Geochemical properties of aquifers and other geological formations in the UK.

Phase 1: Assessment of available data

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Technical Report NC/01/64

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BRITISH GEOLOGICAL SURVEY
Commissioned Report CR/02/224N

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This document is a report describing the water in the aquifer and how it was modelled.

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SUMMARY

This report presents an assessment of the possibility of producing a comprehensive reference manual of data for the intrinsic geochemical properties of British aquifers and aquitards. The data which would be included would be for the geochemical parameters of greatest significance for contaminant transport and risk assessment modelling applied to groundwater protection and pollution issues. Current landfill and contaminated land risk assessment models use estimates of cation exchange capacity (CEC) and the fraction of organic carbon (f_{OC}) to describe the chemical attenuation properties of the geological formations. At present, therefore, these two parameters are the most widely used and they form the heart of the proposed Geochemical Properties Manual (GPM). More sophisticated and chemically complex modelling approaches take greater account of the mineralogical characteristics of the formations and therefore carbonate content, clay content, free mineral oxide content, pyrite content and specific surface area are also considered. The amount of bioavailable iron and manganese in a material is increasingly being considered as a controlling influence on the biologically-mediated degradation of pollutants, for example during monitored natural attenuation (MNA) so measurements of this too are included.

Consultation with contacts in the environmental regulation, waste management and environmental consultancy sectors showed widespread agreement that a compiled GPM would be of benefit to professionals working in these areas. At present there are no authoritative or extensive compilations of such data, and most studies or investigations have to use either estimates with poor uncertainty associated, or expensive direct site-specific measurements. There is no easy way of reliably selecting data which can be used for rapid screening or emergency response assessments.

Review of the extent of existing available data showed that the two abundant and easily accessible sources of relevant data are the BGS corporate data holdings and the collection of Regulation 15 landfill and other risk assessments submitted to the various regions of the Environment Agency. The BGS holdings have been accumulated for a variety of purposes on a range of projects and have not yet been integrated into a single geochemical properties resource. The EA holdings are distributed between the regions and have not been collated. Other data are available in University theses and in consultancy or industry site reports, but again these are distributed and must be individually retrieved. The entire body of data if collated and indexed would provide a foundation for the preparation of a GPM, but the geographical and spatial data coverage would be far from complete.

New experimental determinations of primary data for geochemical parameters are desirable to address the most important gaps in the existing data. After review of published methods for determination of the parameters of interest, preferred standard methods have been recommended for most parameters. Further research is needed to establish standard methods for others. Material from the extensive holdings in the BGS core store could be used to provide suitable sample material for many locations without the need for new and expensive field sampling programmes. Statistical and modelling approaches to estimating data for geochemical parameters in the absence of direct measurements are also discussed. Geostatistics, multiple-regression analysis, and process-based mechanistic models, along with the use of proxy experimental measurements such as near-infra-red spectroscopy, are all considered as possible methods of improving data coverage. None is yet sufficiently established to be used without further investigation and validation.

Recommendations are given for a second phase of the project, with the objectives of establishing the core of a working GPM and beginning a programme of new experimental determinations. Even a substantial experimental programme will not provide comprehensive data coverage within realistic budgetary and time limits, so the programme must be focussed. Early work should concentrate on providing reliable data and useful coverage for CEC and f_{OC} used in the existing models. Finally some areas are suggested for further research work which are beyond the immediate scope of the GPM project, but which would be of significant benefit in the medium to longer term.

1. INTRODUCTION

1.1 Need for and potential use of a Geochemical Properties Manual

Increasing social, economic and legislative requirements for the protection of the quality of groundwater resources have led to a growing need for, and use of, contaminant transport modelling and risk assessment. The trend is likely to continue for the foreseeable future given the current approaches to management of landfill regulation, contaminated-land and monitored natural attenuation (MNA) to name a but a few examples.

It is widely accepted that contaminant transport cannot be described reliably purely in terms of a physical flow model, and so the chemical interaction of the contaminants with the geological formations through which it passes must also be considered. Such geochemical interactions may include, among others, competitive adsorption processes, cation-exchange, mineral dissolution or precipitation reactions and microbiologically catalysed reactions. Whatever modelling approach is used to describe these processes some information about the nature of the surfaces and the intrinsic geochemical properties of the formations concerned is inevitably required.

Direct measurement of the geochemical properties can be difficult, expensive or time-consuming and sometimes all three. Inevitably therefore, comprehensive geochemical characterisation of an individual site is impractical during most modelling or risk assessment studies, although site-specific measurement of a few key properties may be achievable (or necessary). Most often some or all of the geochemical properties must be estimated by analogy or extrapolation from knowledge of similar measurements elsewhere in the same or related formations. Currently much of this existing knowledge and primary data concerning geochemical properties of aquifers, aquitards, etc is dispersed either in the scientific literature, or in site investigation reports held by academic, consultancy and industrial concerns. Many of these reports can be difficult to trace or access easily, and there is no authoritative reference source providing compiled or tabulated data. Consequently estimates for geochemical parameters which are entered into the modelling and risk assessment packages may have poor accuracy and confidence limits, which translate in turn into poor confidence in the output predictions of risk.

The British Geological Survey and the Environment Agency are therefore seeking to collate a set of geochemical data for geological formations across England and Wales. Long-term, national strategic programmes of systematic data collection, analysis, interpretation and publication are the core of the BGS mission. The two organisations have previously collaborated to produce two volumes of data for the physical properties of aquifers (Allen et al., 1997; Jones et al., 2000), known as the Aquifer Properties Manuals and containing an extensive compilation of primary data collected from boreholes and pump-tests. The manuals have become established as valuable primary reference tools both within the Environment Agency and in the wider groundwater community. It is hoped now to provide a similar reference manual for geochemical properties.

It is anticipated that the Geochemical Properties Manual (GPM) will be of use to the Agency, other regulatory authorities (e.g. local authorities), landowners, industry and the environmental consultancy sector. The data sought are for some of the parameters which describe the key processes controlling contaminant migration (or attenuation) in the subsurface, and are required for quantitative assessment of the risks to groundwater from potentially polluting activities using widely available tools (e.g. ConSim, LandSim) and in determining appropriate remedial objectives for land already contaminated.

The Agency’s use of the manual and data is likely to lie in three main areas:

- during emergency response situations (e.g. following a pollution incident or during disease epidemic control incidents, such as foot and mouth) where decisions need to be made extremely rapidly and there is no opportunity for any site investigation;

- to develop catchment-scale assessment methods (e.g. pollutant specific vulnerability indices) that will be required as part of the implementation of the Water Framework Directive (i.e. during characterisation of groundwater bodies, and in developing an appropriate ‘programme of measures’ where a groundwater body is of ‘poor chemical status’);

- as a reference data set when reviewing submitted assessments for contaminated land management, or pollution prevention.

1.2 Vision of completed manual

It is intended that a completed Geochemical Properties Manual should provide a systematic compilation of existing primary data for the intrinsic geochemical properties of aquifers and related geological formations. These will include not only the main water-bearing aquifers, but also geological clay formations and other aquitards or aquicludes. Soils or engineering materials will not be included. The restriction to intrinsic properties is significant. Many of the models use data which are expressed in a contaminant-specific form (e.g. as partition coefficients, K_d) and there are several compilations of such data. However while contaminant specific parameters can often be derived from a knowledge of the contaminant and the intrinsic properties of the aquifer, the opposite is not necessarily true. Intrinsic properties therefore provide a more durable, model-independent description than the contaminant-specific data. The parameters to be considered are discussed fully in Section 3.

Full geographical coverage of the UK will be sought so that the completed manual may serve in the future as a reference document for all areas. The majority of data are likely to come from England because of the higher dependence on groundwater, but data and formations in Wales and Scotland will also be included where relevant information exists. However, attention may be focussed and prioritised on those areas of the country which have a greater incidence of relevant groundwater risk assessments. A variety of methods will be used to identify such areas, possibly including consideration of authorised discharges, landfills, FMD burial sites, sewage sludge application, sheep-dip disposal and waste pesticide disposal.

The completed manual will have two components; a high-quality printed handbook containing explanation and interpretation, and a digital compilation of the data. The digital database should include a geographically referenced GIS-type user interface to facilitate retrieval of the data. The entire manual would be published as a joint BGS/EA publication, priced to try to ensure wide distribution and uptake.

1.3 Difficulties in practical realisation of manual

There are two fundamental difficulties which have to be addressed during the consideration of a Geochemical Properties Manual: the likely paucity of original primary data and the intrinsic spatial heterogeneity of the formations.

Even a brief superficial assessment reveals that there are fewer data available for geochemical properties than was the case for the physical properties, where pump-test records provided a considerable amount of information which could be obtained from the EA regions. The lack of data is partly attributable to the historically lower degree of attention paid to groundwater quality issues, as opposed to resource issues, and to the increased complexity and difficulty of geochemical modelling compared with physical pump-test analysis. The situation is changing, with far more measurements now being made, notably as part of the requirement for groundwater risk assessments at landfill sites under Regulation 15 of the Waste Management Licensing Regulations, 1994. The availability of data has been assessed in some detail as part of this Phase of the project, but even without precise data it is possible to say that the density of primary data will not be sufficient to support geographical and geological coverage. Related overseas data may provide some additional insight but it is likely that significant new experimental work will be required.

Even where data are available, the potential variability of geochemical properties, on a relatively small scale (less than metre scale) must be recognised and will impact on the reliability of interpolation and extrapolation of parameter values. Many aquifers are known to exhibit high degrees of heterogeneity. An indication of the variability which can be expected must also therefore be included in the manual New experimental measurements are likely to be needed to address this too.

1.4 Aims and objectives of Phase 1

Development and production of a comprehensive Geochemical Properties Manual is a significant undertaking, which will require a certain minimum level of investment, for example in database and application development, regardless of how many data are available. It is clearly prudent to assess the feasibility of developing a viable manual before committing more substantial resources to the project. Phase 1 of the project was therefore conceived as a Scoping Study, with the aim of assessing more thoroughly the current state of knowledge for geochemical properties data and establishing in detail the scope of work required. Phase 1 thus had the following specific objectives:

(i) Identify the extent, availability, location and geographical coverage of pre-existing data for the parameters of interest;

(ii) Review published and standard test methods for measurement of the relevant parameters, and thus identify the preferred methods to be used for acquisition of new data;

(iii) Consult on, and develop an outline plan for, the nature and format of the full Geochemical Properties Manual.

The conclusions of Phase 1 can then be used to define the nature of the work programme to be undertaken in Phase 2 and beyond. Provisionally, it was anticipated that the full project should be of 3 years duration (2002-2005), to include systematic extraction, collation and evaluation of the existing data from the sources identified, some new laboratory measurements of key missing data and the preparation of the geochemical properties manual. Exactly how much effort should be directed towards each aspect will be one of the important conclusions of this Phase.

2. THEORETICAL BACKGROUND

2.1 Introduction

There is no point in collecting aquifer chemical properties data if it is not going to be used. One of the main benefits of an aquifer chemical property database for the UK would be that it could be used in contaminant transport models in the place of site-specific measurements (which even for well-studied sites are unlikely to be very comprehensive). If this is to be the case, as we believe it should be during initial assessments, then it is important from the outset to have a vision of the link between measurements and modelling. Ideally the parameters should be as intrinsic/generic as possible and not related to a single model since the models used will change with time and application.

While ‘simple’ models such as LANDSIM are by their nature very basic in terms of their capabilities (in a chemical sense), the ‘real world’ is very complex and so a number of simplifications and assumptions have to be made in order to apply such simple models to the real world.

Adsorption and ion exchange reactions are one of the principal mechanisms by which the movement of chemicals is retarded, or slowed down, in the environment. Precipitation, degradation, dispersion and volatilisation are others. Collectively these processes are sometimes called ‘natural attenuation’. Models which describe the natural attenuation of chemicals in the environment are called reactive transport or contaminant transport models. Implicit in these models is some definition of the amount of adsorption, ion exchange, precipitation or degradation taking place.

The simplest and perhaps most widely used way of describing adsorption is through the ‘K_d concept’. This is one of the options in the LANDSIM contaminant transport model widely used and promoted for the rapid assessment of the possible impact of landfills on groundwater (Environment Agency, 2001). The use of cation exchange capacity (CEC) is another option for describing the retardation in LANDSIM. However, even relatively straightforward concepts such as that of K_d and cation exchange used by LANDSIM and other contaminant transport codes are the source of some confusion and misunderstanding. It is probably easier to understand these concepts if their underlying basis is appreciated. Mineral precipitation is only included in contaminant transport models that include quite detailed geochemical concepts such as that of solubility products (and hence implicitly also activity coefficients, since solubility depends on the ‘ionic strength’ or salt content of natural waters). Degradation models can either be customised models concentrating on organic degradation (e.g. Bioplume III) or general purpose geochemical models such as PHREEQC-2 or the Geochemist’s Workbench which can be programmed to deal with a wide variety of degradation and other reactions.

Here we explain some of the underlying concepts of adsorption and ion exchange including the relationship between the K_d and CEC approaches, their limitations and some of the implicit assumptions made when using them. This is important in view of the excellent and widely-used reactive transport software now available and their ease of use. It is all too easy for the implicit assumptions or ‘silent’ variables in these models to be forgotten or ignored and the model to become a ‘black box’, with the assessor relying on the results obtained without understanding how they have been obtained.

2.2 The partition coefficient or K_d

The solid/solution *partition coefficient* or K_d is a measure of the partitioning of a substance between solid and solution phases

$$K_d = q/c \tag{1}$$

where q is the concentration in the solid phase and c is the concentration in solution. Units vary but q is usually in units of mg/kg solid or mol/kg solid and c is in units of mg/L or mol/L. K_d therefore has units of L/kg (numerically equivalent to mL/g). The K_d concept is sound: there is a finite K_d for each reactive solute. It is how it is applied that causes most concern because it is frequently assumed to be a constant value when in fact it is not. K_d can vary with changes in the concentration of the solute, with competition from other adsorbed solutes and with the nature of the rock/matrix. It can also vary through more subtle effects such as changes in ionic strength.

The concentration q does not refer to the total concentration of substance in the solid phase but just that which is in rapid equilibrium with the solution. This is usually located on the particle surfaces and is often called the adsorbed or exchangeable phase. Substances embedded deep within an insoluble solid phase are essentially isolated from the solution and therefore 'do not count'. Implicit in the definition of K_d is some sort of reaction of the substance between the solid and solution phases. The simplest suitable reaction can be written as

$$S + \quad M = SM \tag{2}$$

with

$$K = (SM)/(S)(M) \tag{3}$$

where S stands for a surface site, M is the adsorbed chemical and K is the corresponding equilibrium constant. Parentheses refer to activities. Already implicit in this formulation is that one surface 'site' reacts with one molecule of M (however we define these things). Using this formulation and assuming activity coefficients of one, c_s=[S] (concentration of 'free' sites) and c=[M] where [ ] refer to concentrations on a 'per litre of solution' basis.

K_d is important in environmental science because it is a direct measure of the scavenging ability of a solid phase for a substance; conversely, K_d is also a measure of the tendency for a solid phase to release or desorb a substance from an already contaminated solid surface. These concepts are important in terms of contaminant attenuation and cleanup, respectively. The concepts underly the behaviour of many chemicals in the natural environment but are also the basis for many important industrial processes including some of those involved in water treatment, e.g. phosphate and arsenic removal. Few chemicals do not interact with soils and aquifers to some extent, although the exceptions, such as Cl, NO_3 and some solvents, are very important exceptions (it is their lack of interactions which makes them especially problematic in groundwater). K_d therefore partially controls (or reflects) the concentration of dissolved substances in groundwater.

K_d is also directly related to the rate at which a substance can move through a porous medium such as a soil or aquifer. If the substance is adsorbed to a solid particle and if this is immobile, the adsorbed substance (q) will not (normally) move, only the dissolved part (c) will. Hence high K_d values mean slow movement.

The total amount of substance is given by summing the sorbed and dissolved parts

$$c_T = q\,(\rho/\varepsilon) + c \tag{4}$$

where c_T is the total concentration (mol/L solution) and ρ is the bulk density of the aquifer material and ε is the water-filled porosity. The factor ρ/ε converts the amount of material in the solid phase to units of mol/L solution.

2.3 Activity and concentration scales

While mass balances ('the book-keeping') necessarily refer to concentrations of chemicals in solution, the chemical behaviour of these chemicals as reflected in the 'laws of mass action' relate to their activities or ‘effective concentration’. These two are related through an activity coefficient which is a kind of ‘fudge factor’

$$a_i = f_i c_i \tag{5}$$

where a_i is the activity of species i with concentration c_i and f_i is its activity coefficient. Fortunately there are good models for calculating these activity coefficients for dissolved, charged substances, e.g. the Debye-Hückel and Davies models.

2.4 Adsorption isotherms

An *adsorption isotherm* is the relationship between the amount of a substance adsorbed and its concentration in solution (or in the gas phase) measured at a constant temperature, i.e. normally plotted as q (y-axis) against c (x-axis). *Multicomponent* adsorption refers to the simultaneous adsorption of several chemicals. This is sometimes called *competitive adsorption.* In the case of multicomponent adsorption, the amount of a substance adsorbed not only depends on its own concentration but also on the concentrations of the other adsorbing substances. This situation is common in environmental systems.

2.4.1 The Langmuir isotherm

Most adsorption isotherms are based on a *site* model. Consider a lattice of adsorption sites (Figure 2.1) and monocomponent adsorption. Molecules (or charged molecules = ions) are in constant motion in solution and randomly hit the surface; the more molecules in solution the greater the probability that one will hit an empty surface site. There is a certain probability that when a molecule hits an empty surface site it will stick. This probability depends on the ‘stickiness’ of the molecule for the surface, the concentration of molecules in solution and the fraction of empty sites

$$\text{Rate at which molecules ‘stick’ to an empty site} = k_{\text{on}}\, c\, (1 - \theta)$$

where k_{on} is a rate constant reflecting the ‘stickiness’ of the surface for the solute in question and θ is the fraction of *filled* sites. Note that when most sites are filled, i.e. θ approaches 1, there is little likelihood of the molecule sticking no matter what its ‘stickiness’.

There is also a probability that adsorbed molecules will desorb from the surface. This is simply proportional to the fraction of filled sites

$$\text{Rate at which molecule desorbs from a filled site} = k_{\text{off}}\, \theta$$

where k_{off} reflects the rate at which sorbed molecules are released once they have become attached. At equilibrium, the number of molecules sticking will equal the number of molecules leaving. Therefore

$$k_{\text{on}}\, c\, (1 - \theta) = k_{\text{off}}\, \theta \tag{6}$$

or

$$\theta / (1 - \theta) = K_{\text{L}} c \tag{7}$$

This is known as the Langmuir isotherm and K_{L} is the Langmuir adsorption constant, sometimes called the affinity constant. θ is dimensionless but it is often useful to express it with dimensions

$$q = K_{\text{L}}\, c\, M \,/\, (1 + K_{\text{L}}\, c) \tag{8}$$

where c is the amount of adsorption in say mg/kg solid or mol/kg solid and M is the total number adsorption sites or adsorption maximum in the same units.

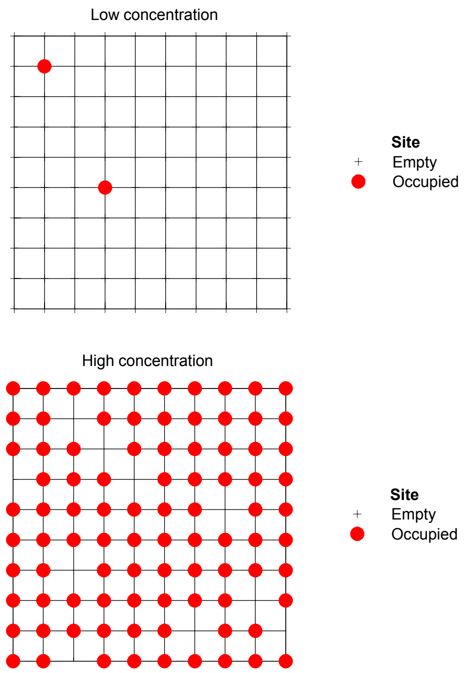

Figure 2.1. **A hypothetical view of a lattice of adsorption sites on a surface. The Langmuir adsorption isotherm can be simply derived by considering the probability that a solute molecule randomly landing on the surface will land on an empty site: almost certain at low concentrations and low surface coverages (top) and very unlikely at high concentrations and high surface coverages (bottom).**

This isotherm can also be simply derived from Eq. (3) by noting that the total number of sites is given by SM + S.

The Langmuir isotherm has a characteristic shape – it is linear at low concentrations, then becomes noticeably curved and then asymptotically approaches the adsorption maximum, *M*, at high concentrations (Figure 2.2). The isotherm is a nonlinear isotherm since a plot of *q* vs *c* is not linear over its entire range.

Many other equations are used for adsorption isotherms but the Langmuir isotherm is fundamental to them all. It has two parameters, K_L and *M*. Note that combining equations (1) and (8)

$$K_d = K_L M / (1+K_L c) \tag{9}$$

In this case, K_d is not a constant but decreases with increasing concentration – it asymptotically approaches zero at high concentrations. If a surface is nearly saturated then little further adsorption can or will take place and the surface behaves like a non-adsorbing surface. This equation differs from that given on p85 of the EA guidance publication on Natural Attenuation (Carey et al., 2000).

In a multicomponent system, the Langmuir isotherm may be extended in a straightforward way which for component *i* is

$$q_i = K_{L,i}\, c_i\, M / (1 + \Sigma K_{L,j}\, c_j) \tag{10}$$

where each component has a distinct K_L and the summation is over all *j* adsorbed species. Multicomponent adsorption is also often called *competitive adsorption* since the various components all compete with one another for adsorption sites.

