteristic times for pressure changes to propagate through system order of 10s to 100 years,
- Flow responds less quickly than pressure, controlled by aquifer hydraulic conductivity and porosity, regional gradients
- Encroachment of saltwater interface associated with sea level rise takes a long time (order of 10 000 years) controlled by aquifer properties (K,n_k) and offshore gradients
- Offshore horizontal gradients become very low, saltwater encroachment controlled by hydrodynamic dispersion (advection associated with density gradients and diffusion)
- Hydraulic heads and freshwater flow systems probably close to steady-state
- Saltwater interface not at steady-state

North Sea type aquifer

- No direct hydraulic connectivity between aquifers and sea, connectivity controlled by thickness and bulk vertical permeability of semi-confining layers
- Base level history defined by location and elevation of rivers and lakes in offshore North Sea during the Late Quaternary through early Holocene, base level defined by sea level when rivers and lakes inundated by rising North Sea, aquifers did not become coastal aquifers until some time during the Holocene
- Changes in sea level propagate through system at rates dominated by properties (K and S) of semi-confining layers overlying aquifer, hydraulic heads stabilize not so quickly, characteristic times for pressure changes to propagate through the system are of the order of 100s to 1000 years
- Fresh water flow system controlled by hydraulic properties of semi-confining layer
- Saltwater encroachment into aquifer controlled by competing upward hydraulic gradients in flow system and downward chemical gradients
- Hydraulic head probably not at steady-state, in response to rising sea level changes in hydraulic head must propagate first through semi-confining layer and then through aquifer.
- Saltwater interface not at steady-state, time to steady-state unknown, governed by different processes than Atlantic type aquifers,
- North Sea type aquifers may never develop a true interface, but instead have very broad and deep transition zone.

14 Hydrochemical modelling as a tool for understanding palaeowaters

14.1 Introduction

The rapidly increasing power of computers, combined with the development of increasingly sophisticated analytical models for geochemical systems have made hydrogeochemical modelling a valuable tool in understanding the formation processes and evolution of hydrogeological systems. This chapter first discusses the recent developments and approaches to modelling groundwater chemistry. Then three case studies are described in which the application of hydrogeochemical modelling to aquifers studied in the PALAEAUX project is illustrated.

Groundwater quality is the result of a complex interplay of several physical and chemical processes. In general, groundwater quality may be traced along a flowpath from the sampling point back to the source area. Along the flowpath a number of physical and chemical processes take place, *viz.* there is a residence time related to small flow velocities of the order of 1 m a^{-1}, there is mixing with other waters due to dispersion and diffusion, and all the time there is chemical interaction between water and sediment in response to variations in flow velocities and paths and water qualities. The correct interpretation of ^{14}C ages is of particular interest in the framework of PALAEAUX. Carbon-14 allows an age to be estimated for waters in many of the studied aquifers. However, carbon is affected by geochemical reactions, and ^{14}C ages must be corrected. Carbonate reactions, ion exchange and redox reactions, and their interplay, are definitely important reactions to be considered.

Two types of models are currently used for describing hydrogeochemical reactions (Plummer, 1992; Parkhurst and Plummer, 1993). One type of model *balances* the reactions that have occurred between two sampling points. The analyzed water qualities are entered together with a set of feasible reactions, and the computer program calculates mass transfers for the indicated reactions. The answer will always be a description of the observed water qualities, although analysis inaccuracies may prevent a solution being found. This type of modelling is also termed *inverse* modelling.

The other type of model calculates the evolution of water qualities during *transport*, based on a set of reactions, and given initial and boundary water qualities. The results can be compared with observed water qualities, and may be completely wrong. The comparison will show how well we understand the chemical and physical processes that are active in the subsoil. This type of modelling is also called *forward* modelling.

14.1.1 Mass balance models

Mass balance models try to find reaction schemes for the observed concentration changes between two sampling points. The extent of each chemical reaction α_r (mol/l), multiplied by the stoichiometric coefficient $b_{r,i}$ for component i, adds a term $b_{r,i} \times \alpha_r$ to the change in concentration between two wells:

$$\Delta m_{T,i} = m_{T,i(\text{final})} - m_{T,i(\text{initial})} = \Sigma_r\, b_{r,i} \times \alpha_r$$

where $m_{T,i}$ indicates the total concentration of component i. For example if gypsum ($CaSO_4 \cdot 2H_2O$) and calcite ($CaCO_3$) react, we have:

$$\Delta m_{T,\mathrm{Ca}} = 1 \times \alpha_{\mathrm{gypsum}} + 1 \times \alpha_{\mathrm{calcite}}$$

$$\Delta m_{T,\mathrm{SO}_4} = 1 \times \alpha_{\mathrm{gypsum}}$$

$$\Delta m_{T,TIC} = 1 \times \alpha_{\mathrm{calcite}}$$

(*TIC* is total inorganic carbon). The extent of the reaction α_r may be positive (indicates dissolution) or negative (indicates precipitation). The set of linear equations is solved for the α_r.

Computer models that solve the mass balance equations are BALANCE (Parkhurst *et al.*, 1982), NETPATH (Plummer *et al.*, 1994) and PHREEQC (Parkhurst, 1995). All three programs have specific features. The oldest program, BALANCE, is still useful as it allows for an easy definition of reactions or parameters which are not part of the standard database. An input file can be constructed with an interactive version (BALNINPT). NETPATH is particularly useful as it contains reactions for isotopes of C, N, O, Sr and S in the standard database. NETPATH also contains an input processor which allows a database of water samples to be maintained.

Both BALANCE and NETPATH require that the reactions *exactly* match. This means that in the above given reaction set for calcite and gypsum, the change in Ca^{2+} concentration must be *exactly* equal to the sum of the changes of SO_4^{2-} and *TIC*. Analysis inaccuracies must be polished away, otherwise these programs print out “no model could be found”. PHREEQC adds another capability to mass balance modelling by allowing for analysis inaccuracies. PHREEQC thus will find a “solution” for any mass balance problem, provided that the uncertainty for a parameter is stated to be large enough to allow for adaptation of concentration differences to the reactions.

Mass balance models have been applied to a wide range of problems: to spring water quality that is the result of weathering in granite area (Garrels and Mackenzie, 1967), to evaporating lakes (examples in Plummer *et al.*, 1994), and to reactions along flowlines in aquifers, especially for finding the extent of dedolomitization as result of dissolution of gypsum (Plummer *et al.*, 1990), carbonate reactions and C isotope evolution (Plummer *et al.*, 1990, 1994; McMahon and Chapelle, 1991).

Several aspects of mass balance models require attention. One is that the models do not consider thermodynamic constraints on mass balance calculations. The user must check that the saturation state of the water is in agreement with the calculated dissolution or precipitation reaction. For example, that plagioclase is not precipitating while the solution is subsaturated. Or, that calcite is not dissolving while the water is supersaturated. Another aspect of the mass balance models is that they assume that steady state exists; water samples along a flow path are usually taken at the same time and differences in water chemistry are assumed to be solely due to reactions with minerals and not to temporal variations in the composition of water entering the system.

Still another aspect of these type of models is that they give the *net* extent of the reactions between two points, and assume a homogeneous reaction between the points of analysis. No provision is made for reaction inversion, meaning that α_r is negative in part of the flowline, and positive in other part(s). This option is not hypothetical. Soils may contain a weathering profile with a sequence of different minerals in different horizons. In the upper horizons the primary minerals of the rock may have dissolved completely, and only secondary minerals remain as weathering residues. These dissolve in downward percolating soil water. In the lower soil horizons the rock minerals continue weathering, and again secondary minerals are formed which possibly have dissolved in upper horizons. Water sampled in a spring will thus have passed a stage of dissolution of secondary minerals, and another stage where the same minerals precipitated (or formed) while primary minerals dissolved (weathered). Also for carbonate reactions in freshening aquifers, a sequence of dissolution and precipitation stages may take place. Initially, calcite will dissolve in soil water. When salt water is flushed downstream in the aquifer, proton exchange occurs, which leads to supersaturation with respect to calcite. On the other hand, other parts of the same flowline may again show dissolution of calcite in the aquifer due to cation exchange.

14.1.2 Hydrogeochemical transport models

Hydrogeochemical transport models solve the advection-reaction-dispersion (ARD) equation. For one dimension the equation is:

$$\frac{C}{t} = -v\frac{C}{x} - \frac{q}{t} + D\frac{{}^{2}C}{x^{2}}$$

where the left hand side gives the change in concentration with time at a given position, while the three components of the right hand side contain the terms advection, reaction and dispersion respectively. C is the concentration in solution (mol L^{-1}), q the concentration in the solid also expressed as porewater concentration (mol L^{-1}), v is the porewater flow velocity (m s^{-1}), D is the dispersion coefficient (m^2 s^{-1}), and t and x are time (s) and distance (m), respectively. Classically, the equation is solved for three dimensions and for relatively simple reactions (MODFLOW, MOC and MICROFEM are popular programs with modules for reaction calculations), or in one dimension and for more complicated reactions (PHREEQM). In recent years a great progress is being made in incorporating the full spectre of hydrogeochemical reactions in 2 and 3D simulations (Yeh and Tripathi, 1989; Walter *et al.*, 1992; Engesgaard and Traberg, 1996; Wunderly *et al.*, 1996).

The results of forward modelling depend completely on the appropriateness of the reactions which are included in the model. The first models had ion exchange as sole reaction (Valocchi *et al.*, 1981), then calcite dissolution and precipitation was incorporated as an equilibrium reaction (Schulz and Reardon, 1983; Appelo and Willemsen, 1987), and subsequently other, more complicated reactions were included as the models evolved and computers were made faster (Appelo and Postma, 1993; Parkhurst, 1995; Wunderly *et al.*, 1996). The most recent advances are inclusion of surface complexation, which is essential for modelling of trace metal behavior, and of kinetics in a completely free, user definable manner (Parkhurst and Appelo, 1997).

14.2 Application to the East Midlands aquifer

14.2.1 Introduction

The possibilities of using inverse geochemical modelling with PHREEQC to interpret the evolution of some aspects of the groundwater chemistry of the East Midlands aquifer are tested.

The geochemistry of the East Midlands aquifer is described in (Edmunds and Smedley, in press; Edmunds *et al.*, 1982, Bath *et al.*, 1987). The aquifer is confined and may be considered as one single hydraulic unit. The natural flow gradients are from the south-west to the north-east. The sandstones range from coarse to very fine, but mostly are of medium grain-size and moderately sorted. Quartz and K-feldspar are the dominant detrital minerals, but plagioclase, muscovite, biotite and lithic clasts may also be present (Bath *et al.*, 1987). Late alterations of the detrital K-feldspar to illite-chlorite is commonly observed, especially in core material from the deeper part of the aquifer and dedolomitization has taken place since deposition by successive groundwater fluxes. These secondary calcites, in turn, may then have reacted near outcrop leading to decalcification of the sandstones. The groundwater chemistry tends to be strongly influenced by the presence of the trace quantities of these two carbonates (Edmunds *et al.*, 1982, Bath *et al.*, 1987) Textural evidence is also found for the former presence of anhydrite within the sandstone, largely removed as a result of successive fluxes of groundwater.

Modelling is carried out along flowlines. Initially it was checked if the inverse model was able to reach a solution. Earlier modelling with NETPATH already indicated that variation in climatic and anthropogenic influences at different times throughout the recharge history of the aquifer would have resulted in different input compositions and thus render the waters down the hydraulic gradient not strictly evolutionary. This reduces the reliability of the inverse model and can lead to the absence of any solution. In a second step the influence of ion exchange and feldspar dissolution processes on the capability of reaching a solution with the inverse model was evaluated. Due to the large amount of dissolution/precipitation processes involved, it was not possible to formulate the problem in such a way that a unique solution could be found. Therefore in the third step the amount of solutions was reduced by incorporating thermodynamic constraints. The acceptable solutions are discussed.

14.2.2 PHREEQC inverse geochemical modelling

Inverse modelling attempts to account for the chemical changes that occur as a water evolves along a flow path. Assuming two water analyses represent start and ending water compositions along a flow path, inverse modelling is used to calculate the moles of minerals and gases that must enter or leave the solution to account for differences in composition. PHREEQC allows uncertainties in the analytical data to be defined, such that inverse models are constrained to satisfy mole balances for each element and valence state and charge balance for the solution, but only within the specified uncertainties. In PHREEQC 2.0 isotope balance, but not isotope fractionation, can be included in the calculations (Parkhurst, 1995).

14.2.3 Description of the modelled problem

Inverse modelling is carried out along a flowline. The chemical processes determining the evolution of the groundwater chemistry are estimated. Therefore precipitation or dissolution of selected minerals is allowed to take place. The following minerals were included; their selection is based on the mineralogy of the aquifer described in Edmunds *et al.* (1982), Bath *et al.* (1987) and Edmunds and Smedley (in press):

- Quartz (as the main mineral);
- minerals of the carbonate system: Calcite, Dolomite, $CO_2(g)$;
- Gypsum;
- feldspars: Albite, Anorthite and also K-mica replacing a representative of the K-feldspars;
- Illite and Chlorite;
- ion exchange system: NaX – CaX_2.

A strong constraint to the inverse solution of the model was the ^{13}C-balance. The amount that the ^{13}C in the samples increased or decreased with the amount added or withdrawn caused by the dissolution or precipitation of calcite, dolomite and CO_2, should balance. The ^{13}C-content of dolomite is −2‰, for calcite −7.0‰ (Edmunds and Smedley, in press) with an assumed uncertainty of respectively 1.0‰ and 0.5‰. For $CO_2(g)$ in a confined section of the aquifer a value of −16.0‰ was calculated (Bath *et al.*, 1979) with an acceptable uncertainty of 2.0‰. The modelled solutions should involve a minimal amount of phases.

The evolution of the groundwater quality along three flowlines (Fig. 14.1) is modelled.

- Flowpath 1: sampling points Ordsall 1 – Hayton 1 – Peartree. Ordsall 1 is modern water, Hayton 1 is pre-industrial (Holocene) water and Peartree is catalogued as late Pleistocene water.
- Flowpath 2: sampling points Markham Clinton 1 – Rampton – Cottam. Markham Clinton 1 is pre-industrial water while both Rampton and Cottam are late Pleistocene water.
- Flowpath 3: sampling points Markham Clinton 1 – Grove 2 – Gainsborough 2. Markham Clinton 1 and Grove 2 being pre-industrial (Holocene) water and Gainsborough 2 being late Pleistocene water.

The composition of the groundwater samples is shown in Table 14.1. An uncertainty of 0.05 (5%) was defined, except for potassium and the alkalinity where respective uncertainties of 0.15 and 0.5 were assumed.

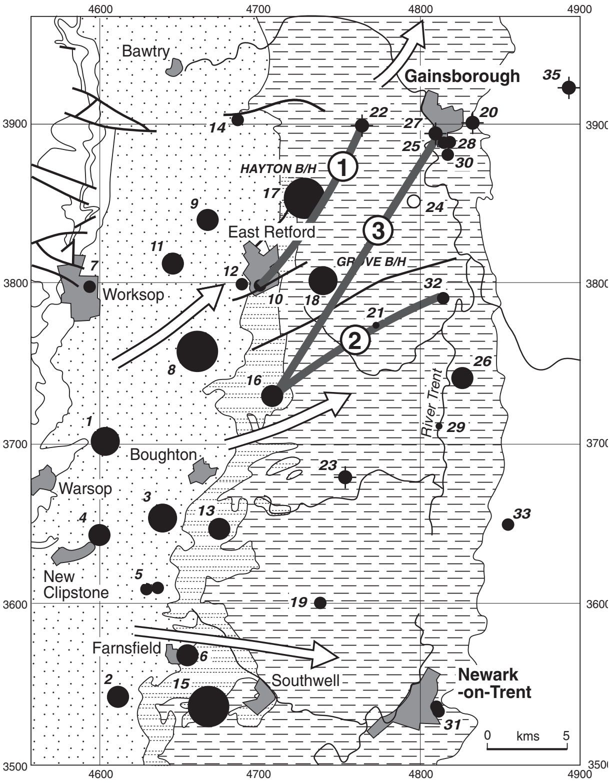


Figure 14.1. Location of the flowpaths and the sampling points for the PHREEQC-inverse modelling.

For the initial part of each flow path it is assumed that $CO_2(g)$ is available and dissolution of $CO_2(g)$ is possible during the inverse calculation. This was the case for the inverse pairs Ordsall 1 – Hayton, Markham Clinton 1 – Rampton and Markham Clinton 1 – Grove 2. For the modelled couples further down the flowpath no $CO_2(g)$ was available.

14.2.4 Results

The ability of the model to produce solutions is tested (Table 14.2). It is assumed that finding no solutions for the posed problem would be caused by the fact that the

Table 14.1. Geochemical data input for the PHREEQC-model.

	T	pH	Eh	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}	Cl^-	Si	^{13}C
	°C		mV	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	‰
Ordsall 1	10.9	7.87	266	47.9	19.5	10	2.7	143	38.8	35.4	3.4	−11.7
Hayton	11.9	7.74	396	41.5	36.1	6.4	9.0	219	90.3	6.1	3.3	−12.4
Peartree	14.3	7.72	39	53.6	20.7	9.4	5.1	195	74.5	9.7	3.4	−9.9
Markham Clinton 1	11.8	8.23	416	16.8	23.8	4.2	4.4	169	7.6	7.8	3.4	−11.6
Rampton	14.1	7.82	101	37.2	21.2	8.9	4.4	173	55.5	7.0	3.5	−8.8
Cottam	17.9	7.66	96	50.1	27.0	11.5	4.6	190	89.2	10.4	4.0	−10.8
Grove 2	13.3	7.89	104	27.1	28.0	5.4	7.1	215	22.7	6.3	3.3	−11.8
Gainsborough 2	17.4	7.48	164	85.3	34.3	18.5	5.4	199	201	24.9	4.3	−10.4

Isotope balance

^{13}C calcite: −7.0‰ (± 0.5‰); ^{13}C dolomite: −2.0‰ (± 1.0‰); ^{13}C CO_2: −16.0‰ (± 2.0‰)

Table 14.2. Amount of solutions for the modelled inverse couples.

	Amount of solution		
	Total	**Excl. feldspar dissolution**	**Excl. ion-exchange**
Flowpath 1			
Ordsall 1- Hayton	51	0	14
Hayton- Peartree	22	0	15
Flowpath 2			
Markham Clinton 1 – Rampton	10	0	3
Rampton– Cottam	0	0	0
Flowpath 3			
Markham Clinton 1 – Grove 2	12	0	9
Grove 2 – Gainsborough 2	18	0	11

flow line conditions are not met, that mixing of water in depth occurred or that the water types are not evolutionary.

The model was not able to reach a solution for the Rampton – Cottam couple while also for the Markham Clinton 1 – Rampton couple few solutions were found. For flowpath 1 an important amount of solutions were found for both couples.

For the evaluation of the importance of feldspar dissolution and ion exchange both processes are consecutively taken out of the model. If feldspar dissolution is not allowed to take place none of the inverse couples reaches a solution. This indicates that feldspar dissolution is an important part of the geochemical processes along these flowpaths. Eliminating ion exchange on the other hand still allows the model to reach solutions.

The PHREEQC-model does not include thermodynamic constraints on the mass balance equations. Some of the solutions include mineral dissolution or precipitation, which are highly unlikely in the given circumstances. These solutions should be excluded. To reduce the amount of solutions the following thermodynamic constraints were taken into account:

- solutions including precipitation of Albite or Anorthite are excluded since the conditions for stability in the aquifer conditions are not likely to be met;
- ion exchange was only allowed if Ca^{2+} was replacing Na^+; the access of Ca^{2+} in the solution makes it a reasonable constraint.

For two inverse couples two (nearly identical) solutions were restrained, for another two inverse couples one solution was acceptable. For the couple Markham Clinton 1 – Cottam there was no solution.

The resulting solutions are shown in Figs. 14.2 (a) and (b).

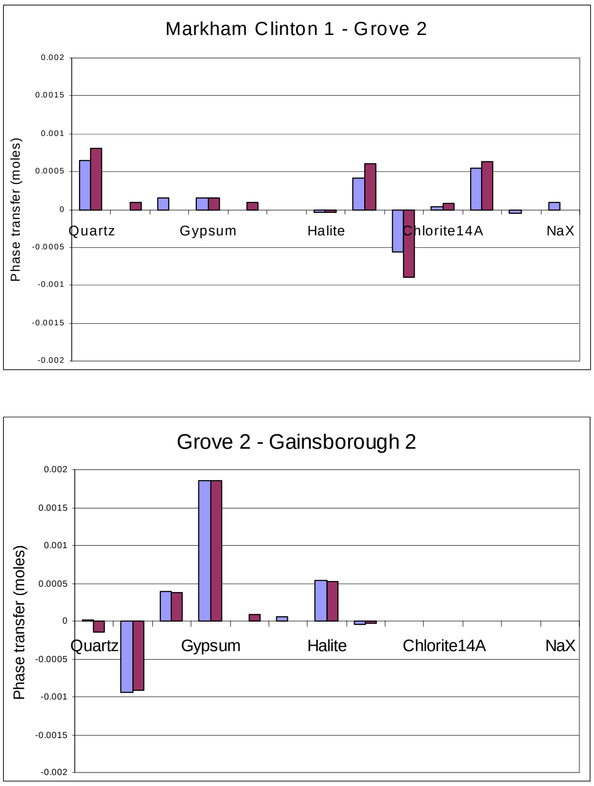


Figure 14.2 (**a**). Solution of the PHREEQC-model along flowpath 1 . Upper: inverse couple Ordsall 1 – Hayton. Lower: inverse couple Hayton – Peartree. (**b**). Solution of the PHREEQC-model along flowpath 3. Upper: inverse couple Markham Clinton 1 – Grove 2. Lower: inverse couple Grove 2 – Gainsborough 2

14.2.5 Discussion

Since for flowpath 2 no solutions are found, flowpath 2 is excluded and the discussion is restricted to the inverse couples of flowpath 1 and 3.

The *carbonate system* is in both flowpaths (1 and 3) dominated by the dissolution of dolomite. Initially in both flowpaths CO_2 dissolves, but further down along the flowpath CO_2 is not involved or precipitates. When *dissolution of gypsum* is quantitatively important access Ca^{2+} forces calcite to precipitate. This is very obvious for the couple Grove 2 – Gainsborough 2 where dissolution of gypsum seems to be the dominating process.

Three out of four inverse couples indicate *quartz* dissolving in important quantities. Since quartz has extremely sluggish reaction kinetics it is unlikely that it is able to control dissolved silica concentrations. The source of silica in these cases might be caused by the dissolution of less stable forms of SiO_2 such as chalcedony or amorphous quartz, or it might be caused by supersaturation.

Ion exchange is in none of the four inverse couples modelled. It can be concluded that this process, if occurring at all, is likely to be of minor importance along these flowpaths. Even when ion exchange is eliminated during the modelling, several solutions for each inverse couple are found. This was also indicated by the lack of solutions when only ion exchange was allowed and feldspar dissolution was eliminated.

Feldspar dissolution and precipitation of illite is one of the main processes occurring in three out of four cases. In both flowpaths dissolution of K-mica (which replaces a representative of the K-feldspars) is initially dominating, while smaller amounts of albite/anorthite are dissolving along the whole of the flowpaths. Evidence for the ongoing feldspar dissolution and precipitation of illite was found in cores from the Gamston borehole drilled near the confined/unconfined boundary. SEM photographs clearly indicate the overgrowth of illite-smectite over K-feldspar (Fig. 14.3(a), in Fig. 14.3(b) the altering of biotite to illite is also illustrated. The precipitation of halite between Ordsall 1 and Hayton is not realistic and probably a

Figure 14.3. SEM photographs of sample of the Sherwood sandstone taken from Gamston borehole: (**a**)biotite altering to illite (**b**) illite smectite overgrowth on quartz and K-feldspar.

consequence of the *Cl- contamination* in recently infiltrated groundwater occurring at Ordsall 1.

In conclusion the modelled examples are inevitably far from representative for the geochemistry of the aquifer. Major shortcomings are:

- the results from each simulation only relate to two samples, and not to the aquifer as a whole;
- not all minerals are included in the inverse model, only the interaction with defined minerals and processes can be modelled;
- thermodynamic as well as kinetic constraints are not modelled.

However, the inverse modelling makes a mass balance of the reactions in the aquifer possible and increases insight in the occurring processes. The conclusions from the four inverse couples along 2 flowpaths are:

- the geochemistry of the carbonate system dominated by the dissolution of dolomite, and precipitation of calcite in the case of important dissolution of gypsum, as described earlier is confirmed;
- feldspar dissolution was found as an important processes determining the geochemistry;
- in none of the modelled cases ion exchange was involved.

The dissolution of feldspars leading to the precipitation of illite is confirmed by SEM photographs of core samples from the aquifer. Kaolinite, also observed as a major secondary phase, is not included in the model runs. Further evidence from this aquifer is given in Chapters 5, 11 and 12.

14.3 Application to the Ledo-Panisleian aquifer

14.3.1 Forward modelling with PHREEQM

The geochemical/mixing cell model PHREEQM (Appelo & Postma, 1993) has been used to simulate the freshening of the Bartonian clay and the subsequent recharge to the underlying aquifer (Walraevens & Cardenal, in press). A flow line has been selected, starting from the top of the Bartonian clay in the westerly recharge area at Ursel, and directed towards the NNE within the aquifer. Model results have been compared with groundwater quality observations of the aquifer. The modelling has allowed it to be shown that the present groundwater quality distribution in the Ledo-Paniselian aquifer mainly corresponds to cation exchange processes in the overlying Bartonian clay and, to a smaller extent, also within the aquifer. Other effects that have been considered in the model as well, are related with the oxidizing conditions prevailing in the clay, responsible for the observed presence of gypsum, and the reducing conditions in the aquifer, causing sulphate reduction. Calcite precipitation/dissolution processes have also been considered.

Groundwater flow conditions in the Bartonian clay largely differ from those in the Ledo-Paniselian aquifer, with respect to in flow velocity and length of flow path (comparing the thickness of the clay, in the order of tens of metres, to the length of the flow path within the aquifer, which is tens of kilometres). Therefore, the modelling was divided in two parts. First, the freshening of the clay was simulated in a vertical column; subsequently, the different watertypes leaking out of the Bartonian clay were flushed through a horizontal column of the Ledo-Paniselian aquifer, simulating the subhorizontal flow in it.

An overview of the model boundaries is given in Table 14.3. For both clay and aquifer, the initial pore water quality was sea water, equilibrated with calcite and 0.75 mmol kg^{-1} H_2O of NH_4^+ production. This solution was also equilibrated with the exchange complex in the clay and in the sandy aquifer, respectively. For recharge, pure water equilibrated with calcite and a P_{CO2} of $10^{-2.0}$ atm, was used. The flow velocities were deduced from the flow model. The cation exchange parameters were computed from observations of CEC and adsorbed cations, on samples of a cored boring in the recharge area of Ursel.

The evolution of the distribution of exchangeable cations adsorbed to the Bartonian clay, and of the composition of the porewater leaking out of it during the flushing, are shown in Fig 14.4. After the clay has been flushed 100 times, the distribution on the clay's adsorption complex is similar to the one found in the boring at Ursel. At that moment, the pore water solution leaving the clay contains Mg^{2+} and Ca^{2+} as main cations, with no significant Na^+ content. This water is strongly different from the one found at present in the Ledo-Paniselian aquifer in the recharge area of Ursel, in which Mg^{2+} is almost absent. The clay must be flushed near 400 times to obtain this observed watertype. This indicates the existence of preferential pathways in the Bartonian clay, through which flow is faster. The flow line in the analyzed boring must be part of a slower pathway, where the freshening is still in progress.

Hydraulic and hydrochemical conditions for modelling the freshening of the Bartonian clay and Ledo-Paniselian aquifer

Infiltration water

Ca^{2+} = 2.1 mM L^{-1}
HCO_3^- = 4.17 meq L^{-1}
pH = 7.3156
$\log P_{CO2}$ = -2.00

Initial pore water (sea water equilibrated with calcite and 0.75 mM NH_4^+ production):

Ca^{2+} = 9.8 K^+ = 10.6 Cl^- = 566 (mM)
Mg^{2+} = 55.1 SO_4^{2-} = 29.3 NH_4^+ = 0.75
Na^+ = 486 HCO_3^- = 1.6   pH = 7.86

BARTONIAN CLAY

- Column length: 20 m
- Number of cells: 4 (5 m each one)
- Flow velocity: 0.12 m a^{-1}
- Time step: 41.7 years
- Dispersivity: 1.5 m
- Diffusion coef.: 10^{-9} m^2 s^{-1}
- Cation Exchange Capacity: 27 meq/100 g
- Gypsum dissolution: 0.45 mM/cell
- Calcite equilibrium

Exchange parameters (calc from Walraevens, 1987)

$\log K_{NaX}$ = 20.0 (reference value)
$\log K_{KX}$ = 20.5768
$\log K_{CaX2}$ = 41.1727
$\log K_{MgX2}$ = 40.8810
$\log K_{NH4X}$ = 20.6 (Appelo & Postma, 1993)
$\log K_{HX}$ = 22.5 (C.A.J. Appelo, pers. comm.)

LEDO-PANISELIAN AQUIFER

- Column length: 20 km
- Number of cells: 20 (1 km each one)
- Flow velocity: 3.35 m a^{-1}
- Time step: 299 years
- Dispersivity: 1500 m
- Cation Exchange Capacity: 5.5 meq/100 g
- SO_4^{2-} reduction: 1.7 mM/cell in first 4 cells
- Calcite equilibrium

Exchange parameters (Std coefficients in PHREEQM)

$\log K_{NaX}$ = 20.0
$\log K_{CaX2}$ = 40.8
$\log K_{MgX2}$ = 40.6
$\log K_{NH4X}$ = 20.6
$\log K_{HX}$ = 22.5

Table 14.3. Model boundaries of Bartonian clay and Ledo-Paniselian aquifer

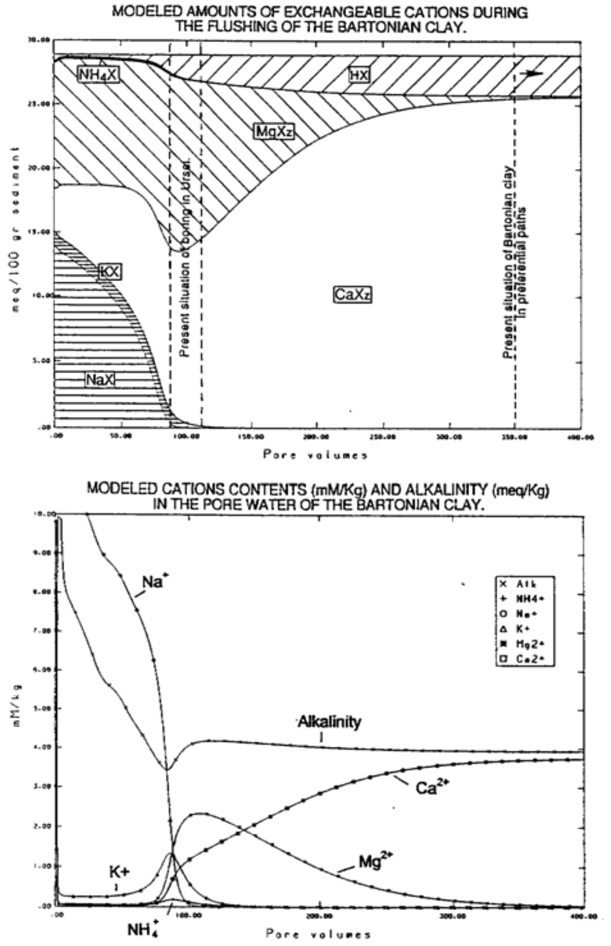


Figure 14.4 Evolution of exchangeable cation distribution and the composition of the porewater leaking out of the Bartonian clay during flushing

When the different solutions leaking out from the Bartonian clay, after flushing it 100 times, are used to flush the Ledo-Paniselian aquifer, the modelled groundwater quality distribution in the aquifer does not correspond at all to the observations. The clay must be flushed near 400 times to obtain the present distribution in the aquifer (Fig. 14.5). This is again confirming the previous conclusion. The deviation between model results and observations, which can be noticed in Fig 14.5 for the most northerly part of the aquifer (most downstream 5 km), is resulting from the lower velocities in the deeper parts of the aquifer, which are not accounted for in the modelling results presented here.

14.3.2 Inverse modelling with PHREEQC

It is crucial for inverse chemical modelling and subsequent radiocarbon dating of groundwaters to correctly assess dissolved total inorganic carbon (TIC) and $\delta^{13}C$ in the water at the time of infiltration. The climatic conditions during the late Pleistocene have varied significantly, giving rise to a large possible range of soil carbon dioxide pressures and $\delta^{13}C$ values of soil CO_2 gas. This concomittant variability of soil CO_2 pressure and $\delta^{13}C$ has, to the best of our knowledge, never been taken into account in radiocarbon dating of groundwater.

Based on previous work by Cerling (1984), Cerling *et al.* (1991) and Hesterberg & Siegenthaler (1991), it can be shown that $\delta^{13}C$ of soil CO_2 can be written as:

$$ {}^{13}\mathrm{C}_{\mathrm{soil}} \quad \frac{c_{\mathrm{atm}}\left(\; {}^{13}\mathrm{C}_{\mathrm{atm}} \quad 1\right) \quad {}_{D}\left(c_{\mathrm{soil}} \quad c_{\mathrm{atm}}\right)\left(\; {}^{13}\mathrm{C}_{\mathrm{p}} \quad 1\right)}{c_{\mathrm{soil}}} $$

where *c* is CO_2 concentration in ppmV, α_D diffusive fractionation factor (1.0044) and the subscripts atm and p refer to atmospheric and produced CO_2. The influence of the variability of $\delta^{13}C$ of soil CO_2 on recharge TIC, for various calcite dissolution regimes, is shown in Fig 14.15. Details about derivations and modelling, which are not described here, can be found in van der Kemp *et al.* (1998).

14.3.3 Method

Inverse chemical models were calculated for 14 water sample analyses (Walraevens, 1987, 1990) from the Ledo-Paniselian aquifer, with the computer code PHREEQC (Parkhurst & Appelo, 1998). Sample point locations are shown in Fig 14.7. Three different evolution scenarios for chemical and isotopic evolution of recharge TIC were taken into account: chemically and isotopically open system dissolution of calcite (co,io), chemically open but isotopically closed system dissolution of calcite (co,ic) and chemically closed system dissolution of calcite (cc), see Fig 14.6. Phases and constraints, used in the modelling, are shown in Table 14.2. A water sample is considered to be a mixture of infiltration water (0.1% seawater) and an old seawater component plus the result of a number of chemical reactions that occurred in the subsurface. Inverse chemical modelling reveals the mixing fraction between fresh recharge water and seawater together with the mole transfers for the various chemical reactions. Each model found, is accompanied by a statistical criterion (sum of residuals) which gives an indication about the feasibility of the model. By varying the soil CO_2 pressure of the infiltration water, the models and the sum of residuals change. Hence, the best model (with the lowest sum of residuals) can be found. Sulphate reduction was only considered for the old seawater component. Frequently low sea levels during the Pleistocene make sulphate reduction in the younger waters (affected by pyrite oxidation in Bartonian clay in the recharge area) not very likely, because of frequent aeration of a large part of the aquifer.

An example of how the sum of residuals changes with the logarithm of soil CO_2 pressure of the infiltration water is shown in Fig 14.8, for sample 31. These calculations were done for all samples and the best CO_2 pressures (lowest sum of residuals) are plotted as a function of $\delta^{18}O$ of the water (corrected for seawater content with $\delta^{18}O$ = 0‰) in Fig 14.9. Despite the scatter, higher CO_2 pressures clearly correlate with less negative $\delta^{18}O$, implying warmer conditions. Relative cation exchange reactions for the various water samples, in order of magnesium exchange, is depicted in Fig 14.10. Older samples (less flushing), show magnesium uptake whereas the younger samples (more flushing) show release of magnesium from exchanger sites. Proton exchange plays an important role in most of the models. Large uptake of protons by exchanger sites is seen in models of younger samples, as a result of vigorous pyrite oxidation in the recharge area. Models of older samples show release of protons by exchanger sites, due

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Figure 14.5 Comparison of observed concentrations of main cations in Ledo-Paniselian aquifer, to modelled concentrations after flushing Bartonian clay 400 times

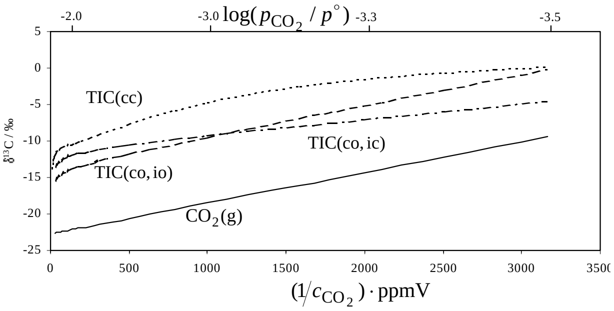

Figure 14.6. Influence of soil CO_2 concentration on $\delta^{13}C$ of soil CO_2 and TIC. Chemically open system dissolution of calcite and isotopic equilibrium with soil CO_2:(co,io); Chemically open system dissolution of calcite, no isotopic exchange with soil CO_2 (co,ic); chemically closed system dissolution of calcite (cc). $\delta^{13}C_p = -27‰$. TIC in the fully open system is 9.5‰ heavier (at 11°C) than soil gas when CO_2 pressure is smaller than 0.01 atm, due to fractionation in the HCO_3^- species. At higher CO_2 pressure the $H_2CO_3^*$ species contributes increasingly to TIC, and $\delta^{13}C$ of TIC becomes lighter. In the isotopic closed sytem, TIC originates half from soil CO_2 and half from calcite, with (for figure 1) $\delta^{13}C = 1.67‰$. $\delta^{13}C$ of TIC is therefore the average of the two contributions, while at higher CO_2 pressure the larger contribution of H_2CO_3 lightens TIC again. Lastly, in the chemical and isotopic closed system, the $\delta^{13}C$ of TIC is *grosso modo* the average of the isotopic open curve and of calcite, with again some rounding due to increased importance of the $H_2CO_3^*$ species at higher initial CO_2 pressure.

to calcite dissolution driven by cation exchange reactions, see Appelo (1994).

Radiocarbon ages as calculated from chemical open system dissolution of calcite during infiltration are shown in Fig 14.11. The maximum ages correspond to full isotopic exchange of recharge TIC with soil CO_2, while minimum ages are without isotopic exchange with soil CO_2. Minimum ages were calculated with +0.8 pmc error on the ^{14}C analyses, maximum ages with −0.8 pmc. Ages derived from chemically closed system dissolution, which are not shown here, are comparable to those obtained in the chemical open case without isotopic exchange.

14.4 Application to the Aveiro Cretaceous aquifer

For this aquifer the calculations use the geochemical mole-balance model, PHREEQC-2 (Parkhurst and Appelo, 1999) to evaluate the geochemical evolution of a water sample in the Aveiro Cretaceous aquifer. This model incorporates uncertainties in mole-balance modelling to evaluate geochemical reactions in the aquifer.

The natural hydrogeochemical evolution in the aquifer trends from calcium bicarbonate waters with low pH (~5.5) and temperature around 18°C in the unconfined part of the aquifer to sodium bicarbonate or sodium chloride waters in the areas close to the coast, with pH in the range from 7.5 to 8.5 and temperature higher than 21°C. These groundwaters have their origin in part associated with the infiltration of rainwater of Atlantic origin and the flushing of older sea water.

The conceptual model for the geochemical evolution of the water in the aquifer is that calcium bicarbonate water originated from rain water infiltration and dissolution of soil CO_2 recharges the aquifer. This water flows along the flow path reacting very slowly in a closed system with the carbonate and silicate minerals and mixing with old sea water trapped in the clay minerals, evolving to a sodium bicarbonate type water in the areas close to the coast.

According to this conceptual model it was selected one initial water was selected, considered to be representa-

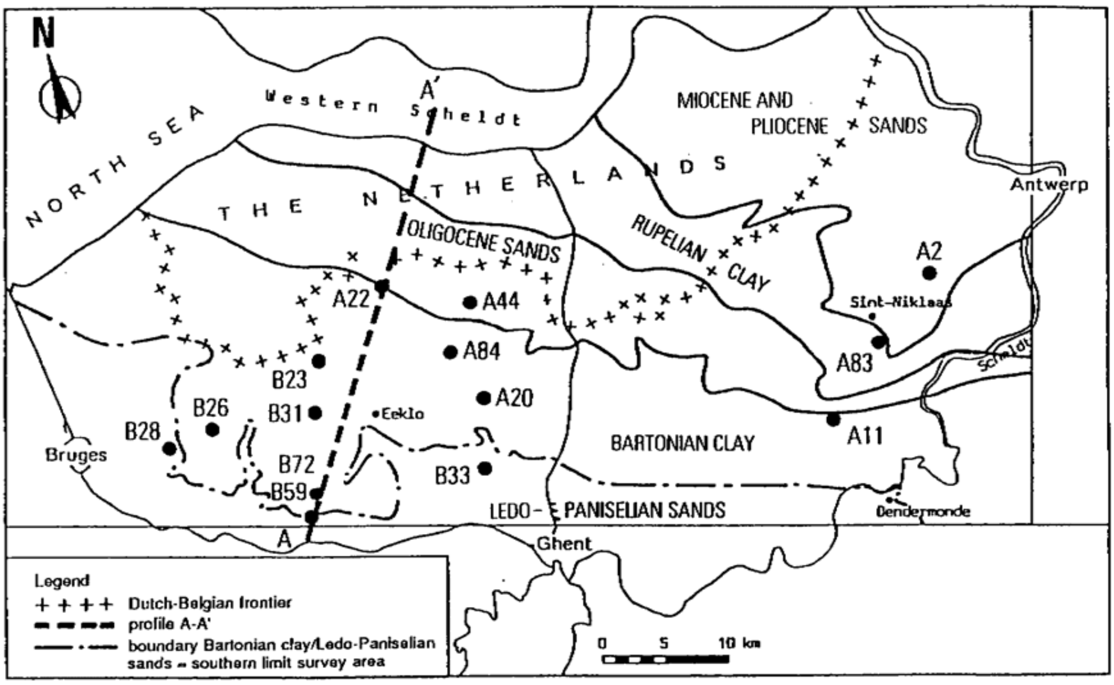

Figure 14.7. Sample point locations.

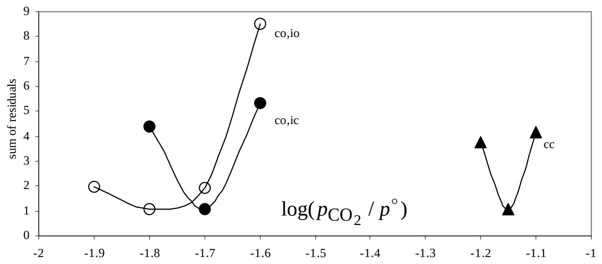

Figure 14.8. Sum of residuals as a function of log p_{CO2} of the infiltration water (water sample 31) for the three types of TIC evolution at infiltration.

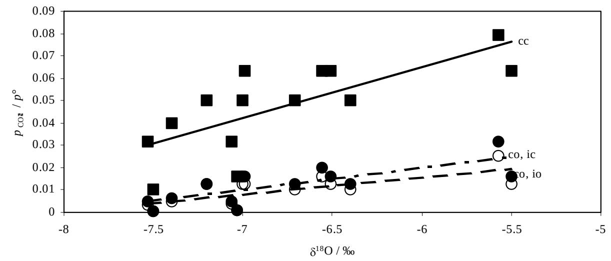

Figure 14.9. Soil CO_2 pressure at infiltration derived from inverse chemical modelling (3 types of calcite / soil CO_2 equilibria) as a function of $\delta^{18}O$ of the water, corrected for seawater content with $\delta^{18}O$ = 0‰.

Table 14.2 Mineral phases, exchange species and constraints used in the modelling.
(+) enters the solution, (-) leaves the solution.

phases:	calcite (+), goethite, pyrite, $(FeS_2)_4(O_2)_{15}(H_2O)_2$ (+), $(CH_2O)_{106}(NH_3)_{16}$ (+)
exchange species:	CaX_2, MgX_2, NaX, KX, NH_4X, and HX
constraints:	Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, Fe_T, SO_4^{2-}, S^{2-}, Cl^-, TIC, alk
^{13}C	seawater 1.5 ± 0.1‰, infiltration water see Fig 14.15, watersamples (Walraevens, 1987), calcite 1.67 ± 0.5‰, organic matter −25 ± 2‰

tive of the local recharge water (solution 1) and sea water was considered as an intermediate term (solution 2). Sea water in this case is used as a source of chloride and sodium. This way there is no need to force halite dissolution in the aquifer to account for the increase in chloride concentration along the flow path.

A Na-Cl water from a deep borehole on the coast was considered as the final term (solution 3) of the chemical evolution of the initial water sample along the flow path. All the major and minor element data for solutions 1 and 3 are from Condesso de Melo *et al.* (1998, 1999), while the isotopic data for the same solutions are from Carreira (1999). Data for averaged sea water composition are from Appelo and Postma (1996). All the chemical data used for solutions 1, 2 and 3 are summarized in Table 14.5.

Mineralogical studies by Rocha (1993) show that the principal mineral assemblage (<38 mm) in the aquifer is calcite, dolomite, K-feldspar and plagioclase. Gypsum, anhydrite, jarosite, melanterite, pyrite and goethite might occur as accessory minerals. Kaolinite, smectite and illite are the most abundant clay minerals. Cation exchange determinations by Oliveira (1997) showed the importance of cation exchange processes in the chemical evolution of the aquifer.

Detailed hydrochemical studies by Condesso de Melo *et al.* (1998, 1999) indicated an aquifer with very slow chemical kinetics for the water-rock interactions resulting

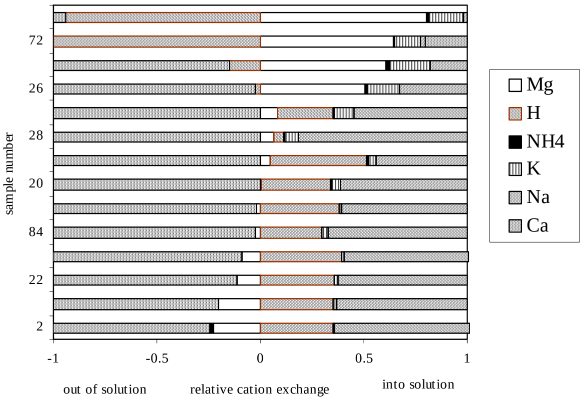

Figure 14.10. Relative cation exchange reactions derived from inverse chemical modelling. (co, io) case.

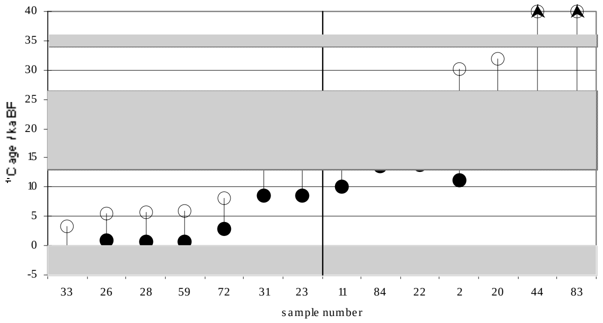

Figure 14.11. Maximum and minimum ^{14}C ages of the different samples co,io and co,ic approximations respectively. An error of ±0.8 pmc was taken into account on the ^{14}C analyses. Shaded areas are impossible or unlikely timespans for substantial infiltration.

Table 14.5. Chemical data for solutions 1, 2 and 3 in the Aveiro Cretaceous aquifer (mg L^{-1} unless otherwise shown).

	Solution 1	**Solution 2**	**Solution 3**
	AC9 S. M. Aveiro	**Seawater**	**AC4 S.M. Ílhavo**
pH	6.82	8.22	8.18
T (ºC)	18.4	16.0	23.7
Na	0.72	485.0	10.92
K	0.15	10.6	0.25
Ca	0.48	10.7	0.07
Mg	0.23	55.1	0.09
Si	0.22	0.002	0.17
Al	1.7×10^{-4}	3.7×10^{-5}	1.9×10^{-4}
HCO_3	1.40	2.4	3.93
Cl	0.67	566.0	5.92
SO_4	0.15	29.3	0.87
$\delta^{13}C$ (‰)	−14.75±0.1	0.00±0.01	−9.87±0.1
^{14}C (pmc)	43.60±0.4	-	0.90±0.3

Table 14.6. Species and dissolution constraints for each reactant in the Aveiro Cretaceous aquifer.

Reactants:	Chemical Formula:	Constraint:
Calcite	$CaCO_3$	Dissolve $\delta^{13}C$= 0.0±1.0
Dolomite	$CaMg(CO_3)_2$	Dissolve $\delta^{13}C$= -2.0±1.0
K-Feldspar	$KAlSi_3O_8$	Dissolve
SiO_2 (a)		-
Gypsum	$CaSO_4 \cdot 2H_2O$	-
Cation Exchange:		-
	NaX, KX, CaX_2, MgX_2, HX	-
Kaolinite	$Al_2Si_2O_5(OH)_4$	Precipitate
Illite	$K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$	Precipitate

Table 14.7. Mole balance results calculated with 5% uncertainty for chemical data.

	Mole transfer (mmol kg^{-1} H_2O)		
		Min.	**Max.**
Calcite	2.14	0.00	2.34
Dolomite	0.00	0.00	1.17
SiO_2(a)	–0.06	–0.12	–0.04
Gypsum	0.45	0.45	0.45
K-feldspar	0.24×10^{-4}	0.67×10^{-5}	0.03
NaX	5.81	5.47	6.14
KX	-	-	-
MgX_2	–0.65	–1.86	–0.60
CaX_2	–3.10	–3.32	–1.84
HX	1.68	1.20	1.96
Kaolinite	0.00	–0.01	0.00
Illite	0.00	–0.01	0.00

from the mainly siliciclastic composition of the aquifer sediments. Calcite dissolution and cation exchange are the other processes responsible for the groundwater chemical composition.

According to these previous studies a set of reactants was selected for the inverse modelling exercise. The chemical formulae for each reactant and the dissolution constraints are summarized in Table 14.6. While calcite, dolomite and K-feldspar were just allowed to dissolve, the clay minerals were forced to precipitate.

The uncertainty assigned for the chemical data is 5%, with the exception of alkalinity which was assigned an uncertainty of 100% due to possible errors of determination at the field site.

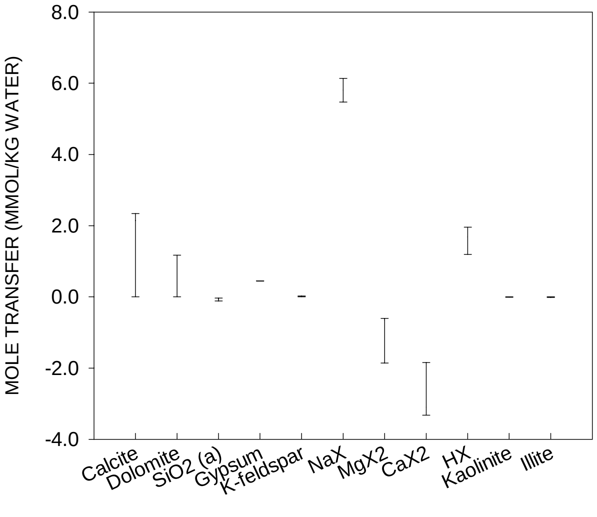

Figure 14.12. Mole transfer of reactant phases in the Aveiro Cretaceous aquifer with 5% uncertainty.

PHREEQC-2 inverse modelling results for the Aveiro Cretaceous aquifer suggest a final mixture of 99% of initial solution (recharge water) with 1% of seawater. In addition, the dominant reactions determined by mole-balance modelling are calcite and K-feldspar dissolution, silica precipitation, gypsum dissolution and cation exchange. According to the model dolomite dissolution, and kaolinite and illite precipitation might also occur.

Modelling results for cation exchange process confirm that sodium is being released into solution and replaced by magnesium and calcium in the clay minerals.

Feldspar dissolution is slowly releasing some aluminium and silica into solution but they will precipitate in silica minerals, kaolinite and illite. Calcite and dolomite dissolution are releasing calcium and magnesium into solution.

The mole transfer between the initial and final solution are summarized in Table 14.7. The maximum range of this mole transfer is plotted in Fig. 14.12.

Other models for the aquifer suggested very small differences in the mole balance. Inverse modelling in the Aveiro Cretaceous aquifer was a valuable way of confirming the principal processes that contribute to the geochemical evolution of the aquifer.

15 Investigation of aquifer and groundwater stratification

15.1 Introduction

The question of vertical stratification both in age and in quality was identified at the outset of the PALAEAUX project as an important topic requiring separate consideration. Not least, the conventional methods of sampling of groundwaters, from pumped boreholes inevitably lead to mixtures of waters and one of the objectives in the project was to minimize misinterpretations of the results. This chapter describes the application and interpretation of geophysical logging in boreholes to provide information for PALAEAUX project purposes. In particular the effects of vertical and lateral variation in lithology on the development of aquifers and the stratification of groundwater chemistry arising from geological layering are discussed. It also discusses groundwater flow systems and how their hydraulic interaction with the rock mass develops aquifer permeability through both current, (present day) and former groundwater circulations. It also shows how the borehole is an observation point in the aquifer flow system whose location, construction and hydraulics influence the chemical composition of water pumped, and where aquifer crossflow and wellbore fluid invasion of aquifer horizons can take place with implications for sampling waters from individual horizons. Geophysical formation and fluid logging techniques that can be used to examine aquifer and groundwater stratification and guide water sampling are discussed. Examples of aquifer layering, wellbore flow, permeability variation, and the influence of aquifer lithology and geological structure on groundwater movement and water sampling, are shown from a selection of PALAEAUX studies.

15.2 Palaeowater and aquifer layering

Palaeowater, has been defined earlier as water mainly >10 000 years old with a distinctive isotopic signature (see Chapter 1), It remains in certain aquifers where it has not totally flowed away or has been replaced by younger groundwater. It is therefore to be found in aquifers that are either large enough to accommodate groundwater flow system transit times in excess of about 10 000 years, or preserved in low permeability strata in smaller aquifers, or in permeable strata where 'trapped' by geological structure (e.g. synclines, closed basins, faulted contacts). This latter environment is a particularly useful ASR (aquifer storage and recovery) target. The palaeowater entered the ground as rainfall recharge >10 000 years ago. Intergranular groundwater flow in sandstone aquifers at depth may be of the order of 1 m a^{-1} hence aquifer systems >10 km in length could contain palaeowaters.

Rock layering is a fundamental geological property. It arises through normal crustal processes of sediment supply, transport and deposition. Generally the variation in lithology and rock properties is much greater in the vertical dimension than developed laterally. A sand body or a limestone, for example, is usually deposited thinly over a considerable area and will be succeeded by a different lithology. Furthermore the time scale represented in the vertical dimension is normally much greater than that represented horizontally along the layers, hence variations recorded in the vertical sequence are normally much greater than those observed laterally.

The layering (stratigraphy) controls subsequent water movement through the rock mass because groundwater will flow through the porous and permeable horizons rather than through the impermeable layers. This is normally through the pore space between grains (intergranular porosity) as in a sandstone, or it may be through the void volume of joints and fractures (fracture or secondary porosity) as in hard rocks such as e.g. limestones, granites, or it may be through a combination of the routes as in fractured sandstones and the Chalk. In addition water will move faster through higher permeability layers (e.g. coarse sandstones, fractured and fissured limestones) than through lower permeability layers (e.g. fine sandstones, siltstones, mudstones). The water movement through the particular layers develops the permeability of those routes through physical and chemical interaction. Hence the permeability distribution is controlled not only by the lithology and solubility of the rock and available openings but also by the groundwater circulation.

Water pumped from boreholes penetrating one or more aquifers represents a mixture of waters from the different layers at depth, each likely to have different circulation histories and transit times. The water pumped may for example be a mixture of modern recharged waters obtained from shallow depth and deeper circulating groundwaters that are older, and possibly palaeowaters. The actual chemical composition of the mix relates to the water composition of the individual layers penetrated, and their relative contribution to the borehole when pumped.

15.3 Groundwater flow systems

Groundwater circulating through the rock mass is part of the global water circulation between atmosphere, land and ocean which is the subsurface flow part of the hydrological cycle. Its movement is driven by gravitational and hydraulic forces. Hubbert (1940) and Toth (1962, 1963) showed all groundwater flow systems contain 3 elements: an intake or recharge region, usually at highest elevation, a throughflow or transfer zone at intermediate elevation, and a discharge or outlet region at lowest elevation. Within the rock mass the overall groundwater flow direction is determined by the distribution of the fluid potential which is normally related to the topography. Groundwater flows from upland topographic highs to lowland coastal regions, or beyond, where it may discharges, given suitable outlets. The groundwater movement within any rock type is influenced by this underlying regional hydraulic control, but local flow directions and circulation routes depend upon the hydrogeological properties of each layer and system geometry (i.e. lithology and geological structure).

If the topography is complex and hilly, several local flow systems will exist as part of the regional circulation,(Freeze and Witherspoon, 1967, Freeze and Cherry, 1979), and a water level elevation difference of only a few metres (well within the range of seasonal changes) can determine whether water enters a local or a regional circulation. Such flow systems are evident from study of contour maps of water level or piezometric surface. However these maps are two dimensional whereas in reality groundwater is flowing in three dimensions having a component of downward flow in recharge zones, horizontal flow in the throughflow zone and a component of upward flow in discharge areas.

15.4 Aquifer crossflow and vertical wellbore flow

Because of the hydraulic (elevation) control of groundwater movement, and the presence of different geological layers, usually dipping according to the structure, the hydraulic head of different layers varies from place to place and a hydraulic gradient often exists between different water-bearing layers at depth. As a result, vertical flow, both upward and downwards, tends to take place in the aquifer across low permeability strata to equilibrate the hydraulic head differences. The water movement from higher head layers to lower in the rock mass is termed *aquifer crossflow*. In porous rocks it takes place through pore space and the result is that low head pore fluids become replaced by fluids from higher potential layers. In fractured rocks the fluid movement follows fracture- and joint-openings. The invading water may have quite different chemistry.

When boreholes are drilled into the rock mass and interconnect different water-bearing layers having different hydraulic heads, water flows strongly in the borehole, upwards or downwards to equalize the hydraulic head differences. The movement can be rapid and substantial and is termed *wellbore flow*. Artesian boreholes are an obvious visible example of upward wellbore flow where it overflows the surface.

Most boreholes exhibit some wellbore flow that is not evident at the surface but is nevertheless taking place in the borehole and is evident when logged. Figure 15.1 is an example of upward wellbore flow from a Permian sandstone and breccia sequence in the Dumfries Basin, Scotland. There are 3 boreholes at the site penetrating the same units to a depth of 150 m. Borehole 1 is deeper than the other holes and penetrates an additional sandstone (Sandstone 1). The breccias have low intergranular hydraulic conductivity (1×10^{-6} cm s^{-1}) whilst the sandstones have much higher values up to 6.6×10^{-4} cm s^{-1}.

Gamma ray and resistivity logs resolved the layering shown, and identified the breccias by a higher gamma ray and lower resistivity on account of their high content of Palaeozoic mudstone, which was evidently exposed nearby at the time of deposition. Fluid temperature, fluid EC and flowmeter logs of the 3 boreholes are shown in the figure. Borehole 1 revealed upflow from 148 m depth with loss of flow into sandstone horizons at 128 m and 65 m. The heat-pulse flowmeter measurement (track 4) shows the upflow which is ~25 m^3 hr^{-1} (24 m min^{-1}) at 148 m. The pumped logs in Fig. 15.1 represent profiles of pumped fluid temperature (TEMPQ),pumped fluid EC (ECQ), and impellor flowmeter recorded whilst pumping in each borehole. The flowmeter log shows stepwise increases in velocity (flowrate) at the sandstone/breccia junctions and the biggest single contribution to the borehole (~40% of total pumped) is from 65 m depth. Although the pumped fluid ECQ is very similar at each borehole the downhole fluid EC is quite different at dif-

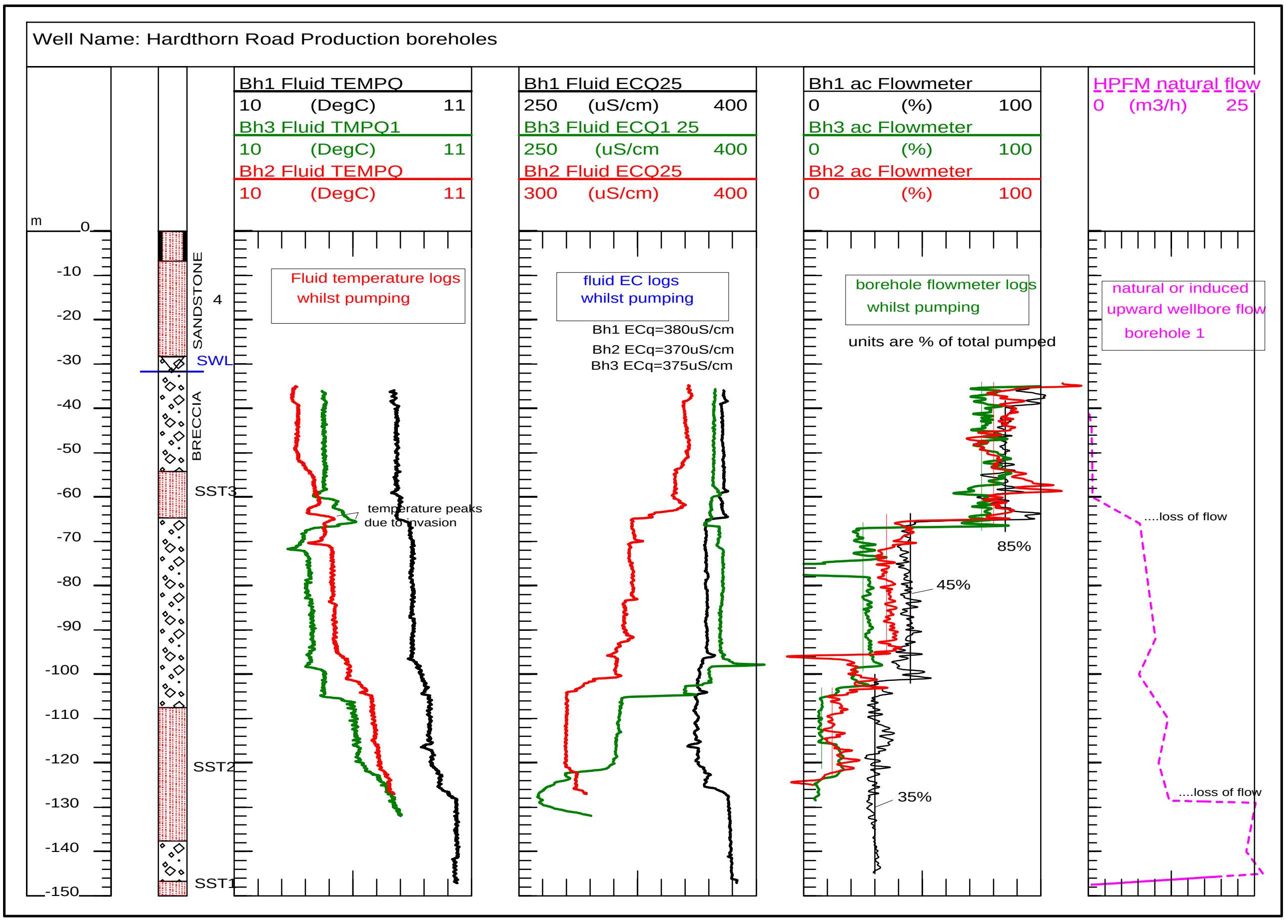

Figure 15.1. Upward wellbore flow borehole 1, Permian sandstone aquifer, Scotland, UK

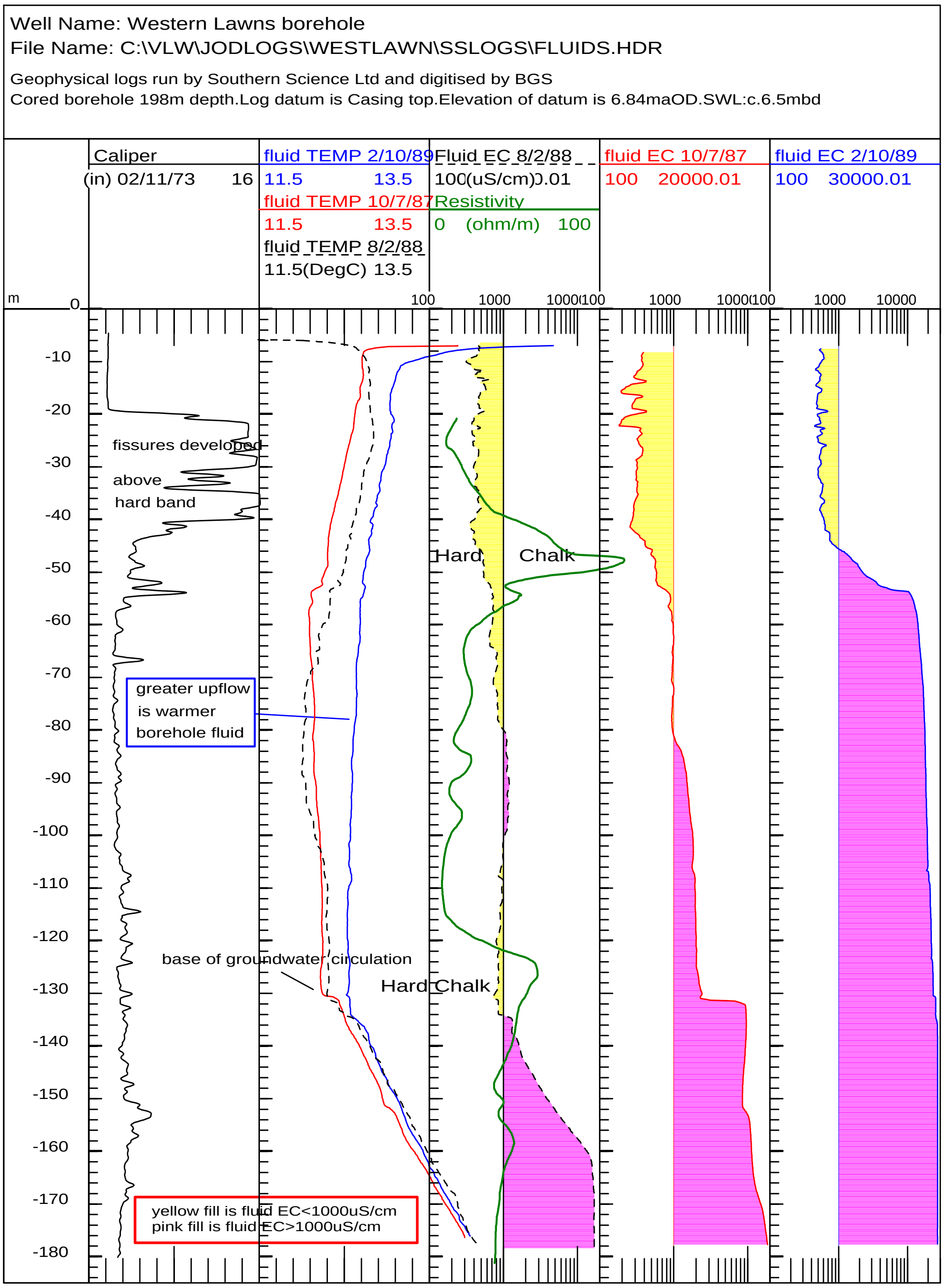

Figure 15.2. Borehole fluid salinity changes during the year in response to hydraulic head change; Chalk aquifer, Western Lawns, near Brighton, UK

ferent depth confirming different circulations for the separate sandstone horizons.

The upward wellbore flow in borehole 1 from the deep sandstone layer is evident from its elevated fluid temperature. The fluid temperature peaks at 65 m flanked by cooler water, above and below in borehole 2 and 3 when pumped (indicated on the Fig. 15.1) reveal the invasion of sandstone 3 by the warmer waters from sandstone 1 even though sandstone 1 is not penetrated in either of these holes. Clearly water samples collected from sandstone 3 will contain a proportion of older water derived from sandstone 1 due to the wellbore flow in borehole 1.

The wellbore flow invasion of low hydraulic head horizons by waters of higher hydraulic head , on a time scale that is quicker than is taking place through the rock mass can lead to some exaggerated effects in boreholes penetrating layers having strong salinity contrasts, as typically occurs in coastal regions. Figure 15.2 shows an example from an unconfined Chalk aquifer studied near Brighton, UK where salinity changes in relation to water level are significant. The freshwater head within the aquifer flow system is highest in March when a “saline interface” (arbitrarily defined by electrical conductivity >1000 µS cm^{-1}) is at 140 m depth. In October seasonal groundwater recession and inland pumping has reduced water level to a minimum and the “saline interface” has risen in the borehole to ~50 m depth. The exaggerated fluid EC changes are observed because of the layering of the Chalk aquifer, its fissuring and fracturing and because the borehole represents an open conduit of high permeability for wellbore flow. The effects observed are due to the wellbore flow. They are not taking place as such in the aquifer matrix, but they do reveal the potential for such changes to take place in the aquifer given suitable pathways. The logging shows that water samples taken from the borehole will vary with both time and depth of collection depending upon the relative water head, and will not be representative of waters in the aquifer matrix at that depth.

The effect of aquifer crossflow and wellbore flow is the production of a mixed groundwater. Such mixing may not be recognized unless the chemical characteristics of individual layers are determined and vertical flows taking place in sampling boreholes are recognized. This is important for PALAEAUX studies where the chemistry, isotopic character and age of groundwaters of individual aquifers is examined, towards the end of aquifer flowlines, near coastlines where groundwaters are more evolved and vertical mixing is prevalent.

The circulation of groundwater through different rock layers, and by different routes, some shallow, some deeper means that the residence time of groundwater in different parts of a flow system may be different. This introduces a vertical and horizontal stratification of the chemistry and isotopic character of the groundwater circulating due to various water-rock interactions that take place. In addition, important chemical changes and groundwater evolution takes place as water moves along individual layers down the flowlines The groundwater body thus evolves a *chemical* stratification because of the geological layering and the hydraulic circulation.

15.5 Vertical fluid movement in coastal aquifers and boreholes

Upward wellbore flow and aquifer crossflow is particularly prevalent in coastal situations because sea level imposes a minimum head reference for the groundwater flow systems and groundwater flowing along the layers from inland is normally at higher potential. The natural upflow is manifest as springs and seepages of freshwater at the coastline or offshore, the temperature and salinity of which is often anomalous relative to that of the adjacent seawater.

In addition, the lateral movement of groundwater in coastal regions is often slow because of low hydraulic gradient. Differences in salinity, temperature, density and viscosity then become increasingly significant factors in controlling the direction and rate of water movement. Custodio (1995) showed that decreasing groundwater temperature in a 100 m borehole column by 1ºC, within the normal range of groundwater temperatures, (10–30ºC) decreased water head by 25 mm; and replacing the freshwater column by seawater depressed the water head by 2.5 m. Water levels of coastal boreholes are also strongly influenced by tidal loading displaying semi-diurnal or diurnal changes of up to several metres in response to the sea tide. The amplitude and time lag of the induced sinusoidal changes further promotes wellbore and aquifer crossflow and the mixing of individual groundwaters of coastal regions. Effects of earlier climate and circulation history on aquifer permeability development

Groundwater flow systems are controlled by hydraulic river- and sea base levels and in certain aquifers in coastal situations the hydraulic interaction with the rock mass can be observed by examining the distribution of permeability by using geophysical logging techniques.

The principle effect of the glacial conditions which have existed over most of the past 100 000 years was that global sea level fluctuated significantly being at times as much as 130 m lower than at present. The effect of the changing sea level was to alter base level for river system development and groundwater circulations alike, with groundwater flow routes and river drainage adjusting to lowered base levels during cold periods, followed by subsequent inundation, and associated conversion of river valleys to estuaries, and then to coastline during sea level rises as the glaciers melted. The precise effects recorded in aquifers depend upon the location relative to the ice cover and in areas close to and under the ice, estimated to be >1000 m thick, (Boulton *et al.*, 1996), the land was depressed by the weight of ice, and subsequently rebounded when the glaciers melted and the load was removed.

During melting large quantities of glacial meltwater may have been injected into underlying and adjacent permeable materials and developed permeability under high hydraulic heads (Boulton *et al.*, 1996) Some of the injected meltwater is preserved in aquifer systems today where it has a characteristic isotopic cold climate composition (Chapter 2). With the melting, ice-depressed areas rebounded and interacted with the rising sea level to provide complex base levels for river system and groundwater circulations.

In terms of water quality the effect of changing sea level was significant and led to quality stratification. Rising sea level salinated unconfined freshwater aquifers from the coastline and advanced inland as sea level continued to rise. Confining beds of confined aquifers slowed or prevented direct salination so that freshwater was sometimes preserved in confined aquifers offshore, sometimes for considerable distances (Fetter, 1980; Kohout, 1977; Person, *et al.*, 1998) With falling sea level refreshening of salinated aquifers commenced from the unconfined parts, but seawaters trapped in low-permeability strata or in geological fold structures may have been only partly flushed before being overlain by younger, better quality lower density waters produced by the freshwater flow from inland which fluctuated according to the climate. Thus a complex groundwater salinity and age distribution may exist with depth in coastal regions. However it is stressed that lower sea levels and a greater offshore extension of freshwater bodies was the norm during most of the late Pleistocene.

Hence climate, sea level change, geological structure, geological layering and the properties of the layers themselves combine to influence the origin and quality of waters resident in aquifers at the present day.

15.6 Former drainage and groundwater circulation

When the colder climate coastlines are drawn (see Chapter 17) it can be appreciated that the present river systems and aquifers onshore represent only a part of the former much larger catchments which developed to the remoter coastlines. The offshore bathymetry is not a reliable guide to the former drainage because of subsequent scouring, infill and marine planation. Rather the former drainage pattern is revealed by the shape and morphology of buried and infilled channels, determined by offshore seismic surveys and drilling. This demonstrates in some areas that the present-day on shore catchments represent only perhaps the top 30%–50% of the former drainage basins, depending upon the offshore slope, which existed when sea level was at –130 m OD. Figure 15.3 is a comparison of onshore and offshore drainage of a part of N. Kent and under the adjacent Thames Estuary, UK where it is evident

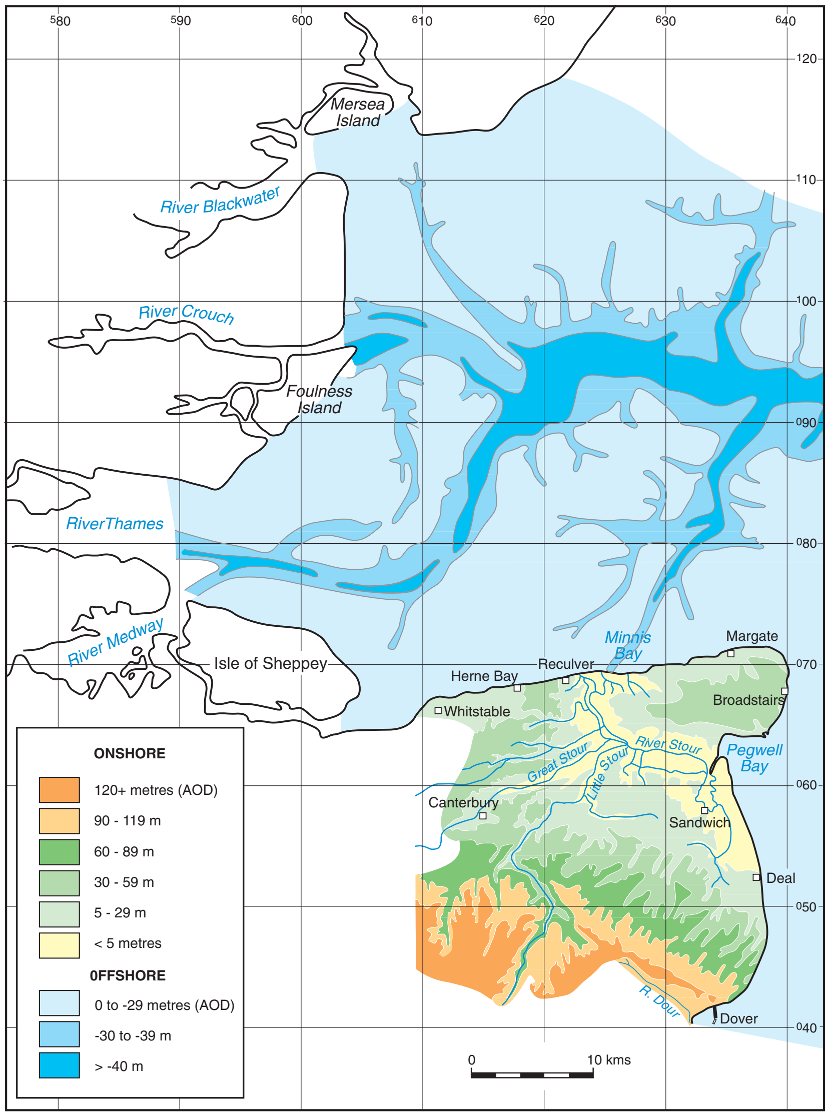

Figure 15.3. Onshore and offshore drainage pattern, North Kent and Thames Estuary, UK

both are part of the same drainage system. Certain aquifers (e.g. Chalk, limestones) retain the imprint of their prior circulation history through the development of permeability at certain horizons, because of the base level hydraulic control of the groundwater flow systems. In the example the offshore drainage channels suggest earlier base levels of –50 m OD and –100 m OD and these positions are reflected by the form of fluid logs of boreholes onshore near the coast (see Fig. 15.4, Table 15.1).

15.7 Tools for examining aquifer layering and identifying water-bearing horizons

There are several techniques that can be used to examine the nature of aquifer layers, and to identify horizons of water movement and detect wellbore flow in boreholes. These include hydraulic testing, hydraulic head measurements, water level and water quality monitoring and geophysical borehole logging.