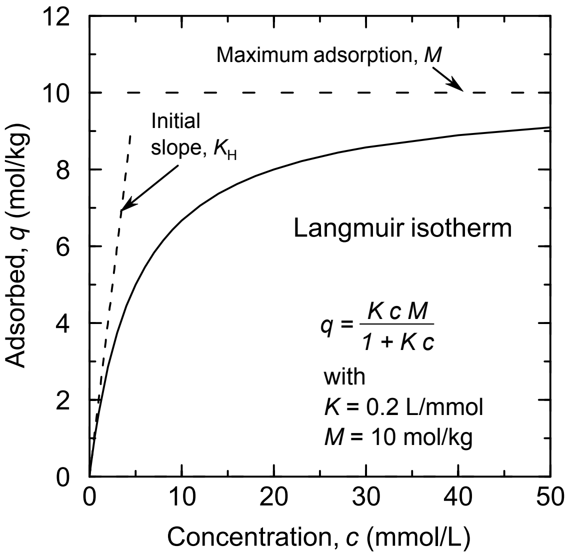

Figure 2.2. **A typical plot of an adsorption isotherm showing the amount adsorbed plotted against its solution concentration. The line shows the form of the Langmuir isotherm with the given parameters. The Langmuir *K* parameter shown here is written as K_L in the main text.**

2.4.2 The linear isotherm

The linear isotherm is simply

$$q = K_H c \tag{11}$$

where K_H is the linear (Henry's) adsorption constant. Clearly this is a special case of the Langmuir isotherm for low concentrations where

$$K_H = K_L M \tag{12}$$

i.e. the slope of the isotherm is a measure of both the Langmuir adsorption constant *and* the number of sites. Using Figure 2.3, the linear isotherm represents the case where practically every molecule hitting the surface hits an empty site.

It is only possible to separate these two from the curvature in the isotherm. If there is no significant curvature, it is not possible to separate these parameters. The linear isotherm is a special case – it is unreasonable to expect the linear isotherm to work at high concentrations because that would mean that there are an infinite number of adsorption sites and that is impossible. It is also reasonable to expect the linear isotherm to be true at low concentrations and this is found to be true in practice in a very wide range of conditions even when there are many substances adsorbed and when there is some heterogeneity. The only case where it manifestly does not apply is for the binding of cations to pure natural organic matter ('humics').

Note that for a linear isotherm

$$K_d = K_H \tag{13}$$

and so in this case K_d is a constant independent of concentration.

2.4.3 The multisite Langmuir isotherm

The Langmuir isotherm assumes that all surface sites have the same affinity for the chemical of interest. This is rarely the case in practice – most soils and aquifer solids contain a variety of minerals, each with their own characteristic adsorption affinities. Even individual minerals are made up of various crystal planes each potentially with its own affinity and some substances, like humic materials, are so heterogeneous that there may be literally thousands of different types of sites.

We can calculate the overall amount of adsorption by summing the contributions of each the different types of sites. Using the Langmuir model, this means we need to know the affinity (K_j) of each type of site present and the number of them (M_j).

$$q_i = \Sigma[K_{Li}\, c\, M_j / (1 + K_{Lj}\, c)] \tag{14}$$

where j extends over all site types present. Eqn (14) is known as the multisite Langmuir isotherm for a single component. You need to know the number (M_j) and binding affinity (K_{Lj}) of each type of sites. Normally the maximum number of sites for which these parameters can be resolved from an experimental isotherm is 3 or less.

2.4.4 The Freundlich isotherm

In practice because of the experimental errors inherent in all experimental data, it becomes difficult to estimate reliably more than about three sets of K_{Lj}'s and M_j's parameters by fitting to experimental isotherm data. While there are ways that attempt to do this in a sensible way, a slightly different approach is to assume a continuous distribution of site affinities of some particular shape. One such distribution is called the Sips distribution which looks somewhat like a normal distribution. Integrating this over the full range of affinities gives the so-called Langmuir-Freundlich isotherm:

$$q = (K_L\, c)^n\, M / [1 + (K_L\, c)^n] \tag{15}$$

where n is known as the heterogeneity factor and normally $0 < n \leq 1$. The smaller the value of n, the broader the Sips distribution, i.e. the more heterogeneous it is. This isotherm is like the Langmuir isotherm in that it approaches a maximum adsorption, M, which is useful since this is a reasonable thing to expect. The Langmuir-Freundlich isotherm has three parameters: K, M and n. Note that when $n=1$, the isotherm reverts to the Langmuir isotherm.

The limiting case of the Langmuir-Freundlich isotherm at low c can be derived from Eqn (15). It is

$$q = (K\, c)^n\, M = K_F c^n \tag{16}$$

Eqn (16) is known as the Freundlich isotherm and is probably the most widely used and most successful isotherm for simple applications to real world situations. It implicitly takes into account the heterogeneity or variability found in real-world situations. A plot of log s vs log c (called a 'Freundlich' plot) is linear with a slope n and an intercept at log $c=0$ equal to log K_F (Figure2.3). The smaller the slope of the Freundlich plot, the more the apparent heterogeneity of the material. The Freundlich isotherm has been widely used for trace metal adsorption to soils and sediments. Typically n is in the range 0.5–0.8. It has also been widely used for describing the sorption of organics including pesticides to soils. For $n <> 1$, the Freundlich isotherm is nonlinear. Note that when $n=1$, it reverts to the Linear isotherm.

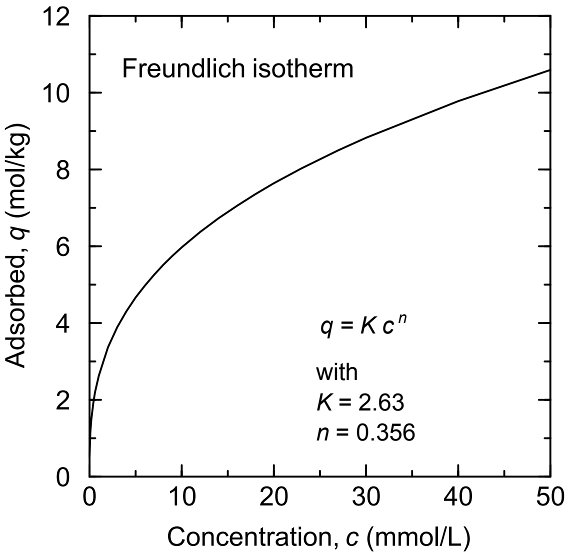

Figure 2.3. **A typical plot of an adsorption isotherm showing the amount adsorbed plotted against its solution concentration. The line shows the form of the Freundlich isotherm with the given parameters. The Freundlich *K* parameter shown here is written as K_F in the main text.**

Just to confuse the situation, the Freundlich isotherm is sometimes written as

$$q = K_F c^{1/N} \tag{17}$$

where $N=1/n$ with correspondingly transformed limits. This is an archaic form and best not used.

Inspection of Eqn (16) shows that $K_F = K_L{}^n M$, i.e. K_F is a complex factor that implicitly includes both an affinity factor and a site density factor. It also has awkward non-integral dimensions.

The K_d for the Freundlich isotherm is given by

$$K_d = K_F c^{n-1} \tag{18}$$

which illustrates that like the Langmuir isotherm, the K_d decreases with increasing concentration. Again, this equation differs from that given on p85 of the EA guidance publication on Natural Attenuation (Carey et al., 2000).

Although the Freundlich isotherm does not have as good a ‘theoretical pedigree’ as the Langmuir isotherm, it has actually been shown to work better than the Langmuir isotherm in many ‘real world’ situations. It is probably the best isotherm for most organics transport modelling, e.g. pesticides. Remember when $n=1$, it reverts to a linear isotherm and so also represents the constant K_d situation. It also often works well for trace metal binding by soils and aquifer materials albeit at constant pH.

2.4.5 Multicomponent Freundlich isotherm

It was widely appreciated that trace metal sorption is often strongly pH dependent and so attempts have been made to extend the traditional Freundlich isotherm to include this. This involves extending the Freundlich isotherm to two or even three components. These extensions are known as the two-species Freundlich isotherms and three-species Freundlich isotherms, respectively.

$$\text{Two species Freundlich: } q_i = K_{F2}\, c_i^{ni}\, c_j^{nj} \tag{19}$$

$$\text{Three species Freundlich: } q_j = K_{F3}\, c_i^{ni}\, c_j^{nj}\, c_k^{nk} \tag{20}$$

When, as is usually the case, the coefficients n_j and n_k are negative, the components j and k are known as competitors and increasing their concentrations will decrease the amount of component i adsorbed.

It is easy to see how this equation could be extended to 4 or more species but there is a problem. As new components are added, K_{Fi} changes its value and so any tabulation of K_{F} values will depend on how many components are included. This makes it awkward to extend to systems other than those under study. In the above example, $K_{F2} = K_{F3}\, c_k^{\ nk}$. Therefore, K_{F} has no pretensions of being an intrinsic property of the material, i.e. a property of the interaction of a single molecule with the surface.

2.4.6 *Adsorption stoichiometry*

It has been implicit in the isotherms discussed above that one molecule occupies one surface site but sometimes a molecule has to bridge between two or more surface sites. This ratio is known as the *adsorption stoichiometry*. For a 2:1 stoichiometry, we have to calculate the probability that two molecules will hit adjacent sites at the same time. In this case, it is possible to show that the Langmuir model becomes

$$\theta/(1-\theta) = (K_{\mathrm{L}}c)^{½}. \tag{21}$$

2.4.7 *Multi-component binding to a heterogeneous surface*

An isotherm that does attempt to preserve K's as intrinsic adsorption or binding constants is the NICA isotherm (Kinniburgh et al., 1999). This extends the above equations to multi-component binding to a heterogeneous surface either using the continuous distribution model. The following isotherm equation can be derived which for the binding of component i gives

$$\theta_i = \frac{(\widetilde{K}_i c_i)^{n_i}}{\sum_i (\widetilde{K}_i c_i)^{n_i}} \times \frac{(\sum_i (\widetilde{K}_i c_i)^{n_i})^p}{1 + (\sum_i (\widetilde{K}_i c_i)^{n_i})^p} \tag{22}$$

$\widetilde{K}_i$ is the median affinity parameter and n_{i} is the 'non-ideality' parameter for component i and p is the heterogeneity parameter which is a characteristic of the surface.

Note that all of isotherms described above can be viewed as special cases of the NICA isotherm. Comparing with the NICA model enables some of the assumptions in the simpler models to be understood better.

A discrete site model that behaves somewhat like the NICA isotherm can be derived where the number of types of site is relatively small (Tipping, 1998).

2.5 Ion exchange

In the models discussed, the chemicals may be charged or not. Many chemicals, especially organic chemicals such as pesticides, are not charged. Also, no mention was made of any surface charge on the mineral. There are many circumstances where both the adsorbing chemical and the mineral surface are electrically charged and this leads to special types of interaction. These depend to a large extent on the nature of the charge – is it formed deep inside the mineral or a the surface. Below we discuss this in some detail and follow its consequences in terms of the types of equation that can be used to describe the binding.

2.5.1 Permanent charge cation exchangers

The adsorbed molecules were envisaged to bind to so-called empty sites. In practice, they probably displaced some solvent (water) molecules. A more interesting case is ion exchange. A few minerals, most notably certain clay minerals, are not neutrally charged. This contradicts Pauling's rule which states that there should be a local neutralisation of charge within minerals. Clay minerals negate this rule through the isomorphous (=similar-sized) substitution of Al^{3+} for Si^{4+} and Mg^{2+} for Al^{3+} within their structures. Because the substitution is in both cases of cations with a lower positive charge, the clays ends up with a net negative electrical charge. The amount of this negative charge depends on the amount of isomorphous substitution but for clays is up to about 1 eq/kg although typically less than half this. This quantity is called the *cation exchange capacity* or CEC. This type of charge is called *permanent charge* because it does not depend on the solution chemistry but is fixed by pre-existing and unchangeable structural features.

This negative charge is balanced by the adsorption of cations (positively-charged ions) which are attracted to the negative charge which emanates from the clay surface. Indeed, the charge always has to be completely balanced by adsorbed cations – there are no 'empty' sites and the mineral and accompanying solution must always have a net zero charge. When there is more than one type of cation present in solution (as in the real world), all cations present will play some part in neutralizing the net negative charge of clays. The various ions present all compete with each other for exchange 'sites' with the loading of each dependent on its concentration in solution, its charge and its intrinsic affinity for the clay surface (Figure 2.4).

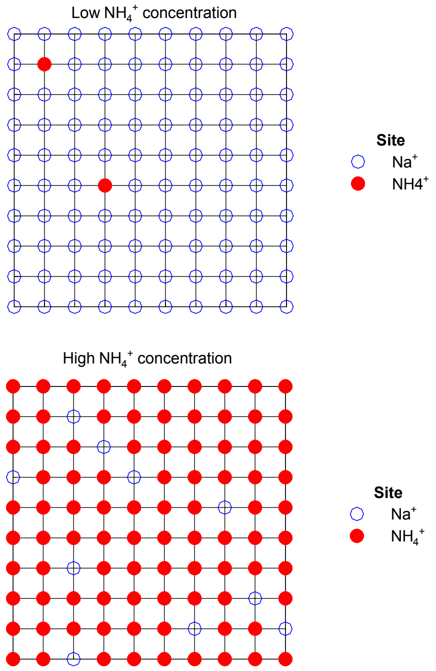

Figure 2.4 A hypothetical view of a lattice of ion exchange sites on a surface. The ion exchange isotherm can be simply derived by considering the probability that a target ion such as NH_4^+ randomly landing on the surface will land on a site occupied by a different type of ion (Na^+): almost certain at low target concentrations and low surface coverages of the target ion (top) and very unlikely at high concentrations and high surface coverages (bottom). Note that there are no 'empty' sites: this figure refers to a permanent charge cation exchanger.

Homovalent exchange

Homovalent exchange refers to the exchange of equally charged ions. In a simple binary system consisting of just Na^+ and NH_4^+, the ion exchange equation is given as

$$Na^+ + NH_4X = NaX + NH_4^+ \tag{23}$$

where X represents the negatively charged clay exchanger (X^-). An equilibrium constant for this reaction can be written as

$$K_{GT} = \{NaX\}(NH_4^+)/\{NH_4X\}(Na^+) \tag{24}$$

where {} represent surface activities and () represent solution activities.

Various models exist, the three most important are the Gaines-Thomas, Vanselow and Gapon models. Probably the most widely used is the Gaines-Thomas model (e.g. as in PHREEQC-2) which assumes that the surface activity of a particular component is given by its *equivalent fraction* in the exchanger phase (the Vanselow model uses the mole fraction which is the same in the case of homovalent exchange but not in the case of heterovalent exchange), e.g. $\{NaX\} = n_{Na}/(n_{Na} + n_{NH4})$ and n_i is the number of moles of *i* bound.

$$\theta_{NH4}/(1-\theta_{NH4}) = \theta_{NH4}/\theta_{Na} = K_{GT}\,(a_{NH4}/a_{Na}) \tag{25}$$

Note that the θ's here are exchangeable fractions. In this case of binary, homovalent exchange, the relative occupancy of the two ions is simply given by the ratios of the two solution activities. As far as an NH_4^+ ion is concerned, if it hits a site occupied by a Na^+ ion, it displaces it. In that sense, the Na^+ sites behave like empty sites.

The amount of NH_4^+ bound, n_{NH4}, is now given by

$$n_{NH4} = K_{GT}\,AR\,CEC\,/(1 + K_{GT}\,AR) \tag{26}$$

where *CEC* is the cation exchange capacity and *AR* is the activity *ratio*, a_{NH4}/a_{Na}. For homovalent exchange, the AR is very close to the concentration ratio because the activity coefficients of similarly charged ions are very similar (D-H theory). Note the similarity between this equation and the Langmuir isotherm, Eqn (8). The only difference is that the activity of one species (Langmuir isotherm) has been replaced by the activity ratio of two species (homovalent, binary ion exchange isotherm)

The K_d for NH_4^+ is then given by

$$K_d = n_{NH4}/c_{NH4} = K_{GT}\,CEC\,\alpha_1 \tag{27}$$

where

$$\alpha_1 = (f_{NH4}/f_{Na})\,(1/c_{Na})\,/(1 + K_{GT}\,AR). \tag{28}$$

Note that the K_d is not constant but depends inversely on the concentration of Na^+, the competitor, as well as the concentration of NH_4 through the AR term. At *very low NH_4 concentrations*, $1 + K_{GT}$ AR approaches 1 and so $K_d \sim K_{GT}$ CEC/c_{Na}, i.e. K_d/c_{Na} is constant and for a constant Na concentration is directly proportional to the CEC and K_{GT}. At higher NH_4 concentrations, which are common in pollution plumes, K_d varies with the concentration of NH_4 and Na in a more complicated way.

Cation exchange isotherms are often plotted in completely normalised form, i.e. the equivalent fraction of an ion in an exchanger versus its equivalent fraction in solution.

Heterovalent exchange

Heterovalent exchange refers to the exchange of unequally charged ions. This situation is more complex than for homovalent exchange. For example, for calcium-ammonium exchange

$$\mathrm{CaX_2 + 2NH_4^+ = Ca^{2+} + 2NH_4X} \tag{29}$$

where as before X represents the negatively charged clay exchanger (X^-). An equilibrium constant for this reaction can be written as

$$K_{\mathrm{GT}} = \{\mathrm{NH4X}\}^2(\mathrm{Ca}^{2+}) \,/\, \{\mathrm{CaX_2}\}(\mathrm{NH_4^+})^2 \tag{30}$$

where according to the Gaines-Thomas convention, e.g. $\{\mathrm{NH4X}\} = n_{\mathrm{NH4}}/(2\mathrm{n}_{\mathrm{Ca}} + \mathrm{n}_{\mathrm{NH4}})$

In this case, the activity ratio, AR, is given by

$$AR = a_{\mathrm{NH4}}{}^2/a_{\mathrm{Ca}} = (f_{\mathrm{NH4}}{}^2/f_{\mathrm{Ca}})\ (c_{\mathrm{NH4}}{}^2/c_{\mathrm{Ca}}) \tag{31}$$

The K_d for NH_4 binding is now given by

$$K_{\mathrm{d}} = K_{\mathrm{GT}}\ CEC\ \alpha_2 \tag{32}$$

where

$$\alpha_2 = [AR\ /2c_{\mathrm{NH4}}]\ [\sqrt{}(1 + 4\ K_{\mathrm{GT}}\ AR) - 1] \tag{33}$$

As for monovalent exchange, at low NH_4 concentrations and a constant Ca concentration, K_{d} again directly depends simply on K_{GT} and CEC whereas at higher NH_4 concentrations, it also depends on a complicated function of the NH_4 and Ca concentrations.

The CEC is an important characteristic of a clay, soil or aquifer. For pure clay minerals, the CEC varies from just a few meq/kg for kaolinite up to 1000 meq/kg for smectites such as montmorillonite. Loamy soils typically have CECs of 100-500 meq/kg.

2.5.2 Variable charge exchangers – surface complexation

Many natural solids, notably oxide minerals and organic matter, do not have a permanent electrical charge due to isomorphous substitution but can acquire a surface electrical charge through the preferential binding of certain ions, called *potential determining ions* (pdi's), at the solid surface. The resultant surface charge varies continuously with the concentration of these pdi's in solution. The most important pdi's are H^+ and OH^- which give the surface a net positive or negative charge, respectively, which varies with solution pH (pH-dependent charge). The CEC of these materials is not a constant but increases with increasing pH and can even be negative. This has important implications for both the laboratory determination of CEC (what pH is it measured at?) and for its application in models (what is the field pH and does it vary with space or time?).

The theory for ion binding to these materials is somewhat different from that of permanent charge cation exchangers and is often called *surface complexation* theory. It is rather similar to the Langmuir isotherm in that it allows for 'free' or unfilled sites but because the surface charge and surface potential vary with the number and type of ions adsorbed, the binding constant, K_{i}, also systematically varies

$$K_{\mathrm{i}} = K_{\mathrm{i,int}} \exp(-z_i\ e\ \psi\ /\ kT) \tag{34}$$

where ψ is the surface electrical potential, $K_{i,int}$ is the intrinsic binding constant for ion *i*, i.e. K_i at zero surface potential or charge. This complicates the calculations because K_i now varies with solution chemistry and so adsorption or binding has to be solved iteratively. A further complication is that ψ varies with distance from the surface and different ions bind at different distances from the surface which gives rise to models with one, two, three or more different sorption planes, each with their characteristic ψ. Well-known surface complexation models are the diffuse double layer model, the Basic Stern model, the Triple Plane model, the Triple layer model and the Constant Capacitance model.

A characteristic of many variable charge materials, including iron, aluminium and manganese oxides common in the environment, is that $K_{i,int}$ can be very large on account of some specific chemical interaction with the surface. This is called *specific adsorption*. Some surfaces can even bind some cations when they have a net positive charge, contrary to what might be expected. Therefore it is wrong to say that because a surface has a positive charge (pH less than the so-called 'point of charge') that it will not adsorb cations such as Cd^{2+}. It might do so. Oxides can also bind anions such as phosphate very strongly especially at low pH.

Variable charge materials normally have a net surface charge as a result of specific adsorption. Since the overall charge of a particle must be zero, this charge is exactly balanced by the binding of an equal number of *counterions* of opposite charge, e.g. Cl^- or HCO_3^- on a positive surface. This is called non-specific adsorption since it merely responds to the net electrical charge (positives attract negatives and *vice versa*) and does not involve any chemical interactions. It can in principle be negative for like-charged ions but this is normally very small. The overall amount of a chemical bound therefore consists of the sum of specifically and non-specifically bound chemical.

An important practical difference between cation exchange and surface complexation is that while ion exchange does show a characteristic selectivity sequence for different ions, often following their sequence in the periodic table, e.g. $Cs^+>K^+>Na^+>Li^+$. the differences are not so great, perhaps an order of magnitude or so. Surface complexation, on the other hand, can give selectivity differences of six orders of magnitude or more and so can be very important for some elements.