One of the features of the PALAEAUX study has been the recognition that geophysical logging techniques (formation, fluid and flowmeter measurements, and water depth-sampling) provide a useful tool to examine aquifer and groundwater layering, and water movements and investigate former groundwater circulations.

Geophysical log identification of fluid movement

The groundwaters of different layers display different fluid EC and temperature characteristics because of their different circulation histories. Deeper circulations are usually warmer and more mineralized on account of longer residence time than shallower more recently recharged groundwaters. These differences are observed by fluid EC (electrical conductivity) and fluid TEMP (fluid temperature) measurements.

It is important to appreciate that fluid EC/TEMP profiles are transient, being shaped by the prevailing borehole hydraulics and represent those obtained under the prevailing hydraulic conditions when the measurements were made. When the hydraulics are changed e.g. by pumping, the profiles alter and water inflow positions can be determined by comparison and overlay plotting. When pumped the fluid inflow proportions can be determined by borehole flowmeter measurements Fluid logging techniques and interpretations are not widely discussed in the litera-

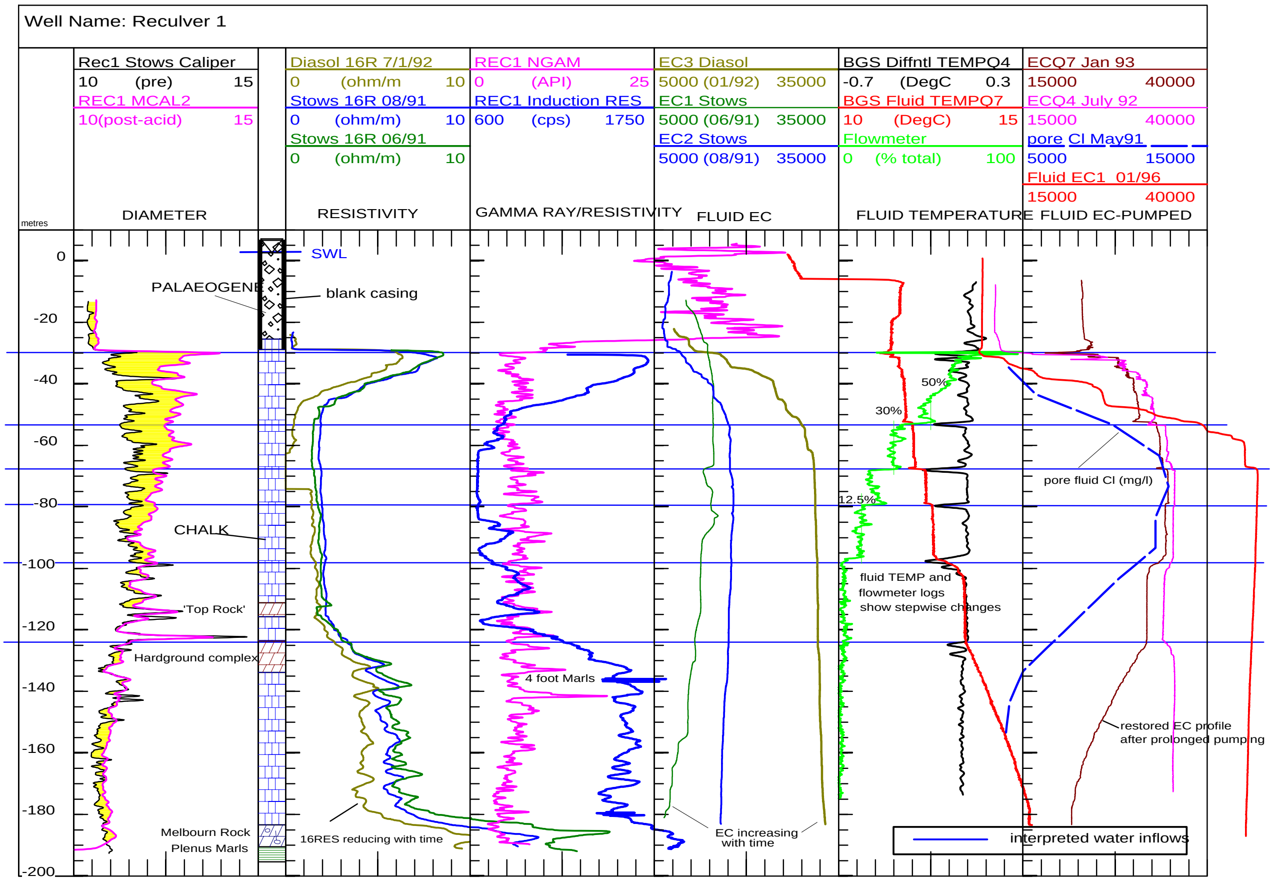

Figure 15.4. Fluid and formation logs, Reculver 1 borehole, N. Kent, UK

ture but examples are given by Tate *et al.* (1970), Keys & MacCary and Michalski (1989).

Groundwater temperatures initially relate to recharge input temperatures and reflect mean air temperature, but once in the ground become influenced by rock thermal conductivity and the depth to which the groundwater flow systems circulate. In the UK and Denmark typical northern Europe groundwater temperature down to depths of 100 m or so is normally 8–12°C, warmer in the south than the north. In Spain and Portugal temperatures are 15–25°C and in France are intermediate from north to south.

In uniform aquifers fluid temperature increases linearly with depth according to the geothermal gradient and according to the thermal conductivity of the rock layers. Geothermal gradients, although variable, are generally 2.0 to 3.0ºC/100 m. Where natural or induced wellbore flow occurs, the geothermal gradient is disturbed and the flow from one horizon to another is usually seen as a reduction or elimination of the natural temperature gradient between the two horizons Hence straight, vertical sections of TEMP (and EC) profiles usually signify wellbore flow, which may be up or down. Borehole flowmeter or head measurements can determine the direction of movement and it can sometimes be inferred from the fluid log profiles themselves. Custodio (1995) showed that if the vertical velocity is low (<10 m h^{-1}) distortion of the geothermal gradient was not be evident even though wellbore flow is taking place. Inflow of water into the borehole is usually seen as a change in temperature or EC on fluid logs at the point of inflow (Figs. 15.1 and 15.4)

Table 15.1. Inflow horizons determined by flowmeter logging at Reculver in the Chalk of North Kent: borehole 1 and 2.

Borehole 1			Borehole 2		
Depth mbd	**OD**	**inflow %**	**Depth mbd**	**OD**	**inflow %**
36-38	–30 to –32	25	36	–32	20
44-51	–38 to –45	10	56	–52	40
58	–52	22			
74	–68	15	59	–55	8
84	–78	14	65	–61	6
			75	–71	7
102	–96	10	102	–98	18
128	–122	4			

Fluid EC is rapid and convenient and reflects the concentration of mobile ions in the borehole fluid and approximates to the TDS or salinity. Shallow circulating waters normally have low EC (unless polluted) and are generally cooler. Lower EC waters at depth that are cooler may be indicative of more rapidly moving groundwaters in fracture or fissures which are by-passing matrix pore routes.

The fluid EC profile is used to define freshwater/saline water interfaces in coastal boreholes. In some aquifers the fluid EC/TEMP profile can be used to identify Pleistocene and Holocene waters directly. This is evident where they display both lower EC and warmer temperature at depth showing the palaeowater is emplaced in

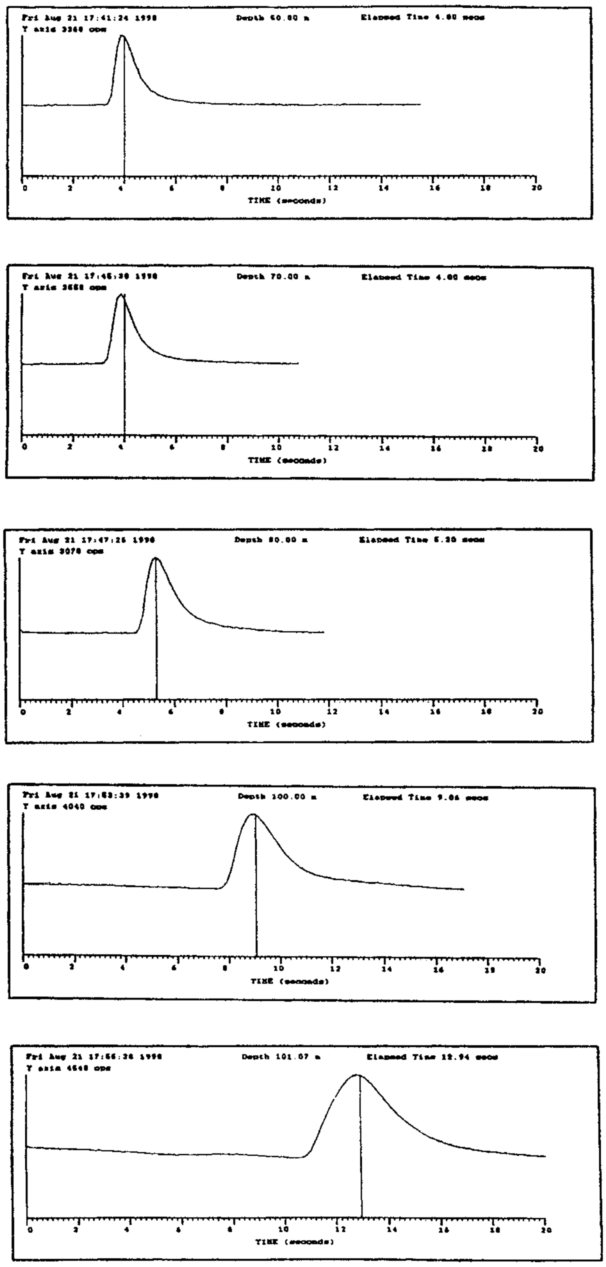

Figure 15.5. Heat-pulse flowmeter response to upward wellbore flow.

low permeability strata overlain by more mobile higher salinity waters, or they occupy aquifers some distance down the flowlines and have younger waters upgradient. In the Sherwood Sandstone aquifer of the East Midlands, UK, Pleistocene and Holocene age waters are distinguished by low EC and warmer temperature (deep circulation) relative to shallower circulating modern groundwaters having higher EC on account of the present-day closer proximity of current recharge to the coastline (sea salt deposition) as well as anthropogenic and industrial effects on the modern recharge.

Borehole flowmeter measurements

Borehole flowmeters provide a continuous record of the velocity of the natural or induced vertical flow in boreholes or wellscreen, and provide a quantitative assessment of the water inflows from particular layers at depth when pumped. The inflow proportions relate directly to the layer permeability.

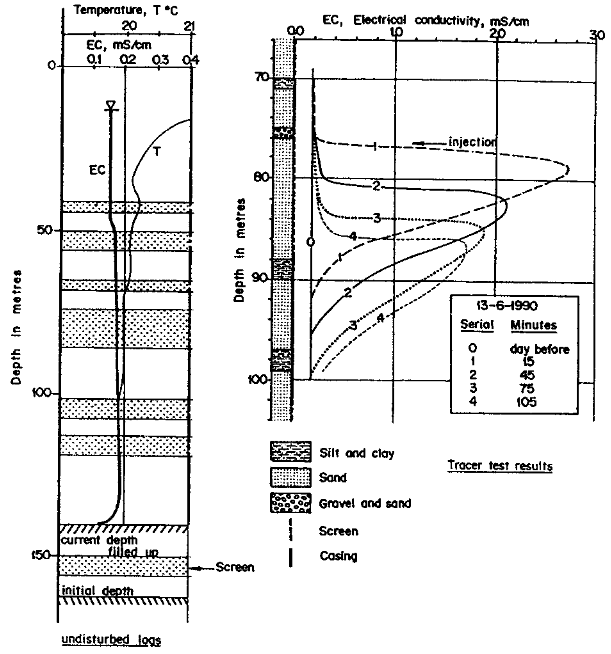

Figure 15.6. Wellbore downflow detected by saline tracer injection and fluid EC logging, from Custodio (1995).

Where inflows occur the vertical velocity increases and this is identified by the flowmeter measurement (Figs. 15.1 and 15.4). When corrected for hole diameter changes the measurements may show a gradual increase in velocity profile signifying an intergranular contribution to flow from e.g. granular material, or may show step-wise, incremental changes in velocity where individual inflow is, for example, concentrated at bedding plane fissures and fractures in e.g. hard rocks (Fig. 15.1), or display a combination of both.

Very slow natural flow may be measured using tracers. These may be thermal e.g. heat-pulse flowmeter (Fig. 15.5 showing upflow), or chemical e.g. salt or radio-isotope, (Fig. 15.6 showing the slow downward flow of a salt tracer injected into a borehole in Spain (Custodio *et al.*, 1995)

15.8 Implications for groundwater sampling and interpretation

The existence of wellbore flow has important implications for the representative sampling of groundwaters from different layers and its existence is strongly influenced by the borehole construction. Open and long-screen borehole constructions penetrating layers of different hydraulic head permit short-circuiting and allow wellbore fluid invasion of the low head layers. This can also occur in short-screen boreholes if the gravel pack extends up to near the surface or crosses several aquifer layers without intervening clay seals. Head differences of only a few centimetres can generate substantial flow volumes in large diameter boreholes.

In efforts to obtain water samples representative of groundwater in the aquifer boreholes are usually purged (pumped) for a period of time to remove typically several well volumes of ‘stagnant water’. It is evident that this may not always (if perhaps ever) remove invaded waters (including drilling fluids) from horizons in open and long-screened boreholes in which wellbore flow has and is taking place.

Often only pumping boreholes are selected for water sampling on the basis that they provide samples more representative of water in the aquifers than in observation-only boreholes. This might be true but as indicated pumped samples only represent a mixture of waters from all contributing horizons in proportion to their relative permeabilities. Unless there is only one inflow horizon they will not be fully representative, and are likely to be biased towards the composition of groundwaters from the highest permeability layers. Likewise samples taken from intermittently pumped boreholes might contain waters penetrated during the rest period. Schmidt (1977) drew attention to the fact that water quality of pumped boreholes was not always constant with time. Bias in groundwater sampling data caused by open boreholes and long-screen boreholes is described by Tellam *et al.* (1992), Segar (1993), and by Church and Gramato (1996).

A clear distinction between borehole fluid and aquifer water should be made in water sampling programmes. Aquifer pore fluids can be extracted by centrifugation from core, and represent matrix waters which may or may not have equilibrated with that in fissures (Edmunds and Bath, 1976). Fluids obtained by centrifuging may not be representative of waters in fissured and fractured porous materials, but together with borehole fluid sampling provide a means of characterizing the groundwaters in dual-porosity systems.

Change in quality of groundwater from pumping boreholes with time is direct evidence of lateral and /or vertical stratification of water quality, either in the pumping borehole or within its capture zone. In such boreholes fluid logging can help by determining the downhole layering, component inflows and contributions.

Samples of individual aquifer waters are therefore best obtained by pumping from individual purpose-built piezometers open to that layer and sealed above and below, and these can also provide individual head measurements for the layers. However these are not always available nor can they be used for other purposes. Most often samples have to be taken from openhole or multi-screened boreholes and in these geophysical fluid logging can help determine the provenance of the sample by establishing the downhole layering and component inflows.

Several techniques for obtaining water samples from specific horizons in boreholes are described in the literature, and precautions and protocols for sampling are described by several authors including Mazor (1991).

15.9 Illustrative examples from PALAEAUX

15.9.1 Density-driven wellbore flow, confined Chalk aquifer, UK

Figure 15.4 is an example of density invasion of the lower part of an open hole coastal borehole by more saline waters from a higher level. In this example formation logs are shown in tracks 1-3 and fluid logs in tracks 4-6. The borehole was drilled in May 1991 on the southern edge of the Thames Estuary, UK and penetrated Palaeocene strata (32 m) which confined the Chalk aquifer. Spot cores were taken in the Chalk and the pore fluid chloride profile shown in track 6 (blue curve), revealed an upper zone of brackish porewater (0 to –55 m OD) overlying a middle zone of saline water (–55 to –100 m OD) overlying a lower brackish water zone. The hole was acidized and the effect of acidization on the caliper logs is shown by the yellow infill which emphasizes the change in borehole shape.

The borehole has been logged on several occasions and after clearance pumping resistivity showed a decreasing formation resistivity with time. At the same time fluid EC logging showed an increasing salinity which became relatively constant below –60 m OD. The borehole was then test pumped for a period of 204 days during which time fluid EC logging showed the EC profile changed again and restored the original tripartite zonation indicated by the original pore fluid chloride measurements (track 6). Relogging after the borehole had stood for 3 years (track 6 1996 curve) again showed invasion of the lower parts of the borehole below –60 m OD by relatively constant high EC fluid. The increased EC again representing density downflow invasion of the lower brackish zone by waters from the middle saline zone.

The fluid and flowmeter logging during the test pumping was particularly important at this site. It displayed stepwise changes in fluid EC and TEMP and velocity (tracks 4 and 5), indicating the water inflows were from specific fissured horizons rather than from intergranular contribution. The interpreted water inflows are represented in the diagram by horizontal blue lines. Analysis of the flowmeter logging in this borehole, and also in borehole 2, drilled 1.8 km to the east is summarized in Table 15.1 This revealed that 60% of the water movement was taking place above –55 m OD, and the remaining 40% was from above –105 m OD. These depths of higher permeability development within the confined Chalk aquifer relate closely to important base levels of the main drainage channels recognized offshore by seismic study and drilling evidence (Bridgland and d'Olier, 1995, see Fig. 15.3). Borehole 2 was fluid logged and depth-sampled immediately after drilling. Its fluid log salinity profile matched that of the pore fluid extracted from core showing that the fluid logging and sampling soon after drilling is representative of the layering, but logging in 1998 showed the profile had changed.

15.9.2 Palaeowater and saline intrusion, unconfined Chalk, UK

Figure 15.7 is an example of geophysical formation and fluid logging in an unconfined Chalk aquifer that has been compiled into a hydrogeophysical cross section It shows layering within the Chalk identified by focused resistivity measurements which relate to the presence of harder (more cemented) and softer (marl) bands some of which are named. It shows typical fluid salinity and temperature changes with depth and salinity increasing approaching the coast which is located at the right hand end of the figure just to the south of East Street borehole

The temperature logs (shown in red) show the coolest groundwater is found in the upper parts of the aquifer. The temperature log in the Victoria Gardens borehole was run whilst pumping and it shows sharper EC and TEMP changes. Flowmeter logs run in the Victoria Gardens borehole when pumping, shown alongside, indicate the bulk of the groundwater movement is taking place above –50 m OD with ~65% of the flow occurring above –30 m OD. Below –110 m OD the relatively undisturbed geothermal gradient indicates there is little groundwater movement, and the borehole flowmeter reveals this is <12% of the total.

The logs run in the East Street borehole closest to the coastline show saline water (emphasized by blue infill) has

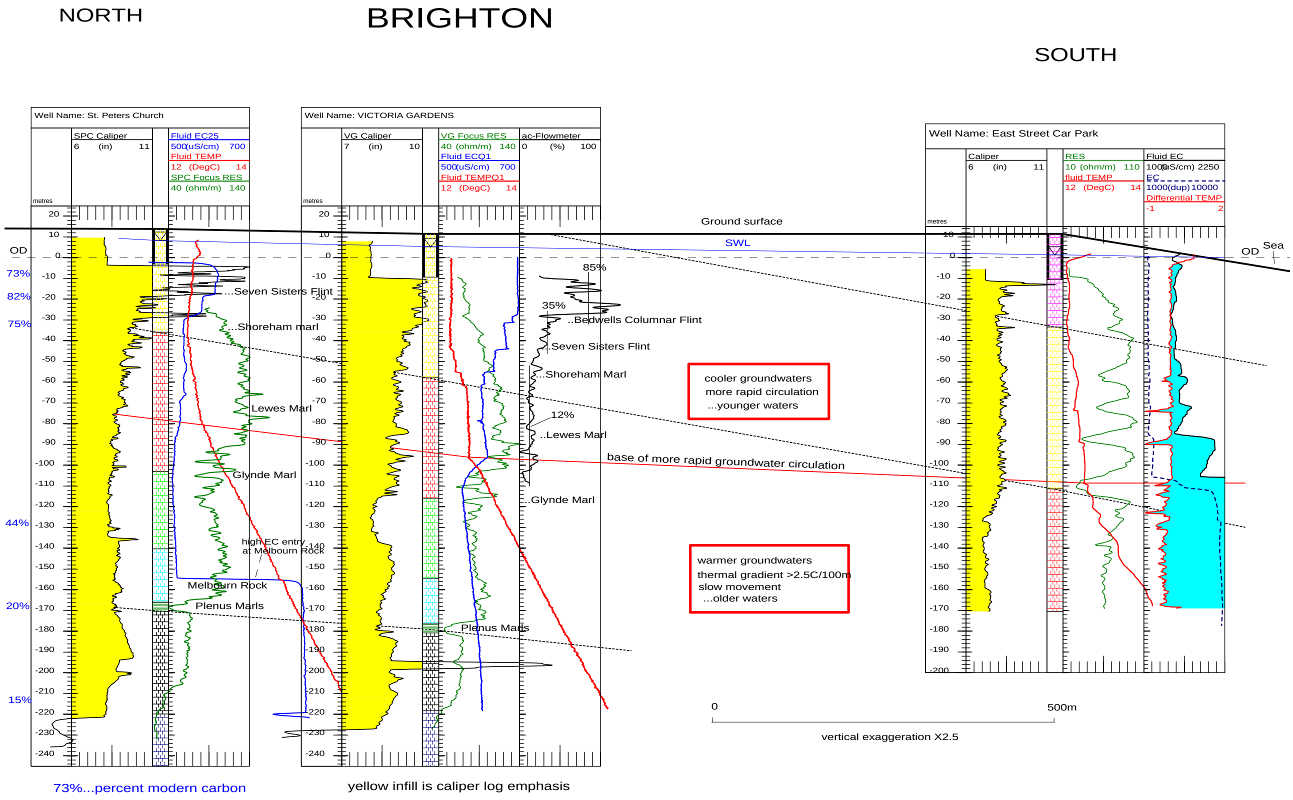

Figure 15.7. N-S hydrogeophysical cross-section showing horizons of water movement and saline intrusion; unconfined Chalk aquifer, Brighton, UK.

entered fissured horizons. The more saline fluid entering the borehole has influenced the electrical resistivity log measurement so that it becomes difficult to identify the named lithological horizons recognized in the two inland boreholes by the resistivity log profile. The differential TEMP log emphasizes small temperature changes and reveals that the higher salinity water is cooler as is the modern seawater. The back-up EC curve (1000–10 000 µS cm^{-1} scale) shows water in the borehole below –110 m OD is relatively constant EC, revealing a density-driven downward flow. The sharp increase in temperature at the base of the cooler groundwater at –90 to –110 m OD is taken to identify the base of more rapidly circulating groundwater. The percentage modern carbon content of depth-samples collected from the groundwater (>70%) shown at the left hand side of the figure confirms this more rapid movement of the younger waters.

In the St Peters Church borehole high EC water enters at and below –154 m OD and represents water entering along a fissure or fracture associated with the Melbourn Rock hard band. This higher EC log feature is not always present and is a transient response to relative head difference presumably caused by adjacent pumping. It is never seen in the Victoria Gardens borehole which is nearer the sea thus suggesting it is a discrete fluid movement through fracturing and may not represent a general diffuse movement of higher salinity water in the aquifer at that depth, but an advance of more saline water along a fissured or fractured horizon connected seaward. Borehole imaging would identify the nature and orientation of the feature responsible

15.9.3 Groundwater stratification and sampling in an unconsolidated granular aquifer, Denmark.

The Ribe Formation in Denmark was investigated at the Skærbæk and Fjand sites. At Skærbæk an irrigation well for a large farm penetrates a thick sequence of sands, clays and tills and is screened against a quartz sand aquifer from 192–232 m depth (Fig. 15.8). The gamma ray (total) log and the spectral gamma (uranium) log curves relate to the lithological layering. The borehole was pumped and the flowmeter curve revealed a smooth intergranular inflow contribution across the screened interval. It was intended to sample waters of the screened interval using the packer baffle technique but the pumping assembly could not be installed due to a diameter constriction. Samples were collected instead by placing a pump at shallow depth to generate flow whilst a sampling pump was used to take samples at 232, 212 and 192 m depth. The geochemistry and isotope composition of the waters obtained showed no significant difference between waters at the top and bottom of the aquifer which is consistent with the uniform nature suggested by the gamma ray logs.

At the Fjand site (Fig. 15.9) a nested well 800 m from the coastline, containing 6 individual piezometers, each open to 3 m of aquifer, was used to monitor water quality of different sand layers down to 175 m depth. The piezometers are shown in the figure and the sand layers are identified by the lower gamma ray mostly above 80 m depth. From 80–170 m the gamma ray log shows a thick fine-grained clay and silt lithology, but a deep sand layer is present below 170 m depth. The piezometric head of all six piezometers is above ground level in winter when

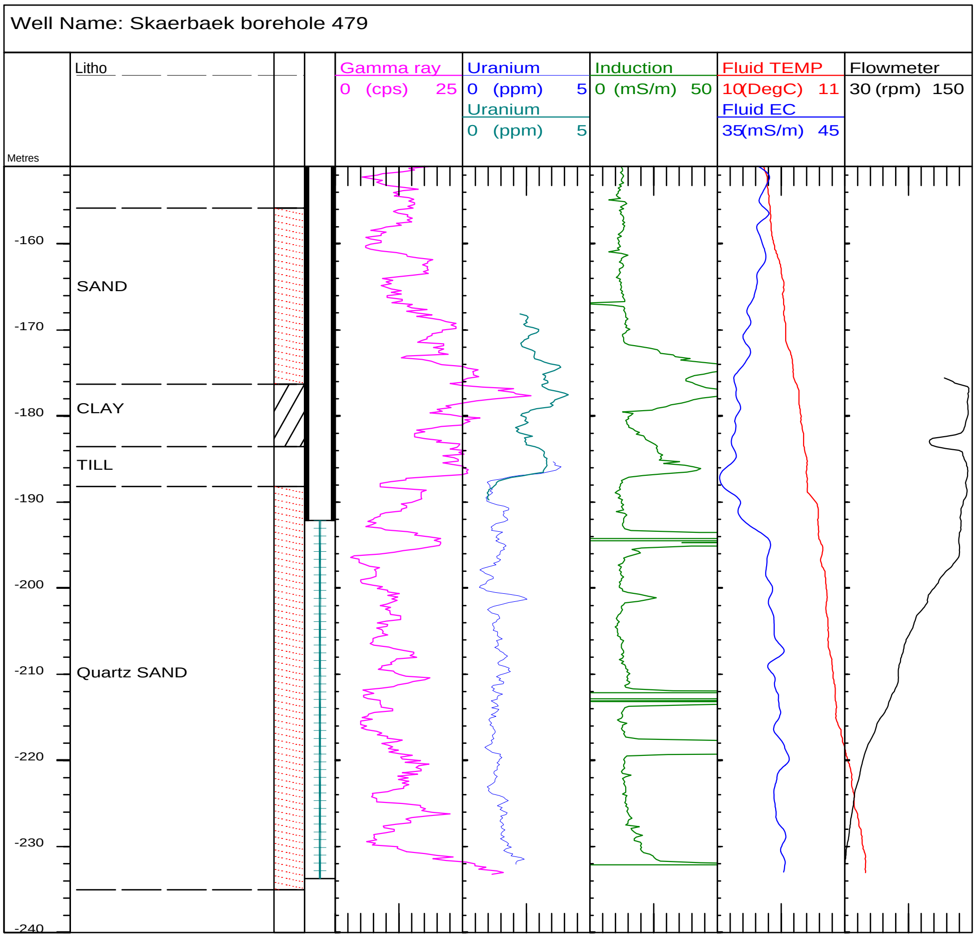

Figure 15.8. Unconsolidated aquifer showing wellscreen and intergranular flow contribution, Ribe Formation, Denmark.

samples can be collected simply by opening the valves. The deepest piezometer (6) has however a high dissolved organic carbon content and its water is brown. A wellfield tapping this aquifer had to be abandoned due to the water discoloration, and piezometer 6 is kept flowing to minimize potential contamination of the overlying sand aquifers.

The piezometric level of the top 4 piezometers is very similar but decreases successively with depth showing a downward hydraulic potential. Their piezometric level falls to ~3.3 m below surface in July and ~3.5 m below surface in October. The level in piezometer 5 lags behind and is only 1.4 mbs in July and 2.1 mbs in October. The piezometric level of deep sand layer 6 remains above surface all year (+0.5 m in October) thus maintaining upward flow. Downward flow of cool water from piezometer 1 to piezometer 5 and upward flow of warmer water from piezometer 6 and 5 is indicated by the fluid TEMP profile which was run in piezometer 6. The fluid EC log, although instrumentally noisy, shows the cooler water is also lower EC.

All six piezometers were sampled and analysed for major ions and CFC-gases and continuously monitored for pH, O_2, Eh and SEC during sampling. The results showed a low CFC concentration in piezometer well corresponding to groundwater recharge in the 1960s. No CFC were detected in piezometer 2, 3 and 4 yet low but significant higher concentrations were measured in piezometer 5, screened from 74–77 m below surface. This suggested a short-circuit between piezometer 1 and piezometer 5.

To investigate, two sampling pumps were used to sample at different depths in piezometer 5. The lower pump was placed at 69 m below surface, and the upper at 50 m depth. It was demonstrated that the two pumps sampled significantly different waters. The lower pump samples anoxic, high pH and high SEC waters, whilst the upper one sampled oxic groundwater close to saturation with the atmosphere and relatively low pH and SEC. The results indicated the piezometer receives water from different levels and leakage was in fact detected visibly from a pipe connection at 1.9 m below surface from the surficial aquifer during sampling The head in the surficial aquifer is higher than that of the aquifer at 70 m resulting in a continuous flow of water down the piezometer. Heat-pulse flowmeter measurements indicated that several damaged or leaky pipe connections were in fact present.

The fluid temperature log (TEMP) run in the deep piezometer suggests a further complication. The fluid temperature gradient across the thick clay aquitard from 80-170 m is only 0.4°C/100 m which together with evidence of upward hydraulic potential of the bottom sand layer suggests upward movement of water from the bottom sand layer either inside or outside piezometer 6 to the sand layer of piezometer 4. No flow was detected inside the piezometer by flowmeter logging and it is therefore most likely the flow responsible for the temperature profile, takes place in the annulus or in the developed zone

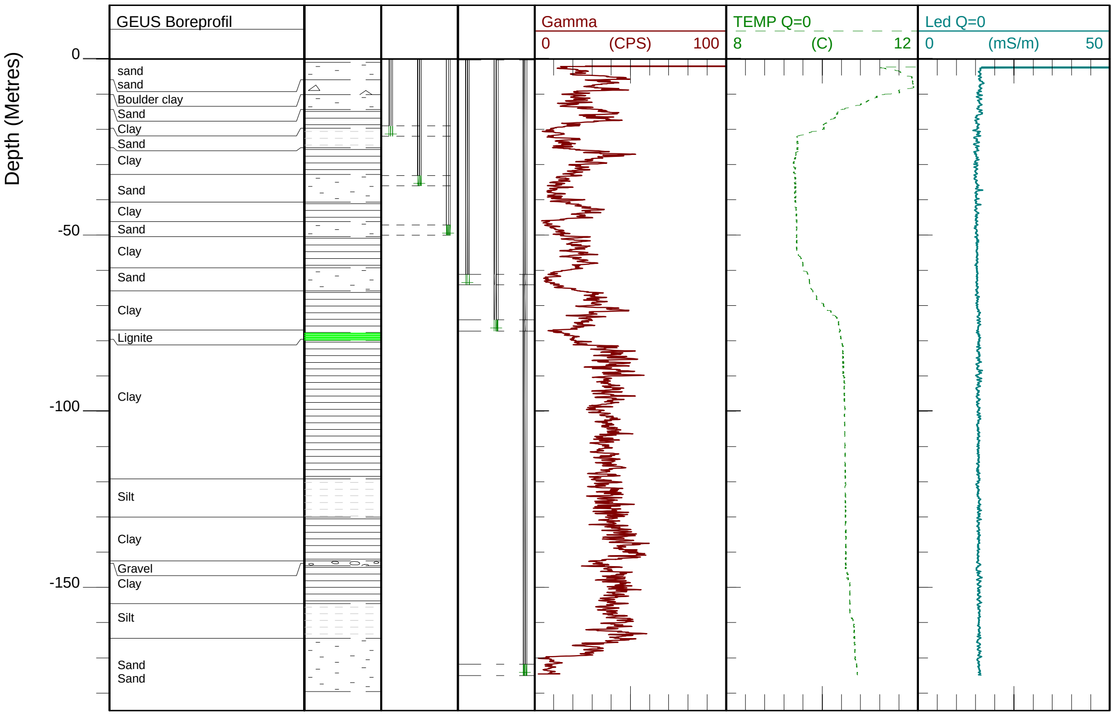

Figure 15.9. Geophysical logs showing geological layering and piezometer placement, unconsolidated Ribe Formation, Fjand area, Denmark.

around the well. If correct the water sampled in piezometer 5 could represent a mixture of sand 5 waters and waters from the shallowest and deepest aquifers which are separated by more than 150 m in space and >5000 years in time. A further complicating factor is that the piezometric head varies throughout the year in all aquifers, due to abstraction and recharge, so that the rate of flow and direction of flow inside the piezometer can change. Hence the groundwater chemistry needs to be considered in relation to the groundwater flow systems and the particular hydraulics of the well construction,. Information on which is provided by the logging techniques and by the hydraulic head measurements.

15.9.4 Saline interface and upflow associated with geological structure, S'Albufera ,Mallorca

Figure 7.20 shows a hydrogeophysical cross-section of the S'Albufera area of Mallorca where fluid EC and TEMP logs were run in more than 30 boreholes penetrating Holocene and Pleistocene sands overlying Palaeogene limestones. The fluid EC logs identified brackish to saline waters present in the sands, and identify a saline interface at –50 to –100m depth in the underlying carbonate aquifer. Fluid temperature logging indicated areas of recent recharging downflow but also revealed locally much warmer water upflowing in the vicinity of a fault between borehole S-21 and S-20 where in one borehole water enters at –140 m depth at 27.4°C (2–6°C warmer than adjacent holes). This water is higher EC (>10 000 µS cm^{-1}) than water below. The upflow is cooled at a further inflow at –80 m which is a higher EC.

15.10 Summary and conclusions

Virtually all rocks show some form of layering and are capable of becoming aquifers if the rock mass contains openings through which groundwater may circulate.

Groundwater movement takes place selectively though favourable lithology horizons (aquifers) and groundwater flow systems become established by the groundwater circulation from recharge regions at higher elevation to regions of groundwater discharge at lower elevations. The regional direction of water movement is controlled by the topography but the depth of circulation and local directions of groundwater movement are influenced by the lithology and geological structure.

The diverse flow routes and circulation histories produced by the layering and structure generate differences in groundwater chemistry both vertically and laterally due to different residence times for water-rock interaction to take place. The groundwater circulating through the rock mass thus becomes chemically stratified.

Individual groundwater circulations tend to have different hydraulic (head) potentials so that aquifer crossflow takes place within the rock mass through available routes, to equilibrate the head differences.

When boreholes are drilled into rock masses and penetrate several water-bearing layers, vertical fluid movement takes place in the borehole to similarly equilibrate the head differences. This fluid movement is wellbore flow and takes place on a more rapid time-scale than crossflow within the rock mass. The effect of these movements (up or down) is to mix the groundwaters.

Boreholes in coastal regions are especially susceptible to the mixing effects of aquifer crossflow and wellbore flow because they are located near the end of aquifer flowlines, close to sea level, where hydraulic head is at a minimum and flow from inland is at higher potential. In addition hydraulic gradients in coastal regions are often flat and water levels are strongly influenced by tidal loading which further promotes vertical flow.

The implication of aquifer crossflow and borehole wellbore flow for water sampling is that groundwaters tend to become mixed and there is a tendency for waters of high hydraulic head to enter and mix with waters of lower head horizons. These waters may be chemically quite different, of different isotopic composition and different age.

Unless groundwaters of individual layers are examined in boreholes and downhole log measurements made, the existence of aquifer crossflow and wellbore invasion may not be appreciated.

Geophysical logging provides information on the geological and aquifer layering.

Fluid logging EC\TEMP\FLOWMETER measurements identify water inflows and distinguish waters of different quality and temperature. These differences in turn are indicative of different groundwater circulation routes and provide information on the Groundwater Flow System present

Interpretation of fluid logs and direct measurement using borehole flowmeters can determine the hydraulic influences affecting the borehole fluids

In some aquifers the fluid EC and TEMP logs themselves provide direct indication of Pleistocene or Holocene waters in the rock mass by their profiles. This has been shown to be the case in certain coastal situations where present-day circulating groundwater is higher EC and cooler and overlies typically lower EC (pre-industrial recharged) waters that are warmer because they are preserved at depth in low-permeability strata at depth.

For representative sampling of individual aquifer horizons, purpose-built piezometers or single screened boreholes, sealed above and below and open only to the interval of interest are best.

These are costly and where not available and sampling has to be performed in open or long screened boreholes, it should be considered that fluid invasion will probably have occurred since construction. An indication of the direction of wellbore flow can be gained by consideration of the hydrogeological setting Geophysical formation and fluid logging should be performed to determine the aquifer layering and the distribution of water inflows. Individual water-bearing horizons can then be identified and their groundwaters sampled accordingly to establish the separate components of the mixture pumped. Water sampling can then be targetted and samples collected by dynamic depth-sampling, packer-pumping or by separation pumping techniques to minimize wellbore flow influence. Water returned from low head horizons might still however be wholly or partly invaded water.

Comparison of fluid logs with formation logs and well-to-well comparisons also provides information on the permeability distribution within the aquifer. Such comparisons indicate that permeable routes were established by groundwater circulation to lower river and sea base levels in the past and are now occupied and exploited by present day groundwater circulation that is also developing permeable routes at shallower levels.

16 Modern groundwater advance in European coastal aquifers

16.1 Introduction

Large parts of the global groundwater resources participate in the hydrological cycle continuously discharging groundwater to rivers, lakes and the sea, other parts are more or less isolated with no or very little exchange with the active system. In the present study all selected coastal European aquifers take part in the hydrological cycle, although some waters deep in the aquifers entered the subsurface more than ten thousand years ago during the last glaciation, and today mainly participate in the hydrological cycle due to aquifer exploitation. In some areas high quality deep groundwaters are threatened by the advance of modern contaminated groundwater, and overexploitation may allow the quality of the deep resources to deteriorate. Modern groundwater is defined as groundwater with a significant human input i.e. groundwater that generally is less than about fifty years old.

This chapter considers the advance of modern groundwaters into European aquifers and how to recognize the interfaces between modern water and older waters. The different environmental tracers, also contaminants, that may be used to fingerprint or date the modern components are also considered.

16.2 Human influence on groundwater chemistry

Generally, human influence can be recognized in groundwater recharged within the last fifty years (Plummer *et al.*, 1993), and at depths generally not exceeding 50–100 m (e.g. Seiler & Lindner, 1995), while uncontaminated pristine groundwaters are found at greater depths (e.g. Edmunds *et al.*, 1982). Pristine groundwaters in coastal areas can be regarded very simply as diluted seawater or evaporated rainwater only with addition of elements from the dissolution of minerals and organic matter in soils and rocks (Appelo & Postma, 1993). The chemical and isotopic composition of such waters define the baseline conditions for the aquifers, serving as the basis on which the human impact can be recognized (Edmunds *et al.*, 1987). The deep groundwater resources generally define the baseline conditions as they are protected against contamination from human activities at the ground surface (Herweijer *et al.*, 1985; Edmunds *et al.*, 1987). Deep groundwaters in contrast to many near surface modern waters generally need little treatment to be used as drinking water.

During the last half of the nineteenth century human activities have been so intense that the upper young groundwater resources globally show the influence of man. Not all these influences are harmful to man and the environment, but some contaminants are very critical and an increasing number of water supply wells are either shut down, or the abstracted water has to receive extensive treatment before the water can be sent to the consumer. Should boreholes have to be abandoned new uncontaminated groundwaters have to be found. New water supply wells are often drilled to greater depths to have better protection against surface pollution. These deeper systems are, as already mentioned, often vulnerable to overexploitation and mining, which if not carefully monitored and managed can lead to severe problems e.g. pollution by younger waters from above (Custodio, 1992; Custodio *et al.*, 1998; Chapter 18). Consequently, description of the groundwater flow systems, and the location of contaminated and pristine waters are essential. During the delineation of the different water qualities and the description of the flow systems the recognition of the human input and the use of environmental tracers and dating tools are important. The objective of this paper is to describe how to distinguish between modern contaminated groundwater and old pristine waters by the help of some common contaminants and useful environmental tracers, and to estimate the advance of modern groundwater into coastal European aquifer systems.

Table 16.1. Examples of human impact indicators and contaminants found in young groundwater

Agricultural impacts	Industrial impacts (including landfills)
Nitrate, sulphate, phosphate, potassium, chloride, pesticides, TOC, TDS, trace elements, pathogens	VOCs (Volatile Organic Carbons e.g. chlorinated solvents, BTXs), surfactants, sulphate, chloride, nitrate, TOC, trace elements e.g. heavy metals, NAPL´s, pathogens

16.3 Tools for recognition of modern groundwater

16.3.1 Human impact indicators

Although anthropogenic effects on the chemistry of the atmosphere and precipitation have been significant for the past approximately two hundred years, as recognized in e.g. sediments and ice cores (Graedel & Crutzen, 1993), this generally does not lead to recognizable changes in the groundwater chemistry for most of this period. Significant global changes in groundwater chemistry due to human activities have occurred only during the past approxi-

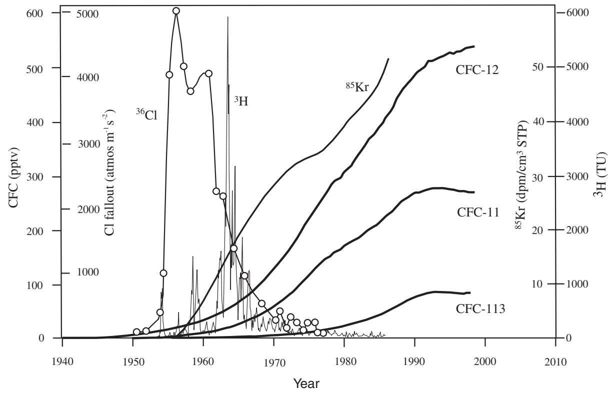

Figure 16.1. Atmosphere concentrations of CFC gases at Niwot Ridge, Co, USA, (McCarthy, 1977, AFEAS, 1993, Elkins, 1993**)** and ^{85}Kr (Loosli *et al.*, 1991) and precipitation concentrations of ^{3}H in Ottawa, Canada (Plummer *et al.*, 1993).

mately 40-50 years, exemplified by the presence of anthropogenic tracers with an atmospheric origin i.e. ^{3}H, ^{85}Kr, and CFC-gases (Fig 16.1), and a large range of contaminants from agricultural and industrial activities e.g. pesticides, nitrate, sulphate, chloride and chlorinated solvents (e.g. Freeze & Cherry, 1979; Robertson *et al.*, 1989; Loosli *et al.*, 1991; Plummer *et al.*, 1993; Wilson & Mackay, 1993; Ekwurzel *et al.*, 1994; Böhlke & Denver, 1995; Edmunds, 1996; Cook & Solomon, 1997; Clark & Fritz, 1997; Busenberg & Plummer, 1997; Loosli, 1999; Plummer & Busenberg, 1999). These tracers and the age-range of the past 40–50 years are therefore used here as the definition of modern (or young) groundwater.

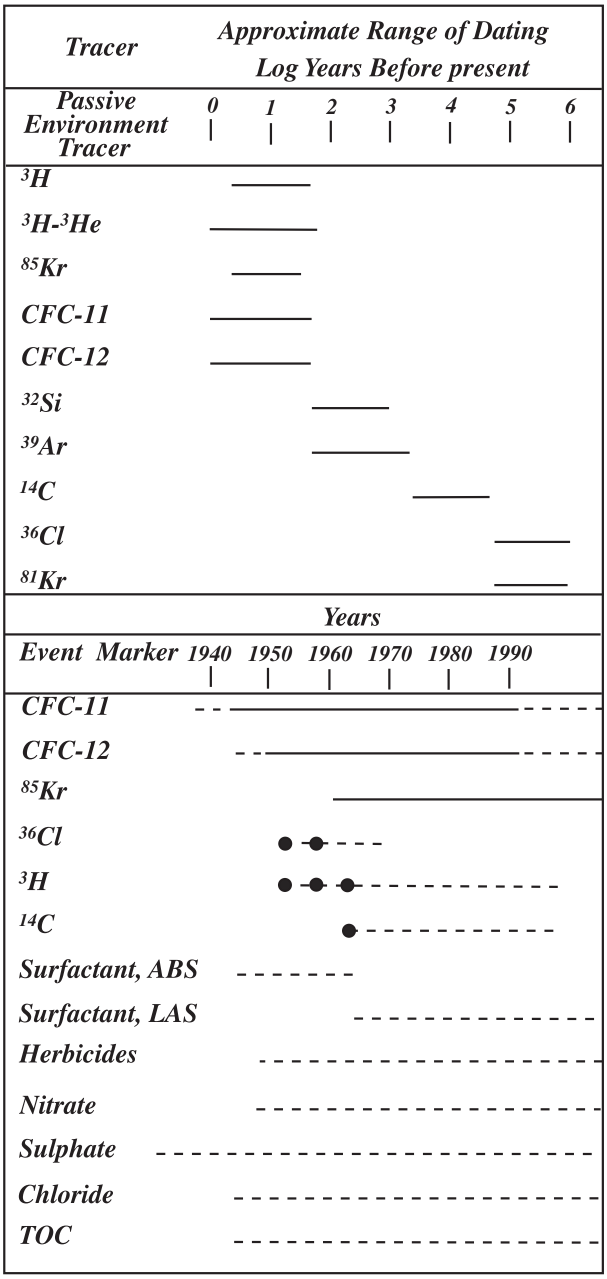

Figure 16.2. Approximate range of absolute and relative dating applications of selected environmental tracers and event markers (in years). Modified after Plummer *et al.* (1993).

16.3.2 Dating tools, environmental tracers and event markers

Some environmental tracers found in groundwater can provide absolute ages whereas other tracers only provide relative ages i.e. determine whether the main part of the water sample is recharged before or after a known event.

Plummer *et al.* (1993) divides dating techniques for dating of young (modern) groundwater into environmental tracers, which yield a continuous record of water age with distance along a flow path (e.g. ^{85}Kr, CFCs, ^{3}H/^{3}He), and event markers which assign an age to only the specific point in the flow system, where the result of the event is located (e.g. the 1963 ^{3}H bomb peak), or indicate relative ages (e.g. nitrate and pesticides, Fig 16.2).

The most important and widely used dating tool to date has been ^{3}H. The value of this method though to some extent decreases with the decreasing atmospheric input (Fig 16.1). However, a low level ^{3}H background (around 2 TU) in the southern hemisphere enables low level ^{3}H measurements (detection limit down to 0.03–0.04 TU, Taylor *et al.*, 1998), making ^{3}H an important and relevant tool even at the low present day ^{3}H levels. As supplements to the ^{3}H technique a number of studies in recent years have shown the strong potentials of alternative environmental tracers such as ^{3}H/^{3}He, ^{85}Kr, CFCs and ^{4}He (e.g. Loosli *et al.*, 1991; Busenberg & Plummer, 1992; Ekwurzel *et al.*, 1994; Cook *et al.*, 1995; Solomon *et al.*, 1996; Cook & Solomon, 1997; Loosli *et al.*, 1999; Plummer & Busenberg, 1999).

The concentrations in air (^{85}Kr, CFC-11, 12 and 113) and precipitation (^{3}H) of the most important dating tools in young groundwater are shown in Fig 16.1 for comparison. The steady increasing concentrations of the CFC gases and ^{85}Kr give these tracers some advantages compared to ^{3}H because first of all they can be used for absolute age dating and secondly they are not as sensitive to dispersion in the aquifers as the very pronounced ^{3}H peak (Plummer *et al.*, 1993). For the last four decades it has not been possible to use the ^{3}H concentration in groundwater in itself for absolute dating due to the varying input function. Only when combining ^{3}H and ^{3}He (the “daughter product” of ^{3}H) can absolute ages be obtained. However, if the ^{3}H input function stabilizes around a fixed value e.g. the estimated pre-bomb value of 5–10 TU, ^{3}H values in themselves can be used in the future for absolute dating of groundwater.

As shown in Fig 16.1 the fast increase of the CFC-concentrations in the atmosphere changed abruptly about ten years ago as a result of the Montreal protocol limiting the use of CFC-gases. The CFC-11 and CFC-113 concentrations in the atmosphere have been nearly constant during the nineties, and for CFC-11 even a slow decrease has been observed. This of course makes it difficult to use CFC-11 and CFC-113 as absolute dating tools. CFC-12 concentrations in the atmosphere still increase slowly. CFC-12 concentrations are also expected to level off and slowly decrease for the next several decades. This expected development of the CFC concentrations will complicate and limit the use of the CFC gases as absolute age dating tools in the future, due to increasing uncertainties, however the CFC gases will continue to be a valuable tracer and modern water indicator for several decades, because of their long life-time in the atmosphere.

In contrast to ^{3}H and the CFC gases the significant increase in the atmospheric ^{85}Kr concentrations since about 1955 are expected to continue in the future. This is due to the continuous release from nuclear installations (Loosli *et al.*, 1991, 1999). This makes the ^{85}Kr tracer a potentially very strong and widely applicable tool in the future for absolute dating of young groundwater if sampling and analysis procedures can be simplified and sample volumes can be decreased (Thonnard *et al.*, 1997, Loosli *et al.*, 1999). Today only a few research laboratories are able to perform ^{85}Kr analyses on water samples, and groundwater studies on ^{85}Kr are still relatively few (e.g. Rozanski & Florkowski, 1978; Loosli *et al.*, 1989, 1991, 1999; Smethie *et al.*, 1992; Ekwurzel *et al.*, 1994).

In the PALAEAUX study ^{3}H has been the most widely used tracer and dating tool for modern groundwater, while ^{85}Kr and CFC gases have been used only at a few sites.

16.4 Contaminants in aquifers and aquitards

Several compounds introduced by man may also be used to distinguish modern impacts (e.g. Back & Baedecker, 1989; Alley, 1993). These are mainly contaminants from agriculture, sewage or industry (e.g. Plummer *et al.*, 1993; Edmunds, 1996). Such "tracers" are not globally applicable but depend on e.g. industry, land use and agricultural practices. However, many of these components are often found in groundwater below farm lands, landfills or industrial areas and leave significant imprints on the groundwater chemistry (Christensen *et al.*, 1994; Lesage *et al.*, 1997; Mackay & Smith, 1993, and they are present in a large proportion of modern groundwaters.

The contaminants found in aquifers can be considered in three main groups although only the first group (the most mobile) are of use in the PALAEAUX context:

16.4.1 Solutes

Solutes are contaminants which easily dissolve in water (they include inorganic and organic species and species adsorbed on colloids). Pesticides and nitrate are typical examples (e.g. Rao & Alley, 1993; Hallberg & Keeney, 1993), which locally can be recognized in groundwater infiltrated during the past 40–50 years (e.g. Plummer *et al.*, 1993; Böhlke & Denver, 1995). In an illustrative study Böhlke & Denver (1995) established a 40 year record of the recharge rates of nitrate by the use of a combination of CFCs and ^{3}H age-dating in an Atlantic coastal plain, Maryland, USA.

Solutes move with the water in which they are dissolved but are more or less dispersed and delayed by physical and chemical processes in the aquifers depending on the aquifer characteristics and the reactivity of the solute. In fractured/fissured rocks the solutes are strongly delayed due to diffusion of the solutes from the flow zones into the matrix. Soluble contaminants (especially nitrate) are the only group commonly observed in the PALAEAUX project and they are described together with the general hydrochemistry in the different country contributions, therefore they will not be described in more detail here.

16.4.2 Non Aqueous Phase Liquids (NAPLs)

These are contaminants where only a minor fraction can be dissolved in water, the main part is a separate phase immiscible with water. The Non Aqueous Phase Liquids is further divided into LNAPLs and DNAPLs i.e. light and dense liquids respectively. Typical examples are oil (LNAPL) and the chlorinated solvent TCE (DNAPL), Pankow & Cherry (1996). The density of the LNAPLs is less than the water density and they therefore float on the water table. The density of the DNAPLs are higher than for water and they sink to the impermeable bottom of the aquifer. Although the main part of the NAPLs are immiscible with water they slowly release a small part to be dissolved in water, where severe deterioration of the water quality it may result. DNAPLs especially often result in serious contamination problems (Pankow & Cherry, 1996). The DNAPLs are able to penetrate fractures with apertures of a few microns relatively easy (Kueper & McWhorter, 1991; Hinsby *et al.*, 1996; Pankow & Cherry, 1996) and furthermore due to their large density they are able to sink relatively deep into the aquifers, where they may contaminate old groundwaters (Bishop *et al.*, 1993; Lawrence *et al.*, 1996; Pankow & Cherry, 1996). Such DNAPL source zones are capable of contaminating very large amounts of groundwater with highly toxic components to concentrations far above the drinking water standards. Thousands of plumes from such DNAPL source zones have been identified in North America (Conant & Cherry, 1997) and they can be found in nearly all parts of the world, e.g. the chlorinated solvents like TCE (Trichloroethylene) are widely distributed and used. Aquifers that have been polluted with DNAPLs are virtually impossible to clean-up and the aquifers will be contaminated for decades or even centuries.

16.4.3 Microbial contaminants and populations

Pathogens are an obvious indicator of modern groundwater but their mobility rapidly decreases with depth and are not of importance in the present context where the first arrival times of human impacts are relevant.

While there has been a considerable amount of work done on the native microbial populations in shallow aquifers and e.g. their effect on degradation of organic pollutants (Ghiorse & Wilson, 1988), the microbiology of the deep subsurface is a relatively new research area and little is known about the microbiology of deep aquifers (Ghiorse, 1989). However, a pioneering interdisciplinary baseline study of deep aquifers (up to 300 m below surface) shows that active diverse microbial populations different from those in shallow aquifers indeed are present in deep aquifer systems (Ghiorse, 1989). Generally, problems with microbial contaminants in deep aquifers are not common and they are not considered as a problem in the aquifers studied in PALAEAUX. However, mismanagement could introduce pathogens into even deep aquifer systems, and they should be considered in the planning of deep aquifer exploitation and development.

16.5 Modern groundwater advance in European aquifers

The advance of modern shallow groundwaters has important implications for the management and exploitation of the European groundwater resources, due to the risk of severe contamination and deterioration of pristine high quality groundwaters in deeper parts of the aquifers. This section provides a short overview of the advance of modern groundwaters in the European aquifers studied in PALAEAUX.

Table 16.2. Selected information and advance of modern waters in PALAEAUX aquifers.

Aquifer name	Period & type of sediment/rock	Aquifer type	Porosity type	Aquifer thickness (m)	Aquifer depth (m bsl)	Depth of advance (m bs)	Human impact indicators
Ledo-Paninselian	Tertiary Sand	S	P/S	50-80	0-150	<20*	^3H
Glattal	Quaternary Gravel	U	P/S	10	100	100	^3H, $^3H/^3He$, ^{85}Kr, ^{39}Ar
Ribe Formation	Tertiary Sand	S	P/S	<10-40	170-230 [100-205]	70	^3H, (^{14}C, ^{13}C) NO_3, TDS, CFCs
Amurga	Tertiary Basalt		S/D				
Doñana	Plio-Quat. Sand	S	P/S	50-150	0-50	20-40	^3H, NO_3, ^{14}C,
Inca-Sa Pobla	Mioc.+ Quat. Lst & Sand	S	S/D	100-300	20-50	10-40	^{13}C
Tarragona	Trias-Quat. Lst & Sand		P/S and S/D				
Cambrian-Vendian	Cambrian & Precambrian Sand & Siltstone	C	S/D	6-20			
Dogger	Jurassic Lst		S/D				
Dogger (Atl.)	Jurassic Lst	S	S/D	40	0->200	25-35	^3H, NO_3, ^{14}C
Landenian	Tertiary Sand		P/S		[20->200]		
Chalk (South)	Cret.aceous Chalk		S/D				NO_3, TOC, Cl,
Chalk (East)	Cretaceous Chalk	S	S/D	>200 ?	0->800 ?	100 ?	^{36}Cl, ^3H
East Midlands	Permian/Triassic Sst		S/D				Trace elem.
Aveiro	Cretaceous Sst	S	P/S	100-200	20->100	50-60	^3H,^{14}C,
Lower Tagus &	Tertiary Sst/Lst		S/D				NO_3,TDS
Sado			S/D				Trace elem.

Aquifer type: C - confined, U - unconfined, S - semiconfined
Porosity: P/S - primary/single, S/D - secondary/dual
* Located in the leaking confining clay layer above the aquifer.

The advance of modern groundwaters depends primarily on the climate, the geological setting and the degree of exploitation. The spatial distribution and variability of the hydraulic conductivity and porosity in granular aquifers and the fissure distribution in fissured aquifers are key parameters that control the groundwater flow. Other important parameters are the presence and type of confining layers and the depth to the main aquifer.

The contaminants found in many modern groundwaters behave in different ways and give rise to a variety of problems depending on the type of contaminant and the geochemical and geophysical characteristics of the aquifers. Therefore a sound and relatively detailed knowledge of the regional geology and the physical and chemical aquifer characteristics is needed in order to understand and describe the groundwater flow systems and the contaminant transport.

The 18 aquifers selected for the PALAEAUX study include a considerable variation of aquifer types and provide a good representation of different aquifers in Europe. They include granular and fissured, single and dual porosity, marine and terrestrial sediments, as well as metamorphic and volcanic rocks. Mesozoic and Tertiary carbonates and sand(stones) are the most common and important aquifers. The study includes confined, semi-confined and unconfined aquifers at depths of between only a few tens of metres up to several hundred metres. This provide a good basis for a general assessment and comparison of the advance of the modern groundwaters into the sedimentary basins and the human impact on the aquifer systems in different aquifer types of Europe. Table 16.2 summarizes selected basic data on the aquifers studied under PALAEAUX and the modern groundwater advance in these aquifers. It should be noted however that some generalizations have had to be made.

Generally, the advance of modern groundwaters are easiest to predict and describe in granular aquifers with a primary porosity (Fig 16.3) although more difficult granular aquifers e.g. where glaciotectonic processes disturbed the sediments to a considerable extent (Hinsby *et al.*, 1999*a,b*). The problem of predicting modern groundwater advance is more pronounced in aquifers with a dual (fracture and matrix) porosity. The situation is illustrated diagramatically in Fig. 16.4. where different rates of movement and concentration gradients are implied between the matrix and fissures. It should be noted, however, that nature may be more complex and that several of the aquifer systems in the PALAEAUX study in reality may be more complex.

The observed differences between the study sites illustrated in Table 16.2 are primarily a consequence of differences in the hydrogeological setting. For instance upward flow (inverse hydraulic gradients) in the Inca-sa Pobla discharge area on the island of Mallorca, Spain prevents the downward advance of modern contaminated groundwater. In contrast the significant advances of the modern groundwaters in the Glattal and East Midlands aquifers are due to highly permeable zones above and in the aquifers and a relatively high infiltration in the recharge area.

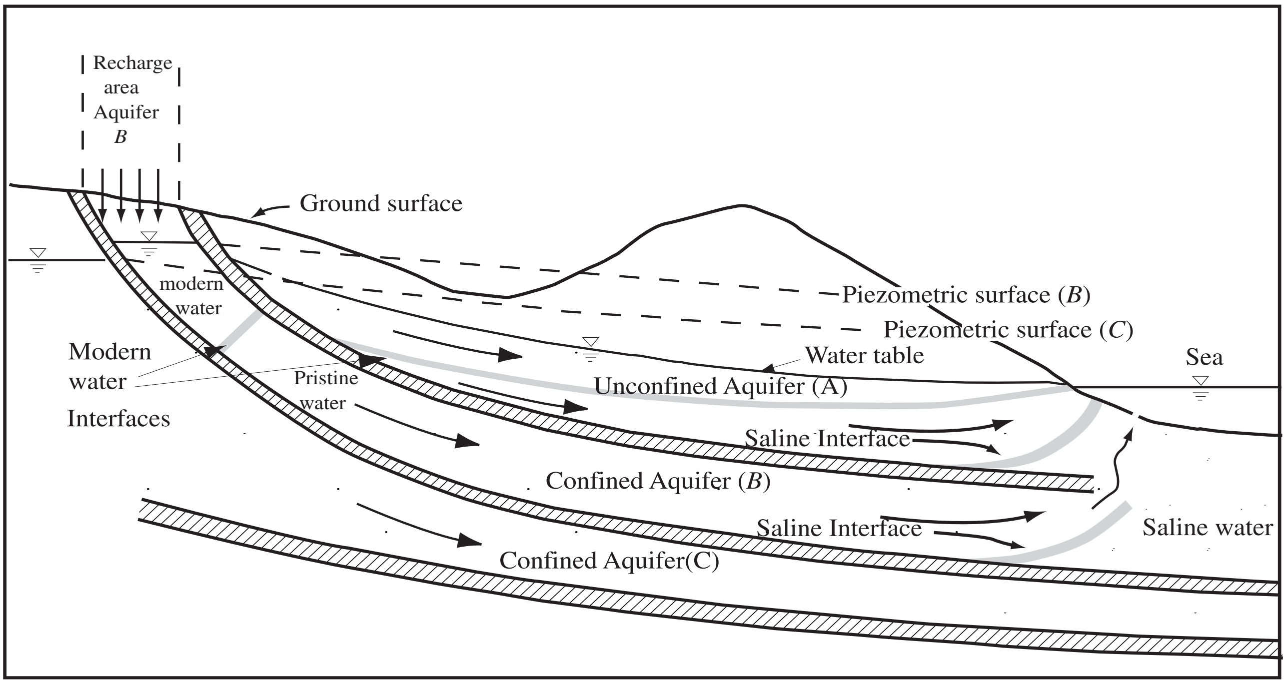

Figure 16.3. Conceptual model of a coastal unconsolidated granular aquifer system with an unconfined and two semi-confined aquifers illustrating a setting where a piston flow model approximation may be applicable. The modern/pristine water interface in the recharge area of the confined aquifer (B) and the sea water interfaces in the discharge area at the coast are indicated. Modified after Bear (1979).

To illustrate similarities and differences between modern water advance in the studied aquifers in a little more detail five aquifers representing different situations have been selected for further description.

16.5.1 Ribe Formation, Denmark

In the Ribe Formation there are no indications that modern groundwaters have reached the aquifer. The deepest certain recognition of groundwater with a modern input as recognized by ^{3}H and supported by $^{14}C/^{13}C$ and chloride is in a screened interval at a depth between 65 and 73 m below the surface in the unconfined recharge area (Fig 16.5). An even deeper well screened between 89 and 92 m below surface has a low but significant ^{3}H content indicating a component of modern groundwater. This water may have been infiltrated in the early 1950s, however, a more reasonable explanation is probably that the measured ^{3}H

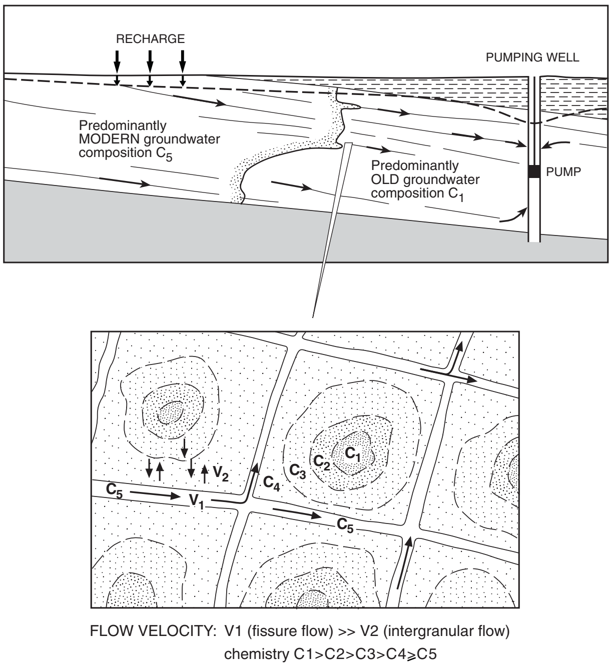

Figure 16.4. Fissured/double porosity flow with interfaces at two scales.

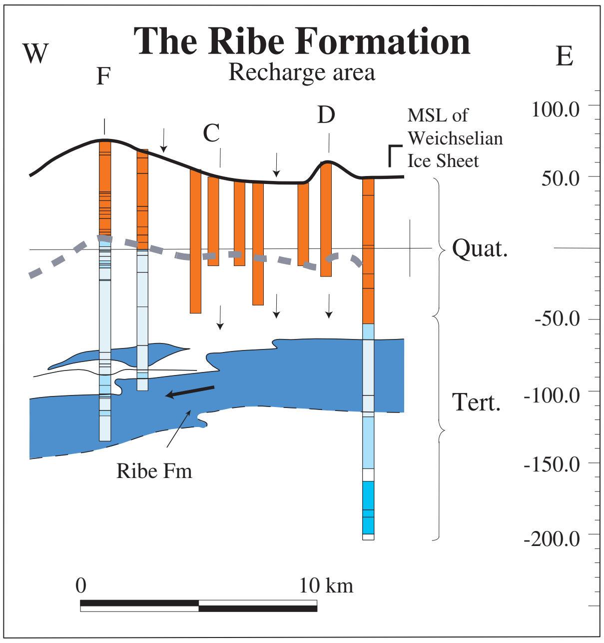

Figure 16.5. Close up of the recharge area to the Ribe Formation showing the estimated location of the modern water interface.

result from small contributions of younger water from layers above the screen either through a slightly damaged screen or draw down to the screen through the gravel pack in the developed zone around the well.

In the study of the groundwaters above the Ribe Formation the most important indicators of modern groundwater have been ^{3}H, ^{14}C/^{13}C, CFCs and the combined impact from agriculture (e.g. NO_3, SO_4, Cl, TDS and TOC). It has been observed in several studies in Danish aquifers that groundwater impacted by agriculture typically show a 2–4 times increase in total dissolved solids (e.g. Hinsby, 1988; Postma *et al.*, 1991). Pesticides, are other contaminants that relatively often are found in Danish groundwaters, but they have not been analysed for in this study. However, pesticides have been found to maximum depth of about 70 m below the surface in Denmark, corresponding to the depths where ^{3}H disappears (GEUS, 1995), and to the modern groundwater advance in the recharge area to the Ribe Formation found in this study. This indicates that the depth of the modern water interface we observe in the recharge area to the Ribe Formation generally is the maximum depth of the advance of the modern groundwaters in Denmark. As the recharge area to the Ribe Formation is located in one of the areas with

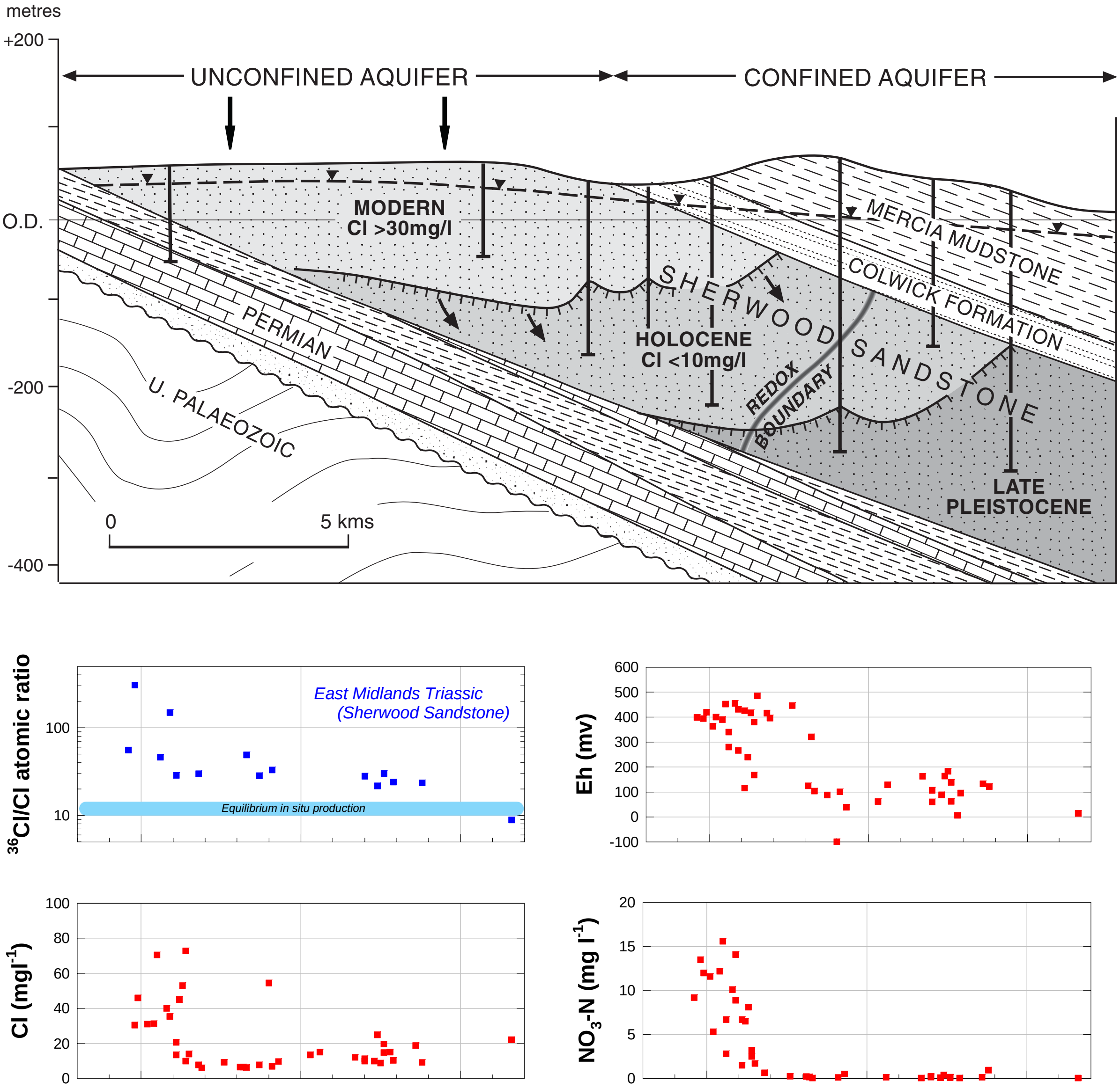

Figure 16.6. The confined/unconfined boundary region of the East Midlands Triassic aquifer, UK where modern waters may be traced as they are introduced mainly by pumping into the confined section. The aquifer is confined by marls and mudstones (Mercia Mudstones of Triassic age) and is underlain by marls and dolomitic carbonates of Permian age. The position of pumping wells is shown schematically, to illustrate the heterogeneous nature of the well field. Waters of Holocene and late Pleistocene age can be distinguished both isotopically and chemically and may still be identified in the deeper well sections (e.g. from depth sampled borehole profiles, see Fig. 5.12). The relative position of the redox boundary is shown. This remains at present within the waters of Holocene age, although modern waters are being drawn towards it by abstraction of the older (non-renewable) palaeowater. Examples are given of four indicators (Cl^-, ^{36}Cl, NO_3^-, Eh) of the modern water influx across the whole aquifer to show the limits of modern water and the situation of the redox boundary.

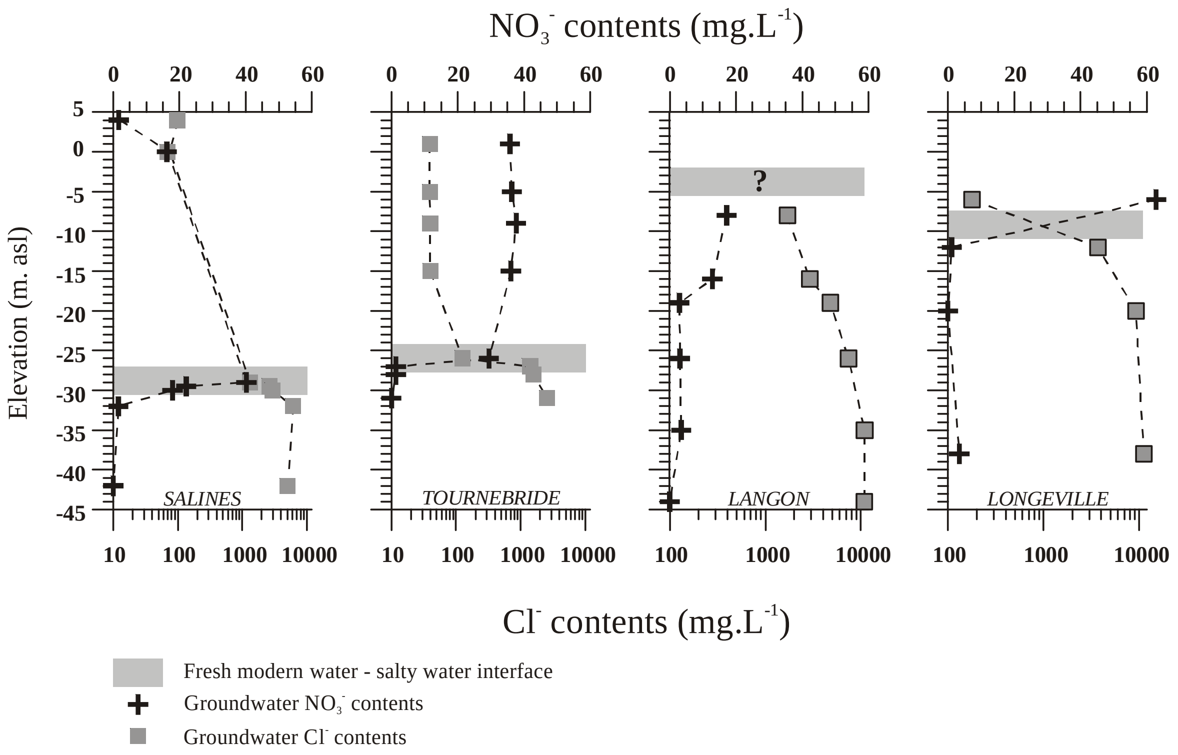

Figure 16.7. Illustration of the advance of a modern water interface in the Dogger aquifer at the French Atlantic coast.

the largest estimated infiltration the climate data are in agreement with this conclusion.

The observation of pesticides at such relatively large depths is in accordance with recent research that shows that some pesticides either degrade very slowly or do not degrade at all in some unpolluted groundwaters (e.g. Agertved *et al.*, 1992; Klint *et al.*, 1993; Aamand *et al.*, 1999), and with the possible use of pesticides as tracers even for the older parts of modern groundwaters infiltrated in the 1950s and 60s (Plummer *et al.*, 1993). That is pesticides may eventually advance into even deep aquifers. In contrast the nitrate contents are generally reduced by mainly organic matter or pyrite before they reach the deep aquifers. However, nitrate is generally followed by other major inorganic ions such as chloride and sulphate, and the reducing agents (organic matter, pyrite) produces an increase in sulphate and dissolved inorganic carbon in the groundwater, when nitrate is reduced i.e. agricultural activities can generally be observed on the inorganic groundwater chemistry (e.g. Appelo & Postma, 1993).

16.5.2 East Midlands Triassic Sandstone Aquifer, UK.

An example of the scale of movement of modern water with several contaminants derived from industrial and agricultural activities into an environment with well documented palaeowater is provided by the East Midlands (Sherwood Sandstone) Triassic aquifer in Eastern England (Edmunds *et al.*, 1984) In Fig. 16.6 the modern contamination in this aquifer can be recognized by a range of indicators which include in particular NO_3^- (shown here) and TOC, The imprint of industrial activity, aerosols and rain can be clearly seen near to outcrop in the concentrations of Cl (Fig 16.6). The isotopic signature of ^{36}Cl, derived from sea-level thermonuclear testing and above a background value of about 30×10^{-15} for the atomic ratio of ^{36}Cl/Cl confirms the presence of recent water and modern water is also confirmed by tritium ^{3}H in the same waters (Edmunds *et al.*, 1984, 1994, Andrews *et al.*, 1994) . Thus both chemical and isotopic tracers together are important for defining the palaeo/modern water interface or mixtures of different water types.

16.5.3 Dogger aquifer, western France

The modern influence of human and agricultural activities is clearly demonstrated in some areas of the Dogger aquifer along the Atlantic coast. The unconfined part of this aquifer is characterized by recent groundwater with high nitrate and tritium contents. At the limit of the Callovian marls, the hydrochemical stratification of groundwater from the confined part of the aquifer allows a distinction to be made between two water-bodies: fresh water with high nitrate concentrations is recognized in the upper 15–25 m while marine solution with high chloride contents is found deeper in the aquifer (Fig. 16.7). The isotopic study (^{3}H, ^{13}C and ^{14}C) of the two water-bodies provides evidence of two distinct periods of recharge. The nitrate-rich fresh water is of modern age as defined by ^{14}C activities, over ca. 70 pmc, and with detectable ^{3}H contents. In contrast, the deep marine solution, nitrate- and tritium-free (the low nitrate possibly the result of a reducing environment), is characterized by ^{14}C activities over 50 pmc, indicating a recharge period older than that of the fresh water. In this system, there no evidence of natural process leading to the mixing of modern contaminated water with the salty solution. However, this mixing may occur by intensive pumping of the fresh water, which maylead to the displacement of the saline wedge toward the unconfined aquifer during the summer period.

16.6 Discussion

16.6.1 Modern groundwater indicators

The occurrence of Pleistocene, Holocene and Modern groundwaters in aquifers are controlled by the geological setting, climate and human activities. The advance of modern contaminated groundwaters i.e. the depth to the interface between modern contaminated waters and pristine "palaeowaters" therefore may vary considerably from place to place. To estimate the advance of modern contaminated waters a sound knowledge of the geological and climatological setting and their variability as well as the human development of the aquifer is needed. However, the modern water interface or the extent to which a given water is influenced by modern waters can be recognized and defined quite well by the use of isotopic and chemical tracers either in the water molecule or dissolved in the water. Some tracers are globally applicable but others are only applicable locally depending on e.g. land use and industry. Therefore a sound knowledge of the regional conditions will help to select the best tracers at a given site. Generally the advance of modern groundwaters can be recognized all over the world by using tracers carefully selected on the basis of regional conditions. This however, does not mean that the systems are easy to understand and describe. The complexity of most geological settings often leave us with only a fragmental understanding of the systems. In such cases the use of multiple tracers is inevitable in order to understand the systems. Groundwater flow models for the description of water and solute transport and for managing the aquifers give little meaning in these settings unless they are calibrated by tracers and combined with geochemical studies.