2.6 Sorption and transport

If a substance is adsorbed, it cannot move with the mobile water. Therefore it is not surprising that there is a direct relationship between sorption and transport (for a detailed discussion, see Appelo and Postma, 1993). For a chemical obeying a linear isotherm (constant K_d), its velocity of movement, v_i, is directly related to the rate of movement of water, v_{H2O}, and the slope of the isotherm which in this case is given by the K_d

$$v_i = v_{H2O} / R_f \tag{35}$$

and R_f is the retardation factor given by

$$R_f = 1 + (\rho/\varepsilon)\, K_d \tag{36}$$

where ρ/ε is the solid/solution ratio often about 5–10 kg/L for soils and aquifers, i.e. for $K_d = 1$ L/kg, R_f is 6–11 or the chemical in question moves 6 to 11 times slower than water. If a non-dimensional K_d, K_d', is defined by expressing q in terms of mol/L pore water rather than in mol/kg solid then

$$R_f = 1 + K_d' \tag{37}$$

This shows clearly that K_d' is directly related to the additional retardation experienced by the chemical over that experienced by a non-adsorbed solute ($R_f = 1$).

Complications arise when the isotherm is nonlinear. Then the K_d varies with concentration and so does R_f with the retardation being greatest where the isotherm slope is greatest, i.e. the speed of movement of a chemical depends on its concentration. Since the concentration is constantly changing as a result of dilution, adsorption/desorption, degradation etc so is its speed. We should therefore write $K_d(c)$ and $R_f(c)$ to indicate that these parameters vary with the concentration of the chemical itself or with the concentration of others in solution especially competitors.

The shape of the isotherm becomes very important for transport calculations, particularly whether the shape is concave or convex concentration (to the x-axis). With a Langmuir isotherm, (dq/dc) is greatest at low concentrations and so the retardation is greatest there. When a slug of contaminant moves as a plume into an uncontaminated aquifer, the front of the plume will have the lowest concentrations and will move slowly with the high concentrations in the centre of the plume moving fastest. There is therefore a tendency for the high concentrations to overtake the low concentrations. This leads to a very steep or self-sharpening front sometimes called a sharp front or shock wave.

With binary ion exchange, the shape of the normalised isotherm reflects the relative strength of binding of the two ions and can be either concave or convex to the solution concentrations axis depending on whether the incoming ion is preferred to the bound ion (*favourable* exchange) or *vice versa* (*unfavourable* exchange). There is some symmetry here: if Na-Ca exchange is unfavourable, then Na-Ca exchange must be favourable so adsorption fronts are quite different from desorption fronts. The shape of the isotherm usually varies with the concentration of salts present – it becomes more non-linear at low concentrations.

2.6.1 Transport with favourable exchange

Favourable exchange leads to the development of self-sharpening front. The number of pore volumes, V, of component i that must pass through an aquifer before i emerges at with its initial concentration can be related to the number of pore volumes of water, V_0, that has passed through

$$V/V_0 - 1 = (CEC/A_0)\,(\Delta\beta_i/\Delta\alpha_i) \tag{38}$$

where A_0 is the total normality (anion concentration) of the inflowing solution, β is the equivalent fraction of i on the exchange sites and α is the equivalent fraction of i in solution. $[\Delta\beta_i/\Delta\alpha_i]$ is the slope of the normalised isotherm either side of the sharp front, i.e. $(\beta_2 - \beta_1)/(\alpha_2 - \alpha_1)$. $V/V_0 - 1$ is a measure of the number of pore volumes after the arrival of a conservative solute, such as Cl, that component i arrives at a given place. It has been called the *flushing factor*, *Ψ condition* and *throughput parameter.*

CEC/A_0 is a measure of the overall importance of adsorbed and solution ions in general rather than for a specific substance. It is closely related to the total time to exhaust the CEC, $T_{exhaust}$, as used in LANDSIM:

$$T_{exhaust} = CEC_{avail}/LR \tag{39}$$

where CEC_{avail} is the 'available' CEC of the aquifer in the system (meq) and LR is the loading rate in meq/s. In LANDSIM, it is assumed that LR is dominated by a single cation, e.g. NH_4^+, i.e. it does not consider multi-component ion exchange. The 'available' CEC relates to the geometry of the clay liner and the wetting properties, and is the total CEC of the liner, not the CEC of a sample.

The higher the CEC, the longer it will take for i to emerge. Also the lower the total normality (salt content) of the inflowing/recharging groundwater, the slower that solute i will emerge.

2.6.2 Transport with unfavourable exchange

With unfavourable exchange, a weakly bound ion (e.g. NH_4^+) attempts to move through a column already containing a strongly bound ion (e.g. Ca^{2+}). Movement of the NH_4^+ at low concentrations is relatively fast and at high concentrations is relatively low leading to a long forward tail or diffuse front in the effluent. The shape of this curve is independent of concentration. It is possible to derive the exchange isotherm by integration of this curve.

The flushing factor for the elution of an ion undergoing unfavourable exchangeable exchange, i.e. is given by

$$V/V_0 - 1 = (CEC/A_0)\,(\mathrm{d}\beta_\mathrm{i}/\mathrm{d}\alpha_\mathrm{i}) \tag{40}$$

where $\mathrm{d}\beta_\mathrm{i}/\mathrm{d}\alpha_\mathrm{i}$ is the slope of the normalised exchange isotherm at the concentration given by α_i.

2.6.3 Transport with multicomponent ion exchange

The theory of multicomponent ion exchange chromatography is now well understood and is discussed by Appelo and Postma (1993). Analytical solutions for homovalent ion exchange are available but more generally the results must be calculated numerically. Movement of a multicomponent solution, like a polluted groundwater, through a soil or aquifer is characterised by a series of diffuse fronts (unfavourable exchange), sharp fronts (favourable exchange) for each component with plateaus of constant composition in between.

Most major anions in groundwaters are not strongly adsorbed by soils or aquifers and so pass through the aquifer unretarded. These are eluted from a column after one pore volume. Because of the electroneutrality constraint, they must always drag along an equal number of cations. As the input solution changes normality (i.e. the concentration of anions), so the number of cations changes too. Cation exchange equations can be used to derive the proportions of the various cations that are eluted at the normality front.

2.7 Software

There is now an abundance of good software available for calculating sorption and transport in environmental systems. PHREEQC-2 is one of the best and is freely available over the web. It can calculate both chemical speciation including ion exchange and simple surface complexation as well as 1D transport. It can deal with complex chemical situations but only simple transport ones. Other models specialise in the transport part. PHREEQC-2 is being linked with more detailed 3D hydrogeological transport models to provide a comprehensive reactive transport model (e.g. PHAST).

The advantage of these chemical models is that they do the chemistry ‘correctly’, e.g. keep charge and mass balances, calculate competitive interactions, solubilities, activities etc. This provides a degree of robustness. A disadvantage is that they are complex. However, much of this complexity can be hidden from the use with a well-designed user interface and the use of default values so it is not the limitation that might appear. In the medium to long term, the benefits of these more rigorous models are likely to outweigh their disadvantages.

2.8 Conclusions

The K_d or partition coefficient is simply calculated from the ratio of adsorbed to solution concentrations. It is an important parameter that determines the ‘solubility’ of a chemical and its ease of movement in a soil or aquifer.

Under special conditions (a linear isotherm, no competition, low concentrations), K_d is independent of the concentration of other chemicals in solution but more normally K_d varies with the concentration of both the chemical of concern and that of others. This is true of nonlinear isotherms and is particularly common at high concentrations. If competition is involved, then both the concentration of the sorbing chemical and of all the competitors are important.

Charged chemicals (ions) frequently bind to charged surfaces. This surface charge can be derived in two ways – permanent charge due to isomorphous substitution as on many clays and a variable surface charge due to specific adsorption as on many oxides. The former gives rise to cation exchange and the latter to surface complexation. In both these cases, K_d will vary with the concentration of some other ion either as a competitor or as a potential determining ion.

An implication of this is that K_d must not be assumed to be a constant. It almost certainly is not an intrinsic property of the mineral itself but will also depend on the solution chemistry. Therefore whenever laboratory K_d measurements are used in a model, it must be clearly demonstrated that an appropriate K_d is being used. In practice, when a chemical is bound by a cation exchange process, the K_d will *always* vary with the concentration of competitor cation(s) and maybe with the concentration of the ion itself and so K_d is not a very good way of capturing this. Better would be the ion exchange constant(s) for the reactions involved, the CEC and measurement of all the main competitors especially Ca, Mg and Na.

The concept of K_d itself is not a bad one – it is the assumption that it is *constant* that can be misleading and lead to erroneous conclusions. It has been demonstrated in the discussion above how the K_d can be expected to vary in a systematic way depending on the processes involved. It is often therefore better to deal with this variation explicitly by using more sophisticated solid/solution partition models rather than rely on a 'constant' K_d approach. Where a constant K_d is assumed, it is incumbent on the user to establish that the K_d does not vary systematically with the relevant environmental variables.

3. PARAMETERS FOR CONTAMINANT TRANSPORT MODELLING

3.1 Introduction

While much remains uncertain about how to apply contaminant transport models to the ‘real world’, the basic physical and chemical principles underlying contaminant transport are now well understood. The key to all such approaches lies in the ability to predict the partitioning of a chemical between solid (stationary) and solution (mobile) phases. The chemical processes that control this partitioning are also quite well understood although there are plenty of areas where uncertainty remains, e.g. coprecipitates and solid solutions.

However, contaminant transport programs differ in the degree to which they *calculate* this partitioning as opposed to expecting its *specification by the user*. Programs such as MT3D and LANDSIM that expect K_d values or simple isotherms to be specified by the user belong to the latter group since they avoid the problem of how to estimate the K_d or the isotherm to use, especially given that the K_d may depend on the type of processes operating as well as the solution chemistry (Section 2). In essence, forcing the user to enter a K_d is side-stepping one of the main difficulties in applying contaminant transport models – how to anticipate the solid/solution partitioning and its variation spatially.

The alternative is to try to estimate the partitioning from more fundamental properties of the solid and solution phases. This approach is widely adopted for organic compounds through the QSAR-log K_{oc} approach and has also been used to estimate metal ion binding by oxides and natural organic matter (Section 6.3).

3.2 A dominant subset of environmental particles

Although it might seem at first sight that the number of minerals and substances in the natural environment is impossibly large to characterise properly, in practice this is not quite such a gargantuan task as it first appears. Strong chemical reactivity arises either from:

(i) a *moderately high and reversible solubility*, for example carbonates such as calcite, dolomite and siderite; oxides of iron, aluminium, manganese and silica; sulphides of iron, but not rock salt which is so soluble that it rarely precipitates, or rutile and zircon which are too insoluble to dissolve at significant; or

(ii) *very small particles with high surface areas*, e.g. oxides of iron, aluminium and manganese; natural ‘humic’ type colloids; phyllosilicate clays like montmorillonite, vermiculite, biotite or illite and chlorite. The specific surface area of the smallest particles (colloids) is orders of magnitude greater than that of sand-sized minerals and dominates many aspects of the surface chemistry and reactivity of soils and aquifer materials. Often the bulk of soils and aquifers is simply that, rather unreactive bulk material.

The components in the natural environment which most commonly exhibit strong chemical reactivity combine these characteristics and in addition, often are abundant and common.

A strongly varying solubility under various pH, redox and other environmental conditions makes certain minerals especially important, and the classes identified above all fall in this category. Carbonate solubility is strongly dependent on the atmospheric $pCO_2(g)$. The solubility of iron oxides has both a strong pH and redox dependence. All sulphides are very sensitive to redox conditions and iron sulphides are abundant in the natural environment.

Iron oxides and humic substances are also ubiquitous in the natural environment. Aluminium oxides are also very abundant, and although aluminium oxides are not so visually obvious as iron oxides, they are more soluble (and toxic) than iron oxides under both moderately acid and alkaline conditions. All oxides have somewhat similar surface properties irrespective of their basic ‘building block’. The reactivity of clays is largely determined by their cation exchange capacity (CEC) and all phyllosilicate clays behave somewhat similarly irrespective of their precise structure. Therefore the overall CEC is the single most important factor that characterises clays.

Therefore the subset of parameters selected for routine determination, namely:

- CEC
- organic carbon content
- carbonate content
- free iron and aluminium oxide content
- pyrite content
- bioavailable (readily soluble) iron and manganese
- specific surface area

have a particularly strong influence on the environmental fate of a wide range of chemicals.

Having established that a rather small subset of natural minerals and particles have a disproportionate influence, it is instructive to see how geochemical programs deal with them. This is largely governed by the chemical processes operating. We discuss these below with particular reference to how the geochemical speciation and mass transport program, PHREEQC-2, deals with them.

Two major approaches are possible: the individual component approach and the whole soil/aquifer material approach. The individual component approach is closely related to the dominant particle concept. This assumes that the behaviour of the whole system can be calculated from the sum of the behaviour of the individual components (this is the implicit approach in most chemical speciation programs such as PHREEQC-2). For this to be true, the interactions between the behaviour of the individual components must be negligible. This is often true but not always true, e.g. interactions may be important in the organic matter-clay-oxide system. Where the individual components cannot be quantified, then the soil or aquifer has to be treated as a whole. Because of the (unknown) heterogeneity of such systems, valid predictions based on this approach are necessarily likely to be of a much narrower scope. Here we concentrate on the individual component approach.

3.3 PHREEQC-2 implementation

The various processes that control solute concentrations in natural waters can be grouped under the following headings (PHREEQC-2 keywords in parentheses): precipitation and dissolution of a pure mineral (`EQUILIBRIUM_PHASES`) or coprecipitation/co-dissolution (`SOLID_SOLUTIONS`), adsorption (`SURFACE`), ion exchange (`EXCHANGE`), degradation (`KINETICS`). Each is controlled by a different set of equations and requires different input parameters (Table 3.1).

Table 3.1. **The processes considered by the general purpose speciation and mass transport program, PHREEQC-2, and their data requirements.**

Process	PHREEQC-2 keyword(s)	Data Requirement(s)	
		Generic needs	Site-specific needs
Solution speciation including redox	`SOLUTION`	Thermodynamic data (log K's etc.) for each species (various databases supplied)	Total element and ligand concentrations in water (from comprehensive chemical analysis)
Mixing of waters from different sources	`MIX`	None	Mixing fractions (from water fluxes)
Irreversible reaction	`REACTION`	List of substances reacting & equations (likely to be known from local geology)	Amount of substance reacting (difficult to know *a priori* but estimate from mineralogy)
Solubility of pure minerals (precipitation and dissolution)	`EQUILIBRIUM_ PHASES`	Thermodynamic data (solubility products) (various thermodynamic databases supplied for pure minerals)	Amount and identity of each reactive mineral phase needs to be known (from XRD and bulk chemical analysis)
Solubility of impure minerals (precipitation and dissolution)	`SOLID_ SOLUTIONS`	As above plus choice of model for 'non-ideal' behaviour. Assump-tions also need to be made about the type of equilibrium existing during growth and dissolution.	Data for chemical composition of mineral & solution phases would help calibration (difficult but can be estimated from electron microprobe analysis or selective dissolution)
Gas solubility	`EQUILIBRIUM_ PHASES and GAS_PHASE`	Thermodynamic data (Henry's law constants or log K_H's) (supplied for common gases)	Partial pressure of the various components or the composition of the gas phase (field/lab measure-ments of gas composition)
Adsorption	`SURFACE and SURFACE_ SPECIES`	Need to be able to specify precisely the adsorption reaction (appropriate 'model' is not always obvious) (site density may be known from crystallography or literature)	Amount of oxides present from selective dissolution, XRD analysis etc.
Ion exchange	`EXCHANGE and EXCHANGE_ SPECIES`	Specify ion exchange reaction (CEC's and log K's known for a range of reference materials)	Cation exchange capacity and log K's (from specific lab expts or estimated from clay content and type if known, or some other highly-correlated parameter)
Kinetics	`KINETICS and RATES`	Specify reaction(s) and supply parameters. Non-standard but some available in literature or supplied with PHREEQC-2	Difficult to generalise and may be related to particle size (basic principles are often quite well understood and can be 'tuned' for specific examples)
Biodegradation	see `KINETICS`	Basic principles quite well understood but need to establish particular reaction stoichiometry which can be difficult in strongly heterogeneous systems	Microbial activity (difficult to estimate a priori – use inverse modelling)
Oxidation/reduction	`EQUILIBRIUM_ PHASES and SOLUTION`	Fix *pe* or the concentration/partial pressure of a redox-sensitive species	Often determined by diffusion of oxygen (difficult to fix), availability of electron donors/acceptors (organic matter, nitrate, Fe(III) etc.). Invariably controlled by biological activity (difficult but can look constrain by measurement of by-products)
Transport	`TRANSPORT and ADVECTION`	1D transport depends on water flux and porosity. Diffusion coefficients known from literature	Assumes flow is known (use a hydrogeological model or recharge rate and assume piston flow; porosity from literature, direct measurement or inference; can use knowledge of 'fraction of immobile water if known. Dispersion coefficient usually not known but not critical
Evaporation	`REACTION`	No chemical reaction need be specified	Specify amount of water 'disappearing' (estimate from evaporation model)

Most of the processes outlined in the Table 3.1 require both generic and site-specific information. Even some of the 'generic' data may need to be tuned to the specific site of interest. However, this may be possible to do with more accuracy and confidence than, for example, extrapolating with a statistical model that has no in-built constraints related to the 'real world' (and could make totally unrealistic predictions if the extrapolation is great). Furthermore, the modelling approach will improve as more data are collected with time. Indeed, it can usefully be used to help guide the collection of 'critical' data by highlighting unknowns that are likely to play a key role.

One parameter from the list considered in this project, but which is usually not considered by the chemical speciation and modelling packages such as PHREEQC, is bioavailable Fe and Mn. Natural attenuation is a low-technology approach to groundwater remediation that makes use of natural degradation processes which can often be biologically mediated, and the major chemical models do not include biological processes. In the absence of oxygen one of the most common degradation processes within contaminant plumes involves biologically mediated oxidation of organic compounds by mineral oxidants, Fe^{III} and Mn^{III} or Mn^{IV}. These oxidants, particularly Fe^{III} are widely available in mineral form in aquifers and are often present in much larger quantities than soluble oxidants (O_2, NO_3^-, SO_4^{2-}). However, not all of the Fe/Mn minerals present are available to microbes for use in biodegradation reactions and only a fraction of the total Fe/Mn minerals present may be reducible under field conditions. Therefore, to evaluate the potential contribution of mineral oxides to natural attenuation at a given site, methods of determination that resolve the bioavailable fraction are required. By quantifying bioavailable Fe/Mn, these methods may provide a basis on which to predict the buffering of aquifer contaminant plumes and to understand redox processes at contaminated sites (Heron et al., 1994a).

3.4 Summary

The parameters suggested for collation and measurement are fundamental parameters that characterise basic features of all environmental materials, and specifically soils and aquifer materials. The large number of scientific papers concerned with these parameters, especially in relation to modelling, attests to their significance. They do not of themselves define the complete behaviour of the particles since they are largely related to extensive properties such as *abundance* rather than model-dependent characteristics such as log K values.

The data collected will therefore have to be combined with some model-specific parameters, as outlined in Table 3.1. The best models and their parameters will evolve with time and it will be necessary to update that aspect of the modelling approach but the intrinsic properties, such as the abundance of iron oxides, are of such obvious importance that they should have long-term applicability and benefits.

4. AVAILABILITY OF EXISTING DATA

4.1 BGS data holdings

An assessment of existing internal data holdings at the British Geological Survey (BGS) has identified several relevant data holdings. The six main databases of greatest significance are summarised in Table 4.1. All the data were collected for other purposes then contaminant transport modelling and risk assessment but nevertheless the primary data provide valuable information for the geochemical properties manual. The quantity of each measured parameter; their spatial distribution and lithostratigraphy are identified where possible. Geographical coverage is variable, depending on the purpose and scope of the original investigations. Further details of the nature and coverage of the data are provided in the following descriptions. A summary metadata compilation of the data is provided in Appendix 1.

Table 4.1 BGS Databases and relevant geochemical parameters measured

Database Name	Geochemical data included
Geotechnical Database	Carbonate content, Organic carbon, Clay content
Minerals Programme Geochemistry Database	Loss-on-ignition(LOI)
Dalradian Carbonate Rock Geochemistry Database	Carbonate content, Major oxide
Nirex Database	
Chemical Analyses of Various Limestone samples from the UK	Carbonate content, oxides (inc Fe_2O_3)
East Dorset, Shaftsbury and Hampshire Grain Size Database	Clay content

Geotechnical Database

The Geotechnical Database contains geotechnical data extracted from Site Investigation reports. The database currently contains 1230 values for organic matter content (%), 698 values for carbonate content (%), and 14,905 values for clay content (%). The organic content has been determined by a range of BS accredited methods, such as the British Standard Walkley and Black method (see discussion in next Section). Carbonate content is determined by BS accredited rapid titration, gravimetric or calcimeter (Collin's modification of Schleibers apparatus) methods (BS 1377: Part 3: 1990). The clay content is the <2µm particle-size fraction and is determined by settling.

The database is located in Oracle under tables prefixed BGS.GTCH2001. The chemical data table format is currently being replaced and therefore not available in Oracle, but is presently available in Access. The grain size analysis and chemical table relate back to a borehole table, geology table and sample table so the data can be related to its position, depth, geology, and analysis type.