^{3}H and nitrate have been the two most important and widely used indicators of modern waters in the PALAEAUX project, although others (e.g. ^{85}Kr, ^{36}Cl/Cl, Cl and CFC's) have been included too in some aquifers. ^{3}H is nearly a perfect tracer as it is part of the water molecule and not influenced by water/rock interactions. Low level detection limits (0.03-0.04 TU) as obtained in a laboratory in the Southern Hemisphere (Taylor, 1998) still give the tritium measurements large value even today, where the atmospheric tritium level are very close to the low prebomb values. Nitrate is also a valuable tracer and it is widely used as an indicator of agricultural impact. However, nitrate is dissolved in the water and takes part in geochemical reactions in the aquifer, e.g. it can be reduced quite fast by organic matter and/or pyrite in the aquifers (Trudell *et al.*, 1986; Postma *et al.*, 1991), i.e. nitrate should not be the only tracer used for indication of modern waters. If significant nitrate concentrations were originally present in the groundwater this would generally be recognizable by other major ions such as sulphate and dissolved inorganic carbon in the waters (e.g. Appelo & Postma, 1993).

CFCs and ^{85}Kr are valuable modern water indicators as supplements to ^{3}H and nitrate especially as they can be used as absolute age-dating tools in many aquifers. However, sampling techniques are relatively complicated for both these techniques and demand special training. Furthermore the stagnating or decreasing CFC concentrations in the atmosphere result in problems for the absolute age-dating of the youngest (<10 a) groundwater by the CFC-method. Another problem related to the use of CFC gases as absolute age-dating tools are the possible degradation of all CFC-gases in some anoxic environments (Oster, 1995; Hinsby *et al.*, 1997, 1999). CFC gases are generally not recommended as absolute age-dating tools under anoxic conditions unless it is documented that no degradation of the CFC gases occur in the aquifer. If however all CFC gases used for age-dating (CFC-11, -12 and –113) estimate similar groundwater ages no degradation of CFC gases are expected.

Problems with ^{85}Kr include the large amount needed for analysis (500–1000 L) and the complicated analysis. However, new analysing techniques might reduce the sample size considerably (Thonnard *et al.*, 1997) and ^{85}Kr must be considered as a very promising tool for absolute age-dating of young groundwater in the future. ^{85}Kr concentrations in the atmosphere originating from nuclear installations are expected to increase steadily in the future (Loosli *et al.*, 1991; Loosli *et al.*, 1999) in contrast to ^{3}H and CFCs which are expected to stagnate and decrease, respectively.

To complete the picture we should mention the potential tracer and absolute age-dating tool SF_6 (sulphur hexafluoride). SF_6 has not been used in the PALAEAUX project as it is a relatively new and not very well studied tracer. However, it might have some potential in the future, due to a fast growing concentration in the atmosphere and its conservative behaviour in the atmosphere and the groundwater environments (Busenberg & Plummer, 1997).

16.6.2 Protection and development

The distribution of modern water indicators in the PALAEAUX aquifers show that the deeper parts generally seem to be quite well protected against contamination from above at least in unstressed situations. This is generally due to the existence of confining layers, natural attenuation and/or present day shallow circulation in the groundwater systems. However, excessive development of the deep aquifers stresses the systems considerably and may in some cases lead to overexploitation and contamination. Likewise wells that punctuate aquitards or penetrate highly conductive fractures sometimes result in intrusion of saltwater or contaminants especially in places with heavy pumping.

Recent investigations of contaminant transport in aquifers e.g. from land fills illustrate the efficiency of natural attenuation in the removal of many contaminants from groundwater (e.g. Christensen *et al.*, 1994), however the degradation of contaminants in aquifers depends very much on the geochemical and microbiological environments. For instance some pesticides or some of their even more toxic metabolites do not degrade or degrade only very slowly especially in anoxic unpolluted groundwater environments (e.g. Agertved *et al.*, 1992; Klint *et al.*, 1993; Aamand *et al.*, 1999). Such contaminants therefore may with time contaminate even deep aquifer systems (GEUS, 1998). The knowledge of the fate of contaminants in groundwater should be used when planning the abstraction and development of aquifers, and when defining groundwater protection zones. It is therefore important to investigate the behaviour of the different contaminants thoroughly i.e. not only to register the attenuation of the primary contaminants but also to follow the fate and degradation of their metabolites in order not to ignore the existence of any toxic substances.

The globally increasing demand for freshwater resources put a large pressure on aquifers, where the main part of the worlds easy accessible fresh water resources are stored. Consequently the abstraction of high quality groundwater resources, the focus of the present project-must be optimized globally in order to exploit the resources to an optimal but sustainable extent. This puts emphasis on the strongly needed development of a) integrated groundwater and surface water modelling tools and b)dating and tracer tools for the calibration of the models, and understanding of the groundwater flow systems. Geophysical and geological measurements and mapping techniques for a proper description of the geological setting and the hydraulic parameters that influences groundwater flow are equally important. Integrated hydrological models can only be as good as the geological models on which they build.

16.7 Conclusion

The recognition and location of the modern water interface is of key importance in the management of groundwater resource in order to avoid inadvertent severe contamination of the pristine parts of aquifers. In the aquifers studied in PALAEAUX the interface is located at depths from approximately 10 to 100 m below the surface. The shallowest interfaces seem to be on the island of Mallorca, Spain, and in the Ledo-Paniselian aquifer in Belgium and the Netherlands, while the deepest is from Switzerland and Great Britain. The observed differences between the sites are primarily a consequence of differences in the hydrogeological setting, e.g. upward flow in the Inca sa Pobla discharge area on the island of Mallorca prevents the downward advance of modern contaminated groundwater, and in the Ledo-Paniselian aquifer the confining Bartoon clay close to ground surface in the recharge area prevents the advance of the modern water interface. The modern water interface is not recognized in the Bartoon clay but the interface must be located in this unit, as there generally are no modern water indicators observed in the Ledo-Paniselian sand aquifer below. In contrast the relatively deep advance of the modern groundwaters in the East Midlands aquifer is due mainly the large abstraction at outcrop and near the confined/unconfined boundary.

The isotopes ^{3}H, ^{3}H/^{3}He and ^{85}Kr, and the CFC-gases, presently seem to be the most important of the environmental tracers and dating tools globally applicable for the study and recognition of modern groundwater. The dissolved components nitrate, TOC, TDS, pesticides, chlorinated solvents and trace elements are important as indicators of human contamination as well. However, although these tracers are quite common they are not present everywhere.

All of the tracer and dating techniques mentioned above and used in the PALAEAUX project have large potentials in the study of modern groundwater and in location of the modern water interfaces. Generally though the groundwater investigations do not allow for analysis of all relevant tracers. To get an optimal amount of information from the applied tracers it is therefore important to carefully select the tracers on the basis of the local conditions and the purpose of the study. However, the use of multiple tracers is generally recommended to eliminate errors and to constrain possible conclusions as much as possible.

Of the more sensitive methods, the ^{85}Kr method might be considered as having the largest potential in the future, especially if new analysing methods demanding only relatively small amounts of water (1–5 L) are developed. This is due to the fact that the steady and significant increasing ^{85}Kr concentration in the atmosphere are expected to continue, and that no microbial degradation of ^{85}Kr can occur in the aquifers. However, low level ^{3}H measurements and CFC gases will probably also be important tools during the next decades due to their relatively easy and inexpensive measuring techniques. In the aquifers studied in the PALAEAUX project the concentrations of inorganic ions, and organic contaminants are quite often sufficient to indicate, qualitatively, the presence of a modern water component. However, in cases where mixing occurs, or quantitative information is needed e.g. an absolute age estimate, dating tools such as ^{3}H, ^{85}Kr and CFC-gases are necessary.

Deep pristine coastal groundwaters are a valuable resource, that should be carefully managed in order to protect the high quality waters against overexploitation and contamination. One of the main issues is to control the position of the modern water interface. The main tools used for this are groundwater flow models and monitoring of water quality at strategic locations. Management schemes and groundwater protection zones for important aquifers should be outlined. Finally, as the information on the behaviour of resistant contaminants in aquifers increases the gained knowledge should be utilized in the sustainable management of the aquifers and in the planning of potential land use restrictions.

17 Groundwater evolution at the European coastline

17.1 Introduction

The hydrogeological conditions near the European coasts have been considered elsewhere in this report mainly on a national basis, reflecting the need to identify the contributions of each partner. This chapter is an attempt at integration, to consider the implications of the new PALAEAUX results at a European scale, region by region. To achieve this the results are presented as a series of maps (Fig. 17.1) supported in some areas by cross sections across the coastlines to demonstrate the likely occurrence of palaeowaters. For each region the modern bathymetry has been used as the basis for reconstruction of the coastline at or near the Last Glacial Maximum (the chosen time slice varies from region to region). Other significant features which had an impact on groundwater movement, such as geological structure offshore, ice limits and palaeodrainage are also shown.

The main objective is to present the hydrogeological results of the present PALAEAUX project against the relevant data from other studies on the late Pleistocene and Holocene. This is important since for most hydrogeological investigations only the modern coastline is considered as the boundary.

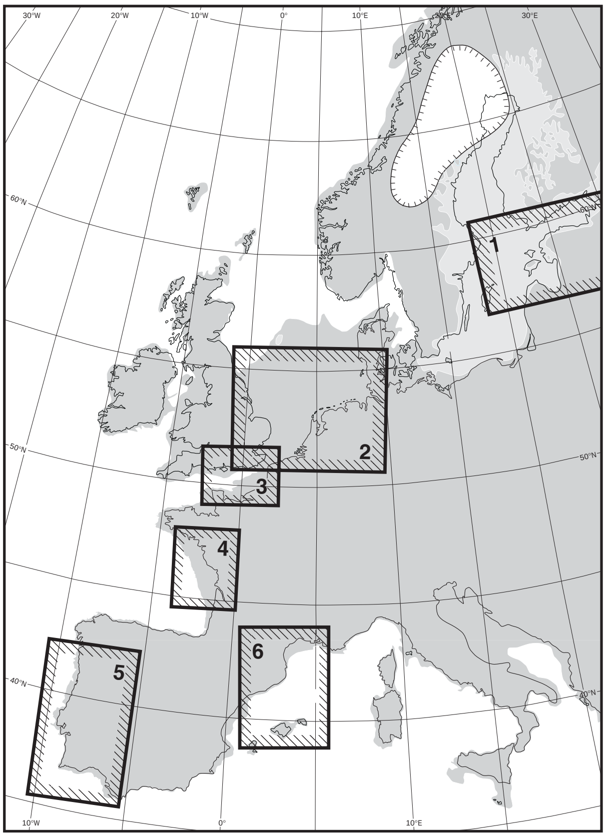

Figure 17.1. Map of Europe showing the areas discussed in detail in this chapter: (1) Baltic; (2) North Sea; (3) Channel; (4) French Atlantic Coast; (5) Portugal/SW Spain; (6) W Mediterranean.

17.2 Baltic Region

17.2.1 Aquifers of the northern Baltic coast in Estonia

The hydrogeological cross-section in Estonia (Fig. 2.2) consists of three principal hydrostratigraphical units.

(i) Quaternary deposits. The sandy and clayey Quaternary deposits and peat form porous aquifers with mainly unconfined groundwater which are directly influenced by meteorological conditions. All infiltration water percolates into the Quaternary cover and the greater part of groundwater discharge flows through it. The upper portion of the Quaternary cover is unsaturated.

(ii) The bedrock. The terrigeneous and carbonate Palaeozoic and Proterozoic rocks form porous, fissured and karstified, mostly confined aquifers, which are isolated from each other with aquitards of different isolation capacity. In the karst cavities near the surface, shallow groundwater flows very fast and its chemical composition is close to that of the surface water. However, the deeper strata contain pre-Quaternary groundwater, which is high in total dissolved solids (TDS) and moves very slowly under natural conditions.

(iii) The crystalline basement. Predominantly pre-Quaternary groundwater in the fissures of igneous and metamorphic rocks containing high rate TDS and under natural conditions is effectively stagnant. The lower portion of the crystalline basement serves as an impermeable base for the whole overlying water-bearing formation in Estonia.

For the PALAEAUX project the principal study object in Estonia has been the Cambrian-Vendian aquifer system (C-V), whose sandstones and siltstones are divided into an upper, Voronka (Vr), and a lower, Gdov (Gd), aquifer in East Estonia. They are separated by the Kotlin aquitard (Kt). The Cambrian-Vendian aquifer system thins out in southern and western Estonia but in northern Estonia its thickness amounts to 90 m. This aquifer system outcrops along the northern coast of Estonia beneath the Gulf of Finland. The Vendian strata are, as a rule, well protected from surface pollution by the Lükati-Lontova aquitard and they are the most important source of good drinking water for North-Estonia. However, in places the water-bearing bedrock formation has been penetrated by a quite dense set of ancient buried valleys filled mostly with loamy till but sometimes glacio-fluvial gravel occurs in lower portion of valleys.

17.2.2 Palaeohydrological conditions of the late Pleistocene

The palaeohydrology of the Baltic Sea basin at around 11 600 a BP is shown in Plate 17.1. To contrast with the coastal areas of north-west Europe and the Mediterranean, where groundwater circulation during the LGM was in many cases activated because of an emerged shoreline due to sea level lowering, in the Baltic area the groundwa-

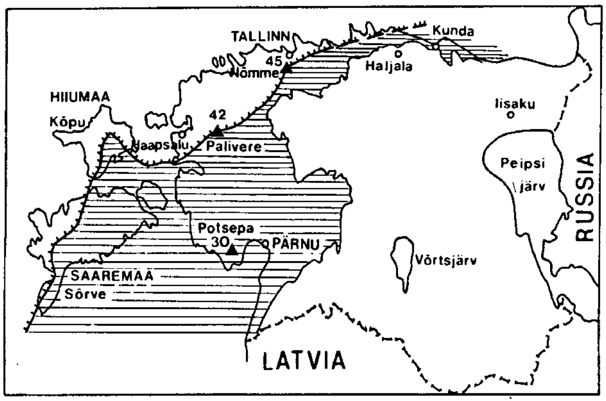

Figure 17.2. Palaeogeographic scheme showing the maximum extent of the Fennoscandian ice sheet in Estonia at the Palivere stadial (about 11.6 to 11.7 ka BP). The hatching denotes the area under the ice dammed lake. Triangles mark the elevation of aqueoglacial forms above the present sea level (from Raukas, 1997).

ter recharge and circulation ceased or was strongly inhibited at this time due to ice cover and/or permafrost.

During the LGM the whole Baltic area and northern Poland was covered by the Fennoscandian ice sheet (Fig. 11.7). Different reconstructions of the ice sheet have yielded different results. According to the ice model, proposed by Denton & Huges (1981), the ice thickness over the Baltic States area at that time was about 2500 to 2800 m. A new modified ice sheet model by Lambeck *et al.* (1998), based on sea-level data and on the geological record of crustal response to glacial unloading since the time of the LGM, shows that the ice sheet thickness over the Baltic States area at 18 ka BP was only about 600 to 800 m. The final ice recession from the south-western Baltic basin occurred 13.5 to 13 ka BP (Berglund, 1979). The Estonian territory became ice free during a time span between 13 and 11 ka BP (Raukas, 1996). The rapid deglaciation produced huge volumes of meltwater and icebergs and therefore during the last stages of ice sheet retreat practically the whole area in front of the ice margin was covered with vast ice dammed lakes which, starting at least from the Palivere stage (Fig. 17.2) formed the eastern part of the Baltic Ice Lake.

Due to the stadial-oscillatory character of deglaciation, the level of the Baltic Ice Lake changed rapidly several times. Thereby, the level of the lake was mainly controlled by the presence or absence of glacial ice in the area of Mount Billigen in Central Sweden (Fig. 11.18). During this very dynamic time period in the history of the Baltic Sea the water level was dammed above sea level during three periods, 12 to 11.2 ka BP, 10.8 to 10.3 ka BP and 9 to 8 ka BP (Björck, 1995). This damming was caused by the ice sheet itself and the isostatic uplift of the functioning threshold. The complex threshold history combined with the fact that the uplift centre of the late Weichselian-Fennoscandian ice-sheet is situated in the northern part of the Baltic basin, and the southernmost region of the Baltic is regarded as a submergence region, means that the early Baltic Sea history was characterized by both regressions and transgressions, often occurring at the same time in different parts of the basin (Björck, 1995, Raukas, 1996).

At the end of the Younger Dryas cold stage the rapid amelioration of the climate caused rapid retreat of the ice margin, and the Baltic Ice Lake drained catastrophically into the North Sea via the Öresund Strait. Its surface was lowered by 26–28 m within only a few years (Björck, 1995). An open sound north of Billingen provided direct connection between the Baltic basin and the North Sea (Strömberg, 1989). The final drainage according to Björck & Digerfeldt (1986) is dated at 10.5 to 10.4 ka BP. However, as a result of further dating (Wohlfarth *et al.*, 1993) the age of the event has been adjusted slightly to ca 10.3 ka BP (Björck, 1995). A marine incursion into the Baltic, identified by marine fauna, occurred briefly, from about 10.3 to 9.5 ka BP, forming the low salinity Yoldia Sea. According to those data, the development of the Baltic Sea between 13 and 8 ka BP can be divided into three main stages: the Baltic Ice Lake stage, 13 to 10.3 ka BP; the Yoldia Sea stage, 10.3 to 9.5 ka BP and the Ancylus Lake stage, 9.5 to 8 ka BP.

In the context of the PALAEAUX project it is important to stress that, in spite of several drastic changes in the Baltic Sea level (Fig. 11.19) and the high glacioisostatic uplift rate in north Estonia during and after the last deglaciation (13 mm a^{-1} in preboreal time and 2-3 mm a^{-1} at the present time in the north-west Estonia (Raukas & Miidel, 1995)), the main discharge area of the coastal aquifer into the Gulf of Finland has been submerged during all stages of the Baltic Sea.

The results of isotope and geochemical investigations and noble gas analyses, performed in the frame of PALAEAUX project show, that the water in this Cambrian-Vendian aquifer complex in northern Estonia recharged during the last glaciation (see Chapter 2). During the Late Weichselian the base of the ice sheet over the Cambrian-Vendian outcrop area in Estonia was in a molten state for about 11 ka (Jõeleht, 1998). During this time the hydraulic head was controlled by the thickness of the ice. Although the Cambrian-Vendian aquifer system itself has high hydraulic conductivity, it is surrounded by areas of low hydraulic conductivity and therefore the hydraulic head in the outcrop area of aquifer system was probably close to floating point, e.g. about 90% of ice thickness (Piotrowsky, 1977). Taking into account also the postglacial uplift and the present depth of the Cambrian-Vendian aquifer system (about 100 m bsl), the hydraulic gradient was around 0.0031 (Jõeleht, 1998). Thus, the recharge of the Cambrian-Vendian aquifer most probably occurred during the glaciation, most probably by subglacial drainage through the tunnel valleys (Chapter 3).

17.2.3 Impacts due to development

Since the Cambrian-Vendian aquifer belongs to the subzone of slow groundwater flow, prior to human exploitation the groundwater had high quality as pure glacial meltwater

In 1998, in Estonia about 200 000 m^3 of groundwater were abstracted from bored wells per day, meeting up to 70% of the municipal, industrial and domestic requirement for drinking water (Vallner, 1997). Approximately 90% of this water was used for supplying towns and settlements, the remaining portion was consumed in agricultural regions. On average, 80 000 m^3/d were abstracted from the Cambrian-Vendian aquifer system, and 50 000 m^3/d from the Silurian-Ordovician aquifer system. Only in Tallinn and Narva the consumption of purified surface water exceeded that of groundwater. Everywhere else groundwater has always been the principal source of public and private water supply.

Basin-wide hydraulic head depressions have been the most obvious result of intensive groundwater abstraction (Vallner, 1994; Vallner, Savitski, 1997). Since 1947 the potentiometric surface of the Cambrian-Vendian aquifer system has quickly fallen showing maxima of depressurization in Tallinn and Kohtla-Järve. In these places the head was withdrawn to depths of 30 and 56 m below the mean sea level, respectively. During the last five years the potentiometric surface of the Cambrian-Vendian aquifer system has risen by 10–15 m due to reduction of the pumping rate.

Owing to the head lowering, the groundwater inflow into the Cambrian-Vendian aquifer system from adjacent strata has grown significantly. Drawdown contours show that half of the increased inflow is coming from the sea, and consequently, the remaining portion must consist of downward, upward, and southward lateral flows. The downward flow provides the Cambrian-Vendian aquifer system mostly with fresh water, but the rising flow may also be connected with upconing of brines from the crystalline basement; the lateral flows induce the transport of connate brines from the deeper parts of the aquifers or sea water intrusion to the groundwater intakes.

In Tallinn, the outcrop of the Cambrian-Vendian aquifer system is situated on the sea bed near shore intakes, and therefore, saline sea water may intrude into production wells. Nevertheless, indisputable evidence of this feared phenomenon is still lacking at present. An increase in TDS from 0.5 to 1.3 g L^{-1} has been registered in well water in the northern part of Tallinn but data from isotope analyses confirm that it is caused by upconing of brines from the crystalline basement or the lowest Vendian strata.

However, so long as the potentiometric surface of the Cambrian-Vendian aquifer system is below sea level, the salt water encroachment continues and must eventually reach the inland intakes. Only if the potentiometric surface rises above sea level, will the sea water intrusion cease. At the pumping intensity of 70 000 m^3/d in the Tallinn area, the lateral salt-water encroachment most likely will reach the coastal wells within ten years.

In principle, sea water intrusion could be hindered by rearranging a basin pumping pattern. If pumping were to be concentrated as far as possible from the seashore, deeper drawdown would increase the recharge of the aquifer from overlying inland strata, whereas reduced pumping near the coast might allow the water level to rise to aid in repelling the entrance of sea water. Therefore, it is highly advisable to tap the Cambrian-Vendian aquifer system by groups of new wells at a distance of 10–20 km or even more from the sea. It is recommendable to recharge deep aquifers artificially. In many places in North Estonia the water table of the Silurian and Ordovician aquifers is 20–80 m higher than the potentiometric surface of underlying deep aquifers. Upper and deep aquifers should be linked by recharge wells. Then shallow groundwater would intrude without any pumping into deep aquifers and their reserves will increase.

The measures described will postpone and mitigate, but not prevent, the unfavourable phenomena of sea water intrusion. However, this is an optimum way to obtain up to 50 000 m^3 good drinking water per day from the Cambrian-Vendian aquifer for the next 50 years which should meet the needs of Tallinn.

In north-east Estonia where the oil shale industrial enterprises have concentrated the Cambrian-Vendian aquifer system has been the principal source of public drinking water supply whereas the streamwater and other aquifers are heavily polluted. Here the eastern part of the Gdov aquifer contains brackish water with TDS reaching 1.2 g L^{-1} In waterworks this water is mixed with fresh Quaternary water gained from the territory of the Kurtna Landscape Reserve. This way an acceptable chloride concentration in public drinking water is obtained in Ahtme and Jõhvi.

It is likely that in the oil shale region the need in drinking water may be met mostly by intensive pumping from the Cambrian-Vendian strata. Here their submarine outcrop is situated further away from the intakes and the sea water encroachment is not as acute as in Tallinn. In addition, shifting the of groundwater intakes inland would significantly postpone the salt-water intrusion into the aquifers.

The high-quality palaeowater abstracted from the Cambrian-Vendian aquifer system should be considered as a valuable non-renewable mineral like as petroleum, coal, the use of which is dictated by economic and social considerations (Vallner, 1999). If necessary, pumping from deep aquifers may continue at present levels or even increase, but society must be aware that the deep groundwater gained will ultimately be replaced mostly by sea water or deep connate brine. In view of this complex situation in which everything is mutually dependent, a well-founded long-term integrated water management plan is urgently needed for Estonia. This means that the surface water, groundwater, and environmental problems should be considered jointly both in the local and a wider regional context. Such an integrated plan would enhance the authenticity of proposed projects, but requires the purposeful research in the field of hydrogeology, water engineering, and environmental technology.

17.3 North Sea Basin

The palaeohydrology of the North Sea Basin at around 10 000 a BP is shown in Plate. 17.2. Almost the whole area was subaerial with the coastline lying at this time to the north of 54°N (Cameron *et al.*, 1992). The Weichselian ice extent at the Last Glacial Maximum extended onto the present day east coastal areas of UK and Denmark, affecting areas which are the subject of interest in the PALAEAUX study. During and immediately following the LGM, the area was drained by the two major river systems of the Rhine (flowing south-west out of the English Channel) and the Elbe, flowing north-west via the Heligoland Channel.

The present day bathymetry is at best an approximation to the former subaerial topography. Glacio-isostatic adjustments have led to rise of the land surface although the long term rate of subsidence of the North Sea Basin over the Pleistocene as a whole is between 0.35–0.50 m ka^{-1} (Cameron, 1992). Sea-bed erosion has also caused some modification of the original late Pleistocene and Holocene deposits and features. The relatively flat-lying topography and the subsiding basin structure over most of the area has not allowed significant freshwater flushing of the region. The base levels locally may have been enhanced by channel formation (eg Heligoland Channel to probably as much as –90 m below OD, Konradi, pers.comm.) or at the time of the LGM by offshore deeps caused by glacial scouring (Silver Pit to –95 m OD present

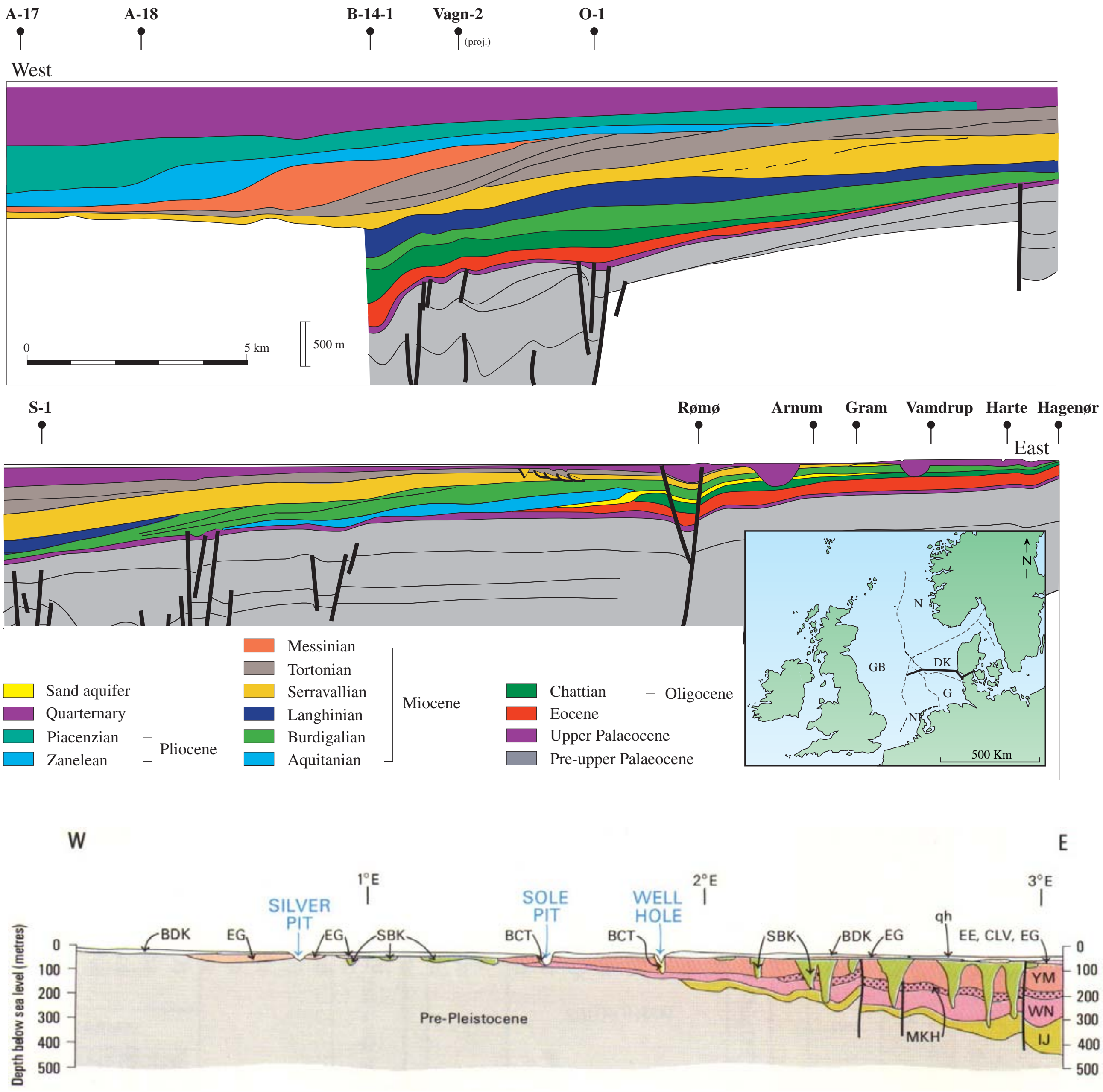

Figure 17.3. Cross sections through the Pleistocene formations in relation to older strata off the East Coast of England and the west coast of Denmark, based on Cameron *et al.*, 1992 and unpublished data from GEUS. The Chalk outcrops in the Silver Pit and the flow in the Ribe formation (arrowed) may be controlled by the glacio-tectonic features.

depth) which may have been formed by outbursts of glacial melt-waters close to the ice margin (Wingfield, 1990).

17.3.1 Aquifers of the North Sea margins

The aquifers studied in PALAEAUX can be used to investigate the impacts of the late Pleistocene and Holocene on groundwater evolution. Much of the area is underlain by Holocene, Plio-Pleistocene or Neogene deposits and these younger formations could have contained fresh or saline formation water depending on the depositional history. The principal aquifers of interest are shown in Plate 17.2. In the UK these are the Triassic aquifer of the East Midlands (A-A') the Chalk of Lincolnshire (B-B') and Yorkshire (C-C') and in North Kent (E-E'). In the Netherlands and in Denmark two aquifers of Cenozoic age, the Ledo-Paniselian (F-F') and the Ribe Formation (G-G'), are investigated. Offshore sections referred to in the text are also shown off Denmark (G'-G'') and the English Coast (D-D').

17.3.2 Palaeohydrological conditions

The outcrop area Chalk of north-east England lay just under the stationary front of the Devensian ice and there is strong evidence of glacial and periglacial activity on groundwater in the area (Younger and McHugh, 1995). The base level for groundwater movement during the

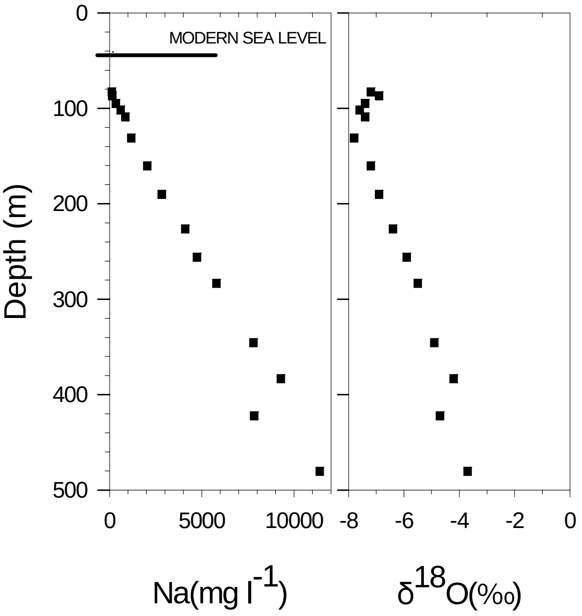

Figure 17.4. Profile of $\delta^{18}O$ and Na (equivalent to Cl) at Trunch, through the Chalk of the Norfolk Coast England.

Devensian prior to the LGM could have been controlled by the sea levels in the northern North Sea which were -60 to –80 m OD. Some reactivation of the flow system may also have occurred by drainage towards the Silver Pit (Plate. 17.2) where the Chalk is exposed (Wingfield, 1990), although this may only have been exposed during the period around the glacial maximum due to glacial scouring. This feature is shown in Fig. 17.3 in relation to similar controls on groundwater flow on the Danish coast. Further south the topography is relatively flat with the present North Sea bed around –20 to –30 m OD. In East Anglia where the Chalk is covered by 40 m drift deposits at the coastline, evidence from interstitial waters of freshwater movement is detectable to a depth of around -100 m OD (Fig. 17.4). To this depth the pore waters are less than 2000 mg L^{-1} Cl and with a $\delta^{18}O$ of –7.8‰ indicating the possible influence of late Pleistocene water. Below this depth a diffusional gradient between this freshwater and a marine connate water is found (Bath and Edmunds, 1981). The present day base level in the Thames estuary is around –40 m OD although in-filled channels may have cut through the exposed sediments (Bridgland and d'Olier, 1995).

Observations on the Ledo-Paniselian aquifer show the fresh/salt-water interface to be displaced to more than 25 km from the recharge area (Fig. 4.11). This must be due to different flow conditions during the early Weichselian, when the base drainage level in the Flemish Valley was 20 m lower, due to a lower erosion profile. In the Belgian area, there was no ice cover during the LGM, but the development of a permafrost layer caused by low land surface temperatures had limited the recharge of the aquifer system. As a consequence, hydraulic heads under the permafrost layer were decreased and thus flow velocities and groundwater fluxes were much smaller.

In Fig. 17.3 a section of the Danish Coast (southern Jylland) west from the island of Rømø is shown based on seismic surveys and boreholes. This is based on a new (1998) seismic line which shows excellent glacio-tectonic features that are considered to have an influence on the hydraulic conductivity and discharge in the Ribe formation (see Fig. 3.2).

The groundwater flow in the Ribe Formation at present and at the end of the last glaciation, is and has been very dependent on the hydraulic continuity of the Ribe Formation sands beyond the coastline. In the southern part of the Danish North Sea sector and the north-eastern part of the German sector the Ribe Formation seems to pinch out relatively close to the present coastline and continue in mainly marine clays and silt (Fig. 17.3), whereas in the northern part of the Danish sector e.g. west of the Fjand site (see Figs 3.1 and 3.2) the Ribe Formation are recognized on seismic surveys 15 km offshore where it still may be as thick as 50 m. Generally, the Ribe Formation is embedded in clay and silt sediments of low permeability, i.e. groundwater flow in offshore parts of the Ribe Formation may have been limited even at the end of the last glaciation, when permafrost vanished and meltwater runoff was high. On the other hand glacial processes and glaciotectonic features caused by moving glaciers and meltwaters e.g. incision valleys, which are very common across the North Sea as well as in Poland, Northern Germany and Denmark (e.g. Cameron *et al.*, 1993; Lykke-Andersen, 1995; Piotrowski, 1997) and thrusted sediment blocks may create hydraulic connections and favourable conditions for groundwater flow. Likewise, faulting and folding of the Cenozoic sediments e.g. induced by movements of the Permian salt formations at greater depths in the Southern North Sea may greatly influence the hydraulic connectivity of the different layers and especially during the end of the last glaciation it may have influenced the groundwater flow systems considerably. These tectonic features may have caused cross flow between aquifers and discharge either directly to the Palaeo-Elbe (Plate 17.2) or to Palaeo-Elbe tributaries.

Favourable conditions for Pleistocene freshwater that may be trapped or perhaps even still flowing very slowly in coastal areas of the Danish North Sea sector seem to be most probable in the northern part of the Danish sector (Chapter 3). However, the fact that brackish water (3000 mg L^{-1} chloride) is found 300 m below the island of Rømø (approximately 10 km from the west coast of Jylland) show that some fresh water input to this deep lying thin "offshore" aquifer occurred during the late Pleistocene and perhaps at a very slow rate even today.

During the Last Glacial Maximum the southern part of the North Sea as well as most of the Central North Sea was above sea level. The ultimate base level for erosion and for the ground water table therefore was situated over 400 km to the north The melt water from the southern rim of the Scandinavian ice sheet drained via the Palaeo-Elbe River and its tributaries to the sea (Plate 17.2). The Palaeo-Elbe crossed the southern North Sea in what is now the depression of the Heligoland Channel from the present mouth of the Elbe, in north-westerly direction passing east of the Dogger bank and continuing to the Devil's Hole deep.

17.3.3 Sea level rise and glacio-eustatic effects on groundwaters

The establishment of precise piezometric changes during the late Pleistocene is made almost impossible due to interactions between land subsidence due to sedimentation, glacio-eustatic changes (including ice loading and rebound, crustal warping as well as freshwater loading by ice-dammed lakes and sea level rise. A generalized curve based on Jelgersma (1979) is shown in Fig. 17.5.

The eastern and southern North Sea may have undergone greater subsidence due to sediment thickness, whereas the British coast may have been an area of net uplift (Bridgland and d'Olier, 1995)

17.3.4 Initial conditions prior to development

The evidence from the present study shows that fresh groundwater occurs in the Chalk aquifer to a depth in excess of –100 m OD near to the coast in north Yorkshire but that salinity increases at such depths further south in Yorkshire. Groundwater is most saline in the low-lying Holderness Peninsula and lack of modern groundwater circulation, together with limited radiocarbon evidence, suggest that this is of pre-Holocene age. To the south of the Humber Estuary, groundwater salinity and probable ages are variable. Saline zones of pre-industrial origin have been identified in north Lincolnshire along the Estuary margin and in south Lincolnshire, but saline groundwater in the industrial area of Immingham-Grimsby has been mainly induced by modern pumping. In East Anglia the earlier evidence from the Trunch borehole (Fig. 17.4) also suggests some movement of late-Pleistocene fresh water near the present coast in the confined Chalk to a depth of -100 m OD (Bath and Edmunds, 1981)

In the Ledo-Paniselian, freshwater is found to a depth of about 150 m. Modern recharge of the Ledo-Paniselian aquifer (Section F-F') is relatively limited (40 mm a^{-1}), due to the slow velocities of downward flow through the Bartonian Clay. Moreover, the hydraulic conductivity of the aquifer is relatively low (2.7 m day^{-1}). Under the present-day flow conditions, the original seawater may have been displaced over a distance of around 15 km, between the recharge area and the polder boundary, during the last 10 000 a (Van Camp & Walraevens, in press). Under persisting present flow conditions, the freshening could advance further under the polder area, but very slowly, and on a timescale of a few thousand years only over a few kilometres.

17.3.5 Impacts due to development

There are clear indications from the UK coastal area in Yorkshire that modern sea water has been induced, around the Humber estuary.

17.4 Channel

During most of the Late Pleistocene, Britain and Europe were joined over a large area. The palaeohydrology of the English Channel at around 10 000 a BP is shown in Plate. 17.3. The topography of the Channel at the beginning of the Holocene may be expressed approximately by the bathymetric contours which are shown in black. These contours are based on modern soundings but modification of topography due to scouring and sedimentation during the Devensian (or earlier), may have occurred and the drainage may not expressed by these contours (Hamblin *et al.*, 1992). However the main feature is the Northern Palaeovalley which at the start of the Holocene is likely to have a sea level at –60 m OD. During the Devensian sea level was expected to have oscillated between ca –120 and –60 m OD and conditions in this valley would have changed from freshwater through estuarine to marine, possibly similar to the Bristol Channel at the present day. The open sea would have lain well to the west of the Cherbourg peninsular and the overall climate would have been more continental than today.

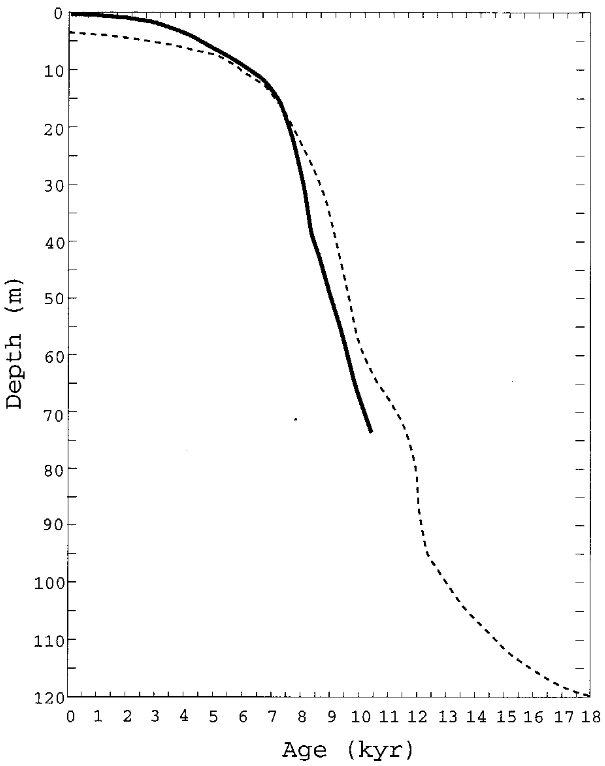

Figure 17.5. Comparison of sea-level curves from the Southern North Sea and Barbados since the Last Glacial Maximum. The solid line shows the Southern North Sea curve based on data compiled from several sources: Streif (1990), Jelgersma (1979) and Konradi (in prep). The dashed line shows the sea-level curve from Barbados (Fairbanks, 1989).

Drainage and erosional features in the exposed Channel developed similar to those at the present day on-shore. Over much of the offshore areas evidence is found of a river system which is an extension of the present day, for example offshore of the Sussex-Hampshire coast (Bellamy, 1995). Two major river systems joined the northern Palaeovalley: the Solent and the Seine. The Solent river used to flow from Dorset and to the north of the Isle of Wight (Velegrakis *et al.*, 1999), but was captured at the time that the Chalk ridge from Dorset to the Isle of Wight was breached during the Devensian. The mid-Channel river flowed westwards from near the present straits of Dover possibly fed by a spillway of glacial meltwater from the North Sea area. The date of separation of Britain from Europe is controversial and probably only fully occurred at the time of the Flandrian transgression around 8000 BP, although partial separation may have occurred in the Late Pleistocene.

17.4.1 Aquifers of South coast of England and Northern France

The principal aquifer system bordering the Channel is the Chalk, which, in modern times is an unconfined aquifer at the coastline over much of southern England and northern France, elsewhere being confined although with fresh groundwater resources in certain regions. The hydrogeology of the Chalk in NW Europe has been described by Downing *et al.*, (1993) and the hydrogeochemistry by Ed-

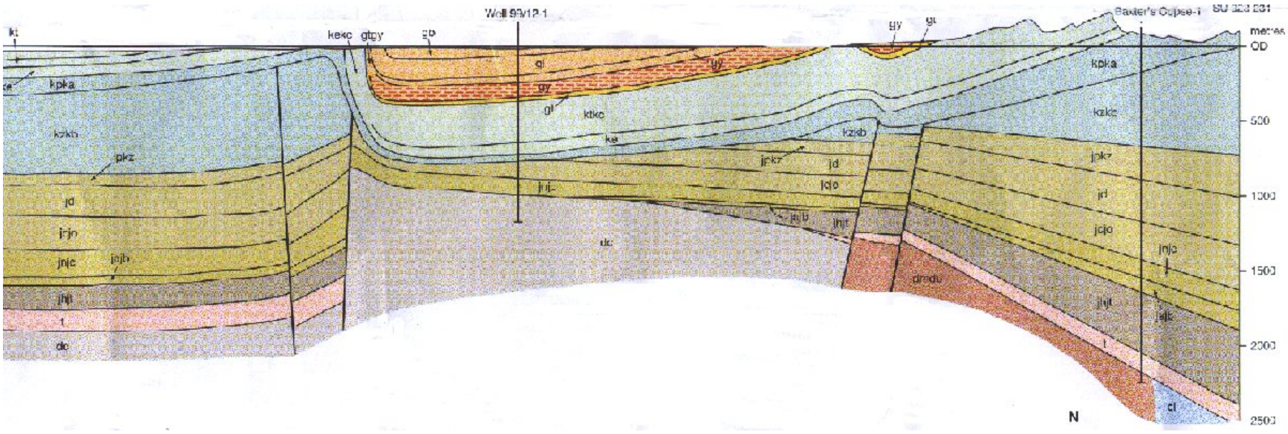

Figure 17.6. Cross section through the monoclinal structure in the northern Channel, showing position of borehole number 99/12-1.

munds *et al.* (1992). The solid geology of the Channel is shown in Fig. 17.6 and over much of the area Drift deposits are thin (<0.5 m) or absent (Hamblin *et al.*, 1992) although overlying Tertiary beds are thick (+300 m). The Chalk extends as part of the Anglo-Paris Basin under the whole area and is affected by roughly east-west folding. The main structure is the Wight-Bray monocline which forms a vertical southern limb to the Hampshire Dieppe Basin. This structure also has several associated minor folds (eg Chichester syncline), and crosses the Northern Palaeovalley.

17.4.2 Palaeohydrological conditions of the late Pleistocene in the Channel basin

The likely exposed area of the Chalk during the late Pleistocene can be see in Plate 17.3. The Northern palaeovalley is considered to have served as a base level for drainage of much of the Chalk of southern England during the late Pleistocene when exposed areas would have acted as recharge areas, possibly interrupted during periglacial times by permafrost. The present day high ground areas of unconfined Chalk, such as the South Downs would, then as now, have operated as the main recharge areas for groundwater flow systems. Groundwater in the Tertiary Beds, Chalk and Greensand to the north would have flowed south towards local base levels in the palaeovalley, some 35 km south of the present coastline at around –60 m OD up to around 10 ka BP. Spring lines would have existed as today along valleys where the Chalk was exposed. Flow would have been influenced by geological structure. The strata dip SW into the Channel and approximately 20 km offshore rise in a monoclinal fold (Figure 17.6), being an extension of the Isle of Wight monocline. This structure is considered responsible for an increased thickness of freshwater upgradient of the structure in the Poole Harbour (Wessex) area. Offshore borehole OS 99/12-1 (Fig. 17.6, Plate 17.3) upgradient of the syncline penetrates some 300 m of Palaeogene strata overlying Chalk and Greensand aquifers. SP and resistivity log indications are that permeable formations in the Palaeogene strata are sea water-saturated, but that the confined Chalk and Greensand layers contain fresher waters (estimated at <10 000 μS cm^{-1}). It is estimated that further upgradient freshwaters would almost certainly be encountered within these formations offshore.

Groundwater in the Chalk to the south (in France) would also have flowed north and although the distance to the palaeovalley here was over 100 km from the modern coastline. The valley of the Seine, joined by the Somme was likely to have been the main area of discharge. Depths of –40 m occur only 25 m from the present day coastline.

Water in the Lower Cretaceous Greensand (Albian) would also have flowed offshore via the monoclinal structure as for the Chalk.

17.4.3 Sea level rise and glacial-isostatic impacts on groundwaters

The sea-level rise in the Channel region was a complex combination of melt water addition and the crustal rebound of the region at the end of the glaciation (Lambeck, 1995). The English Channel was probably fully marine by 7500 BP. All the evidence for the British coastline points towards no significant sea level change since that time with no clear evidence for marine transgressions higher that those of today in that period. During the Flandrian transgression, the hydrogeological behaviour was probably different between the northern and southern palaeocoasts of the Channel. This imbalance is related to the asymmetry existing between the two sides of the Northern Paleovalley. In northern France, the flat landscape and the lower hydraulic gradients at that time mainly explains the invasion of the coastal unconfined aquifers by marine waters recorded in the current study. The low-lying areas of the Normandy coast, near the area studied around Caen, could have allowed limited marine transgression during the late Holocene, and this is recorded in the groundwater. In contrast to southern England, this low-lying valley topography has allowed the record of the sea-level encroachment to be preserved; the areas covered by sea have subsequently been covered by recent sedimentation.

In Southern England, the inferred age of freshwater in the Chalk is late Pleistocene and the age of groundwater in the Albian (7500 BP) suggests that flow was taking place towards the Palaeovalley until the completion of the Flandrian sea level rise, after which time offshore flow slowed down considerably, and since that time has been adjusting to the new head distributions. Saline water would have covered the outcrop and the discharge areas and created a new interface near the modern coasts. It is concluded that fresh water, which had access to the Channel aquifers over a period in excess of 100 000 a has considerably flushed the formation waters over this period.

17.4.4 Initial conditions prior to development

In southern England, freshwater emplaced during lowered sea levels is found at 300 m depth in the Chalk in several places (Sussex, Poole Harbour) where it is preserved by the fold structures (see Chapter 5). These also coincide with areas where the unconfined aquifers are well developed hydrogeologically near the present coast, whereas beneath some confined areas of the Chalk, flow at the present day and during the Pleistocene is much more restricted, mainly due to the structural development. The freshwaters found below 110 m OD at the time the first wells were drilled must have been emplaced at the time of the late Pleistocene but above this the flow is shown from geophysical logging to be the result of present-day head distributions.

It is concluded that there is a strong likelihood of freshwater or brackish water being preserved in the confined Chalk in the present offshore areas. In the higher permeability strata of the Lower Greensand and the Upper Greensand the chance of there being freshwater is even greater.

17.4.5 Impacts due to development

Any saline waters in the south coast areas of England are considered to be exclusively derived from modern sea water as a result of pumping, although a small area of preserved formation water is found north of Bognor Regis.

17.5 Atlantic coast of France

The topography and the solid geology of the Atlantic ocean along the Aquitaine Basin (western France) are indicated on Plate 17.4. During the Last Glacial Maximum (18 ka BP), the shoreline was approximately at −120 m relative to modern sea-level, staying at this level to around 14000 BP (Pinot, 1968) while the ocean level was recognized at −50 m at the beginning of the Holocene (Pirazzoli, 1991).

Along the French Atlantic coast, the fluctuations of the sea-level have been restricted to the continental shelf during the Late Quaternary. In the north of the Aquitaine Basin, the continental shelf gently dips towards the southwest with a mean slope of ca. 0.1%. The exposed formations on the shelf are mainly Tertiary deposits. Moreover, between the latitudes 45.5°N (Gironde estuary) and 46.5°N (southern edge of the Armoricain Massif), the Cretaceous and Jurassic series outcrop both off-shore and on-shore. These formations are affected by faults roughly oriented 120° (Hercynian direction). As the Mesozoic monoclinal sedimentary series dips towards the SW with a slope about 10 times higher than that of the continental shelf, the Jurassic and Cretaceous aquifers do not give rise to any evident discharge areas. If existing, these discharge areas are likely to be some hundreds of kilometres offshore, along the continental slope and/or the continental rise.

During the Flandrian transgression, in the North of the Aquitaine Basin, the salinization of groundwater could only have occured through the direct recharge of aquifers by ocean water in coastal areas where outcrop areas of the aquifers could have been covered by a marine transgression. This case, for instance, corresponds to that of the Dogger aquifer confined under the Marais Poitevin in Vendée, Western France (see Chapter 6). Locally, along the Atlantic coast, the marine water can directly encroach upon the unconfined coastal aquifers where the ocean is hydrodynamically in contact with these groundwater reservoirs. During the transgression, the saline wedge of these unconfined aquifers in equilibrium with the ocean might have moved forward inland in response to sea-level rise these areas subsequently being covered by Recent sediment.

17.6 Atlantic coast of Portugal & South-West Spain

The Iberian Peninsula straddles an important position between Europe and Africa, reflecting its past climate conditions not only the inter-relation between European glacial/interglacial periods and the African pluvial/interpluvial periods, but also the mass exchange of Atlantic and Mediterranean water (Gulf stream).

The map for Portugal and south west Spain (Plate 17.5) contains general information about the local geology, topography and main river basins, as well as the offshore features. The palaeo-coastline at 14 000 a BP corresponds to the bathymetric contour of 100 and 120 m below sea level for the western coast of Portugal and south west Spain, respectively. They correspond to a sea-level rise of +20 m when compared to the minimum sea-level during the Last Glacial Maximum (18 ka. BP).

17.6.1 Aquifers of the Iberian Atlantic Coast

The Aveiro Cretaceous coastal aquifer located in north-western Portugal, covers an area of 600 km^2 in the Lusitanian Basin and dips gently to the NW beneath the present coastline. The extension of the aquifer in the adjacent continental shelf is not well known but boreholes for oil exploration located at 20 km off-shore penetrated a complete Upper Cretaceous succession. The succession is generally carbonate-rich, but upwards intercalations of siliciclastic beds become more frequent. The Upper Cretaceous interval recognized in the northern offshore area cannot be followed onshore (Rasmussen *et al.*, 1998). Faults of approximately N-S orientation affect the complete sequence of Cretaceous sediments. The aquifer is confined for the most part but uplift and erosion of the confining marly clay unit in the east defines the unconfined part of the aquifer. Although the Cretaceous sediments crop out on-shore there is no evidence that they crop out off-shore. However there is the chance that they intersect the continental slope about 50 km from the present coastline.

Located in the SW of the Iberian Peninsula the aquifer system of Doñana, consists of Plio-Quaternary sands and gravels overlapping impervious Miocene marine marls, is the biggest sedimentary aquifer in the area. The aquifer has a surface area of 3400 km^2, a variable thickness from a few meters inland to some 150 m near the coast line, and a roughly triangular shape. It outcrops to the W and N in a rather flat-lying area. To the SE the aquifer deepens and becomes confined under some 50 m thick Holocene estuarine clayey layers, with a confined area of about 1800 km^2. The Quaternary sediments extend seaward occupying the continental shelf (some 2 km wide) between Huelva city (to the W) and Cadiz city (to the E), and also part of the continental rise (down to 500 m depth).

17.6.2 Palaeoclimatic and palaeohydrological conditions during the late Pleistocene

The picture emerging for the last 20 000 years is that of a coastal Iberian continental margin periodically intruded during Heinrich events by a pre-Holocene Canary current carrying large amounts of icebergs originating from a collapsing Laurentine Ice Sheet. On their way along the Portuguese margin, the icebergs rapidly melted, leading to a greatly reduced flux of ice rafting debris (IRD) off southern Portugal.

The limit between the Polar Front and the Gulf Stream at the Last Glacial Maximum (LGM) was located close to the Spanish-Portuguese northern border (40°N) and had a different climatic response in the Iberian littoral zone, north and south of 40°N. According to Zazo *et al.* (1996), during the LGM climatic conditions were less humid and generally cool for the zone north of 40°N. The Younger Dryas event is characterized by cool and slightly humid conditions, evolving towards conditions that are more humid. A temperate and humid climate similar to the present day was reached at the beginning of the Holocene. In contrast the climate for the zone south of 40°N is described as generally dry and cold before 15000 a BP, followed by an amenable climate conditions. The Younger Dryas is recorded as an arid episode.

The late Quaternary depositional history of the Portuguese margin has been reconstructed by Baas *et al.* (1997) using the sedimentological and paleoceanographical data. Pelagic sediments prevail in the Holocene. In pre-Holocene times, settling of biogenetic particulate matter was supplemented with sea level- and climate-controlled input of terrigenous material from local and distant sources by low-concentration turbidity currents, contour currents and icebergs.

Downslope transport of terrigenous material decreased and biogenetic production increased following the sea level rise and sea surface temperature increase during deglaciation. The temporary return to glacial conditions around 10.5 ka was recorded on the Portuguese margin by increased input of terrigenous silt and sand. The Younger Dryas is a meltwater event equivalent to Heinrich events in the central North Atlantic, but only few icebergs reached the Portuguese margin. Minor sediment winnowing occurred on the northern part of the Portuguese margin during the Younger Dryas. Holocene sediments have a typical interglacial signature with a dominance of biogenetic over terrigenous sedimentation.

17.6.3 Sea level rise and impacts on groundwaters

For drawing the palaeo-coastline map (Plate 17.5) available information about the local off- and on-shore geology, topography and main river basins was considered. It was decided to represent the palaeo-coastline at the very end of the glaciation, around 14 000 a BP. The bathymetric contours of 100 m below mean sea level for the western coast of Portugal and 120 m below mean sea level for south-west Spain were inferred from sea level curves suggested by Rodrigues *et al.* (1991) for Portugal and Hernandez Molina *et al.* (1991) for Spain (Fig. 17.7). They correspond to a sea-level rise of +20 m when compared to the minimum sea-level during the Last Glacial Maximum (18 ka BP).

The sea-level changes during the last 20 000 a had a considerable impact in the length of flow paths in the coastal aquifers along the Iberian coast and clearly influenced their flow regimes. Two coastal aquifers have been studied with respect to the impact of sea-level changes in their flow regimes: the Aveiro Cretaceous aquifer in Portugal and the aquifer system of Doñana, in SW Spain.

In both Portugal and south-west Spain five morphologic units have been recorded between 0 and −140 m, reflecting the successive steps of the retreating Polar Front. The relative sea-level curves for both Portugal and Spain follow the same trend with the exception of the period during the Younger Dryas when the drop observed in the Portuguese curve has not been recorded in Spain (Rodrigues *et al.*, 1991). For the same period, the Atlantic had warmer sea surface temperatures than the Mediterranean. The present difference of 5°C higher in the Mediterranean than in the Atlantic was reached around 9500 a BP.

During the Last Glacial Maximum (LGM) the sea level in the south-west of the Iberian Peninsula was lowered by 115–120 m below its present position. This allowed the deposition of deltaic (sands, silts and gravels) and littoral (sands) sediments. At this time the exposed (recharge) area of the aquifer was probably composed of Pliocene sands and Pleistocene sands and gravels. The area was never covered with permafrost. These sediments outcrop

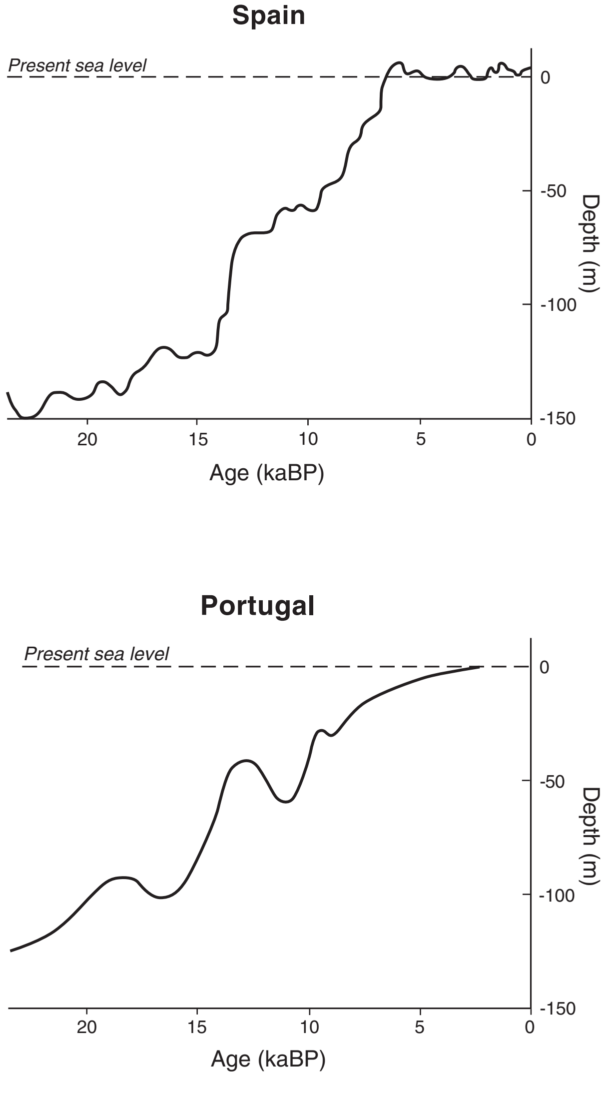

Figure 17.7. Sea level curves for the Iberian peninsular (Portugal and Spain)

nowadays (or are covered by a thin layer of sand and silt) between 30 and 200 m depth in the continental shelf, so during the LGM discharge took place to the sea probably both along the ancient coast line and as submarine outflows.

The postglacial Flandrian transgression started some 15 000 a BP and rose the sea level in two stages before to stabilize some 6000 a BP. During the sea level rise the aquifer sediments were encroached by seawater. But due to synchronous tectonic and sedimentary subsidence, while the western (mainly sandy) part of the aquifer remained above sea level, the SE (mainly gravelly and sandy) part was covered by some 50 m of Holocene estuarine clays.

17.6.4 Initial conditions prior to development

The confined part of the Aveiro aquifer has groundwaters recharged during the Late Pleistocene. Noble gas determinations carried out in groundwater samples of this part of the aquifer by Carreira *et al.* (1996) show an average temperature of 9ºC for these waters, 5ºC less than the present day mean annual temperature in the region.

At the time of the Last Glacial Maximum sea level was –120 m when compared to the present day, giving an increase of at least 35 km more in the length of the flow path and a groundwater gradient twice as high as present day. This might have contributed to the complete flushing of the sea water in the aquifer.

Following the sea level stabilization some 6000 a BP until some 30 years ago, when the human use of the aquifer became important, discharge in the sandy western part of the aquifer took place southward to the sea, northward to La Rocina creek and eastward to the marshy clays, where it uses to discharge as upward flows along the sand-and-clay contact or through the Holocene clays. Groundwater in this area was fresh, and probably of sodium chloride to calcium carbonate type, because of calcium carbonate dissolution by infiltrating local rain.

In the eastern part of the aquifer groundwater flowed from the water table area (in the N) to the confined area (to the S), probably discharging during at least 6000 a along the contact with the Holocene clays or in the centre of the marshland as upward flow through the clays. The upward head gradient was still visible a few decades ago as flowing wells. The SE sector of the confined aquifer is still filled with saline groundwater, which has not been flushed out due to the low fresh water gradient existing since the late Holocene sea level stabilization. So the situation observed in the Doñana aquifer suggests that approximately half of the confined Pleistocene aquifer has been freshened by fresh groundwater flowing to the S and SE from the unconfined area.

17.6.5 Impacts due to development

The Aveiro Cretaceous aquifer lies in one of the most industrialized areas in Portugal with a high population density, and since the 1960s relies on groundwater for most of the urban and industrial water supply.

In recent years a continuous fall in the water table has been observed due to intensive groundwater abstraction, leading in some areas to values of –25 m bmsl. Because it occurs in a coastal aquifer, partially confined and with limited natural recharge it can lead to gradual deterioration of the water quality either because of salt-water intrusion or due to mixing with very high-mineralized waters from deeper aquifer levels, nowadays with higher water potentials.

To prevent the gradual deterioration of the water quality the traditional groundwater abstraction for public supply is being replaced by the use of surface water.

17.7 Mediterranean

The outline palaeogeography and conditions in the western Mediterranean area around 13 000 a BP is shown in Plate 17.6.

17.7.1 Aquifers of the Western Mediterranean, between the Rhone and the Ebre deltas

The geological configuration of the NE coast of the Iberian Peninsula and the Gulf of Lyon is the result of a post-alpine tectonic stress relaxation and extension. The result is a set of NE-SW oriented horst and graben system (Fig. 17.8) which is an extension of the Western-Europe–North-Sea system. As a result, two main aquifer types can be found.

Unconsolidated aquifers

Aquifers are found in unconsolidated sediments, mainly of Plio-Quaternary age but also older, corresponding to coastal piedmonts and alluvial fans; lineal coastal formation, and deltas with two or more aquifer systems. From east to west they are: Rhone, Ter, Muga, Tordera, Besós, Llobregat and Ebre rivers deltas; Maresme, Barcelona, and Tarragona coastal plains. In the Balearic islands: Inca-Sa Pobla and Plà de Palma plains. The largest pre-Quaternary unconsolidated aquifer is the sandy Astian unit (France), the subject of PALAEAUX study, which is covered by Plio-Quaternary sediments.

All the deltas in the area have a common origin. Their exposed area formed mainly after the Flandrian transgression. They also have a similar three layer structure:

(xix) the deepest layer is a permeable unit usually appearing between 70 and 130 m depth, which consists of Pleistocene alluvial terraces, which usually behave as a good confined aquifer;

(xx) the former is covered by a more or less thick (a few tens of m) and extense landward wegde of fluvio-marine silty clay deposited during the sea transgression, which behaves as an aquitard;

(xxi) the uppermost layer is a sandy unit of littoral and deltaic plain origin and 5–30 m thick which behaves as a water table aquifer.

The Astian aquifer is a confined sandy aquifer of 450 km^2. Due to the tectonic features the offshore limit is not well localized. The aquifer is covered by Plio-Quaternary continental sediments which may contain small aquifers. To the east it is in hydraulic contact with karstified dolomitic sediments of Jurassic age.

The Inca-Sa Pobla aquifer system in Mallorca is a 350 km^2 multilayer aquifer consisting of thick carbonate Miocene and Pliocene layers and thinner Plio-Quaternary sands, silts and clay layers. Jointly with the Plà de Palma aquifer, of similar origin but smaller size, it is the result of the Mio-Plio-Quaternary filling of the marine straits formerly dividing the island into two, from SW to NE. The S'Albufera wetland existing nowadays in the NE part of the former strait (in the Alcudia bay) is the sole remains.

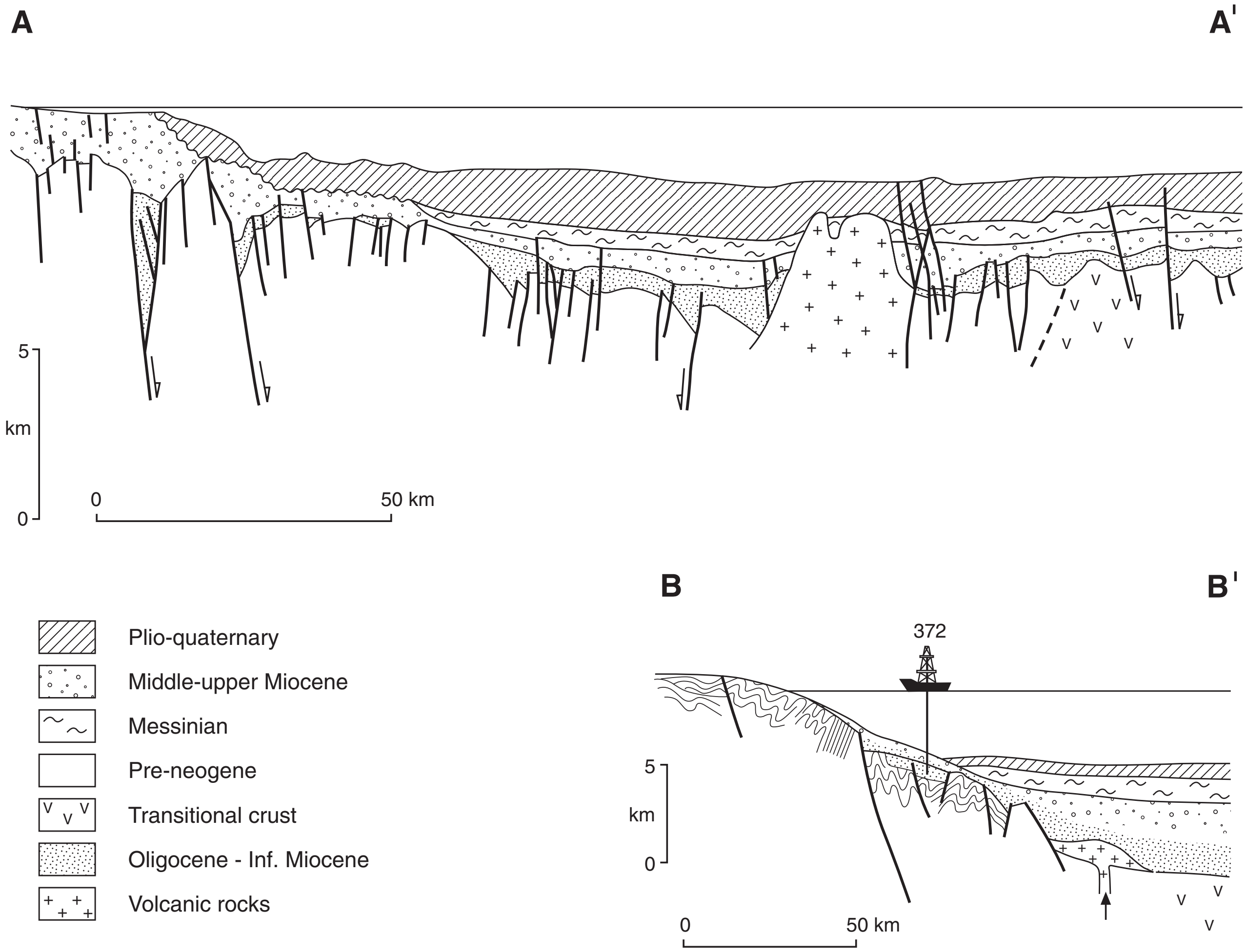

Figure 17.8. Cross sections of western Mediterranean lines which are shown in Plate 17.6.

Fissured and karstic aquifers

Aquifers are widely found in thick fissured and karstified carbonate formations, usually of Triassic, Jurassic and Cretaceous ages. The carbonate rocks usually form NE-SW oriented coastal ranges and dip towards the sea some times giving rise to coastal aquifers confined under the detrital sediments, as well as other stepped coastal massifs discharging directly to the sea. Examples of the first type are the Jurassic limestones in contact with the Astian aquifer in France, and the Cardò massif close to the Ebro delta in continental Spain. Examples of the second case are the Garraf massif close to Barcelona, and the Serra de Tramuntana and Serra de Llevant massifs in Mallorca island.

17.7.2 Palaeohydrological conditions of the late Pleistocene

During the Last Glacial Maximum (LGM) the sea level in the area fell some 120 m below its present position. This allowed the deposition of fluvial terraces, deltaic (sands, silts and gravels) and littoral (sandy bars) sedimentary bodies. The remains of the Pleistocene deltas appear nowadays under the Holocene deltas. The alluvial terraces appear in the bottom of the Holocene deltas and overlying the ancient ones. The alluvial sediments extend several km seaward and outcrop (or are covered by a thin layer of recent sand and silt) in the continental shelf, around 100 m depth. The remains of the Pleistocene littoral sandy bars appear nowadays as relict elongated sandy bodies on the continental shelf.

The exposed area of the sedimentary and carbonate aquifers was never covered with permafrost in this area. During the LGM discharge from the sedimentary and carbonate aquifers took place to the sea, probably both along the ancient coastline and as submarine outflows.

17.7.3 Sea level rise and glacial-isostatic impacts on groundwater

The postglacial Flandrian transgression took place in two main stages before stabilizing some 6000 a BP. During the sea level rise both the sedimentary and the carbonate sediments were encroached by seawater.

The freshwater gradient existing from the time of sea level stabilization to the present was in most cases favourable to the flushing of this saline water to the sea. In some places it is still possible to find undisturbed deep layers (around 400 m deep) where (assumed) very old fresh water is being abstracted. Some wells and boreholes showing these features are available both in the Tarragona and in the Valencia plains and in the surroundings of the Ebre delta. In other cases only Holocene or post-Holocene groundwater is found, as is the case for most of the small deltas (Llobregat, Besós,.).

The flushing of saline water was not possible in the Rhone and the Ebre deltas, the two biggest coastal sedimentary formations in the NW Mediterranean. Due to the low elevation of the river channel (which controls freshwater potential) and to the wide extension of their deep aquifers (Pleistocene alluvial sediments) in the continental shelf, they still contain salt and brackish water.

In the Astian aquifer pre-Holocene saline groundwater is present in its western part probably due to leakage from the underlying Jurassic formation which seems to contain old sea water. In the coastal area of the Inca-Sa Pobla aquifer, saline and salt groundwater of at least Flandrian age is found as well.

17.7.4 Initial conditions prior to development

The human exploitation of the coastal aquifers is several centuries old, but it began to be intensive and to affect the natural behaviour of aquifers at the time of the industrial take off of the area, some 30–50 years ago. Prior to this time most of the sedimentary coastal aquifers have been little used, mainly for irrigation and secondly for human supply, because both uses were satisfied (as is also nowadays) mainly by river water. Groundwater was then of good quality.

17.7.5 Impacts due to development

Intensive groundwater abstraction after the 1960s, both from the detrital and the carbonate aquifers all along the coast, has produced general distortions in the freshwater-saltwater interface, giving place to a marine intrusion process extending widely mainly in the sedimentary units.

Except in the case of the Rhone and Ebre deltas, the rest of the coastal systems contain Holocene and recent freshwater and recently (a few tens of years) encroached seawater as well. The clay layer usually contains connate Holocene marine water more or less diluted by mixing with freshwater by vertical flow between both aquifers. The upper water table aquifer usually contains recent freshwater, in most cases affected by salinization along the coast and by local industrial and agricultural pollution elsewhere, so that its use becomes limited.

The low coastal areas filled up by Quaternary sediments usually have a great local importance as aquifers. They have recent fresh groundwater (up to a few centuries old), quite often locally affected by pollution of different origin: saline intrusion in the coastal fringe, agricultural, industrial and urban (sewage) contamination elsewhere.

As indicated above, old fresh water is still present in some deep layers of the carbonated coastal aquifers to the S of the Ebre delta. But except in these areas, the Mesozoic aquifers usually contain recent to a few centuries old freshwater, as well as brackish and salt water at the coast.

17.8 Conclusions

The PALAEAUX results provide a representative, although incomplete, picture of the status and origin of fresh and saline groundwaters at or near the present European coastline. Some areas are not covered. These include the hard rock areas of the western European seaboard as well as Scandinavia. However, these areas as well as the large areas of carbonate aquifers of the northern Mediterranean were deliberately excluded from the project since they were considered unlikely to retain palaeowaters.

The six regional maps present a summary as far as possible of the conditions existing in the early Holocene, after the impact of glaciation, when groundwaters might be expected to have reached their maximum offshore evolution prior to the encroachment of seawater during the Flandrian transgression. This evolution lasted for some 100 000 a since seawater would have covered the land mass to the same extent. It is important therefore to consider that the present coastline is a very recent phenomenon and that the landmass – as far as groundwater evolution is concerned had a far greater extent than that apparent today.

In the Baltic the groundwater evolution is unique in that freshwater heads *higher* than the present day were the control, plus the fact that there is evidence of melted water at the base of the ice-sheet allowing and promoting recharge during much of the late Pleistocene (with clear isotopic evidence of this).

In the North Sea Basin, there is generally evidence of freshwater movement to depths of 100–150 m but the absence of deeper fresh water (palaeowater) storage may relate to the mainly lower gradients in the basin. An anomaly yet to be satisfactorily explained is why freshwater of Pleistocene age is present to –500 m approximately in the Triassic of the East Midlands.

The channel presents one of the most active regions to illustrate the scope of groundwater movement. Freshwater is found in several areas to a depth of 300 m. Yet the freshwater evolution is heterogeneous and freshwater recharged during the Pleistocene into areas that experienced little or no flow since the late Cretaceous. Offshore flow towards the central palaeovalley is likely to have led to freshwater discharges in the central Channel.

In the two Atlantic coastal areas of France and Porrtugal/Spain a contrast exists due mainly to the proximity of the continental slope. In Portugal freshwaters are found at the coastline, and probably offshore, which contain evidence of recharge during the lowered sea-levels. In France some salinity encroachment is observed during sea-level rise, although some evidence of palaeowaters are preserved, assisted here by lower rates of groundwater recharge.

In the Mediterranean coastal areas including Mallorca island the PALAEAUX study has provided evidence of freshwaters preserved at depth near the coastline, although in several areas these do not contain isotopic confirmation of palaeowater origin. Brackish palaeowaters are also found which may be of value as desalination sources rather than directly as potable water.

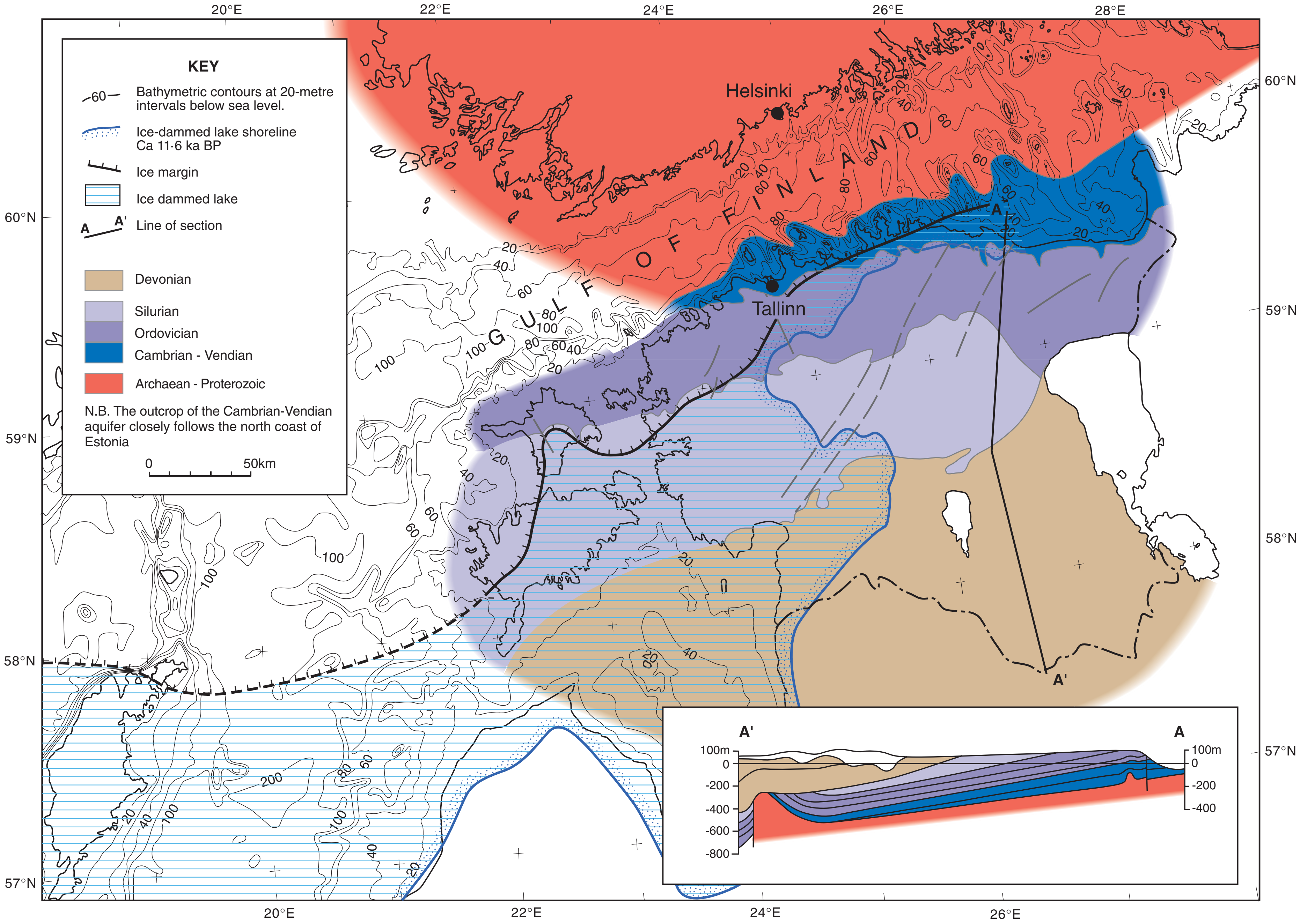

Plate 17.1. Palaeohydrology of the eastern Baltic at around 11 600 a BP.