Carbonate content data coverage (Table A1.1) is concentrated in the south of England (Figure 4.1) with a predominance of samples from Essex and Kent. The samples cover a range of lithostratigraphical groups, however samples are often from drift deposits. The distribution of organic content samples is broader than carbonate content, with more samples from central England (Figure 4.1, Table A1.2). Samples are still concentrated in the southeast, primarily Essex, Greater London and Kent with moderate samples from Staffordshire. Samples from Avon, Gloucestershire, Gwent, and Hampshire are from Quaternary or soil deposits and unlikely to be of use. Samples with measurements for clay content are abundant for southern and central England (Figure 4.1) and the

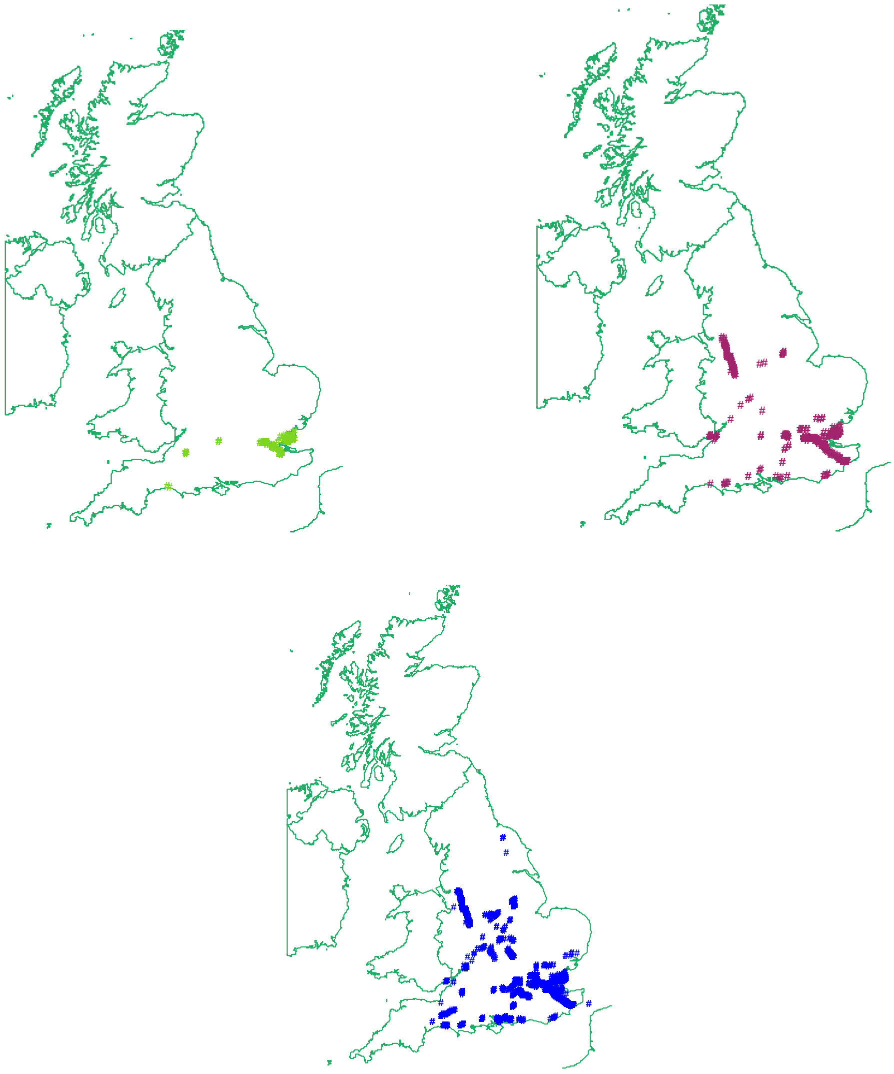

Figure 4.1. Coverage of data holdings in Geotechnical Database; Top Left; Carbonate content distribution. Top Right; Organic carbon content distribution. Bottom; Clay content distribution

majority of samples are from Kent and Greater London, although there are samples that follow major constructions, such as motorways. The samples tend to be close together, however the range of lithostratigraphy covered is extensive (Table A.1.3).

Minerals Programme Geochemistry Database

The Minerals Programme Geochemistry Database contains data relating to the UK landmass and is organized in a relational database structure under Oracle that includes data from G-Base, Minerals Reconnaissance Programme (MRP) and Litho-geochemistry projects. The database primarily contains soil, sediment, and water samples, however there are also rock and drillcore samples. The database contains measurements for organic carbon and carbonate content derived from LOI at 450°C and 1050°C respectively. None of the other required parameters are within the database. There are 1864 rock samples and 1969 drillcore samples for carbonate content and 125 rock samples for organic carbon content, however 102 of these values are recorded as nil.

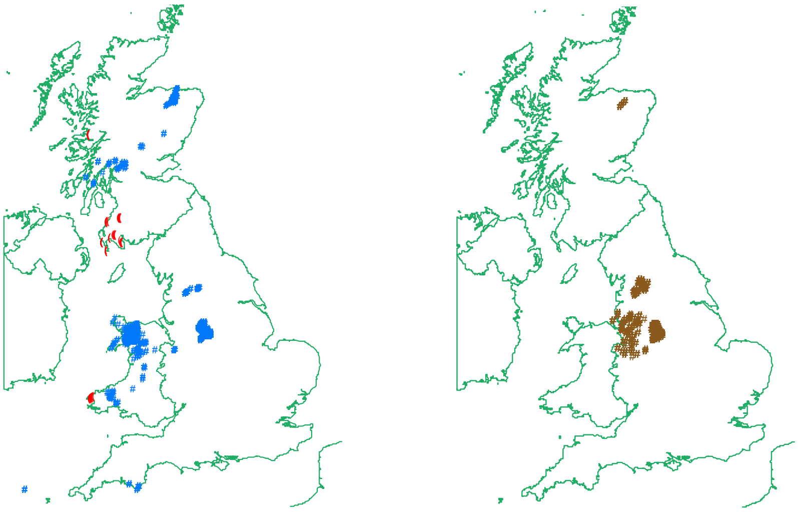

Figure 4.2 **Geographical coverage of data holdings in Geochemistry Database. Left; rock sample distribution for organic content (red) and carbonate content (blue). Right; core sample distribution for carbonate content.**

The organic content samples are concentrated mainly in the Southern Uplands of Scotland (Figure 4.2), however there are 21 samples in western Wales (all nil). Samples measured for carbonate content are located in the Grampians of Scotland, West Midlands and North Wales (Figure 4.2). There is also some coverage in central and southern Wales, and southwest England.

The database covers a range of igneous and metamorphic rocks of Scotland, with rare sedimentary rocks analysed for both carbonate and organic content. There are further carbonate content measurements from borehole and rock samples for the Carboniferous Limestone, Triassic Mudstones and Permian & Triassic Sandstone in England and Wales.

Dalradian Carbonate rocks

The database contains information from the Moine and Dalradian Project on metamorphosed carbonate rocks from the East Grampian highlands of Scotland (Figure 4.3). The database is held locally at BGS Edinburgh and is not accessible from Oracle. The samples are taken primarily from formations within the Appin Group, however there are some samples from the Argyll and Grampian Groups. There are 690 samples measured for major oxide (wt%) and 620 samples measured for carbonate content (%). As the samples are restricted to upland Scotland they are less likely to be useful for the purposes of the project.

Nirex Digital Geoscience Database (NDGD)

During the period 1989 to 1997 Nirex undertook an extensive geological investigation at sites near Sellafield where 30 deep boreholes and 30 shallow boreholes were drilled. The majority of boreholes were drilled to obtain core, resulting in 18.7 km of rock core. The core was tested for petrological, mineralogical, hydrogeological, geophysical and geotechnical parameters. Data resulting from the investigation were compiled into the NDGD under contract for UK Nirex Ltd. The database is currently loaded into an Oracle schema, but protected from public access until the system is upgraded. It has not yet been possible to establish the number of samples held and the analyses performed. Discussions have indicated that all required parameters have been entered into the database except for possibly pyrite content, bio-available Fe and Mn and surface area. The data is restricted to the Sellafield area, and therefore the lithostratigraphy covered is unlikely to be extensive. Updating of the database is planned to begin during late 2002, with no finish date identified at present.

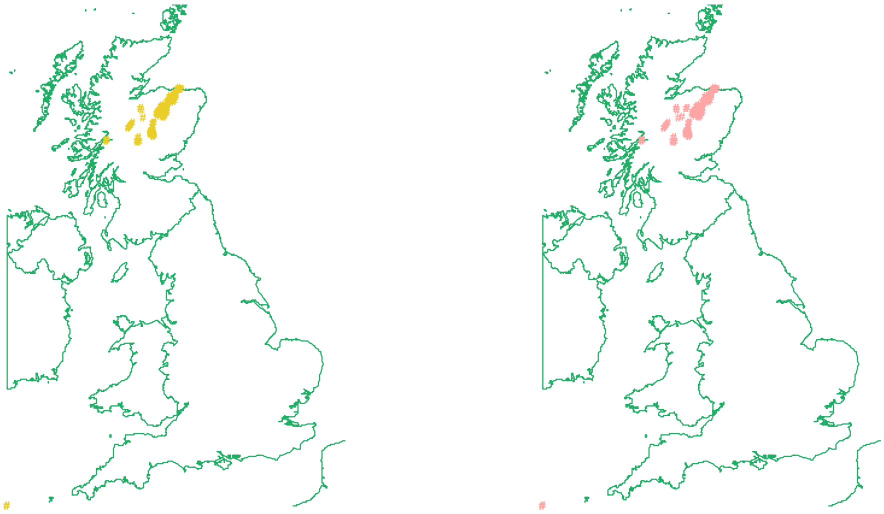

Figure 4.3 **Geographical coverage of data Dalradian Carbonate Rock Database. Left; Samples measured for oxide content. Right; Samples measured for carbonate content.**

Chemical analyses of various limestone samples from the UK

The "Chemical analyses of various limestone samples from the UK" database contains geochemical data from limestone samples throughout the UK. The database is located in Oracle under tables prefixed by BGS.LEGACY_MIDAS_LIMESTONE, and has public access. Any information to be used from the database needs to be checked for confidentiality with the database manager.

There are 3770 chemical analyses of limestone contained in the database, with samples concentrated in areas with limestone deposits at or near surface. The samples are predominantly from central and northern England, however there is an even, but sparse, sample coverage over southern England and Wales (Figure 4.4). There are 3766 measured values for CaO, 1262 for Fe_2O_3 and 2756 for LOI. Limestones sampled include Carboniferous Limestone, Chalk, and Magnesian Limestones.

The database has been managed by several people, therefore much is unknown about sample collection, lithostratigraphies and analysis techniques, such as the LOI temperature. The database is based on IMAU (Industrial Mineral Assessment Unit) data that is likely to be from core or bagged samples from quarry faces.

East Dorset, Shaftsbury and Hampshire Grain Size Database

At present only a small portion of data collected for East Dorset, Shaftsbury and Hampshire is available in digital format. There are 375 measurements for the clay and silt fraction (<63µm) within an Access database at BGS Exeter. These are therefore not measurements of the clay fraction *per se*, but it may be possible to use the fine samples for further analysis to determine the clay fraction. The samples contained within the database are predominantly from National Grid block SY, and several samples from ST, however the exact locations cannot be displayed due to incomplete grid references. The samples measured are from the Bracklesham Group and the Thames Group and cover 13 different lithostratigraphies (Table A1.4).

There is further digital data, however this is in dBase4 format and currently inaccessible, therefore the number or location of measurements is not known. There are hard copies of the digital information, and additional analyses. Approximately 300 extra sample analyses are held at BGS Exeter for Petrockstow, Exeter, and Minehead, but there are no NGR references for samples.

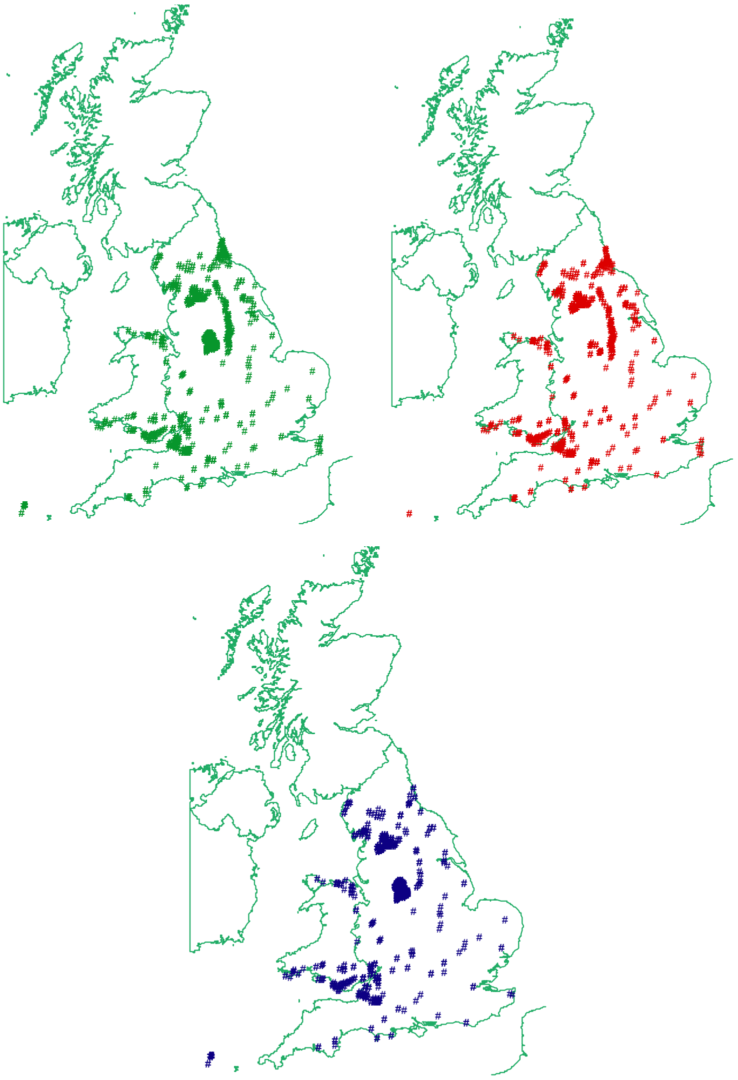

Figure 4.4 **MIDA Limestone Database Samples. Top Left; CaO sample distribution. Top Right; Fe_2O_3 sample distribution. Bottom; LOI sample distribution**

BGS publications and reports

Some 30 BGS reports on relevant subjects were identified by keyword searching of the report titles. These reports listed often relate to a specific location, and therefore are unlikely to contain data for a wide range of lithostratigraphies but may contain data on multiple parameters. There are a few reports that offer a broader coverage of the UK, however these often concentrate on measurement of one parameter type.

Measurements of the required geochemical parameters are often not mentioned in the title or keywords of reports and are not returned from literature searches. Therefore there may be BGS reports not yet identified which contain some or all of the required geochemical parameters. Extracting these data would require a systematic search of BGS reports. There are 17 historical series containing a total of over 18,000 Technical Reports, 9,000 of which are on open file. Of these 17 series, 9 are most likely to contain relevant information. These are the series concerning Onshore geology, Hydrogeology, Fluid processes, Mineral resources, Mineralogy and petrology, Analytical geochemistry, Regional geophysics, Engineering geology, and Applied geochemistry

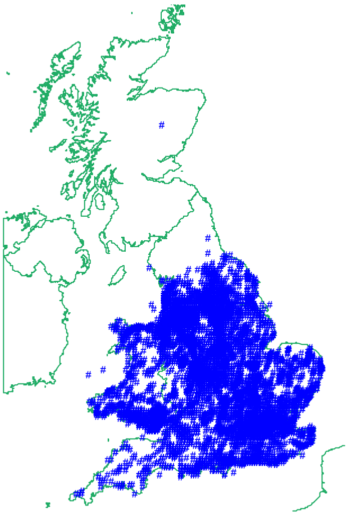

Figure 4.5 Distribution of site investigation reports held at BGS

A full systematic search is likely to yield only a moderate quantity of data for a large amount of work; therefore the benefit of systematic searching would need to be assessed. A more targeted approach is to use the knowledge of report authors. Discussion with staff in relevant programmes has already identified several suitable reports. A few reports contain data on the less frequently measured parameters including pyrite content, free iron oxides and surface area, along with the more common parameters. Salient reports from the Nirex programme that are not available as part of the NDGD cover Bradwell (Essex), Fulbeck (Lincolnshire), Killingholme (South Humberside), and Elstow (Bedfordshire). The Bradwell report contains measurements for clay content, pyrite content, CEC, Fe_2O_3 (%), and surface area. The Killingholme report follows a similar format, except there are no measurements for pyrite and clay content and the lithostratigraphy of samples is not noted. Reports for Fulbeck and Elstow are likely to contain the same measured parameters. It is worth noting that in these reports clay is recorded as the <10µm fraction, rather than the standard <2µm. There are values for London Clay, Oldhaven Beds, Reading Beds, Woolwich Beds, Thanet Sand and Chalk but not all parameters are measured for each sample. There are a further 700 reports from the Nirex core characterisation programme which mostly contain information from the Sellafield area.

There are also some 30,000 site investigation reports containing borehole records, trial pit data, laboratory and test data. There is good report coverage of England and Wales (Figure 4.5). In most cases the factual data from the reports may be available, subject to copyright and confidentiality conditions. The reports are indexed and can be accessed from Oracle in Arc-View, although at present only the report location is shown; the actual data cannot be accessed via this route. Further digital access is planned.

4.2 EA data holdings

Survey of the holdings of geochemical properties data held by the Regions of the Environment Agency indicated that relatively few data are available within the EA. The data that are available are derived almost entirely from landfill risk assessment reports received under the requirements of Regulation 15 of the Waste Management Regulations. As such, almost all the data have been received by the Agency since the implementation of the regulations, within the last 2-3 years, and all the measurements are for the parameters used in the EA's recommended models, i.e. either cation exchange capacity or fraction of organic carbon. Summaries of the coverage of the data are shown in Table A1.5 for cation exchange capacity and Table A1.6. for f_{OC}.

None of the Regions have well developed mechanisms for extracting the data from the Regulation 15 site reports and preparing accessible compilations. In many cases the data were provided to this study simply as photocopied pages from the original reports.

The details of the Regulation 15 requirements mean that all landfill sites, new or established, should have risk assessments completed every four years. It is therefore foreseeable that all Regions of the Environment Agency will continue to receive significant numbers of additional site assessments over the next few years. At present, in the absence of an existing reference compilation of suitable data, many of these assessments will require site-specific measurements to be made and so the body of reports will be an important source of new primary data. Preparation of a comprehensive geochemical properties manual would be substantially assisted if an effective mechanism could be established for capturing the new data.

4.3 UK Academic and commercial data holdings

CEC

Small numbers of data for cation exchange capacity have been identified in doctoral or masters theses from the Universities of Birmingham, Sheffield and Reading. There may also be other departments but the holdings are likely to be on small scale.

The theses at Birmingham have been considered in some detail, and relevant data extracted pending inclusion in a compiled GPM. The data are mostly measurements of cation exchange capacity, but also include some surface area figures, and are mostly derived from samples of the Triassic sandstone in the midlands area.

The holdings of the Groundwater Restoration and Protection Group at Sheffield also undoubtedly contain relevant data. Access to the data has been agreed in principle with researchers at Sheffield, but a meeting to discuss the data in detail has been delayed. Appraisal and extraction of these data should be completed without difficulty during the early stages of Phase 2 of this project.

Fraction of organic carbon

There are a few scattered measurements of fraction of organic carbon in academic dissertations but by far the most significant piece of work is a recent PhD thesis from University College London by Steventon-Barnes (2000) which focussed specifically on the measurement and role of organic carbon in UK aquifers. The study included some 1000 individual determinations but the geographical distribution of the measurements depended on the availability of core material. The coverage of the data is therefore variable with some areas having good data for a number of sites and for depth profiles; other areas, including parts of major aquifers are not covered. Primary measurements are included for at least one sample from each of the Chalk, Lincolnshire Limestone, Triassic Sandstone, Glacial Till, Lower Coal Measures, Lower Greensand, Oxford Clay and some Unconsolidated Deposits. The study therefore represents an extremely important contribution to the compilation of a comprehensive Geochemical Properties Manual.

The thesis has some confidential components (principally concerning the locations of individual sites) and not all the material has been openly published yet, but discussions with the author suggest that the data should become available for inclusion in the GPM within the timescale of the GPM project.

Bioavailable Fe & Mn

There are very few data on Fe/Mn bioavailability for geological formations either in England and Wales or at overseas sites (Table A1.7). Most other data for bioavailable Fe & Mn are for soils rather than aquifer sediments. In the UK the majority of data identified derive from research studies carried out at the Groundwater Protection and Restoration Group, University of Sheffield. In particular, measurements have been made over the length of two cores from different phenolic-contaminated sites on the Triassic sandstone aquifer. For both of these cores there is significant variability of measured Fe/Mn bioavailability with depth (Thornton et al., 2001).

The absence of suitable data arises in large part because the field of MNA and the need for measures of bioavailable Fe/Mn have only developed relatively recently. The problem is exacerbated by the difficulty, complexity and relatively large expense of determination. Fe and Mn have been measured more frequently in other fields such as soil science or exploration geochemistry, but differences in the analytical method can affect the fractions of Fe and Mn which are extracted, making comparison and interpretation more difficult.

Commercial organisations

Discussion with a representatives from a number of environmental consultants and waste management operators showed widespread support for the concept of the GPM. Many of the organisations indicated that they held data from site investigations which would be relevant, but there were sometimes concerns about distribution of the data. Consultancy organisations in particular were cautious in view of the often confidential nature of their investigations and indicated that client approval would be required before data could be released. The other constraint is that the time involved in retrieving the data from archives is difficult to justify for a commercial organisation.

Contacts from the waste management companies suggested that approaches to the other companies would be best received if a co-ordinated enquiry was received through the Environmental Services Association. An approach was made but the level of response during this Phase 1 was low.

Further effort will be required across the sector if useful data is to be obtained. It is also not yet clear from the enquiries completed during this Phase how much of the data held by the consultancy and landfill concerns is derived from the Regulation 15 assessments which have been submitted to the Environment Agency. Such reports are already in the public domain and can be accessed via the respective EA Regions, reducing the level of any imposition on the commercial organisations. Phase 2 of the GPM project should therefore include provision for following-up the initial contacts which have been made with the consultancies and waste operators.

4.4 Available core material suitable for new experimental determinations

BGS Core Store holds a collection of over half a million drill core samples from boreholes drilled in the UK by BGS, commercial and public bodies. These cores are all accessible for further sub-sampling and new experimental determinations, although there may be restrictions where the cores have previously been heavily sampled, or if the quantity of material required for analysis is excessive. The geographical distribution of core samples provides extensive coverage of northern, central and southern England but coverage is less extensive for Scotland, Wales and southwest England (Figure 4.6).

Details of the cores are compiled in the Geoscience Data Index (GDI) and can be displayed in Arc-View. Good geospatial information is generally available including location, National Grid Reference, SOBI (Single Onshore Borehole Index) reference and year of sampling. There is also a depth range for each core. Sample lithostratigraphy is not recorded in the GDI, but there are plans to link the database with the Lexicon (or Rock Classification Scheme, RCS) to facilitate querying for samples from a lithostratigraphy of interest in a particular region. This scheme is currently being implemented and aims to be completed by the end of 2002.

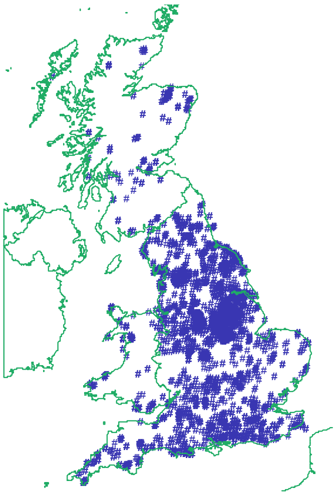

Figure 4.6. Distribution of onshore drill core held in the BGS core store.

For most of the parameters under consideration for the GPM, the stored core can be expected to be perfectly suitable for new experimental determinations. The parameters are generally stable and the quality of measurement is unlikely to be degraded as a result of storage.

The main exception to this assessment of long-term stability is measurement of bioavailable Fe/Mn where changes in redox conditions after drilling may cause significantly erroneous determinations: reduced species in the core may oxidise on exposure to air increasing the oxidised Fe/Mn content. To avoid errors, the core must either be known to have been oxic before core recovery, or it must have been extracted and stored under anaerobic conditions (e.g. under nitrogen). Otherwise, reduced species in the core may oxidise in contact with atmospheric oxygen, increasing oxidised Fe/Mn. Collection and long-term storage of core in so as to preserve anaerobic conditions is both difficult and expensive and so in practice is very rare. Core in the BGS store is not preserved in this way so, for the purposes of bioavailable Fe/Mn determinations, only core which can be shown to have been under aerobic conditions when in situ is likely to give measurements which are representative of the original natural conditions.

4.5 Summary of extent and quality of available pre-existing data

The BGS databases examined have limited spatial coverage, with the Geotechnical database having best coverage of England, and the Geochemistry Database primarily covering Wales and the west Midlands. The parameters resolved from the databases are organic carbon content, carbonate content, clay content, and oxide content for some Scottish samples. The NDGD database could have further measurements for CEC and free mineral oxide, however this is restricted to the Sellafield area.

A search of BGS publication has given limited results with few reports extensively addressing specific geochemical parameters. The most significant of these are the recent joint BGA/EA reports concerning CEC (Gillespie et al., 2001; Gillespie et al., 2000). Other than this, the majority of data contained with reports is likely to be limited in quantity and distribution, and would require a thorough search of the identified series to remove relevant information.

There is currently little available information at BGS for CEC, mineral oxide content, pyrite content, specific surface area and bio-available iron and manganese. The coverage for clay, carbonate and organic carbon content is moderate, but not extensive. There are, however, abundant samples available for new experimental determinations with very good coverage for England and Wales.

5. EXPERIMENTAL DETERMINATION OF PARAMETERS

5.1 Introduction

This section considers the experimental methods available for determination of the parameters which are being considered within the geochemical properties manual. Choice of experimental method can influence the result which is obtained, even if the method is carried out by a skilled analyst. For example, some methods may be better suited to carbonate materials then others, depending on their use of acidic reagents. In order to produce meaningful compilations of data on geological formations of national scale it is clearly desirable that experimental measurements should be as consistent as possible. Here we review the range of experimental methods which is available and identify the relative merits and weaknesses of each. The aim is to try to establish standard methods for the measurement of each parameter by recommending which techniques should be preferred, and in what circumstances.

Intrinsic bias between analytical methods can be identified by use of standard reference materials with known (or accepted) values for given parameters. Reference materials also enable consistency and proficiency testing between different laboratories, even where the same methods are being used. The availability of suitable reference materials for determination of the geochemical properties is considered in the discussion below.

Many of the methods described here have originally been developed for the measurement of the geochemical properties of soils. Soils, by their nature, are normally disaggregated materials whereas aquifer materials are likely to be more consolidated. A number of parameters such as cation-exchange capacity, clay content, free oxide content and surface area are dependent on the particle surface area and particle size distributions within samples. It is therefore possible that to some extent the sample preparation of a consolidated aquifer material will have an effect on the parameter being measured. This is well recognised in the scientific literature. Some examples of the effects are given for specific measurements in the following discussion but the consequences of changes during sample preparation must be considered when reviewing aquifer property data.

5.2 Cation exchange capacity

The Cation Exchange Capacity (CEC), usually expressed in milliequivalents (meq) per 100g of dry sample, is a measure of the quantity of readily exchangeable cations neutralising negative charges in the test material (Rhoades, 1982). A recent review (Gillespie et al., 2000) has shown that there are a variety of methods available for CEC determination. The majority of methods begin with the displacement of existing cations with a saturating salt to provide an index cation on the exchange complex. Thereafter, the methods used to determine the quantity of cations displaced can be divided into two categories; single displacement methods and double displacement methods. In single displacement methods the concentration of exchanged cations or the decrease in concentration of the index cation in solution provides a measure of CEC. Double displacement methods use a second displacing solution to remove the index cation from the sample and the decrease in concentration of the displacing solution or the increase in concentration of the index cation provide a measure of CEC. In the double displacement method the choice of salts can be designed so that the index anion reacts with the displacement cation to form an insoluble salt, which is precipitated from solution (often referred to as compulsive displacement). The advantage of this approach is that there is no need for the repeated washing steps that would otherwise be needed.

Bias in results of CEC measurements is very much associated with the type of material being measured. Gillespie et al. (2000) point to three main problem areas:

- Dissolution of soluble salts, calcium carbonate and gypsum leading to overestimation of CEC

- Specific adsorption of K^+ and NH^{4+} in interlayer positions in vermiculites and micas leading to either an over- or under-estimation of exchangeable K^+ when NH^{4+} is used as the index cation.

- Specific adsorption of trivalent cations such as Al^{3+} or Fe^{3+} on surfaces leading to an underestimation of CEC.

The ammonium ion has been used as the index cation in many methods because its selectivity and extremely weak hydration enables it to move rapidly to a well defined number of exchange sites, sealing off access to other sites. It also has a number benefits related to its practical use (Gillespie et al., 2000). However, as indicated above, for some materials its use leads to significantly biased results. Despite this, the USEPA have recommended the use of a single displacement method with an ammonium index cation for soil CEC determination during long-term monitoring in environmental programmes (Schumacher et al., 1995).

The method that has been adopted as both the British Standard and ISO method [BS, 1997 #53;ISO, 1994 #54] is based on that developed by Bascomb (1964) specifically to overcome the overestimate in CEC introduced by the presence of calcite or gypsum in the samples. The method uses Ba^{2+} as the index ion, introduced in the form of $BaCl_2$. The Ba is subsequently compulsively displaced with Mg^{2+} by adding $MgSO_4$ to form the insoluble salt $BaSO_4$. The index-cation salt is made up in an ethanolic solution with triethanolamine that minimises the soluble-salt interference and the Ba^{2+} ion does not cause collapse of expanded phyllosilicates as the NH_4^+ ion would. It has been shown, however, that this method still suffers from a positive bias in the presence of samples containing high concentration of gypsum. Stuart and Vickers (1989) suggested a modified method to help overcome these problems.

Gillespie et al. (2000) compared three methods of CEC determination applied specifically to a selection of UK aquifer materials: the Bascomb $BaCl_2$ compulsive exchange method, a single displacement method using $SrCl_2$ as the index salt and a Methylene Blue index method that uses an organic dye to displace cations from the sample. Summary results are illustrated in Figure 5.1 using box-and-whisker plots to show the data obtained from five replicate measurements of each material type. The three methods show profound differences for all the materials. The $SrCl_2$ method gave notably higher results than the other two for samples containing high quantities of calcite (Lower chalk and Lincolnshire limestone samples). The results for the two size fractions of the Sherwood sandstone also illustrate that, as has been noted by other workers (Barton and Karathanasis, 1997; Deutschmann et al., 1997), for consolidated materials the sample preparation has a significant effect on the final results produced.

On balance, Gillespie et al. preferred a modified version of the Bascomb $BaCl_2$ compulsive exchange method on the grounds that it was already widely used and proved suitable for a wide range of geological materials They subsequently applied the method to samples of 30 geological formations drawn from across the country. Although 30 samples is by no means a large study, these data do represent a very significant, internally consistent, portion of the overall available body of data for CEC. There is merit in ensuring that future measurements are consistent with them and hence the use of the $BaCl_2$ method is also recommended here as the preferred experimental method for determination of CEC.

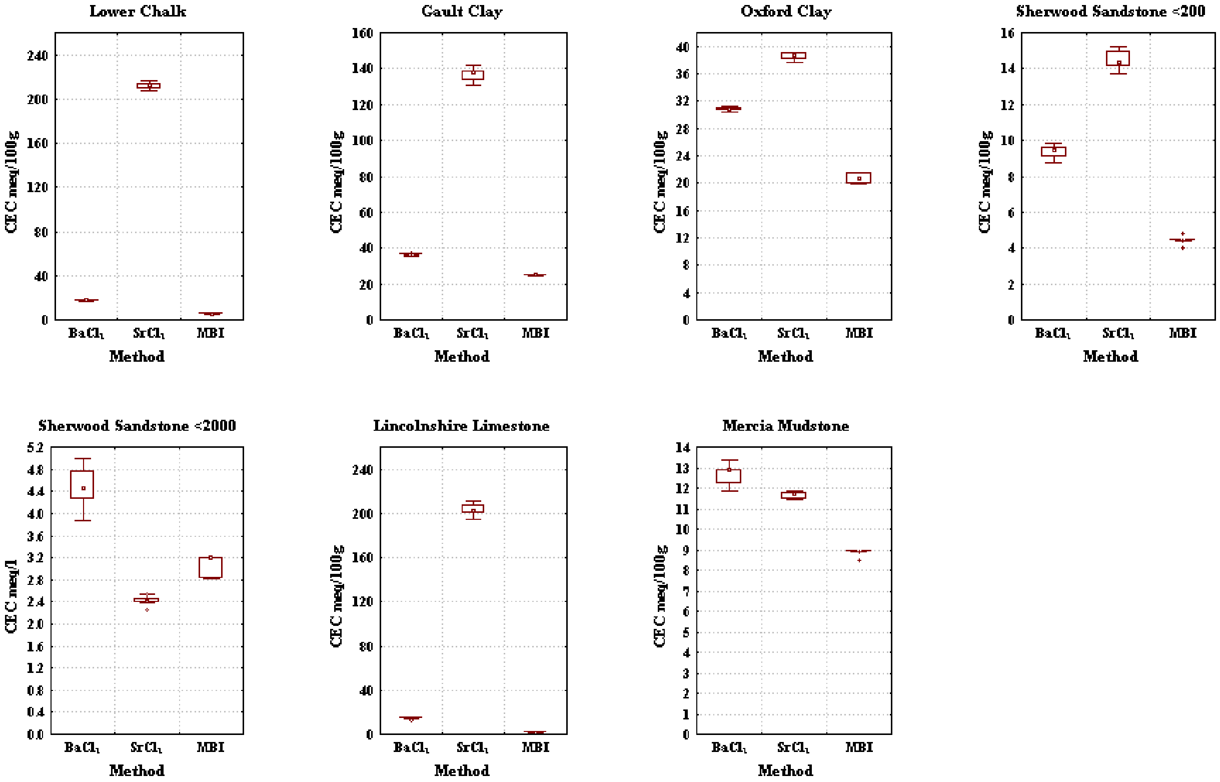

Figure 5.1. **Comparison of CEC measurement method on aquifer materials (from Gillespie et al., 2000)**

The fact that current literature contains many modifications and new methods for CEC measurement (e.g. Barton and Karathanasis, 1997; Bergaya and Vayer, 1997; Cerri et al., 2002; Ciesielski and Sterckeman, 1997; Liu et al., 2001; Skinner et al., 2001; Zhao et al., 1997) supports the view that current standard methodologies are not applicable to all material types. Most of the literature is related to CEC measurement of soils but the CEC of rocks is also being investigated (Deutschmann et al., 1997; Duquette and Hendershot, 1993; Gualtieri et al., 1999; Osman and Suter, 2000).

There are few easily available reference materials for CEC measurement. No such materials are listed in the catalogues for the internationally recognised National Institute of Standards and Technology (NIST, USA) or the Institute for Reference Materials and Measurements (IRMM, Belgium). However, the Chinese National Research Centre for Certified Reference Materials (NRCCRM, China) does list four soils with certified cation exchange capacity data which are available in the UK through the Laboratory of the Government Chemist (LGC). Proficiency-testing schemes operated by the Wageningen Evaluating Programmes for Analytical Laboratories (WEPAL) and the North American Proficiency Testing Program (NAPT) both allow laboratories to evaluate their performance on CEC determination of soils.

5.3 Organic carbon content

The organic carbon fraction in aquifer materials exerts a major influence on the subsurface mobility of organic and organic-associated contaminants. The spatial distribution of total organic carbon (TOC) in aquifer materials must be determined before the transport of hydrophobic organic pollutants in aquifers can be modelled accurately. Solid carbon can occur in aquifer materials in inorganic and organic forms. The organic matter consists of plant, animal and microbial remains in various stages of decomposition along with their highly-altered derivatives (usually referred to as humic matter).

There are number of approaches to the determination of organic C in soil:

(i) by determination of total C after removing inorganic carbon by acid treatment

(ii) by dry combustion in a furnace at moderate temperature with either the weight loss expressed as ‘loss on ignition’ or by quantification of the amount of carbon dioxide produced.

(iii) by organic carbon reduction of chromate ($Cr_2O_7^{2-}$) and subsequent titrimetric determination of the unreacted chromate with ferrous sulphate.

Method (i) has been recently evaluated specifically for aquifer materials (Caughey et al., 1995). Sample replicates were digested with sulfurous acid, dried at 40°C, and then combusted at 950°C using proprietary instrumentation that measured the evolved carbon dioxide. For the three test materials that contained >2% TIC, incomplete acidification resulted in a systematic positive bias of TOC values reported by five of the six laboratories that used the test method. The authors suggest that given time to become proficient with the method, improvements in accuracy should be obtained. The advantage of this approach is that carbonate C is removed before the analysis allowing less potential interference from the inorganic carbon particularly in materials with low organic C compared their inorganic carbon content. This has been confirmed by (Kerven et al., 2000) who showed that a suitable acid pre-treatment of alkaline soils in the sample boats followed by a drying step eliminates the carbonate carbon prior to combustion and the need for an additional measurement. The measurement of carbon in soils by this high temperature combustion in an oxygen atmosphere was shown to be a rapid and reliable method capable of producing results in good agreement with one of the established dichromate oxidation procedures. Nieuwenhuize et al. (1994) have also shown that this approach allows the determination of 60 samples per day by a single analyst and that extensive testing and application showed long-term precisions for organic carbon of about 3%. The accuracy was found to be excellent, irrespective of the calcium carbonate content of the sample.

The first two methods estimate total organic C without discrimination between humic material and elementary C although this is probably not as important in aquifer material as it is in soil measurements. Loss on ignition, whilst very simple to carry out, may provide an overestimate of reactive organic material with samples containing high charcoal content or in certain clay soils where weight loss may be associated with loss of water or hydroxyl groups. In addition, it is necessary to convert the organic matter value obtained from the LOI measurement to an organic carbon content. In a recent study of sediments (Sutherland, 1998), examination of organic matter (OM) to organic carbon (OC) conversion factors for Manoa bed sediments indicated that values typically observed in the soils literature (1.7-2.2 mg/kg) are far too low. Values of OM/OC were found to increase with increasing grain size, and decrease with increasing LOI percentage. Conversion factors obtained for grouped data had a mean of 14.9, a coefficient of variation of 21%, and a range of values between 6.2 and 27.4 mg/kg. It is suggested that these high conversion factors reflect significant water loss by dehydration of Fe, Al, and Mn oxides at a muffle furnace temperature of 450°C. The authors suggested that the blind application of conversion factors developed from soils should be avoided when converting from OM to OC for fluvial bed sediments. This should also be a consideration in aquifer materials, which like sediment materials, have significantly different properties compared to soils.

Schollenberger (1927) introduced a rapid titrimetric method whereby soil organic matter is oxidised by a saturated solution of potassium dichromate in concentrated sulphuric acid, with application of heat. The unreduced chromic acid is then back-titrated with ferrous ammonium sulphate solution. Walkley and Black (1934) and later Walkley (1947) modified this by omitting the heating step, using the heat generated on dilution of the sulphuric acid to provide sufficient energy for the reaction to take place. In soils the procedure is only partly efficient in recovering OC, depending on the sample type; Walkley and Black found a mean recovery of 76% for a range of British and foreign soils, necessitating a multiplication factor of 1.32 to yield a result equivalent to OC by combustion methods. Others have suggested a much broader range varying with soil group (e.g. Allison, 1960). However, in the absence of a specific recommended value the original Walkley and Black figure of 76% is frequently used. Details of the original Walkley and Black method have subsequently been modified by a number of authors (Allison, 1965; Hefferman, 1985; Jackson, 1958; Kaira and Maynard, 1991; McKeague, 1978; Metson, 1956; Nelson and Sommers, 1962; Schumacher et al., 1995).

Recent trends in OC analysis are moving towards the use of dry combustion with CO_2 infra-red detection (e.g. Matejovic, 1993; Wang and Anderson, 1998). In these methods, the combustion temperature and flow of oxygen are optimised to make the combustion specific for OC whilst leaving the IC unreacted. The method has been developed using a two-stage temperature programme to allow both OC and IC to be differentiated and quantified during a single-pass analysis (Neal and Younglove, 1993; Wright and Bailey, 2001). The procedure is potentially extremely cost-effective, offering a greater than 10-fold reduction in time required for sample preparation, analysis, and data acquisition. Results for a variety of soil types, with OC contents ranging from <1 to >4% and IC from <1 to >9%, were found to be correlated highly with results from more established methods (Chichester and Chaison, 1992). Similarly, Matejovic (1997) found the results by this method were in good agreement with those obtained by a laboratory proficiency test at the International Soil-Analytical Exchange, organized by Wageningen Agricultural University.

ISO standard methods have been published for a version of the Walkley and Black wet oxidation method (International Standards Organisation, 1995a) and the dry oxidation method with acid pre-treatment (International Standards Organisation, 1995b). A British standard method has only been published for the dry oxidation method with acid pre-treatment (British Standards Institute, 1995a). The USEPA recommend the use of the Walkley and Black wet oxidation procedure (Schumacher et al., 1995).

The recent review of OC measurement in aquifer materials by Steventon-Barnes (2000) recommended that the most accurate way of determining TOC was by high-temperature oxidation after carbonate removal with acid.

There are more reference materials available for OC than for CEC determination although the number and variety of samples is not very comprehensive. The NRCCRM, supplied through the Laboratory of the Government Chemist, lists a number of soils, sediments and rocks with certified or recommended values for OC. In addition, two recent publications have listed the organic carbon contents of 30 and 22 geological reference materials respectively (Cahill and Autrey, 1988; Jackson and Roof, 1992). Of the laboratory proficiency schemes, while the NAPT scheme provides information on performance on total carbon and soil organic matter, the WEPAL scheme provides information only on the carbonate (not carbon) content of soils.

5.4 Carbonate content

Carbonate carbon can be determined by a number of methods. Traditionally, the simplest method involves the dissolution of carbonates in an excess of standard acid followed by back titration of the remaining acid (Nelson, 1982; Rowell, 1997). Other methods measure the carbon dioxide evolved on acidification volumetrically (British Standards Institute, 1995b; International Standards Organisation, 1995a; Shapiro, 1975), gravimetrically (Peck, 1964), by pressure (Jones and Kaiteris, 1983), thermal conductivity (Amundson et al., 1988; Weliky et al., 1983) or by coulometric titration (Chan, 1986; Engleman et al., 1985). Dry combustion methods with infra-red detection of carbon dioxide (as already discussed in relation to organic carbon analysis) have been developed using a two-stage temperature programme. This method has been used to allow both organic carbon and inorganic carbon to be differentiated and quantified (Chichester and Chaison, 1992; Neal and Younglove, 1993; Wright and Bailey, 2001). Finally, the carbonate content can be determined by difference where a total combustion method provides a value for the total carbon content and the organic carbon content is obtained either by ashing at a lower temperature (Krom and Berner, 1983) or by removal of inorganic carbon by acidification prior to ashing (e.g. Snyder and Trofymow, 1984). In general there is good agreement between most methods although some methods have been shown to have a higher precision and accuracy than others (Engleman et al., 1985). The 'measurement by difference' methodology may also suffer from precision and accuracy problems when measuring a relatively low quantity of inorganic carbon in the presence of high organic carbon in which the result is calculated as a relatively small difference between two high values.