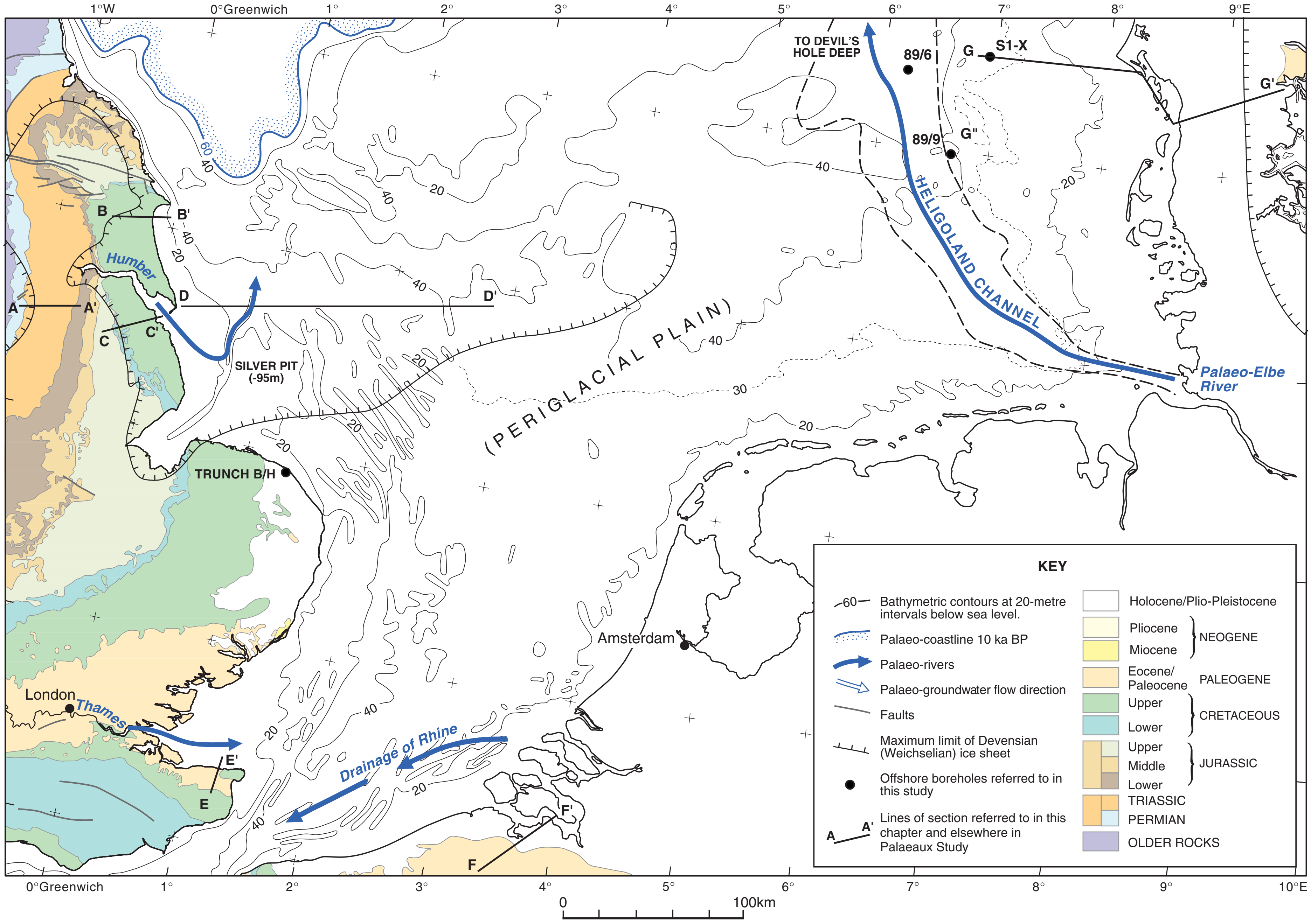

Plate 17.2. Palaeohydrology and related features of the North Sea basin at around 10 000 a BP.

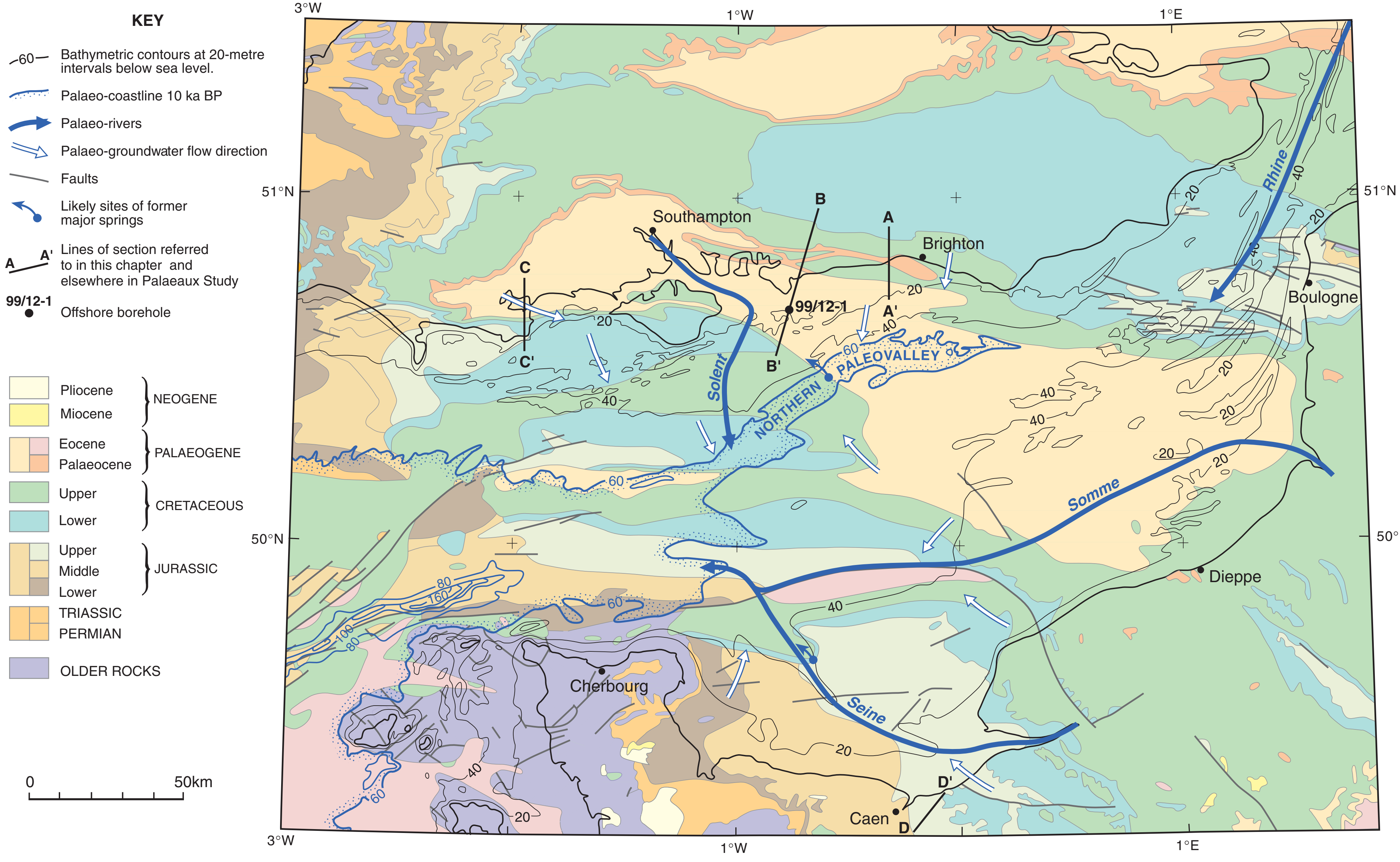

Plate 17.3. Palaeohydrology of the English Channel. at around 10 000 a BP.

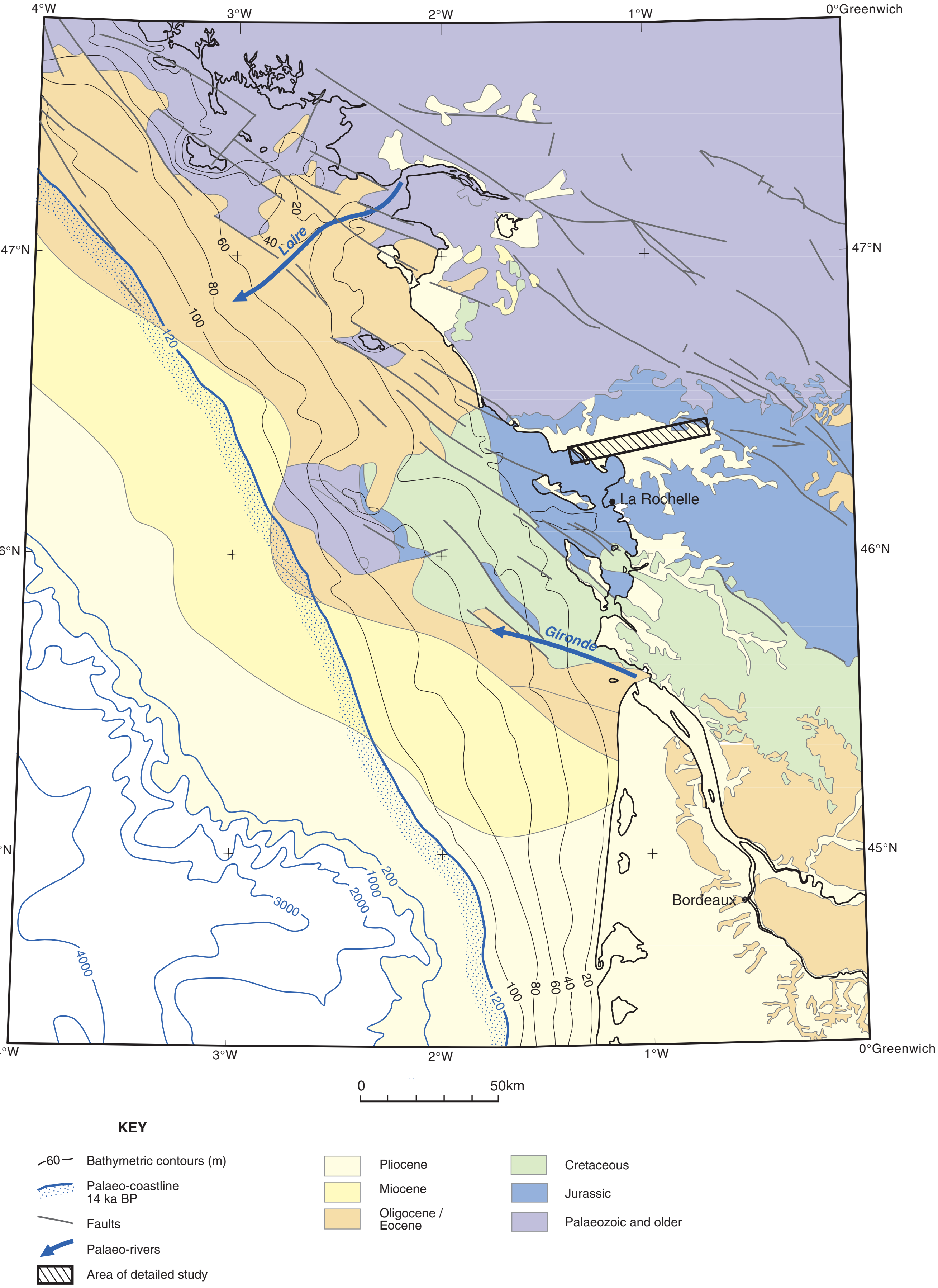

Plate 17.4. Palaeohydrology of the Atlantic coast of France approximately 14 000 a BP.

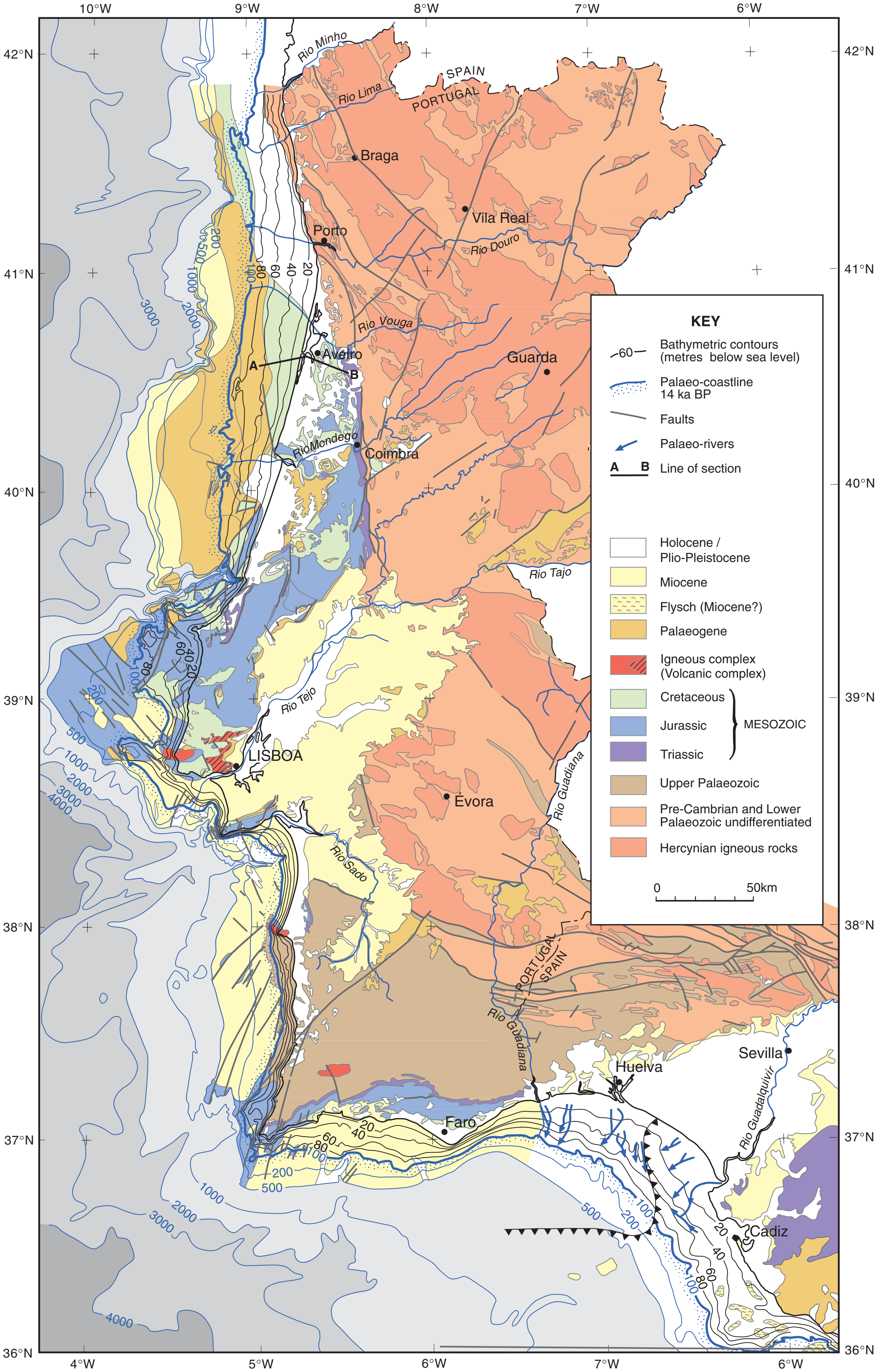

Plate 17.5. Palaeohydrology of the Atlantic coast of the Iberian peninsula. at around 14 000 a BP.

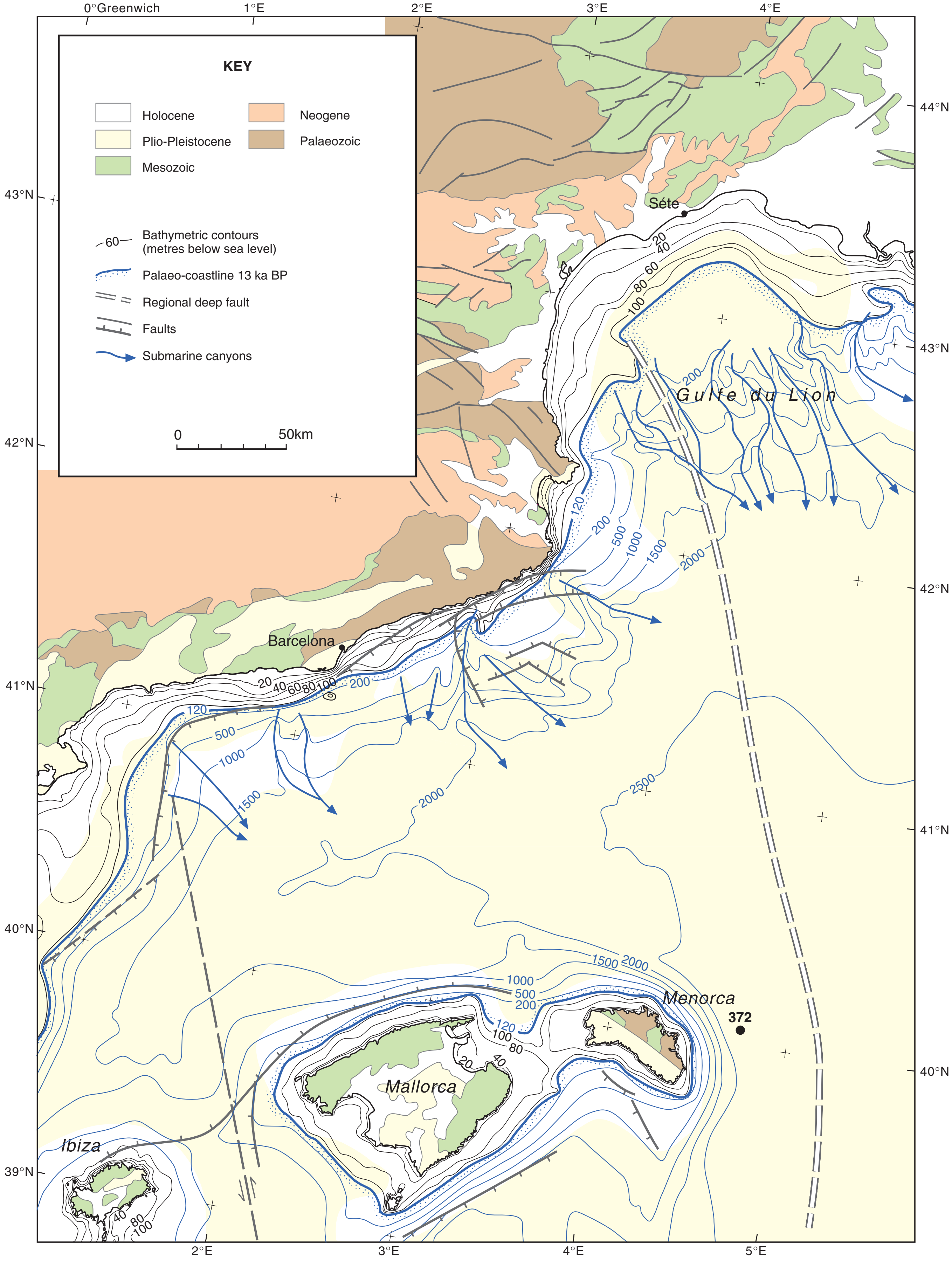

Plate 17.6. Palaeohydrology of the western Mediterranean around 13 000 BP.

18 Management of coastal palaeowater resources

18.1 Introduction

In many countries and regions of Europe and elsewhere the population and its activities tend to concentrate along the coasts. This is due to favourable climatic factors and the availability of flat land, easy transport and arable soil. Moreover, important infrastructures were built in the past when the seas were essential to trade and development. Currently retired people from industrialized regions show a preference for coastal areas and islands in mild, even arid climatic areas, for secondary or permanent residence during the increasing life span after retirement.

Thus, in many coastal areas or in nearby localities there is an intense concurrence for urban, industrial, storage, touristic and farming space, which sometimes coexist uneasily. Moreover the availability of fresh water supply is or may become a main issue, which may condition the sustainability of the regional economy. Common water problems to be solved refer to quantity, quality and seasonality, as well as increasing pollution, aquifer saline intrusion and contamination, and sometimes interferences with valuable ecosystems and the natural environment.

In areas with favourable terrain and climate, agriculture is often a principal consumer of good quality water, as well as a rival to urban water supply. Agriculture is a traditional activity that progressively expands and evolves towards intensive farming, taking advantage of the favourable coastal conditions, such as flat terrain, high local food demand and trade advantages. Often agriculture is politically protected and at the same time is responsible for as well as the origin of the deterioration of groundwater quality by saline intrusion as a result of groundwater abstraction, application of agrochemicals and the infiltration of saline return flows. Coastal urban areas, which demand large quantities of good quality water, create conditions for deterioration and pollution, including intensive abstraction to cause seawater intrusion. All this is well known and the subject of numerous studies. Southern Europe has plenty of examples (see Chilton *et al.*, 1997; Custodio and Bruggeman, 1987; Falkland and Custodio, 1991; van Dam, 1997; Custodio and Galofré, 1993).

Currently deep wells are constructed in coastal aquifers for groundwater exploitation to supply all the varieties of water needs, including industry and agriculture. Drilling down to several hundreds of meters is currently not uncommon. In many situations these wells tap palaeowaters – often without knowing it – and their unique properties are not considered. Palaeowater is a one –time reserve, having originated under climatic and hydrodynamic conditions different from today, free from man–made pollutants. It is worth considering its most beneficial use, setting specific management and protection norms.

The existence of palaeowater in coastal aquifers and islands is the result of physical conditions which allow for a water storage with a very long turnover time. This implies a combination of physical (low permeability formations and layers) and hydraulic (low water head gradients) conditions. The higher hydraulic gradients prevailing during the past low sea stand allowed continental or island fresh water to penetrate into coastal permeable formations, but subsequent and current low natural hydraulic heads prevent its fast renovation.

Palaeowater can be found in Europe in the thick sedimentary basins existing in the continental grabens of Central Europe (e.g. the Rhine and the Danube) and Southern Europe (e.g. the Po and the Tajo). Similar situations are found along the European coast, some of which are described in detail in the present chapter. Important and well developed coastal sedimentary basins are found along the eastern and southern coast of the Baltic Sea, which continue along the North Sea coast. Other well developed coastal basins are found in England, the Netherlands, Belgium and the Atlantic side of France. Along the Iberian Peninsula and the northern part of the Mediterranean sea the closeness of the mountains to the coast reduce the extent of these coastal basins but still some large ones are found such as the Aveiro and Lower Tejo–Sado areas, the Guadiana and Guadalquivir coastal deposits and deltas, and the Mediterranean basins and deltas of the Ebre, Llobregat, Rhone and Po. In all these areas recent, low permeability deposits cover deep aquifers susceptible of containing palaeowater. The actual existence of fresh palaeowater depends on local circumstances and the hydrodynamic changes suffered by each aquifer system, as explained in the present publication.

The wide variety of situations covered by the PALAEAUX Project, from the North of Europe to the southernmost areas in the Iberian Peninsula and the Canary Islands, jointly with the wide range of situations, from large coastal basins to carbonate and volcanic formations, from cold, wet climates to warm, dry areas, from rural to periurban areas, comprise a wide range of situations. This set shows how adequate aquifer management may deal with problems of sustainability, profiting from the unique characteristics of palaeowater in such coastal formations.

Groundwater management may be considered as the set of rules and actions needed to obtain a given set of technical, economical, social and political objectives relative to water supply, wetland preservation and economic development of a region. Often it involves a trade-off among conflicting interests, both in the short and long term, taking into account the sustainable use of the resource and the preservation of its role in natural processes. Management involves scientific principles, technical operation, economic considerations and fulfilment of socio–political constraints.

The objective of this chapter is to discuss the special characteristics of palaeowaters in coastal aquifers and the need to correctly manage them, presenting the main principles to make good use and to protect these groundwater resources.

18.2 Coastal aquifers

Coastal aquifer systems differ from other continental aquifer systems in three main aspects. The first aspect is the particular geological conditions existing in the boundary zone between the continent in which erosion and transport carry sediments towards the coast, and the physical and chemical sedimentation environment due to the base level imposed by the sea and its salinity. The second aspect refers to the discharge of continental water into the seawater body, characterized by its high salinity and greater density; this means that the denser seawater tend to occupy the lower parts of aquifer systems. Seawater in the ground does not flow unless diluted by freshwater, or until relative sea level changes are produced, or the freshwater flow pattern is modified by natural causes (climatic change) or by human influence (pumpage). The third aspect refers to continental water quality since its mixing with only a few percent seawater drastically impairs ability to be used and more that 3 or 4% renders it practically unsuitable for most uses, and only costly desalination processes may upgrade it. In coastal aquifer systems seawater and trapped marine water in aquifers and aquitards may be in direct contact with continental groundwater. This means that in coastal aquifers, in addition to the common knowledge of aquifer properties and hydrodynamical conditions, detailed information on saline water pattern and heads is needed.

In spite of being more complex, coastal aquifers can be studied, known, developed and managed with well known and experienced principles and means, and constitute important key elements in the water supply systems of coastal areas. They play the role of natural sources of water and storage reservoirs, just in areas where surface waterworks and reservoirs are often difficult due to the lack of space and good conditions. The discharge of groundwater may create valuable coastal wetlands and interesting ecological situations, which deserve due consideration.

Coastal aquifers can be developed as a continuous source of water or as a reserve for discontinuous use, or some combination of both. The operation rules depend on the existence and characteristics of other sources of water, the variability of demand and the restrictions imposed by the water distribution network, economic factors and existing rights and legal constraints.

Emergency situations may develop, such as major breakdowns in water supply systems, failure of reservoirs and pipes, long lasting contamination events and general disruption of energy supply. They can be the result of natural events such as earthquakes, landslides, volcanism, floods, tornadoes, catastrophic heavy rains. Additionally, design failures, rupture of toxic waste stores, leakage of chemicals, and even war and terrorist actions due to human activity also create emergencies. In these situations a local, large enough and proven fresh water reserves capable of rapid development are needed. Local aquifers often may accomplish this role. The survival of freshwater supply in Beirut and other Lebanese coastal towns during the long lasting civil war of the 1980s is an example.

Peak water demand situations pose serious problems to water supply in many coastal areas. The most acute correspond to large demand increments due to seasonal irrigation needs and touristic affluence. In some touristic resorts seasonal populations may increase by an order of magnitude, at the time that agricultural demand also increases. The critical season is often the summer, but it can also be the winter, as in the Canaries, where reasonable temperatures attract tourists and out of season irrigated intensive crops find good markets at other latitudes. To cope with peak situations waterworks have to be large enough, which implies operating at undercapacity for a large fraction of time, or to be backed by a separate storage of good quality water to be used at peak time and replenished the rest of the year. Coastal aquifers may fulfil this role, securely and economically, if correctly managed.

Box 18.1. *Palaeowater quality and use: a conflict of use*

In several countries high quality palaeowater may have been used over without recognition of its origin on its non–revewable character. The groundwater in the Triassic sandstone of the East Midlands is being used not only for public supply but for cooling water for power stations where low total dissolved solids in an advantage from the point of view of corrosion and scale control. Similar situations are found for example in the Aveiro aquifer Portugal, where industrial areas are one of the main users of the high quality palaeowaters. In those areas where palaeowaters are recognized it is recommended they are used for drinking purposes and as a strategic reserve.

The risk of seawater intrusion and the potential for saline upconing is an added complexity but this need not hinder aquifer development. Much of what is referred to in reports and in the literature as negative effects of coastal aquifer exploitation is often the result of lack of awareness of the nature of coastal groundwater, poor development and inadequate management. This is one of the myths referring to groundwater, mostly propagated by those who ignore groundwater properties or systematically oppose aquifer use in favour of surface water or desalination. Sea water intrusion can be tolerated to some extent. It is reversible under some circumstances and can be controlled by reducing abstraction rates and careful monitoring, or by reducing the salt water head by pumping out saline water (Custodio and Bruggeman, 1987).

The large freshwater storage volume in many coastal aquifers allows for intensive use during short periods of time (weeks to months) without serious deterioration, and the antecedent conditions may be recovered during the rest period under favourable circumstances, if the discharge of fresh water into the sea is restored.

In coastal areas and islands there may be a temporal excess of fresh water which can be used at other times. The excess is the difference between water availability and demand, including quality restrictions. Excesses refer to the unused part of spring and river flow, discharge from flowing wells and drainage galleries, production of treated and desalinated water, or conveniently treated sewage water. The classical solution to this problem is surface storage.

Freshwater coastal aquifers can often be adequate reservoirs for storage of these waters by means of artificial recharge, by applying the most suited methods and managing clogging effects. The operational cost is a main constraint to the practical feasibility as well as the possible modification of aquifer water quality by substitution or by mixing with the artificially recharged water. This is a complex function of recharge siting, well characteristics and operation.

Storage capacity may also be found in brackish or saline coastal aquifers if this water can be effectively displaced. The body of injected or recharged freshwater presents a mixing zone (dispersion zone) with native water the width of which is controlled by aquifer properties and geometry, local heterogeneities, the buoyancy of freshwater in saline water and the operation of the injection/abstraction wells. However, introducing freshwater from the surface or through interaquifer (natural or forced) leakage also means introducing anthropogenic chemical, biological and radioactive contaminants, some of which may be a health concern, even at low concentrations. Thus, before deciding to use a coastal aquifer containing brackish or saline palaeowater for artificial storage it is worth considering whether this water may not be usable as a source of freshwater by desalination.

Coastal aquifer management has to consider the special characteristics mentioned above, mainly the existence of saline water and the risk of salinization. This includes the knowledge of the origin of salinity and the process of salinization.

18.3 Palaeowaters in coastal aquifer systems

The existence of palaeowaters in a coastal aquifer system is the result of parts of it having a long turnover time due to the right combination of permeability and groundwater head gradients. The long turnover time part of the aquifer system may contain a mixture of recent and old water, or true old water when piston flow dominates (Zuber, 1986; Custodio, 1991). The mixing is often the result of different flow paths converging toward a spring or a well.

Aquifers are often open in relationship with land surface, other aquifers or extensive aquitards. Thus, when palaeowaters are discharged or abstracted they are replaced totally or partially by recent water, or progressively exhausted in the less frequent case in which the aquifer is closed. Only a fraction of the total palaeowater volume is exploitable without mixing with younger water, and this is a function of well emplacement, screen position and abstraction rate. In a given aquifer abstracted palaeowater may be replaced by palaeowater in other aquifers or aquitards – up to some limit – or be replaced by recent recharge, or become a variable mixture of old and new water. In coastal aquifers replacement water – from the ground or by recharge – may be saline water. Palaeowaters are a non–renewable resource, with a given volume, similar to other fluid mineral reserves such as oil and gas.

One of the main beneficial uses of fresh palaeowater, whether it refers to pre–industrial water or to Pleistocene water, is for drinking purposes. Not only do most palaeowaters have the advantage of good biological quality and slowly variable characteristics, common to most groundwaters, but they are free of artificial pollutants such as polycyclic hydrocarbons, halogenated solvents and disinfectants, pesticides and their derivatives, drugs, industrial heavy metals, man–made radioisotopes (fission and activa-

Electrodialysis plant in Playa del Ingles, Gran Canaria, to desalinate brackish palaeowater

Box 18.2. *Use of brackish and saline palaeowater*

Brackish water from the Amurga phonolite massif (see Chapter 8) is used for desalination at the electrodialysis plant near the Maspalomas–El Inglés large touristic complex in the South of Gran Canaria island. This water has no man–made contaminants. The development intends to use groundwater reserves without seawater intrusion and deterioration by possible deep-seated saline water during the economical life of the plant. The desalinated water is mixed with freshwater from other sources and reverse osmosis desalinated sea water. Sewage water is treated and reused for municipal gardening and grass-covered sport areas, as well as for irrigation of crops, mostly under greenhouses.

In the Ebre river delta, in Southern Catalonia, near the enter shore the deep Pleistocene aquifer contains old marine water, which has not been flushed out due to lack of hydraulic gradient. Several attempts have been carried out to develop this marine water for aquaculture (mostly crustaceans and shellfish) as an alternative to direct use of sea water, which needs a costly uptake facility, turbidity control and temperature conditioning. Groundwater is clear, easy to get and with an adequate and constant temperature. But the reducing groundwater environment due to the presence of organic matter in the sediments impairs water quality. This has prevented the widespread use of this water but for some attempts to exploit the relatively warm, constant temperature water exchanging heat with water from other sources.

Natural spring area in the Ebre delta in which freshwater drag along old marine water in the Pleistocene formations

Box 18.3. *Palaeowater as good quality water: the Aveiro Cretaceous Aquifer*

Nowadays one of the public institutions abstracting palaeowaters from the Aveiro Cretaceous aquifer is the Aveiro Harbour Authority which have to supply fresh water to visiting ships.

In the harbour there are two boreholes around 260 m deep to abstract palaeowater. However, while one only exploits the aquifer layers with good quality, low mineralized water ($Cl^- < 30$ mg L^{-1}) at maximum allowed pumping rates of 15 L s^{-1}, the other one exploits less deep aquifer layers, with more mineralized waters ($Cl^- \sim 250–300$ mg L^{-1}) but that allows higher exploitation pumping rates (50 L s^{-1}).

Recently the Harbour Authorities decided to drill a new borehole to replace the latter one, but decided this time to explore uniquely the aquifer layers with low mineralized waters despite their lower productivity.

This is highly representative of the current trend these days to develop new boreholes in the aquifer which exploit less mineralized and lower yielding aquifer layers, rather than more mineralized but better yielding layers.

Sustainable development of the low salinity palaeowaters in Aveiro's deep coastal aquifer depend on correct design, construction and maintenance of wells and needs regulations to be followed by municipalities, which are the local responsible authorities for permits to develop groundwater. Damaged wells and boreholes to be abandoned have to be carefully backfilled and duly cemented.

tion products), pathogens and viruses. This is especially important when safe treatment for potability is not available or difficult (as in rural areas and small towns) or is too costly. In addition, in many areas of Europe there is an increasing popular demand for good quality, tasteless untreated water supply. Often palaeowater is or may be an important source for bottled water.

Unfortunately fresh palaeowater sometimes may contain some components that are undesirable and even toxic, which require treatment before use. This is the result of the long contact time with aquifer minerals under diverse environmental conditions. The result may be an excess of some components such as F, B, an excess of Na with respect to earth-alkaline ions, high Na concentration, sometimes As and V, some heavy metals (mainly Fe and Mn) and perhaps slightly high radioactivity (mainly Rn gas). Under reducing conditions, in addition to heavy metals palaeowaters may contain bisulphide (or hydrogen sulphide under acidic conditions), ammonia and some dissolved gases (CO_2, CH_4). Also the temperature may be quite high due to depth (effect of geothermal gradient); this is an advantage in cold areas but requires some storage detention in warm areas. Hard palaeowater with high equilibrium CO_2 pressure is not only a nuisance for domestic use (laundry, heating) but may produce scaling in pipes. Acidic water enhance corrosion of pipes and appliances.

The use of fresh palaeowater for industrial purposes has similar advantages and drawbacks to those described above for drinking and domestic uses. Water hardness may be a problem and some preliminary water softening pre–treatment may be necessary. In some cases, notably in volcanic aquifers, high silica content is also a nuisance. Palaeowaters are also used for agricultural irrigation and problems are found at high salinities or where unbalanced alkaline–ion concentrations occur. The correction is too expensive except for high value crops.

Industry and agriculture, and also livestock, are much less quality demanding than human consumption, and may use other sources of water. Thus, as a general rule, non–renewable palaeowater resources should be preserved mainly for drinking purposes. This general rule has to be adapted to local circumstances of actual palaeowater conditions and quality, water planning and management alternatives.

The influence of marine salts may result in poor natural quality conditions. Thus, although in many cases palaeowater is fresh and exempt from toxic substances, in other cases it may be saline or brackish, and further it may contain undesirable contents of some substances derived from water-rock interaction, including redox reactions induced by the presence of organic matter in the sediments. But it is still essentially free of man-made chemicals and their degradation products, and also of biological contaminants. In this respect palaeowater, even if the saline content is too high, is a suitable water source for desalination, if natural toxic dissolved components are below reasonable limits. This is currently a situation of growing frequency in some coastal areas and islands, when the climate is arid and there are no other sources of water. Salinity can be of marine origin (unflushed or partly flushed sea water) or the result of scarce recharge where most of rainfall evaporates combined with relative high airborne salts due to the proximity to the coast and winds coming from the sea. This is the case for extensive areas of the Eastern Canary and Cape Verde islands.

Currently reverse osmosis is the most usual desalination method for brackish water but also electrodialysis is applied if water salinity is moderate. This is now common practice in Gran Canaria and Fuerteventura (Canary Islands) and is also developing in Eastern Spain coastal areas and in Mallorca island.

Desalination by means of membrane techniques is cheaper for brackish groundwater than for sea water. But for plant efficiency water salinity has to be relatively constant and troublesome components, such as dissolved silica, must be below reasonable limits or have to be controlled by pre-treatment. The lack of turbidity and the constant temperature together with the lack of anthropogenic and biological contaminants are distinct advantages in utilizing these palaeowaters.

Another possible use of brackish and saline palaeowater is as a source of water for fish farms, where constant, slightly warm temperature is advantageous. Fish and shellfish are however very sensitive to reducing conditions, ammonium and certain trace components such as iron and some heavy metals which may be present in palaeowaters in deltaic sediments. This may hinder the direct use of this water or make it too costly if treatment is needed.

18.4 Development of groundwater in coastal areas

The existence of palaeowater in coastal areas and islands is the result of special local characteristics. Drilling may greatly disturb the existing situation by creating paths for vertical interconnection of aquifers and for the penetration of surface and phreatic waters under natural conditions or as a result of groundwater abstraction. Inadequate drilling may ruin for ever a coastal aquifer as in the Besós delta (Barcelona) and the Pont d'Inca calcarenite aquifer (Mallorca island). Unaware and irresponsible well drillers generally try to get the maximum yield by putting a screen in any permeable layer they find. In hard rock the casing is mostly for isolating the well from the surface, or to protect the pump from falling sediments and rocks; the lower part of the bore, if it stands, may remain uncased. Steel casing corrosion also favours aquifer interconnection, as well as poor welding or inadequate waterproofing of joints.