Published values for carbonate contents of soil and geological reference materials, analysed by various methods, are available from several sources (Cahill and Autrey, 1988; Chan, 1986; Engleman et al., 1985; Jackson and Roof, 1992; Krom and Berner, 1983). In addition, the NRCCRM and NIST catalogues list a number of soil, sediment and rock samples with certified or recommended inorganic carbon data. Proficiency schemes also address carbonate content: the WEPAL scheme provides information on the carbonate content of soils and the GeoPT proficiency testing scheme, run by the International Association of Geoanalysts (IAG), include IC as one of the test determinands for rock samples. The NAPT scheme, on the other hand, provides information on total carbon and soil organic matter only.

5.5 Clay content

The term 'clay mineral' is most commonly used to denote a family of hydrous alumino-silicates (more specifically phyllosilicates)' usually with particle sizes <2 µm. They are chemically and structurally similar to other phyllosilicates known as the true and brittle micas. There are many other materials of similar size which are of geological importance, including other silicates such as quartz and zeolites, as well as non-silicates such as the hydroxide, oxyhydroxides, hydrous oxides and amorphous compounds. These are not clay minerals. However, the clay content of rocks and soils is usually methodologically defined in terms of clay-sized material, as the proportion of the material with a given particle size. The particlesize based definition of clay used by the Canadian Soil survey Committee (CSSC) and the United States Department of Agriculture (USDA) is given in Table 5.1 (McKeague, 1978).

Table 5.1. Particle size definitions of clay mineralogy

CSSC nomenclature	USDA nomenclature	Mean diameter size range
Clay, fine		≤0.2 µm
Clay, coarse		0.2 – 2 µm
	Clay	≤2 µm

Particle size analysis can be divided into three different phases; (i) sample treatment, (ii) sample dispersion and (iii) weight contribution of each size fraction of the total sample weight. Each phase comprises several different processes.

Pretreatments

Numerous pre-treatments have been developed in order to try to achieve complete aggregate dispersion in samples. The pre-treatments are primarily for the removal of cementing and binding agents such as organic matter, iron oxides, carbonates and soluble salts. A detailed discussion is given by Gee and Bauder (1986).

The effect of organic matter on sample dispersion varies greatly with different soil types. Organic matter acts as a binding agent among particles giving the soil the appearance of having a coarser texture. Organic matter is most commonly removed by oxidation using hydrogen peroxide (H_2O_2). Other oxidants that have been used include sodium hyperchlorite (NaOCl), sodium hyperbromite (NaOBr) and potassium permanganate ($KMnO_4$) (Gee and Bauder, 1986).

Iron oxides, such as hematite and goethite, can form strong binding agents on soil particles either as discrete crystals or coatings on particle surfaces (Gee and Bauder, 1986). Iron oxide removal usually involves the reduction and solubilisation of iron using the method of (Mehra and Jackson, 1960) using sodium dithionite, sodium citrate and sodium bicarbonate (DCB). This procedure consists of multiple washings with the DCB solution until the soil is grey, and subsequent washings with sodium citrate and/or sodium chloride to remove up all iron from the system, saturation of ion-exchange sites with sodium, and flocculation of the samples. Iron oxides are an important part of the mineralogical composition of soils and aquifer material and their removal can change the particles size distribution and lead to erroneous interpretations of other soil chemical properties that are commonly related to particle-size analysis (El-Swaify, 1980). The procedure should, therefore, be used with caution.

Carbonates are commonly removed from the soil by washing with dilute 0.2 N HCl, 1 N HCl, or an acidified sodium acetate (1 M NaOAC, pH 5) solution. Sodium acetate is recommended because it is not as harsh as HCl and saturates the exchange sites with sodium. Once again caution should be exercised. Limestone and dolomite particles can be removed resulting in a change in particle size distribution and textural classification of the soil (Kilmer and Alexander, 1949). The difficulties of measurement of the clay content of carbonate-rich lake sediments after removal of carbonates has also been discussed by Murray (2002).

In alkaline soils, soluble salts of calcium, magnesium, and sodium may be present in concentrations high enough to cause particle flocculation. The addition of sodium-based chemical dispersants further hinders aggregate dispersion by increasing the salt content. Therefore, the salts must be removed prior to sample dispersion. Removal of excess salts can be accomplished by multiple washings with deionised water. Gee and Bauder (1986) suggest the washings should be continued until the leachate salt concentration drops below 10 mM.

Measurement

The measurement of particle size and hence the clay content are based on the settling of grains in a liquid medium. The rate at which different particles settle is directly related to their size (radius). Falling particles follow Stoke's law in which it is assumed that the particles are smooth and spherical, that they do not interact with each other, that terminal velocity is reached at the start of the settling process, and that the viscosity of the liquid controls the rate of settling. Separation of the various particle sizes can be achieved by homogenisation of the soil suspension and decanting all that remains above a given depth after a given time. Settling times for different fractions are listed in various texts (e.g. Schumacher et al., 1995).

The most common technique for particle-size analysis (PSA) of silt and clay fractions is the pipette method. This method is perhaps the standard method to which most other PSA techniques have been compared. Both British standard and ISO methods using this procedure have been published (British Standards Institute, 1998; International Standards Organisation, 1998) and the technique is recommended by the USEPA (Schumacher et al., 1995). The method consists of bringing the dispersed sample into suspension after removal of coarser sand and silt fractions by wet sieving. Once suspended, an appropriate settling time is allowed and then the resulting suspension is sampled to a specified depth using a pipette of known volume. The extracted aliquot is dried, weighed, corrected for weight contribution of dispersion agent, and converted into weight percent silt or clay. The major disadvantage of this method is that the procedure is very slow.

With advances in electronic and X-ray technologies and improvements in various sensing devices, several new methods have been developed to enhance the speed of PSA. These methods work on the principles of photo extinction of white light (e.g. Singer et al., 1988), low angled forwards scattering (Fraunhofer diffraction) of laser light (e.g. Beuselinck et al., 1998; Chappell, 1998; Loizeau et al., 1994; Lu et al., 2000; Shillabeer et al., 1992; Vitton and Sadler, 1997), X-ray absorption (e.g. Singer et al., 1988; Vitton and Sadler, 1997), and electrical conductivity (e.g. Pennington and Lewis, 1979). Methods employing photoextinction and X-ray absorption techniques are based on particles settling following Stokes' law. Comparisons of these new methodologies with the standard pipette method (Beuselinck et al., 1998; Buchan et al., 1993; Loizeau et al., 1994; Pennington and Lewis, 1979) show there are differences in the results obtained although in general there is good agreement. Despite the advantages of increased speed of analysis, the pipette procedure still appears to be the most commonly used method.

The accuracy of the method can be checked on propriety material with standardised particle sizes. The difficulty in specification in the accuracy of the method comes from the type of samples being used and chemical pre-treatments being applied. Reference materials for clay content in the aquifer materials of interest in this work are likely to be difficult to obtain.

5.6 Free mineral oxide content

The free mineral oxide content of a geological material is not strictly defined but refers to the crystalline iron and aluminium oxide content of the material that does not include the amorphous iron and manganese oxides. The term 'free' is a reference to the extraction procedure that should be specific for the crystalline Al and Fe (free) oxides and should not extract (bound) Fe and Al by dissolution of primary and clay minerals. Although there have been detailed studies of the specificity of reagents used to extract amorphous Fe and Mn oxides (Chao and Zhou, 1983), it is not clear whether there has been rigorous investigation as to whether the reagents used to extract free mineral oxides do not also extract amorphous oxides. Despite this, the results of the free mineral oxide content are treated as being specific and often the ratio of free oxides to amorphous oxides is used to assess the age of soils where weathering processes are thought to increase the crystalline forms of Al and Fe.

A review of the development of extraction methods has been given by (Schumacher et al., 1995) who shows that methods used for this analysis have quickly gravitated to two procedures. The most popular of these is the method of (Mehra and Jackson, 1960) which uses sodium dithionite, sodium citrate solution buffered to pH 7.3 with sodium bicarbonate. A pH of 7.3 was chosen because the oxidation potential of $Na_2S_2O_4$-$Na_2C_6H_5O_7.2H_2O$ systems buffered with $NaHCO_3$ increases rapidly up to pH 8 while the solubility of Fe_2O_3 decreases rapidly over pH 7. The two curves intersect at about pH 7.3 suggesting that this is the optimum for pH extraction. The other method is that used by the USDA, which involves shaking overnight with citrate-dithionate solution. (Shedrick and McKeague, 1975) found good agreement between this method and that of (Mehra and Jackson, 1960) when used on 14 Canadian soil samples. At the end of the extraction the amount of Al and Fe in solution is determined by AAS or ICP-AES with matrix matched standards. When using either protocol that care must be taken to monitor the shelf life of the $Na_2S_2O_4$ as the reagent deteriorates resulting in low recoveries of Al and Fe. In addition to this, care should be taken in sample preparation as it has been found that over grinding can cause significant errors (Neary and Barnes, 1993)

An alternative approach is the use of dilute acid extraction to selectively extract the desired fraction of free metal oxides. Mineral acid extraction has several clear advantages: it is an simple and easy technique, highly pure reagents are commercially available cheaply, subsequent analysis of extracted metals is easy to carry out on acid aqueous matrices by standard instrumental techniques, and if multi-element techniques such as ICP-OES or ICP-MS are used then a full suite of metals an be analysed simultaneously. Using HCl complexes Fe better but using HNO_3 is also very effective and provides a cleaner matrix for analytical instruments.

There are no ISO or BS methods for this determination and no proficiency testing schemes. The USEPA recommends the standard method used by the USDA (Schumacher et al., 1995). No formal standard materials exist but (Schumacher et al., 1995) suggest that samples from the Agriculture Canada ECSS round-robin samples could be used as check materials (the availability of these materials is not known).

5.7 Pyrite content

The pyrite content of sediments has been investigated as an important part of the studies of the sulphur diagenetic cycle, sulphate reduction and sulphide mineral formation (Duan et al., 1997). Sulphur is known to exist in a number of forms within sediment materials; sulphates, organo-sulphur compounds, elemental sulphur, acid volatile monosulphides and pyrite (Canfield et al., 1986). Methods that use high temperature combustion and oxidation of sulphur species provide information on the total sulphur content but not on the individual sulphur species present (Hern, 1984). An early methodology (Lord, 1982), that was pyrite-specific but time consuming, used a sequential extraction by first removing iron oxide using the method of Mehra and Jackson (1960), followed by iron silicate dissolution with hydrofluoric and boric acids and finally extraction of the pyrite with nitric acid and quantification of the iron content by atomic absorption or colorimetric methods. Canfield et al. (1986) described a method whereby reduced sulphur species (pyrite + acid volatile sulphur + elemental sulphur) are decomposed to hydrogen sulphide in hot acidic $CrCl_2$ solution. The evolved hydrogen sulphide was trapped in a zinc acetate solution forming zinc sulphide that was then determined iodimetrically. The method was shown to be specific for reduced sulphur species. More recently Duan et al. (1997) made modifications to this method in which organic extraction and ethanolic hydrochloric acid distillation steps were added prior to the $CrCl_2$ digestion to remove the elemental sulphur and acid volatile monosulphides respectively allowing the specific pyrite content to be quantified.

These methods for pyrite determination are generally regarded as ‘research’ methods and have not been designed for the routine determination of large batches of samples. It has been shown that the results are dependant on sampling techniques (reducible sulphur species can be oxidised in air) and on the age of the pyrite in the material (Duan et al., 1997). It is likely that development of the methodology would have to be carried out to deal with high carbonate content materials (chalk and limestone) as CO_2 out-gassing during reaction with the acids used in the procedures could cause problems. Although there is some evidence that the reproducibility of these methods is acceptable there are no easily available reference materials or proficiency testing schemes to check the accuracy of pyrite determination.

5.8 Bioavailable iron and manganese

Two classes of methods have been developed for quantifying bioavailable Fe/Mn in geological materials. *Biotic* methods involve incubation of test material with iron-reducing bacteria. Fe/Mn consumption is then measured either directly or indirectly. *Abiotic* methods rely on chemical extractions that simulate bioreduction. They reductively dissolve a fraction of Fe/Mn that can be correlated with the bioavailable fraction.

5.8.1 Abiotic methods

Abiotic extraction methods which have been proposed are listed below, roughly in chronological order of their development.

0.5 M HCl. Several extraction times have been investigated, ranging from 1 hr (Lovley and Phillips, 1986b) through 24 hrs (Heron et al., 1994b) to 3 days (Bekins et al., 2001; Cozzarelli et al., 2001; Tuccillo et al., 1999). This extraction method leaves 95% of crystalline, less bioavailable Fe oxides (hematite, goethite, magnetite) undissolved (Tuccillo et al., 1999).

5 M HCl. Using more concentrated acid at 90°C for 8 hours gives total extractable (non-structural) Fe and Mn (Broholm et al., 1998; Heron et al., 1994a). Fe mineral species that are less bioavailable, possibly magnetite (Fe_3O_4) or clay minerals with Fe in the structure, are extracted by 5 M HCl.

Ammonium oxalate. This method uses a 0.175 M ammonium oxalate – 0.1 M oxalic acid mixture (Tamm's Reagent) in the dark (Chao and Zhou, 1983; Heron et al., 1994b). Significant fractions of less-bioavailable magnetite or organic-complexed iron are dissolved. Therefore, this method is only specific to amorphous iron oxides in the absence of magnetite and organic matter complexes.

Hydroxylamine-hydrochloride. Extraction by 0.25 M hydroxylamine hydrochloride – 0.25 M HCl at 50°C for 30 minutes (Chao and Zhou, 1983). The authors considered this to be the best of five methods tested for extraction of amorphous iron(III) oxides on the basis of the short duration of the test, the minor dissolution of crystalline iron oxides (<1% of the total iron), specificity of the fraction extracted, and the close agreement with the benchmark Tamm's reagent method, which is more difficult to perform. Less magnetite is extracted by this method than with the Tamm's reagent method. It is, therefore, considered more selective for amorphous Fe^{III} oxyhydroxide extraction compared with the latter method. However, this method extracts Fe^{II} as well as Fe^{III} and, therefore, overestimates the amount of amorphous Fe^{III} in reduced environments.

Hydroxylamine (acidic conditions). This is a development by Lovley and Phillips (1987) of the hydroxylamine hydrochloride method listed above. The modifications include reaction time and temperature, although a precise description of the method was not provided. It is reported as an improvement on the basis that, in contrast to acid extraction techniques, it does not extract high concentrations of Fe^{II} along with the Fe^{III}. Some good agreement was found between microbially reduced iron in a set of microcosm experiments and the fraction extracted by hydroxylamine (Lovley and Phillips, 1986a). However, the authors of both hydroxylamine methods reported inability of hydroxylamine to extract all of the amorphous/microbially reducible Fe^{III}. Therefore, the method does not give a quantitative value for microbially reducible Fe^{III}, but may be useful in identifying zones where Fe^{III} is available for microbial reduction. Lovley and Phillips conclude that the development of a technique which fully but selectively extracts all the amorphous Fe^{III} oxyhydroxides may not be possible.

Cr^{II} reagent. This method was proposed by Barcelona and Holm (1991), but Heron et al (1994a) considered the Cr^{II} reagent to be very unstable and reactive. Oxidation capacity determinations 15 to 20 times the expected values were obtained.

Ti^{III}-citrate. 0.05M Ti^{III} – 0.05M citrate – 0.05M EDTA with $NaHCO_3$ as pH buffer (Ryan and Gschwend, 1991) reacted for 24 hrs (Heron et al., 1994b; Tuccillo et al., 1999). The method is reported as extracting substantially larger fractions of hematite and goethite than the 0.5 M HCl method described above (Tuccillo et al., 1999).

Ti^{III}-EDTA. Extraction using a solution of 0.008 M Ti^{III} with 0.05 M EDTA (Crouzet et al., 1998; Graf Pannatier, 1999; Heron et al., 1994a; Heron et al., 1994b). This method is a further development of the Ti^{III}-citrate-EDTA method above using Ti^{III} as the reducing agent together with EDTA as a complexing agent. The citrate ligand and $NaHCO_3$ pH buffer were omitted to simplify the extraction and quantification reactions on the assumption that the buffering capacity of EDTA on its own was sufficient. The substantially reduced concentration of Ti^{III} still gives reasonable excess over the reducible fraction of most iron rich sediments, whilst the EDTA concentration was increased to just below its solubility limit. Excess of EDTA was intended to minimise competition for the Ti^{III} reductant from other cations that may be present.

This method has been found to reduce a well-described fraction of the total Fe/Mn minerals, namely ferrhydrite (98%), akageneite (100%), goethite and hematite (93%), magnetite (9%) and pyrolusite (99%), within an extraction period of 24 hrs (Heron et al., 1994a) although there is the possibility of interference from other reducible species e.g. sulphate and nitrate (Broholm et al., 1998). The detection limit depends on accuracy of the redox titration and on the solid-solution ratio of the extraction: a detection limit of 4 μequiv g^{-1} was calculated for samples with a solid-solution ratio of approximately 1 g sediment to 10 mL of extractant.

Anthraquinone-2,6-disulfonate oxidation. This recently suggested method is reported to provide a closer estimation of bioavailable iron oxides than other extraction methods (Hacherl et al., 2001). Further study of the literature and possibly laboratory trials are required to verify the efficacy.

5.8.2 Biotic methods

Laboratory microcosm assays can be either batch microcosms (e.g. Lovley and Phillips, 1986a), or column experiments (e.g. Benner et al., 2002). These involve anaerobic incubation of aquifer material with amendments such as a carbon source (e.g. acetate), nutrients and iron reducing bacteria.

Bioavailable Ferric Iron Assay is a commercial product form of the microcosm assay (Evans, 2000; Evans et al., 1999; Evans and Koenigsberg, 2001). Reagent, including iron reducing bacteria, and nutrient is supplied in a dried state and incubated for a 30 day period in a test tube containing a sample of the sediment to be tested. Evolved iron(II) is measured using a colorimetric procedure (e.g. phenanthroline) or other method.

5.8.3 Preferred methods

Conceptually, biotic tests employ the same type of microbiological, geochemical and physical processes as occur in the field to quantify reducible Fe/Mn. In contrast, abiotic methods use more aggressive physico-chemical processes to reduce a fraction of Fe/Mn that requires correlation with the microbiologically reducible fraction. Abiotic methods, therefore, attempt to simulate biotic processes and the latter provide a benchmark for the former.

A major disadvantage of biotic methods is the length of time it takes to conduct the assay. Even under conditions highly conducive to bioreduction, as in the case of the CDM assay, a thirty day incubation period is required. This disadvantage underscores the need to develop more rapid and tractable abiotic techniques, using biotic methods as the reference in one of two ways. The first approach employs ideal conditions for the bioreduction (e.g. ideal pH, electron donor concentration, nutrient availability) and quantifies the *potentially* bioavailable fraction. The second approach employs conditions as close as possible to ambient in an attempt to quantify the bioavailable fraction under *actual* aquifer conditions.

The definition of bioavailable Fe/Mn is clearly not straightforward. A range of factors – physical, geochemical, physiological, thermodynamic and mineralogical – controls bioavailability. Several of these controlling factors are environmental and hence vary from site to site. For example, the presence of humic acids or other natural ligands can influence the extent to which biogenic Fe^{II} is adsorbed onto Fe^{III} oxide and act as a barrier to further oxidation (Roden and Urrutia, 2002). Hence, an advantage of biotic methods is that, unlike abiotic techniques, they are able to take into account the influence of some of these ambient conditions. The abiotic methods are perhaps better considered as providing only a 'potential' bioavailability. It seems reasonable, therefore, to calibrate abiotic methods against biotic methods in which the influence of ambient conditions has been eliminated. This allows standardisation of the biotic assay conditions, as with the CDM assay, and has the advantage of being simpler compared to reproducing ambient conditions in the incubation vessel. Caution must be exercised in the application of any laboratory measure of 'potential' bioavailable Fe/Mn to field conditions.

Sample disturbance and sample preparation must also be given careful consideration in the use of any of the methods. Particle size and available surface area have been found to influence bioavailability of iron oxyhydroxides (Banfield and Hamers, 1997; Roden and Zachara, 1996) and are likely to be altered by compaction during transport or preparation methods such as disaggregation. Abiotic methods of determination will likewise be influenced by changes of particle size or surface area that impact availability of surface active sites to reagents.

Nine abiotic methods of determining bioavailable Fe/Mn have been listed above. There is no clear line of distinction between bioavailable and biologically recalcitrant Fe/Mn oxides from the point of view of mineralogy. However, there is a consensus that less crystalline forms (e.g. amorphous iron oxyhydroxides) are more bioavailable than more crystalline forms (e.g. magnetite) (Lovley et al., 1993; Roden and Lovley, 1993). Therefore, a possible, if relatively crude, criterion for selecting a suitable abiotic method of determination would be that it extracts a minimum of magnetite.

- On the basis of this criterion, extraction using 5 M HCl and Tamm's reagent can be eliminated, since they have been found to extract significant fractions of magnetite.

- Lovley's hydroxylamine method is claimed to be an advance on Chao's version so the latter can be eliminated from consideration, although Lovley found that his variation still failed to extract all of the amorphous Fe.

- The Cr^{II} reagent is reported to be unstable and too aggressive and is eliminated for this reason.

- Extraction by Ti-Citrate-EDTA-$NaHCO_3$ is unsuitable since it is reported to extract substantially larger fractions of hematite and goethite compared with 0.5 M HCl.

- Heron's Ti-EDTA method is reported to extract a well-described and appropriate fraction of Fe/Mn minerals and has the added advantages of ease of quantification of the reducing agent and decreasing concentration of reducing agent to a level low enough for an appropriate quantification of reduction (Heron et al., 1994a).

Thus, consideration of the relative advantages and disadvantages of the various proposed abiotic methods results in a short-list of four extraction methods which merit further investigation: dilute HCl, hydroxylamine (acidic conditions), 0.008 M Ti^{III} – 0.05M EDTA and anthraquinone-2,6-disulfonate oxidation. None of these can yet be regarded as having become established as a standard or recognised procedure, so further appraisal is desirable to address their practicability, reliability, cost and correlation with standardised biotic assays.

5.9 Summary

None of the geochemical parameters of interest to the current study has a universally accepted standard method for determination, but the picture is clearer for some than for others.

The two parameters of most immediate concern to the Environment Agency and the groundwater contamination assessment community, CEC and f_{OC}, both have experimental methods which although not universally standard, are well established and can be recommended as the method of choice for future determinations. The availability of reference materials and proficiency schemes is better developed for f_{OC} than for CEC.

Techniques for measurement of carbonate, clay and free metal oxide contents, and specific surface area can also be recommended with some confidence. Although these parameters are not yet so widely used in modelling and risk assessment as CEC and f_{OC}, if they are to be used in future models it is desirable that any data generated should be produced using consistent methods. In a geochemical context some of these measurements are currently made only during research investigations, although they may be regular measurements in other fields (e.g. clay content in a geotechnical context). The analytical behaviour is mostly well understood and the methods proposed can be accomplished using equipment which is commercially available. The availability of reference materials and proficiency schemes is variable, depending on the parameter.

Table 5.2. Summary of recommendations for preferred experimental methods of determining geochemical properties. Fuller discussion provided in main text.

Parameter	Preferred experimental method	Standard reference materials
Cation exchange capacity	Modified British Standard double displacement method using pH-buffered $BaCl_2$-triethanolamine.	Few. 4 Chinese soils
Organic carbon content	Dry combustion (450°C)	Selection of reference materials and published reference values available. NAPT proficiency scheme.
Carbonate content	Dry combustion	Published values for reference materials. WEPAL and GeoPT proficiency schemes.
Clay content	Optical particle-size analysis	Standards available for validation of particle size analysis, but not for clay content of geological formations.
Free metal oxide content	Dilute acid extraction	No formal reference materials. Some round robin samples available.
Pyrite content	No standard method. Analysis mostly research based.	None available
Bioavailable Fe/Mn	No standard method. Further research required to evaluate short-list of suggestions. Simple dilute acid extraction has some potential benefits.	None available

Further research work is needed before recommendations can be made for standard methods for determination of pyrite content or bioavailable Fe and Mn. Unfortunately direct laboratory work to evaluate the methods will necessarily be intensive and time-consuming and is beyond the scope of the current project to development a geochemical properties database and manual. Given the particular interest in bioavailable Fe and Mn as controls on contaminant transport and natural attenuation, additional work to establish a standard method for analysis and a basis for interpretation of bioavailable Fe/Mn measurements is desirable.

A summary of the recommendations concerning each parameter is presented in Table 5.2.

Work could begin immediately on a set of new consistent measurements of those parameters which do have established standard methods, including CEC and f_{OC}. As discussed previously there is no over-riding reason why archived core from the BGS core store could not be used for these measurements in the absence of freshly drilled material. In addition it would be worthwhile to:

- Demonstrate the reliability of the CEC method for materials with high carbonate contents.
- Establish a recognised reference material for CEC determination. This could be a joint venture, supported by both BGS and the EA. Participation of other organisations might also be beneficial.
- Support further research on bioavailable Fe and Mn to establish a recognised, reliable and reproducible method for analysis. The method should if possible be simple and cheap to perform to wide uptake. It would be most appropriate to involve one of the University Research Groups in this work.

6. APPROACHES TO ESTIMATING PARAMETERS FROM INCOMPLETE DATA

6.1 Introduction

Descriptions of soils or aquifers are typically supplied to a contaminant-transport modelling program either in the form of a grid of values of the various properties (porosity, transmissivity, K_d etc) or as the spatially-averaged value for the properties for a particular unit. A question that always arises is how to derive this type of information. Given the overall paucity of relevant direct measurements evidenced in the preceding sections of this report, some assumptions and extrapolations need to be made. Below we discuss different approaches to this problem and the nature of the assumptions involved.

To be worthwhile, the approach adopted needs to capture something about the specific environment of interest but it should also make use of 'the science base' – an understanding of the processes involved – as far as possible. This will make interpolation to new areas more reliable. For example, if we had data for the transport of Zn through an aquifer but not for Pb, we might be able to make use of the Zn data to estimate the transport of Pb. But first we would have to estimate the likely mechanisms controlling the retardation of the two chemicals. If they were the same – most likely cation exchange on clays or sorption to oxides – then we could extrapolate accordingly by adjusting the appropriate binding constant or 'log K' for the reaction based on published studies of the sorption of the two chemicals. This adjustment is likely to be greater if sorption on oxides is involved than if cation exchange is involved since sorption on oxides is more pH-dependent.

There are also likely to be 'adjustments' to be made because the best available literature data may have been obtained under conditions somewhat different from those of interest, e.g. rather than true adsorption data, perhaps only data some kind of selective extraction results (e.g. HCl extractions) might be available.

In essence, we combine the available field information (here some observations on Zn transport and aquifer properties for Zn binding) with our general knowledge about how chemicals behave in the environment. Generic databases are an important part of this approach. Such databases include thermodynamic databases (solution speciation, redox reactions, mineral solubility, sorption, octanol-water partition coefficients, etc.).

This approach has the advantage in that we might be interested in the question of what happens if the pH of a soil drops by one pH unit say and we have no information about the behaviour of Pb or Zn under these more acidic conditions. Then we can use our knowledge of the pH-dependence of the underlying processes – if cation exchange on clays is the dominant sorption process then this will show relatively little pH dependence but if sorption to oxides is dominant then this will show much greater pH dependence. We can adjust our 'log K' appropriately.

If there was a small amount of site-specific information about the pH dependence of Pb sorption available, then this could either be used to refine the process-based model or could be used to derive some statistical relation between log K and pH, for example by linear regression. Which method is likely to be most reliable is hard to say but as more information becomes available and as the understanding of the underlying processes improves, the process-based approach is likely to prove more efficient since it is able to use a broader range of 'data' (knowledge) to constrain the parameter values.

Taking this example forward, if there were no information available about Zn mobility then our task would be even more difficult. In this case, we might know from our 'aquifer properties database' that there in the area of interest there was so much clay and so much iron oxide in the aquifer. We could then resort to generic models of Pb sorption by clays and oxides. If we know nothing about the properties of the aquifer in the area at all, then we would have to assume some average value for the aquifer over the whole country, and so on.

Such 'blind' modelling inevitably involves many assumptions and extrapolations and the uncertainties in the transport estimates are likely to be large. It relies on being able to identify the key processes involved, having a sound understanding of them at a quantitative level, and having software and modellers available to make the necessary predictions. Nevertheless, as our basic knowledge of the underlying processes improves and their capture by modelling software increases, then so will the reliability of predictions. Such an approach can play a particularly useful role in making 'what if?' predictions at a generic level. This may be all that is required.

The problem of predicting parameters for chemical transport in the absence of site-specific data can be divided into categories, in the first instance, according to the level of information which is available:

- *Spatial infilling*: capturing site-specific, geographically-based information about the property of interest existing from nearby areas and interpolating that to the area under consideration;

In the absence of significant information about the parameter of interest, either at the study area or nearby, then purely spatial infilling is impossible and *chemical infilling* is required. Spatial infilling is always necessary to some extent but clearly chemical infilling is the more challenging of these two tasks since it involves an element of spatial infilling as well. Chemical infilling can be further subdivided according to the conceptual approach used to tackle the problem:

- Proxy measurements: direct measurement of an easy-to-measure parameter which can be interpreted to predict the harder-to-measure parameters of interest (clearly sample material must be available for this approach);

- Correlation-based predictions: application of statistical or regression techniques to other known measurements of parameters not directly related to the geochemical properties;

- Process-model based predictions: estimating parameters (physical, chemical or microbiological) using assumptions about the underlying processes involved and (where available) knowledge or estimates of other relevant properties.

There can be overlaps between any or all of these approaches. For example, new measurement of proxy parameters could provide further data used for regression analysis, or knowledge of a process model could be used to constrain the scope of a multiple regression analysis. However, the merits of each approach are different. They are discussed in more detail below.

6.2 Spatial infilling

It is impossible to measure the properties of a soil or aquifer at all locations of interest – which may include 'everywhere' if a spatially-averaged property value is required – and so some form of interpolation or extrapolation from known locations to unknown locations is required. There are many ways of doing this, most of which use a weighted-average of the value of the property at nearby locations ('nearest neighbour weighting'). It is not unreasonable to expect that 'nearby' samples should contribute more to the estimated property value than distant values, although if the nearest sample is already very distant then this might not necessarily be the case. Clearly the definition of 'nearby' and the choice of how the weighting varies with distance is important and will depend on the nature of the spatial variability of the property and the approach adopted.

The spatial variability of soil or aquifer property is best quantified by a systematic study of how the property varies from one point in space to another. This may involve grid sampling, stratified random sampling or some more sophisticated sampling scheme. Clearly the greater the sample density, the greater the information available and the greater the ability to interpolate to unknown points with confidence. Various methods have been used for spatial interpolation (Venables and Ripley, 2002). These include:

(i) *Trend surfaces* fitted by polynomial regression. The 'degree' of the polynomial can be increased to provide greater resolution but such global surfaces tend to give large errors at the margins of area;

(ii) *Local trend surfaces* can be used to avoid the problems of global surfaces. This involves either fitting a polynomial to each predicted point based only on the nearby data points (loess fitting) or by Dirichlet tessellation and the associated Delauney tessellation (tessellation is the process of dividing an area into 'tiles', each of which is associated with a data point and includes all points nearer to that data point than any other);

(iii) *Kriging* is based on the use of the variation of the covariance between pairs of points as a function of their separation for estimating the weights to be applied to nearby points when calculating the value of a predicted point from neighbouring data points (kriging). There are many forms of kriging, the simplest of which assumes a constant trend surface over the area of interest.

The extent of smoothing varies between the methods and can also be varied with a given method by adjusting the implicit model or assumptions. An important characteristic of kriging is the extent of the 'nugget' effect – this is the estimated covariance at zero separation which, if the underlying processes are smooth, should be zero apart from measurement errors. Non-zero nugget effects lead to a discontinuity at the data points and in this case kriging does not interpolate but smoothes.

As the distance between adjacent samples increases it is likely that the differences in the value of a particular property at the two points will increase. Eventually when the distance is so large that the there is no similarity between the two locations, then the difference will become more-or-less independent of separation and will reflect the overall variability of the property of interest.

A plot of the variation against separation or distance apart is known as the *experimental variogram* and the study of this kind of spatial variation in the earth sciences is known as *geostatistics*.

Often the variogram reveals various scales of variation from micro-scale heterogenity (over mm) through local variation (over metres), which may arise from, for example, small-scale fluvial processes, to much larger-scale or regional variation (over tens to hundreds of kilometres) reflecting major geological differences arising from tectonics say. All aquifer properties can be expected to show such spatial variability although the nature of the spatial dependence may either show be similar for the various properties or different depending on whether there is a common underlying process or not. Once the variogram has been established, it can be used to help to interpolate the value of a property at an unmeasured location using a weighted average of neighbouring observations. This is called *kriging* and uses the variogram to weight the influence of adjacent observations – the closer, the greater the influence and vice versa but the exact nature of the weights is given by variogram.

Establishing the nature of the variogram is achieved by measuring a property at many locations and then analysing all pair-wise differences in terms of their separation and orientation (direction). Typically it takes at least 100 observations to establish a reasonably reliable variogram. Therefore variogram analysis and kriging are often not worthwhile for many of the small, sparsely-populated geological datasets currently available and a more pragmatic approach along classical lines is probably best, e.g. the average value of the property for the aquifer of interest.

Recent studies have used the Bayesian maximum entropy approach to combine ‘soft’ but extensive data contained within maps with accurate but sparse analytical data to produce. Such an approach may be applicable to the interpolation of aquifer chemical properties.

6.3 Proxy parameters

As we have discussed, one of the major difficulties in obtaining primary experimental measurements of geochemical parameters is the cost and complexity of some of those measurements, even when suitable sample material is available. If an alternative measurement can be used which will allow derivation or prediction of the parameters of interest then this has the potential to extend geochemical understanding and data more easily and economically.

The cost-benefit balance of using proxy experimental measurements has to be considered carefully. If the proxy data are of low reliability and confidence then it may still be a wiser use of resources to measure the true geochemical parameters directly on a smaller number of samples, even when the proxy measurements are very cheap. If the cost of the proxy measurements is only marginally cheaper than direct measurements then again it may be better to direct effort to making true measurements. However, where the proxy measurements generate data of reasonably high value but at low cost then this may be more cost effective than making the traditional measurements on all samples.

Recent literature has suggested that many of the key geochemical parameters such as organic carbon content, cation exchange capacity, clay content, specific surface area or carbonate content can be accurately predicted using the Near Infra Red (NIR) reflectance spectrum of soils and sediments (e.g. Bendor and Banin, 1995; Chang et al., 2001; Confalonieri et al., 2001). The advantage of this method is that the NIR spectrum of the soil is very quick and simple to obtain, at a fraction of the cost of the standard laboratory methods needed to measure the geochemical parameters of interest (see Section 5). In addition, there are possibilities that the measurement can be made in-situ (Sudduth and Hummel, 1993) or by remote sensing (Bendor and Banin, 1994). In order to predict the geochemical parameters of interest, a multiple regression model has to be established which relates the NIR spectra to the parameter in question. The model must then be calibrated using a proportion of the samples that are measured by traditional means. Some further work is needed to establish the validity of the interpretation of geochemical parameters from the NIR measurements before the technique could be applied routinely to preparation of the GPM.

It is also possible to make use of proxy parameters without the need for new experimental work. There are many circumstances where aquifer materials are sampled and characterised for properties that are not directly linked with their geochemistry. An example is that of engineering geology parameters such as the Atterberg limits. There is evidence to show that these parameters can be related to geochemical parameters such as CEC and organic carbon content (e.g. Dejong et al., 1990; Dejong et al., 1992; Petersen et al., 1996) and can thus be used in a similar manner to the NIR spectra as proxy variables for prediction of geochemical properties.

There are a number of ways in which the geochemical parameters of interest can be estimated from their proxy counterparts.

There is a purely statistical approach that has been shown to be quite successful for a variety of applications (e.g. Walczak and Massart, 2001a; Walczak and Massart, 2001b). These techniques, however, do not provide any insight into which of the proxy variables is contributing to the predicted properties. This is a ’black-box’ methodology in which the propagation of errors into the predicted variable could be difficult to follow.

A better option is to use multivariate regression techniques such as Multiple Linear Regression, Principal Component Regression and Partial Least Squares. Although the final model is entirely empirical, the diagnostic statistics of each of these methods clearly shows how each of the proxy variables contributes to the final prediction of the parameter of interest and the error on the prediction can be clearly defined. This allows the model to be validated by checking the importance of predictor variables with theoretical first principles. There are many examples of this type of approach in soil and sediment applications (e.g. Bengtsson and Ekere, 2001; Brubaker et al., 1992; Goldberg et al., 2000).

Various procedures are available for using basic chemical information to make inferences about the value of some unmeasured property. The most general of these is the Quantitative Structure-Activity Relationship (QSAR) approach which establishes the relationship between the structure or composition of a compound and the activity that the compound displays under various experimental conditions, e.g. solubility, vapour pressure (Eriksson and Hermens, 1995). This approach is widely used in organic chemistry to estimate unmeasured physical and chemical properties of organic compounds (e.g. toxicity, soil sorption properties) from a knowledge of their chemical structure (e.g. hydrophobicity, molecular weight, electronegativity, density) and the behaviour of similar compounds. The use of the octanol-water coefficient to estimate the solubility of a wide range of organic chemicals is well known (Appelo and Postma, 1993). There are too many organic compounds to measure everything for all of them and so the QSAR approach is important.

A variant of the SAR approach (indeed a forerunner of it) is the Linear Free Energy Relationship which uses a plot of the standard free energy of a reaction, ΔG, for a series of related compounds against some chemical property related to the structure of those compounds, e.g. molecular size or ionic radius. Since ΔG is directly related to the equilibrium constant, $\log K$, of a reaction, this provides a way of interpolating the $\log K$ for unknown solutes from known values for other, related solutes.

For example, Dzombak and Morel (1990) used it to estimate the sorption constants for anions on hydrous ferric oxide (HFO) when no reliable data were available. It makes use of the known similarity in the stability of surface complexes between different anions on HFO to constrain the values for the unmeasured ones. The same approach has been used by Tipping (1998) and Milne et al. (in press) for estimating metal binding parameters to natural organic matter. A similar approach could in principle be taken for soils and aquifer materials. However, the LFER approach is not an absolute predictor but rather a good way of interpolating unknown parameters from the known parameter values of a number of related compounds.

The most scientifically sound method for predicting geochemical parameters from proxy variables is through theoretical modelling where the exact physico-chemical processes relating the proxy variables to the geochemical parameter of interest are mathematically modelled (e.g. Benedetti et al., 1996; Ganguly et al., 2001). This has the advantage of having a sound scientific basis for the prediction but, in practice, many of the relationships are very complex and poorly understood giving limiting the use of the model. In some instances, these problems can be alleviated by combining theoretical and empirical approaches.

With all of the different methods discussed here it is necessary to calibrate (in the case of regression models) or validate (in the case of theoretical models) the predicted geochemical parameter of interest against laboratory-based measurements. The chosen method of prediction ultimately will depend on the parameter to be predicted and the nature of the proxy variables that are available.

6.4 Process modelling

Here, the aim is to use our existing knowledge of chemistry to help to infill unknown parameters. This approach differs from the purely statistical and spatially-orientated approaches outlined above which do not explicitly take into account any chemical principles like mass action, mass balance and the similarity in chemical behaviour between different chemical compounds. Of course, the chemical approach may also involve some statistics, e.g. optimization.

Frequently, an established modelling package such as PHREEQC is used. For example, by assuming the composition of an aquifer material, and using speciation model to calculate the adsorption of a component according to an assemblage of individual adsorption models, it is possible to calculate an effective K_d value for the bulk material. The sophistication and precision of the calculations are improved with increasing knowledge, and hence decreasing assumption, about the proportions of the composition used as input parameters for the speciation model. The processes which can be considered, and the way in which they are used in PHREEQC were described in fuller detail in Section 3.

6.5 Summary

Some of the methods discussed here are still considered to be research topics and would require development, which is outside of the scope of this current project. However, prediction methods based on regression are tried and tested and could be used for some simple predictions where data is unavailable. In particular, given the large amount of data available on Atterberg limits of different aquifer materials, a small scale trial of prediction of CEC and organic carbon could be carried out to establish the value in filling in sparsely populated areas of the GPM.

7. DEVELOPMENT OF GEOCHEMICAL PROPERTIES MANUAL

7.1 Prospects for delivery of meaningful manual

During the consultations carried out during this scoping study there was widespread support for the concept of a Geochemical Properties Manual. It was clear that, although there are not as many data as might have been hoped, there are significant data available. The data which do exist are distributed between a variety of organisations and there are no meaningful compilations currently available. A completed GPM can be expected to be of real value and is likely to be used by staff on both the regulatory and operational sides of groundwater protection and waste management activities. It is, therefore, certainly worth pursuing the objective of developing a GPM.

Given the amount of existing primary data for the geochemical properties of the aquifers and other formations in the UK it should be realistic to complete a fully comprehensive, evaluated compilation of all the existing data within a 3 year timescale and within the likely available funding limits. Further details of exactly how this might be achieved are discussed in the sections below.

The counterpoint of the possibility of achieving a comprehensive compilation of existing data is that the geospatial coverage will be far from comprehensive. Many of the parameters have very sparse data and even the most frequently measured, CEC and f_{OC} show major gaps in the geographical distribution and data density. The patchy coverage would represent the major limitation of the GPM if a programme of gap-filling by new measurements of the parameters were not implemented to run alongside the data-compilation programme.

In view of the multiple activities required to produce the GPM as a valuable reference tool and resource, it would be both sensible and practical to follow a phased programme of development. The next stage should concentrate on trying to complete compilation of the existing data. With that in hand attention could be progressively transferred first to evaluation of the quality and coverage of that existing data, then to addressing the problem of missing data by new experimental measurements. Ultimately this could lead to developing new more sophisticated tools for predicting missing data from knowledge of other conditions or parameters. More detailed suggestions of what the next phase should contain are presented in Section 7.3 below.

7.2 Possible nature and presentation of manual

The previously produced manuals of Aquifer Physical Properties comprised both printed reports and data CDs. The printed volumes provide critical discussion and interpretation of the data, ordered by geological formation. The data CDs provide a simple GIS application allowing generation of selected geological map segments with the distribution of data points superimposed. Selecting individual points from the maps allows the original data to be retrieved. This format was relatively successful and accessible but both the printed and CD versions suffer the major disadvantage that they are fixed snapshots of the available data, frozen at the time of publication, and therefore become progressively out of date as new measurements are made. It is also necessary to note that software and IT capabilities have developed significantly during the last five years since production of the Physical Properties Manual.

The underlying concept of the GPM is that there should be a digital and geospatially referenced data compilation, preferably with a method of providing a geographical visualisation of the data. Three possible methods of delivering this vision have identified.

(i) The simplest approach would be to provide an application which builds a small amount of custom code onto a commercial distributable viewer for a GIS package. This approach could be implemented fairly rapidly and with low development costs, but the way in which the data could be visualised would be constrained by the capabilities of the commercial application.

Distribution of the completed GPM would be limited in the same way as the previous Physical Properties Manuals by providing a fixed snapshot dataset.

(ii) More complex would be to build a fully custom visualisation application (perhaps using VBA). This would provide a potentially more flexible application, but would require considerably more effort to develop. It could still have the limitation of providing data at a fixed time point.

(iii) The most sophisticated and forward-looking approach would be to develop an internet based delivery mechanism with controlled access to the data. The technology to achieve this now exists and is becoming more robust. The major advantage would be the opportunity for dynamic data updating. The source database could continue to be developed and populated with new data, which would become available to users immediately.