Drilling in coastal and island aquifers, especially when palaeowater exists, must follow a careful design which includes:

(xxii) Casing and grouting of the upper part to prevent the penetration of surface or phreatic water.

(xxiii) Emplacement of casing with correctly welded or waterproofing of joints.

(xxiv) Restoring the isolation provided by low permeability layers by careful grouting and multiple or telescopic casing if needed to provide good grouting and/or protection against corrosion; corrosion resistant casing may be needed such as plastic or fibreglass.

(xxv) Using thick enough casing to avoid implosion and breakdown by external pressure, especially during well development and pumping.

Any of the available drilling methods can be used if suitable for the formations and the depths, from cable tool percussion to bottom hammer air percussion and rotary systems, but the constraints imposed by casing and grouting have to be considered. Not all drilling methods and rigs are able to ensure a good construction and testing. The ability and experience of the driller is of paramount importance.

Often palaeowater is emplaced in deep formations and deep wells have to be drilled. When the deep well is expected to flow, as in low elevation coastal plains, grouting must be able to resist water pressure and to accommodate the installation of a well cap. Failures are not rare and correction may be costly.

The design of a well, if there is not enough previous local experience, may require an exploratory borehole and geophysical testing and logging.

18.5 Management of coastal aquifer palaeowater

The unique characteristics and one-time reserve circumstances of palaeowaters introduce into the coastal or island aquifer system new constraints since a part of it may need specifically tailored management rules to preserve its existence as long as possible and to get from it the best beneficial use. A consequence is that priorities should be introduced to get its preferential use for drinking purposes, even under peak demand and emergency situations. These constraints may require rules which may be in conflict with what is generally considered the best use of a coastal aquifer, since palaeowater protection for drinking purposes is more important than contributing storage space. This means that rules may be different for different areas or aquifers of the same system.

In order to protect palaeowater existing in coastal and island aquifers, the preservation of isolation and/or low hydraulic gradient conditions leading to its existence is an important management objective. This relative isolation not only refers to barriers to horizontal flow (they may not exist) but mostly to horizontal layers above and below the aquifer containing the palaeowater. Often the most effective natural confinement is due to the presence of thin, low permeability layers in the formations, which greatly reduce vertical permeability. They have to be identified and known, and be the subject of special protection. Such rules are applied, for example, for drilling in the dune area near Amsterdam.

Old cattle watering trough in the Doñana national park, southern Spain, previously fed by a flowing well but now abandoned due to piezometric level drawdown after intensive development in nearby areas. Water discharged was fresh palaeowater.

Box 18.4. *Palaeowater: a finite resource*

In several coastal areas of Europe, but particularly in the south, well-field development has intercepted non-renewable palaeowaters and led to extinction of wetlands and baseflow to rivers. Artificial measures such as importation of water or mining of even deeper resources may provide a short-term remedy, but the need for re-assessment of the long-term water balance is highlighted.

A pumped well discharging palaeowater to sustain the impoundment of a lagoon used by waterfowl in the dry season. Doñana national park, southern Spain.

Isolation preservation means drilling without increasing aquifer interconnection and vertical permeability. This applies not only to exploratory drilling and exploitation boreholes and wells but also to monitoring boreholes. Carefully engineered isolation and grouting, and casing resistant to degradation and failure by corrosion and mechanical stress have to be considered and installed. This

Box 18.5. *Management steps of the Ledo–Paniselian aquifer*

The Ledo–Paniselian aquifer in Belgium is exploited to an increasing extent for public water supply, industrial and domestic uses. The government has set up a monitoring system for the aquifer, including:

- a piezometric monitoring network for monthly measurements of the hydraulic heads
- a water quality control network
- an inventory of pumping wells comprising location, well characteristics and abstraction rates
- the DAWACO database including all mentioned data (De Smet *et al.*, 1997)

The observed hydraulic heads are locally much lower than can be expected from the known pumping data, revealing that the latter are incomplete.

A hydrodynamic modelling system has been developed for managing the Ledo–Peniselian aquifer (Van Camp *et al.*, 1998), comprising:

- a regional multi-layer 3-D model to simulate the groundwater flow in the whole system, both for pumped and non-pumped situations, that can also be used to predict the impact of future exploitation
- a local, radial axisymmetrical model to calculate the drawdown around single wells, that can be used to evaluate the impact of individual wells.

Groundwater abstraction permits are awarded by the administration on the basis of drawdown simulated by the model. In general, it is considered unacceptable to lower pumping levels beneath the top of the aquifer, thus respecting its semi-confined character.

At present, no provisions exist to make special management for palaeowaters. Indeed, groundwater is considered as a renewable resource. However, exploitation of the freshened palaeowaters in the Ledo–Paniselian aquifer induces flow of less freshened groundwater of the over– and underlying aquitards, spoiling the palaeowater reserves, in stead of merely replenishing them with younger fresh groundwater by an accelerated lateral flow from the natural recharge areas.

also means that leaky or abandoned boreholes must be carefully grouted to restore former hydraulic conditions.

Maintaining low hydraulic gradients to delay penetration of other waters, especially recent and saline water, can be achieved by adequate spacing of wells or boreholes on the territory and by avoiding large, concentrated abstractions. This needs some trade off with the convenience of reducing the number of wells and the length of distribution pipes. Except in enclosed aquifers, in which piezometric level drawdown will increase with increasing total water withdrawal, abstracted palaeowater will be replaced by new water, both continental and marine, except for the reduction in storage. In outcropping areas of the aquifer, if they exist, it is not rare that what was formerly rejected recharge (the aquifer was full) is progressively converted into effective recharge that replaces palaeowater as it is being abstracted. Modelling of aquifer behaviour is needed to know the palaeowater volume reduction, the mixing with young water and the different contributions to pumping wells, in order to establish operational rules to optimize the use of the one–time palaeowater reserve.

Regional water head drawdown can be large and may induce consolidation in young formations. The consequence is some degree of subsidence, local or regional, which may modify land flooding characteristics, the coast line and the drainage of coastal areas. Good examples can be found in Thailand, Japan and NE Italy (Venice), and is suspected in the Llobregat delta (Barcelona, NE Spain). In karstic coastal areas water head drawdown (and especially increased water head fluctuations) due to groundwater abstraction may also increase the rate of local, sudden land collapse and sinkhole formation.

18.6 Monitoring needs and data use for management of coastal aquifer palaeowaters

Management of palaeowaters and the interface with modern waters in coastal aquifers needs specific data, including the knowledge of:

(i) geometry of the aquifer system, including the aquitards
(ii) three–dimensional (3–D) head and salinity distribution and evolution, under natural or initial conditions and as a result of development; in some cases also 3-D temperature distribution is needed. This has to be supported by hydrogeophysical logging (temperature and electrical conductivity) as a basis for determining the flow pattern
(iii) constructive and behavioural information of boreholes and wells, and rate of groundwater abstraction with time, since the drilling was carried out
(iv) information on hydrochemistry and environmental isotopes of value for palaeowater characterization and evolution as a consequence of development

Since palaeowater aquifers are commonly confined, water head distribution and evolution can be known through a reduced number of piezometers, but at each site often more than one water head has to be measured since the hydraulic potential may change with depth. Thus, sets of nested or multiple piezometers are often needed, which include measuring water head in each of the aquifers and aquitards in the same vertical line, as well as in fresh and in saline water. If there are other permeable or semipermeable formations below the palaeowater aquifer under consideration, at least one of the piezometers should measure their water heads.

Measurement of water salinity is more complex since it may progressively change, especially when the palaeowater aquifer is developed. Water quality monitoring has to be adapted to the actual salinity distribution and to its future evolution.

Water pumped from boreholes is likely to be a mixture of components from different depths and does not represent the true situation in the aquifer system. Exploitation wells are suited for palaeowater quality sampling provided the water comes from a well-defined depth. In this respect the existence of long screened sections or several screens, which may be the origin of interscreen flows, is an undesirable situation. Also, pumping time must be enough for the water sample to come from the aquifer and not from inside the casing.

Observation boreholes are suited for palaeowater sampling provided the water sample is from the aquifer. This means using a depth sampler lowered to the screen after evacuating a large enough water volume from the borehole. This may not be necessary if groundwater flow through the screen is high enough, a rare condition in palaeowater aquifers except near pumping wells. A good water sample can be also obtained by pumping after extracting several times the water volume inside the borehole between the pump and the screen. It is worth checking that the temperature and electrical conductivity of pumped water stabilizes before sampling.

In short screened boreholes in poorly permeable formations the maximum pumping rate may be quite low, which means a long time to renew the water inside the casing. Thus, in some cases a submersible sampler is recommended after some pumping.

Lost drilling water and residual drilling muds may disturb sampling for a long time since they are difficult to take out. Thus, the selection of the drilling method and the operation of the drilling rig are important since it is necessary to be able to identify if remnants of drilling fluid are still in the borehole. This is easy when drilling water is chemically and isotopically different from aquifer water. Drilling muds often have high pH (due to added chemicals) and this may be a good indicator in unbuffered aquifers. In other cases an added tracer such as bromide or lithium may be of help. Na from additives may also be a useful indicator.

Palaeowater aquifer management needs reliable data, especially:

- water head measurements in the aquifer and related aquifers, and in some cases aquitards; monthly values are generally enough if there is additional data from a few continuous piezometers. When variable salinity water is involved, the density distribution along the borehole column has to be known or deduced;
- sampling for chemical analysis in pumping wells and boreholes, generally once or twice a year, and weekly to monthly for salinity monitoring in a few points together with temperature. Chemical analysis of major ions is generally sufficient, but a more complete analysis and more frequent sampling may be needed, following established norms for water supply monitoring. Environmental isotope analyses are not generally needed for monitoring but for establishing the initial condition and the 3–D distribution of groundwater types. However to know the long term (5 to 10 years) evolution of well fields (including palaeowaters), environmental isotope surveys are required;
- records of abstraction rate by wells or groups of wells, and yearly abstraction. This is easy for supply wells fitted with water meters (if calibrated), but it is more complex for rural and agricultural wells lacking these meters; indirect evaluation has often to be applied, such as irrigated surface.

18.7 Administrative and legal framework

The countries and regions of Europe have different legal water ownership status, from private to public. This influences water administration but is not essential for management since there is always the possibility of setting reasonable limits to private action for the benefit of the community and for preserving the vital and social role of fresh water. Also, public ownership does not necessarily mean good management. The dominant factor is the political will – based on people's will – and the ability of the water administration to really set and apply adequate rules and laws. Good and bad examples can be found both under private and public ownership of groundwater.

The current trend oin freshwater administration and management is the sustainable use of the freshwater resource system. Sustainability is a complex concept which has to be flexible enough to adapt to a continuously changing world subject to scientific and technical development, variable water needs and evolving social requirements.

The application administration to a palaeowater aquifer as a source of fresh water, or of water that can be converted into fresh water, has to include considerations similar to those used in mining: the total quantity is limited and non renewable. Furthermore it can be spoiled by salinization and it is vulnerable to contamination. Thus the exploitation of palaeowater should be linked to the benefits it produces in order to use a part of these benefits (specifically or through general taxation) to pay for the development of a new source of fresh water as palaeowater reserves diminish and, finally, are depleted or replaced. These include direct economic but also indirect and intangible (mostly social) benefits, the influence of which depend on some subjective and political factors. A combination of permits, taxes on abstraction and limitations is needed, adapted to state or regional laws and accepted by the social agents, which are those directly interested and the beneficiaries.

Current administrative and legal systems generally do not provide explicit norms to deal directly with palaeowater, since this is a subject that in general has not been considered by managers and lawyers. But rules can be easily derived from groundwater protection and preservation norms and directives if the objectives are clearly explained and understood, and there is the administrative and political will to set and apply them. These have to consider:

(i) the non–renewable nature of palaeowater,
(ii) its specific value for drinking water due to the absence of harmful anthropogenic substances,
(iii) the vulnerability to salinization and pollution due to faulty and careless drilling, poor well operation and inadequate abstraction pattern,
(iv) the use of other sources of water for non-drinking purposes.

Coastal and island palaeowater aquifer management needs specific rules, over and above those included in regional laws, national water acts and European Union Directives. They include:

(i) drilling norms for wells and boreholes, including their abandonment
(ii) distribution of wells and discharge rates
(iii) aquifer development plans, to be reviewed periodically
(iv) priorities for palaeowater use
(v) monitoring
(vi) specific management rules

The effective implementation of management rules needs the framework and the will to set them. This can be accomplished when the palaeowater aquifer is under the full responsibility of the management organization, but it generally fails when other related aquifers and aquitards cannot be controlled. Rules may include provisions to prevent the indiscriminate exploitation of deep aquifers, which often contain palaeowater. Often this means changes and additions to the existing Water Act or equivalent legislation.

The constitution of aquifer water users' associations, to which the different water rights holders give management capacity, is generally a good solution and perhaps the only stable way to protect the aquifer and to obtain the best use of palaeowater. The users' association should be a public entity under specific statutes and rules and under the guidance of the Water Administration. The association – or similar legal denomination – has to have the capacity to legally represent the water rights holders in administrative and legal affairs and be the subject for technical and economic public support and legal protection. Other water actors have to have a voice as well.

18.8 Summary conclusions

- Coastal aquifers constitute a highly valuable source of water for human needs. They are key elements in water resources management as storage reservoirs.
- Deep coastal aquifers may often contain slowly renovated groundwater, several centuries or millennia old – palaeowater – which is a one time reserve of water which is free of man–made pollutants; it deserves protection as a source of drinking water.
- Along the European shore coastal aquifer palaeowater is freshwater in many circumstances, but when it is brackish or saline it still may be an interesting source for desalination in water-scarce coastal areas.
- Palaeowater in coastal aquifers can be easily contaminated and spoiled by poorly constructed, maintained and operated wells and boreholes.
- European Water Directives have to consider the intrinsic interest of coastal aquifer palaeowaters as a unique, one–time source of drinking water, free of man–made contaminants. Regulations for their protection, use and management are needed.
- Indiscriminate use of deep coastal aquifers has to be avoided and abstractions should be subject to regulation.
- Coastal aquifers can be effectively managed if operational rules for exploitation and well drinking are available and enforced.
- The effective participation of water users in coastal aquifer palaeowater management is essential, as well as the transfer of part of the individual water rights to a common management body under the guidance of the water authority.

18.9 Annex 1: Management of the Astian aquifer, Southern France

The confined Astian aquifer (South of France) consists of micaceous sands, and covers a surface of 438 km^2 towards the Mediterranean coast. This sandy formation is covered by Plio-Quaternary continental deposits and outcrops over only 17 km^2. Almost 600 boreholes are recorded in the Astian sands. The coastal area is a very touristic region. In summer the population multiplies six fold (70 000 permanent residents, plus 325 000 seasonal inhabitants along the coast during summer). As a consequence of the specific geological pattern and the touristic pressure, decreasing piezometric levels have been observed, with increasing salinity coming from present sea water or deep aquifers. Furthermore, casing corrosion adds to this problem by creating paths for vertical interconnection with polluted waters.

Considering this situation the different towns concerned tried to form an aquifer users' association called "Syndicat Mixte d'Études et de Gestion de l'Astien" (SMEGA). A study Commission directed by the "Sous Prefecture" de Béziers and linking the 20 towns concerned, the territorial communities and national technical services, was firstly created in 1988. The objective was to examine who was concerned by the problem (users, borehole owners, drillers), what kind of legislation already existed and the economic implications. Considering the need of financial involvement, the "Syndicat Mixte", including all the partners, was officially created in 1990. The main goals of SMEGA are:

- continuous watch over the Astian aquifer (piezometric level, water quality, data base and mathematical simulation);
- reflection on Astian aquifer management;
- production of information and sensitive data for the users.

The SMEGA is made up of 28 members;

- General Council of Herault (6 persons);
- 20 towns (1 person per town)
- The "Chambre d'Agriculture" (1 person)
- The "Chambre de Commerce et d'Industrie" (1 person).

The financial participation of each member is related to the amount of water used. Subventions are coming from the General Council of Herault, the Water Authority (Agence de l'Eau Rhône–Méditerranée–Corse) and from the French government (Ministry of the Environment and Ministry of Agriculture).

Different works have been carried out. In 1989 the SMEGA collaborated with the DIREN (Direction Regionale Environnement) to obtain a weekly piezometric observation in the dry season with results transmitted to all the users. A database was created. Different mathematical models have been constructed and simulations of the future evolution of the aquifer have been carried out.

Recently (June 1997), a contract was signed by the "Syndicat" with the Prefet representing the French government, the General Council of the Herault and the "Agence de l'Eau". The goal of this contract is to develop

Box 18.6. *User's associations: the Astian aquifer*

The confined Astian aquifer, Southern France, exemplifies the development of a coastal aquifer for human supply of an area subjected to a sharp increase of water demand in summer, which is due to tourism (see Annex 1 for more details). To cope with aquifer impairment a water users' association was created in 1988 with representatives of municipalities and management organizations. A specialist administrating a small budget is in charge of updating the knowledge and preparing proposals based on mathematical modelling, as well as securing the good condition of abstraction wells. No special consideration is however yet paid to palaeowater existence and protection; the goal is to obtain freshwater, so there is room for education.

5 topics included in an integrated programme:

- Quantitative management of the aquifer;
- Borehole quality (old boreholes have to be removed);
- Water savings;
- Training;
- Complementary studies related to the resource.

The SMEGA became the SMETA (Syndicat Mixte d'Études et de Travaux de l'Astien) and a young hydrogeologist was employed. The total economic resources available to deal with the five topics is about 3 million euros per year.

18.10 Annex 2: Groundwater management of the Llobregat delta coastal aquifer

The Llobregat delta coastal aquifer system is a small alluvial formation just at the SW area of Barcelona, the capital of Catalonia, with a Metropolitan area of about 3.5 million inhabitants. In its 80 km^2 of surface (120 km^2 if the lower valley included) there are up to 1000 wells, most of them boreholes penetrating the full thickness of the Quaternary sediments. Details can be found elsewhere (Custodio, 1968; Custodio *et al.*, 1971; Iribar, 1992; Manzano, 1991; Peláez, 1983) and in this report.

Up to 130 hm^3/a were abstracted around 1972 but currently the figure has been reduced to 60 hm^3/a (more than 10% of total water demand in the full area), with an installed capacity of about 4m^3/s. A large part of the current recharge is river infiltration through irrigation canals and the irrigated fields, and also directly from the river bed. The intensive groundwater exploitation maintains a permanent drawdown situation in the confined delta deep aquifer and its water table extension into the lower valley, with water levels commonly below sea level and down to –30 m in the past. The result is the possibility of using up to 100 hm^3 of underground storage capacity in the lower valley to allow to intra-annual regulation. This allows infiltration of surface water, but also creates conditions for easy pollution (river water has quite a high salinity, groundwater hardens by soil CO_2 addition in irrigated fields and by reaction with carbonate sediments) and sea water intrusion through the offshore aquifer outcrop. Thus part of the aquifer suffers from groundwater quality impairment.

Current groundwater use is up to 40% for town supply (actual abstraction depends on the need to complement surface water availability and treatability in a given year) and up to 50% for direct supply of factories, and less than 15% for agriculture.

Low salinity palaeowater existing in the delta deep aquifer was of pre-industrial age but recharged during the Holocene, with flow high enough to flush out Pre–Holocene marine water (Custodio *et al.*, 1992). Development of the good quality groundwater reserves started in the last half of the last century, mostly for house and rural supply and also for agriculture, but soon paper mills and later on synthetic fibre and metal factories were the main developers. Thus palaeowater was rapidly depleted and substituted by recently recharged water except for rural areas close to the coast, where now seawater intrusion is established, but in a few less transmissive areas. As a consequence the coastal aquifer system is now almost depleted of palaeowater, with most of the reserves already used for applications not requiring high quality water.

Box 18.7. *User's Associations: the Llobregat delta aquifer*

As explained in more detail in Annex 2, the good quality water of the large transmissivity, confined (Pleistocene) aquifer of the Llobregat delta since the last century attracted the development for rural and town supply of the existing high grade pre–industrial water. But the intensive exploitation since the first third of this century, and especially since the 1950s, for industrial uses has exhausted the old water, which has been replaced by recently recharged water from the contaminated river and a serious seawater intrusion. The serious loss of water quality affects the currently large local population and damages industrial production. A groundwater user's association was created in the 1970s, now recognized by law as a public entity, with the goal of controlling the aquifer use and protecting it. The results are encouraging, although the old water (not strictly palaeowater) has been mostly exhausted, although the International Airport facilities are still using it in part. Flow and salinity transport models are used to help in the proposal of management actions.

The coastal aquifer system is a key element in the water resources system. This is well understood by the inhabitants of the area and was clearly stated and demonstrated by the Water Authority in the 1960s and 1970s, when most of the management actions developed. The starting point was the awareness of the danger created by the advancing seawater intrusion tongues (an aquifer heterogeneity effect) and the need of reducing industrial production costs by decreasing regional drawdown. At that time the Barcelona's Water Supply Company had already started artificial recharge in the lower valley by conditioning the river bed upstream and by injection into wells of excess treated river water from the treatment plant.

A local well owner's association was promoted in 1975 by a group of factory managers, with the help of the Water Authority, and the later incorporation of the most affected Municipality, Prat del Llobregat. In 1976 a Managing Board was created and started working at the time the Association's Statues were prepared and approved by the Government in 1982, under the possibilities contained in the 1876 Water Act, which considered groundwater the property of the abstractor, and surface water a public domain. After the enforcement of the 1985 Water Act, which considers all water a public domain and promotes groundwater user's associations as a desirable management tool, the Association was enlarged to cover all the area affected by the aquifer system. The Association is dominated by water supply companies (municipal or private) and factories, but farmers are also represented through the large number of wells they have or through the respective municipal representatives. The Association has a Board, a Technical Board and a Jury. At the beginning the main tasks were to keep an updated well inventory and to ask the Water Authority to carry out studies and investment in the area. But little by little the Association has enlarged its own observation network, has carried out studies to protect its rights and has improved the information activities, all of this with a small budget (starting from 3000 to the currently 50 000 euros per year) and the technical contribution of the most active members.

The main tasks accomplished are:

- a complete inventory of wells and updating these

- advisory action and control of new drilling
- cessation of an exploitation of aggregates from the aquifer area
- control of excavation refilling
- periodical survey of groundwater levels and salinity, further to the network operated of the Water Authority
- promotion of groundwater abstraction savings through improvements in industrial processes and controlling water distribution leakages, with the objective of retarding seawater intrusion and reducing exploitation costs
- actions to protect recharge areas and to restore them when affected by major works such as new roads or railways
- actions to grout abandoned and corrosion damaged wells, and to secure the correct drilling of new ones

Seawater intrusion progression is under partial control due to a series of industrial wells abstracting saline water, mostly for cooking purposes. This is a non–ideal situation, which is very sensitive to the closing or abandonment of these wells. Attempts by the Water Authority for an engineered solution to reduce saltwater potential by means of temporarily pumped wells, or by artificial recharge of freshwater (using the upper aquifer as a filter and storage element) have failed until now due to poor design and implementation, and the lack of understanding of the problem by decision makers.

A further problem which is appearing in the last two decades is the foot dragging applied to the Association development and action as a Public Corporation with the capacity to share responsibilities. This is matter of sluggish and uncertain development of the Water Act, unwillingness of some public servants to transfer part of their powers to other organizations and the poor management capabilities of the new decision makers who are more interested in large investments and big water supply schemes than in management of water resources and the good use of existing natural and man made infrastructures. If the lower Llobregat and delta aquifer system is destroyed, this implies the development of an equivalent water system able to provide similar services, in a complex area, with little space for new infrastructures. The investment for this alternative system is reckoned about 250 million euros, or about 0.5 euros m^{-3}.

The preservation of the aquifer system is equivalent to the operation costs of water works. When this is carried out through general and special taxation, it can be expected that the corresponding part is used to preserve the area, directly by the Water Authority or through the Users' Association. But this is something resisted by the Water Administration, which expects the user's to provide or to obtain from other sources additional money, putting them in disadvantage with respect other citizens.

19 General conclusions

The PALAEAUX project has brought together up-to-date geochemical, isotopic and hydrogeological information on coastal groundwaters across Europe in a transect from the Baltic to the Canary Islands. These data have been interpreted in relation to past climatic and environmental conditions as well as extending and challenging concepts about the evolution of groundwater near the present day coastlines. Freshwater of high quality, originating from different climatic conditions to the present day and when the sea level was much lower, is found at depth beneath the present coast in several countries. The implications of the scientific results for management of aquifers in European regions are considered.

The final report is written to give an account of the work carried out by each contractor and the principal conclusions from this work are summarized at the end of each section. In addition the integration of the subject areas covered has been presented in a series of chapters which should also be viewed as syntheses of the work covered. These synthesis chapters therefore combine the role of reviews of the state of the art in those topics considered by the consortium to be central to the PALAEAUX work as well as presenting project results at the European scale. The palaeoclimatic history of Europe is therefore discussed inasmuch as this is relevant to interpretation of groundwater evolution. Isotopic and geochemical methods, together with hydrogeophysical techniques which are both investigative techniques central to the project are reviewed and discussed in relation to the new PALAEAUX results. The chapters on physical and hydrogeochemical modelling should be viewed as conclusion sections which take the interpretation of the different scenarios suggested in the country sections as far as possible with the available data. The evolution of the European groundwaters is then viewed at the regional scale considering the likely controls at the time of the ice retreat and before the sea level rise, generally around 10 000 a BP using as a base a series of coloured maps of the main coastal regions of Europe. Finally the management chapter provides a summary of the applications of the study and lessons that need to be implemented

A number of new techniques have been introduced in the project as a result of the European collaboration. In particular state-of-the-art geochemical and isotopic methods have been applied widely in the partner countries. Among the important and/or innovative techniques are

(xxvi) the use of ^{226}Ra and chemical tracers to improve timescales;

(xxvii) the use of noble gases to determine age, palaeo-temperatures and mechanisms of recharge, including beneath ice cover;

(xxviii) the use of hydrogeophysical logging to demonstrate the three dimensional qualities of palaeowater distribution and to assist in problems involved in sampling.

The conclusions may be further summarized under the following categories, relating to the initial project objectives.

19.1 Aquifers as archives of palaeoclimate and palaeoenvironment

Results from the present study have shown that information on palaeotemperature, past precipitation and recharge regimes as well as air mass circulation can be deduced from the geochemical evidence contained in European coastal aquifers and these results augment conclusions from earlier work. One of the main deductions from the project is that an age gap can be recognized in some aquifers (in UK, Switzerland and Belgium for example) which indicates that no recharge took place at the time of the last glacial maximum (LGM). In the UK East Midlands aquifer, where there is excellent ^{14}C control, no water ages are found between 20 000 and 10 000 a BP and this timescale for an absence of recharge is found elsewhere. This indicates that these areas were free of ice cover but that sealing due to permafrost was effective. Evidence from Estonia however demonstrates that areas beneath ice sheets received recharge during the LGM.

The stable isotopes δ^{18}O and δ^{2}H in several aquifers in northern Europe indicate a sharp distinction, typically of 1–1.5‰ lower, between groundwaters which characterizes the palaeowater component relative to waters from present day hydroclimatic origins. Noble gas recharge temperatures provide convincing evidence in aquifers from northern Europe that recharge occurred during the cooler climates prior to the LGM and that recharge temperatures (soil air temperatures) were some 6°C colder than at the present day. New data from Denmark (6°C) and Belgium (up to 7°C) support the evidence already published for the UK and from Switzerland.

In Estonia groundwaters pumped from the Cambrian-Vendian aquifer, which dips inland south from the Gulf of Finland, contain the lightest known isotopic compositions in Europe. These waters have δ^{18}O values of approximately –22‰ and must represent water recharged directly beneath the Scandinavian ice sheet. Difficulties in interpreting the radiocarbon data prevent the precise dating of the recharge, but the noble gas data indicate a recharge temperature near 0°C.

In southern Europe, in contrast to groundwaters further north a smooth record of radiocarbon ages is found, indicating continuity of recharge through the LGM. Noble gas recharge temperatures in the Aveiro Cretaceous aquifer in Portugal for example, have indicated as elsewhere, that atmospheric cooling of 5–6°C occurred before and during the LGM. However in contrast to northern Europe, an enrichment in δ^{18}O of around 0.6‰ is found in the groundwaters recharged during the late Pleistocene, which is considered to reflect the isotopic enrichment in the Pleistocene ocean water as well as the constancy in the source of moisture from the Azores region of the Atlantic as at the present day. These results emphasize that the stable isotope signal in palaeowaters may either reflect the source or the temperature of the precipitation. Should the age of deeper groundwater in the Canary Islands be confirmed as a palaeowater then the absence of an isotopic shift in this water supports the conclusion from Portugal of a degree of constancy in the circulation of the Atlantic air masses in the late Pleistocene.

19.2 Emplacement of groundwaters - depth and extent

For most of the past 100 000 years the European continent was considerably larger than today and fresh surface waters and related groundwater systems extended tens or even hundreds of kilometres off the modern coastlines, which have only been in place for the past 7000–8000 years (and are still evolving to a minor extent at the present day). Sea levels considerably below those of the present day existed for most of the Devensian period, providing an opportunity for recharge and movement of groundwater beyond the present coastline as well as emplacement to greater depths onshore than allowed by the present day flow regime. The base level for flow exceeded –120 m off the Portuguese coast as well as in the Atlantic islands (Gran Canaria), but in the Channel the maximum base level was –50 to –70 m OD and in the North Sea –30 to –50 relative to modern sea level, although local deeps, due to glacial scouring, may locally have increased this to –90 m. An interface (often a saline/freshwater interface) is found at depth in many European coastal aquifers above which freshwater of late Pleistocene age, as shown by ^{14}C or stable isotope indicators, has penetrated to various depths and is preserved in some of the larger aquifer systems. A second interface (typically freshwater/freshwater) may then be observed which marks the depth limit of circulation of water from the modern era.

The greatest recorded depth of palaeo-fresh water (to about –500 m) is found in the UK East Midlands aquifer. The timescale of this groundwater movement, shown by radiocarbon data which have been calibrated and extended using chemical tracers, probably represents a continuous sequence of recharge over 100 000 a, at least since the previous Eemian high sea levels; this would support the evidence from speleothem growth for infiltration of groundwater through the Devensian glacial period. It is difficult to explain this depth of circulation purely by the lowered Devensian sea level and some of this feature may relate to groundwater emplaced during the previous (Ipswichian) period of glaciation.

In Estonia, the isotopic evidence indicates movement of colder palaeowaters to depths of –250 m. Dissolved gases found in these waters indicates a 2–5 times excess which is interpreted as evidence for recharge beneath the ice sheet, but it is concluded that the pressure dissipation here was likely to have been relieved laterally by tunnel valleys. In Denmark which, like the East Midlands in the UK was close to the stationary margin of the Weichseilian (Devensian) ice sheet, the Ribe Formation now contains water of Holocene age to around –200 m. There is evidence from noble gases of residual late Pleistocene water, although this may now have been largely displaced to the discharge areas near the coast. It has been proposed by Boulton *et al.* (1995) that the greater heads imposed beneath or adjacent to the margins of the European ice sheet could have increased the depth of circulation of groundwater. This model has been closely examined in the present programme from field evidence, geochemical and isotopic data in the aquifers and from modelling. Field evidence in Denmark and Estonia suggests that there has not been any deeper circulation and that most if not all or the pressure release can be explained by lateral flow via tunnel valleys or the may be accounted for by the lateral permeabilities of the sediments forming the near surface aquifers. In the East Midlands where there is clear evidence of penetration to –500 m, the geochemical data support a continuous flow over the whole period of the Devensian (rather than a drastic reorganization of the groundwater over the relatively short period represented by the ice advance). Modelling here suggests that the effect of the ice advance would have been to redirect flow north to south (normal to the ice front) rather than to increase the circulation depth; it is probable however that this area lay to the south of the maximum ice advance.

In several other regions waters of Holocene age have been recorded. In the Dogger aquifer of the Caen and Atlantic coast regions of northern France the fresh water end member is of Holocene age (7500–4500 a BP). This is overlain by a slightly saline water which represents recharge of marine or estuarine water during the Flandrian (Holocene) transgression; some of these areas are now inland due to the deposition of recent sediments. Similar explanations are given for saline water overlying fresh water (of late Pleistocene age) in northern Kent (UK) as well as in Doñana in southern Spain. In this area it is shown that the flow path of groundwater has taken some 6000 years to reach the discharge area which supplies the Doñana wetland area.

In the south coast aquifers of the UK, waters of late Pleistocene and Holocene age are found to depths of between –250 and –300 m in the Chalk. The use of borehole hydrogeophysical logging has helped to confirm the complex stratification that may exist at present day coastlines. Freshwater and saline water (of modern or ancient origins) may be found side by side. This may be related to former drainage patterns with fresh water emplaced along lines of river valleys with older, possibly more saline water preserved in interfluve areas. However structural controls may also be important (in the UK south coast area the Alpine east-west structures locally inhibit coastward flow) and saline water of connate origin may locally be preserved. In the underlying confined Lower Greensand aquifer however fresh water of mid-Holocene age (6500 a BP) is found to –450 m depth near the coastline which is explained as relatively rapid recharge of water moving offshore during the late Pleistocene and early Holocene, which was then slowed down or stopped by the rising sea level.

Indirect evidence is found from the present study that fresh or brackish water, by implication that which was recharged during the late Pleistocene, is found in aquifers currently offshore. Freshwater has been proved historically in Tertiary and Quaternary sediments beneath the Solent (southern England) and has been found in leached drill-core sediments beneath the North Sea to the west of Denmark. Reinterpretation of geophysical logs from the Chalk south of the English coast in the Channel implies that brackish water still exists at depth offshore. From several studies (Portugal, UK, Denmark for example there are strong implications that freshwater may be preserved in confined beds offshore. This would be consistent with results from the drilling off the eastern seaboard of the USA where fresh/brackish waters were proven to depths of 300 m to a distance of 100 m from the modern coasts. The results of modelling show that such features may take tens of thousands of years to erase.

In summary it seems that local geology as well as location/elevation of past recharge areas played, and still play, an important role in the flushing of groundwater, including saline waters derived from earlier periods of recharge. The sea level lowering and subsequent Holocene rise have clearly played an important additional role. There is however no evidence that the impact of ice cover had a major impact on reorganization of groundwater flow.

19.3 Quality of palaeowaters

There is a marked contrast between northern and southern Europe in the total mineralization of palaeowaters, reflecting the different rainfall and recharge conditions as well as the influence of marine aerosols. However the main attributes of palaeowaters are their high bacterial purity, total mineralization less than that of modern waters and being demonstrably free of man-made chemicals. As a result of long residence times, some palaeowaters may be enriched in some beneficial trace elements whilst others especially in reducing environments may have high iron or other species requiring treatment.

In Estonia and in the UK freshwaters found at depths up to 300 m in aquifers of Mesozoic to Palaeozoic, are of lower salinity than the present day recharge; modern waters contain additional solutes resulting from human impacts. The low Cl in the East Midlands aquifer is almost entirely the result of atmospheric inputs and the lack of increasing salinity with depth is strong evidence for a lack of cross-formational flow from adjacent formations containing more mineralized waters. In Spanish coastal areas and especially in Gran Canaria the palaeowaters are typically of high salinity as a result of lower recharge and the impact of marine aerosols. In other areas, especially aquifers in Tertiary and Quaternary sediments (notably in Belgium), the quality reflects the freshening of saline connate or later saline water. As well as any residual salinity, these waters show classical cation exchange sequences related to the expulsion of saline water. These effects are well demonstrated in the present study using hydrogeochemical models.

19.4 The palaeo-modern interface

The development of aquifers in Europe during the past 50–100 years by abstraction from boreholes has generally disturbed flow systems that have evolved over varying geological timescales and especially those derived from the late Pleistocene and Holocene. Inevitably boreholes penetrate time and quality-stratified aquifers resulting in mixed waters which are produced on pumping. In the present programme the extent of this stratification has been demonstrated by hydrogeophysical logging and depth sampling. The use of interstitial water profiles has demonstrated in more detail profiles in water quality.

A specific objective has been to be able to recognize the extent to which waters from the modern (industrial) era have penetrated into the aquifers, often replacing the natural palaeogroundwaters. A range of specific indicators including ^{3}H, ^{3}H/^{3}He, ^{85}Kr and CFCs have been used to detect this water influx but the human impacts may be more easily recognized as a pollution front from general chemical changes in the major ions, TOC, nitrate and trace elements such as B which are largely of anthropogenic origin. In many instances the presence of confining beds affords protection of the palaeowater and later pristine waters.

19.5 Implications for development

In the coastal regions where development pressures are already severe, many problems come together including issues relating to quantity and quality of water, seasonal demand, pollution risks and ecosystem damage. The water balance in many coastal areas may not be fully understood and wells are drilled or deepened without the awareness that palaeowaters belonging to a former recharge regime are being intercepted. In many areas there is induced replenishment as modern (often polluted) waters are drawn in. However in some aquifers the rates of withdrawal exceed the natural recharge and in effect a part of the resource is being mined.

In these areas there is a need for careful drilling to establish the age and quality layering as well as proper well completion. Proper monitoring networks and strategies need to be set up to follow the position of interfaces in both the vertical and lateral planes. Correct management is needed often for seasonal demands – this may be beneficial, allowing winter recovery of water levels. The palaeowater however is a high quality resource and should be treated as a strategic reserve. It should receive priority for potable use and not be wasted for agricultural or industrial purposes which do not require waters of such high purity. Conservation targets are needed to allow for sustainability including ecosystem preservation. Changes may be needed in the administrative and legal framework to safeguard the use of the palaeowater.

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Appendix: Project publications and presentations

The detailed scientific results of this project, after a full peer-review process will be published shortly as a Special Publication of the Geological Society of London.

In addition, the publications and presentations listed below, which have been made (or are to be made shortly) by PALAEAUX partners, have arisen from work funded wholly or in part by the PALAEAUX project.

Appelo, C.A.J. 1997. 'Multicomponent ion-exchange and chromatography in natural systems', pp 193-227. In Lichtner, P.C.; Steefel, C.I.; Oelkers, E.H. ed.), 'Reactive Transport in Porous Media'. Reviews in Mineralogy, Mineralogical Society of America, vol. 34.

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Barbecot, F., Marlin, C., Gibert, E. and Dever, L. 1998. Identification d'un biseau salin dans l'aquifere cotier du Bajocien-Bathonien de la region de Caen (France). CRAS (Compte-Rendus de l'Academie des Sciences de Paris). In press

Barbecot, F., Marlin, C., Gibert, E. and Dever, L. 1998. Halogen geochemistry of a middle Jurassic calcareous aquifer in northern France. Ninth International Symposium on Water-Rock Interaction.

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Viking age rain is excellent drinking water. Jydske Vestkysten, 6.1.1998, p.1.

The hunt for clean water from the ice age. Jydske Vestkysten, 6.1.1998, section 1, p.3.

TV-syd (regional TV station), approx. 5 minutes on the new well on Rømø and the PALAEAUX project in the 22.20 news, 9.2.1998.