It is proposed that development of the GPM should proceed with the intention of providing an internet based application for accessing the data. As the fully working application may take some time to develop, it is also proposed to use the first, simplest option of an augmented commercial viewer in conjunction with the plan to develop internet access. The simpler option is based on existing applications and could be fully operational within the early stages of Phase 2. The working prototype manual could then be used to view and visualise the evolving datasets to aid decisions about where new experimental measurements should be made at the same time as preparations are made for the production of the final internet application.

One further factor to be considered during development would be integration of the Physical Properties data with the Geochemical Properties data into a single software application. This should be pursued if data modelling (to be carried out at the beginning of Phase 2, below) shows integration to be a viable practical option which would not excessively divert resources from population of the geochemical core of the GPM.

7.3 Outline work programme for Phase 2 and beyond

Phase 1 of the project has established that there is a widely recognised need for, and general underlying support for, the preparation of a Geochemical Properties Manual. Phase 2 will be to begin the work of preparing a manual in earnest. The geographical and geological coverage of data already available is variable, with some important gaps. Furthermore many of the data are distributed in different organisations and reports and are not easily accessible. Phase 2 of the project should address these problems by establishing long-term management structures and mechanisms for the capture of geochemical properties data, and by beginning a programme of new experimental measurements.

7.3.1 Phase 2

Anticipating that Phase 2 of the project will have a duration of one year and an overall budget in the region of £100k, then the following specific objectives should be achievable:

(i) Establish a working database and GIS application for data visualisation and analysis;

(ii) Enter known pre-existing data into the data base;

(iii) Complete consultation with industry sources to identify additional existing data;

(iv) Establish a mechanism for routine capture of future data;

(v) Carry out new experimental measurements of CEC and f_{OC} to address highest priority weaknesses in existing data coverage;

(vi) Establish preliminary distribution profiles for the available data.

The work required can be divided into five main tasks, detailed below.

Task 1. Construction of database application

Professional data management staff from BGS the Information Systems discipline will be employed to design and implement a database and supporting application software.

- Data modelling. The current and possible future uses of the data will be assessed in order to design a robust relational data model which will avoid redundancy, enable efficient querying and data retrieval and which will allow flexibility for future extension or changes in application. In order to avoid replication of effort or data, where BGS already hold relevant geochemical properties data within other programme areas, the design may include use of or links to the existing data tables.

- Database construction. The identified structure will be constructed under Oracle and integrated where possible with other relevant BGS database structures such as WellMaster. This should allow the geochemical properties data to be view in relation to, for example, lithological, aquifer physical properties or borehole record data.

- Application development. Two principal applications will be developed. The first, probably under Microsoft Access, will be to enable efficient but rigorous processing and entry of existing holdings or newly obtained data. The second, probably using ArcView, will be a GIS interface to facilitate viewing and retrieval of the data on a geographical or geological basis

- The database and applications will include audit tracking to ensure that the individual data points used in reports, maps or interpretations can be precisely identified. This will prove an important tool for version control of reports or analyses. It will ensure that propagation of any errors which are identified can be followed and corrected.

The effort involved in establishing the correct data structure and visualisation tools at the outset of the project will represent a worthwhile investment. It will underpin all subsequent data collection and analysis throughout all stages of the project and will provide a functional, searchable prototype of the Geochemical Properties Manual right from the early stages of the project, even though the underlying data may still be rather scarce. It will also facilitate any future translation of the database and manual to alternative formats, for example to an internet based access

Task 2. Data capture

Significant progress was made during Phase 1 in establishing the extent and nature of existing data. This task will complete the process and try to verify that all available relevant data have been identified.

- Contacts with consultancies and landfill or contaminated land concerns during Phase 1 produced a low yield of hard data for inclusion in the manual within the timescale of the Scoping Study, although there was a general interest and willingness to co-operate. Further effort will be spent pursuing leads and contacts established during the Scoping Study.

- In cooperation with the appropriate EA staff, a mechanism will be established for trying reliably to capture all new geochemical data which are submitted to the EA regions and areas as part of site investigation reports or impact assessments (e.g. Regulation 15 reports for landfill sites).

- Searches of the scientific literature and overseas data compilations will be extended.

Geochemical properties data for UK formations will be included in the databases. Data from overseas will be assessed to determine whether they provide useful additions to the data or understanding included in the UK manual. Consideration will be given to the use of easily available proxy data for prediction of parameters when primary measurements of geochemical properties are not available.

Task 3. Database population

The existing data holdings identified during Phase 1 will be checked, cleaned if necessary, and entered into the newly created database.

- Source information and metadata will always be included if possible.

- The confidence associated with all data will also be evaluated and an assessment of uncertainty recorded in the database.

At the end of the phase, all existing BGS and EA data, together with the new measurements discussed in Task 4 below, should have been successfully processed and be available for querying.

Task 4. Data analysis

Once the database has been populated it will be possible to start to identify characteristics of the data distributions. Simple summaries of the spatial (geographical and vertical) variation of the parameter values, at lithological, aquifer or local scale will be prepared. These will provide first estimates of the appropriate use of the information in the GPM, and also will help to inform the strategy for obtaining additional data. The task will include an assessment of the effectiveness of estimating missing data from proxy parameters.

Task 5. New analytical measurements

Laboratory measurements will be carried out to obtain new data for those areas or formations identified as being the most serious and urgent omissions or weaknesses in the existing data coverage.

- Although several other parameters are being considered during the compilation of the manual, the laboratory work in Phase 2 is likely to focus almost entirely on additional measurements of CEC and f_{OC} as these are that data needed most urgently for use in the EA's existing preferred risk assessment models.

- As a preliminary estimate, approximately 200 measurements each of CEC and f_{OC} may be possible during Phase 2.

Raw material for the measurements will be obtained from the BGS core archive or by agreement with other accessible sources or site investigations; no new drilling or sampling work will be carried out by this project. The choice of samples to be analysed will be made in consultation between the EA and BGS through the Project Steering Group.

7.3.2 Beyond Phase 2

At the end of Phase 2, the project should have reached a position where a working geochemical properties manual is in place; consideration of historical and existing data has been largely completed and handling of newly generated data is routine. Subsequent phases should thus be able to focus on extending the programme of new experimental measurements, on description and interpretation of the range and spatial variability of the compiled datasets and on preparation of the manual for publication and possible internet delivery.

A detailed programme for subsequent phases should be developed during the course of Phase 2. The programme will need to include:

- Preparation of a critical interpretation of the data providing guidance on the level of confidence which can be applied when the data are used in modelling or risk assessment studies.
- An enhanced experimental programme to provide high standards of consistent data coverage, across all important geological formations for the two most urgently required parameters (CEC and f_{OC}) and as far as resources permit for the other parameters of interest. The programme should be tailored taking account of the detailed patterns of data availability which emerge from populating the database with the existing data during Phase2.
- Conversion of the development versions of the database and visualisation application to a format capable of providing access to, and graphical presentation of, the data via the internet.

7.4 Recommendations for further work

The scoping study has also identified several areas in which it is considered that further work would be highly desirable, although the work does not fall, or would not be achievable, within the remit of the GPM project as currently defined.

- Research into the effectiveness and selectivity of laboratory methods for determination of bioavailable Fe and Mn content in geological materials. Establishment of a recommended standard method and an understanding of the significance of the measurement.
- Evaluation of laboratory methods for determination of pyrite content in geological materials. establishment of a recommended standard method.
- Preparation of an inter-laboratory reference material or materials for determination of cation exchange capacity of geological materials. More than one would be required for setting up a proficiency testing scheme for laboratories.
- Investigation of an alternative to the flawed, but widespread, use of $K_d(NH_3)$ as a single-parameter for assessing the attenuation potential of a material.
- Further evaluation, validation and application of techniques for gap-filling and predicting geochemical parameters from proxy data.

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APPENDIX 1. METADATA CATALOGUE OF EXISTING DATA

Table A1.1. Distribution and lithostratigraphy of carbonate samples from the BGS Geotechnical Database

County	No of samples	Lithostratigraphy		Quaternary/Soils
		Group	Formation	
Dorset	3	Lias Group	Lower Lias	Alluvium
			Dyrham Formation	River Terrace Deposits
Essex	390	Chalk Group	Upper Chalk	Head
		Thames Group	Bagshot Formation	Estuarine Alluvium
			London Clay	Tidal Flat Deposits
				Brickearth
Greater London	67	Thames Group	London Clay	
			Harwich Formation	
		Chalk Group	Upper Chalk	
		Lambeth Group	Reading Formation	
			Woolwich Formation	
			Thanet Beds	
Kent	219	Chalk Group	Upper Chalk	Alluvium
			Middle Chalk	River Terrace Deposits
			Lower Chalk	Head
			Gault Clay Formation	
Oxfordshire	9		Gault Clay Formation	
Wiltshire/Avon	10	Lias Group	Lower Lias	
			Bridport Sand Formation	

Table A1.2. Distribution and lithostratigraphy of organic carbon content samples from the BGS Geotechnical Database.

County	No. of samples	Group	Formation	Quaternary/Soils
Avon	48			Estuarine Alluvium
Buckinghamshire	40	Thames Group	London Clay	Glacial Deposits
		Lambeth Group	Reading Formation	
Cheshire	48	Mercia Mudstone Group	(Middle Keuper Marl)	Till
				Alluvium
				Glacial Sand & Gravel
Derbyshire	1	Mercia Mudstone Group		
Dorset	8	Lias Group	Dyrham Formation	
		Lambeth Group	Reading Formation	
East Sussex	14		Tunbridge Wells Sand Formation	Alluvium
			Ashdown Formation	
Essex	281	Thames Group	London Clay	Estuarine Alluvium
			Bagshot Formation	Head
		Lambeth Group	Woolwich Formation	River Terrace Deposit
			Laminated Beds	Alluvium
			Upnor Formation	Peat
			Reading Formation	Tidal Flat Deposits
				Brickearth
Gloucestershire	1			Made Ground
Gwent	16			Estuarine Alluvium
				Head
				Alluvium
Greater London	299	Lambeth Group	Woolwich Formation	Alluvium
		Thames Group	London Clay	Flood Plain Gravel
			Thanet Beds	
Hampshire	4			Topsoil
Hereford & Worcester	1	Lias Group	Lower Lias	
Hertfordshire	18	Thames Group	London Clay	Channel Fill Deposits
				Alluvium
Kent	258	Lower Greensand Group	Atherfield Clay	Alluvium
			Sandgate Beds	Head
			Folkestone Beds	River Terrace Deposit
		Thames Group	Harwich Formation	Flood Plain Gravel
		Lambeth Group	Woolwich Formation	
			Upnor Formation	
		Wealden Group	Weald Clay	
			Gault Clay Formation	
			Thanet Beds	
Lincolnshire	23	Lias Group	Scunthorpe Mudstone Formation	
			Charmouth Mudstone Formation	
		Mercia Mudstone Group		
			Hydraulic Limestones	
Nottinghamshire	1	Mercia Mudstone Group	Edwalton Formation	
Oxfordshire	10	Lias Group	Middle Lias	
			Gault Clay Formation	

County	No. of samples	Group	Formation	Quaternary/Soils
Staffordshire	138		(Keele Formation)	Till
		Coal Measures	Upper Coal Measures	Glacial Sand & Gravel
		Warwick Group	Halesowen Formation	Glaciofluvial Deposits
		Sherwood Sandstone Group	Chester Pebble Beds	Head
		Mercia Mudstone Group		Peat
				Alluvium
Surrey	12	Lower Greensand Group	Hythe Beds	Alluvium
		Chalk Group	Upper Chalk Formation	
		Bracklesham Group		
Warwickshire	3			Alluvium
				Glacial Deposits
West Sussex	6	Lambeth Group		Brickearth

Table A1.3. Distribution and lithostratigraphy of clay content samples from BGS Geotechnical Database

County	Samples	Group	Formation	Quaternary/Soils
Avon	54	Lias Group	Bridport Sand Formation	Alluvium
			Lower Lias	
Berkshire	74	Lambeth Group	Reading Formation	Flood plain gravel
		Thames Group	London Clay	Brick earth
			Langley Silt Formation	
Buckinghamshire	485	Thames Group	London Clay	Glacial Deposits
		Lambeth Group	Reading Formation	Alluvium
		Chalk Group	Upper Chalk	
		Ancholme Group	Kellaways Formation	
			Oxford Clay	
		Great Oolite Group	Blisworth Limestone	
			Blisworth Clay	
			Upper Estuarine Series	
Cheshire	729	Inferior Oolite	Lower Estuarine Series	
		Mercia Mudstone Group	Middle Keuper Marl (obsolete)	Glacial Deposits
			Lower Keuper Saliferous Beds (obsolete)	Alluvium
			Lower Keuper Marl (Obsolete)	Head
Derbyshire	33	Mercia Mudstone Group		Alluvium
Devon	3	Mercia Mudstone Group		
Dorset	165	Lias Group	Lower Lias	River Terrace Deposits
			Dyrham Formation	
			Bridport Sand Formation	
		Greensand Group		
		Lambeth Group	Upnor Formation	
			Reading Formation	
East Sussex	12		Tunbridge Wells Sand Formation	Colluvium
			Wadhurst Clay Formation	Alluvium
Essex	780	Great Oolite Group	Upper Estuarine Series	Tidal flat deposits
		Lambeth Group	Upnor Formation	River Terrace Deposits
			Reading Formation	Alluvium
			Woolwich Formation	Head
		Thames Group	London Clay	Glacial Deposits
			Bagshot Formation	Brick earth
			Harwich Formation	
			Thanet Beds	
Gloustershire	58	Lias Group	Charmouth Mudstone Formation	Alluvium
			Lower Lias	River Terrace Deposits
Greater London	3885	Chalk Group	Upper Chalk	River Terrace Deposits
		Lambeth Group	Upnor Formation	Alluvium
			Reading Formation	Gravel
			Woolwich Formation	
		Thames Group	London Clay	
			Bagshot Formation	
			Harwich Formation	
Gwent	25	Mercia Mudstone Group	Dolomitic Conglomerate	Glacial Deposits

County	Samples	Group	Formation	Quaternary/Soils
Hampshire	203	Bracklesham Group		Plateau Gravel
		Thames Group	London Clay	Brick earth
		Lambeth Group	Upnor Formation	
			Reading Formation	
		Barton Group	Chama Sand Member	
			Barton Clay	
Hereford & Worcs	6	Mercia Mudstone Group	Blue Anchor Formation	
		Lias Group	Lower Lias	
Hertfordshire	290	Lambeth Group	Upnor Formation	
		Thames Group	London Clay	
Kent	4635	Wealden Group	Weald Clay	Colluvium
		Lower Greensand Group	Hythe Beds	Alluvium
			Sandgate Beds	Head
			Folkestone Beds	
			Atherfield Clay	
		Chalk Group	Upper Chalk	
			Middle Chalk	
			Lower Chalk	
		Thames Group	Harwich Formation	
			London Clay	
		Lambeth Group	Upnor Formation	
			Reading Formation	
			Woolwich Formation	
			Clay with flints	
			Gault Clay Formation	
Leicestershire	74	Mercia Mudstone Group	Cropwell Bishop Formation	Alluvium
			Sneinton Formation	Glacial Deposits
			Gunthorpe Formation	
			Radcliffe Formation	
		Lias Group	Charmouth Mudstone Formation	
Lincolnshire	229	Lias Group	Scunthorpe Mudstone Formation	
			Charmouth Mudstone Formation	
North Yorkshire	28	Lias Group	Redcar Mudstone Formation	
Northamptonshire	81	Lias Group	Whitby Mudstone Formation (Upper Lias)	Glacial Deposits
			Lower Lias	
			Middle Lias	
		Great Oolite Group	Blisworth Clay	
			Blisworth Limestone	
			Upper Estuarine Series	
		Inferior Oolite	Lower Estuarine Series	
Nottinghamshire	38	Penarth Group		Alluvium
		Lias Group	Scunthorpe Mudstone Formation	Head
		Mercia Mudstone Group	Edwalton Formation	Glacial Deposits
			Cropwell Bishop Formation	
			Gunthorpe Formation	
Oxfordshire	9	Lias Group	Middle Lias	
			Lower Lias	
Somerset	92	Lias Group	Lower Lias	

County	Samples	Group	Formation	Quaternary/Soils
			Middle Lias	
			Blue Lias Formation	
			Bridport Sand Formation	
			Charmouth Mudstone Formation	
			Dyrham Formation	
Staffordshire	1861	Warwick Group	Etruria Formation	Glacial Deposits
			Halesowen Formation	Alluvium
		Coal Measures	Upper Coal Measures	Head
		Sherwood Sandstone Group	Chester Pebble Beds	
			Helsby Sandstone Formation	
Surrey	965	Thames Group	Bagshot Formation	Alluvium
			London Clay	Head
		Bracklesham Group		River Terrace Deposits
		Barton Group		
		Lower Greensand Group	Hythe Beds	
			Atherfield Clay	
		Wealden Group	Weald Clay	
			Clay with flints	
Warwickshire	43	Lias Group	Lower Lias	Alluvium
		Mercia Mudstone Group		Head
West Sussex	51	Lambeth Group	Reading Formation	Brickearth
		Thames Group	Harwich Formation	
			London Clay	

Table A1.4. Lithostratigraphy of samples from BGS East Dorset, Shaftsbury and Hampshire grain size database

Lithostratigraphy			Number of Samples
Group	**Formation**	**Member**	
Bracklesham Group		Branksome sand	3
Bracklesham Group	Poole Formation	Broadstone sand	126
Bracklesham Group	Poole Formation	Creekmoor sand	7
Thames Group	London Clay Formation		14
Thames Group	London Clay Formation	Lychett Matrivers sand member	4
Bracklesham Group	Poole Formation	Oakdale clay member	2
Bracklesham Group	Poole Formation	Oakdale sand	125
Bracklesham Group	Poole Formation	Parkstone sand	63
		Unknown	9
Thames Group	London Clay Formation	West Park Farm member	6
Thames Group	London Clay Formation	Warmwell Farm sand member	15
		River Gravel	1

Table A1.5. Distribution of cation exchange capacity (CEC) data held by EA Regions.

Geographical area	NGR	Geological formation	No of data	EA Region
Beaconsfield, Bucks	SU98	Upper Chalk	9 , profile	Thames
Ware, Herts	TL31	Boulder clay	2	Thames
		Upper Chalk	10, profile	
Wrecclesham, Surrey	SU84	Gault clay?	2	Thames
Headley, Hants	SU83	Folkstone beds, Lower Greensand	3	Thames
Redhill, Surrey	SU35	Folkstone beds	1	Thames
		Hythe beds	1	
Hampshirets	SU75	Bracklesham beds	Var	Thames
Offham, Kent,	TQ65	Hythe beds	10	Southern
Canterbury, Kent	TR16	Lower London Tertiaries	13	Southern
Sevenoaks, Kent	TQ51	Gault Clay	5	Southern
Boston, Lincs	TF34	Leadenham Clay	3	Anglian
Arpley, Warrington	SJ58	Clay/silt	12	North-west
		Sherwood sst	range	
Bromborough, Wirral	SJ38	Hydraulic fill	Few	North-west
Carnforth, Lancs	SD47	Salt marsh sed	Few	North-west
Accrington, Lancs	SD73	Accrington mudstone	11	North-west
Calne	SU07	Kimmeridge clay	5	South-west
Stowbridge, W Midlands	SO88	Wildmoor sandstone	6	Midlands
Welford	SP67	Lias clay	3	Midlands

These data are in addition to the systematic measurements of CEC for some 40 selected formations which were made for the joint EA/BGS projects reported by Gillespie et al. (2001; 2000)

Table A1.6. Distribution of fraction of organic carbon (f_{OC}) data held by EA Regions.

Geographical area	NGR	Geological formation	No of data	EA Region
Ware, Herts	TL31	Boulder clay Upper Chalk	6	Thames
Offham, Kent,	TQ65	Hythe beds	7	Southern
Canterbury, Kent	TR16	Lower London Tertiaries	7	Southern
Sevenoaks, Kent	TQ51	Gault Clay	5	Southern
Warrington	SJ58	Clay/silt Sherwood sst	Range range	North-west
Preston	SD54	Glacial drift	Few	North-west
Chester	SJ46	Sherwood sst	4	North-west
Calne	SU07	Kimmeridge clay	5	South-west
Stowbridge,W Midlands	SO88	Wildmoor sandstone	6	Midlands
Evesham, Worcs	SP04	Lower Lias clay	10	Midlands

Table A1.7. Identified existing data for measurements of bioavailable Fe and Mn, both in the UK and overseas.

Geographical area	Geological formation/	No & range of data	Method of determination	References
Wolverhampton	Triassic Sandstone	2 data points 620, 790 μequiv.g^{-1}	Microcosm experiments	University of Sheffield
Wolverhampton	Triassic Sandstone	30 data points 28-176 μmoles.g^{-1}	Ti-EDTA on single core	University of Sheffield
Mansfield	Triassic Sandstone	49 data points 12-255 μmoles.g^{-1}	Ti-EDTA on single core	(Crouzet et al., 1998)
Vejen, Denmark	Galcial meltwater sand with clay and silt inhomogeneities (oxic zone)	20-110 μequiv.g^{-1}	Ti-EDTA on single core	(Heron and Christensen, 1995)
Winterthur, Switzerland	Quarternary glacial fluvial containing 40-60% $CaCO_3$ and silicate minerals	50-150 μequiv.g^{-1}	Ti-EDTA on single core	(Amirbahman et al., 1998)
Bemidji, Minnesota	Glacially deposited, moderately calcareous, silty sand with local lenses of silty material and lenses of coarser sand and pebbles	148 data points c.10-100 μequiv.g^{-1}	0.5 M HCl, 3 days	USGS – (Cozzarelli et al., 2001) (Tuccillo et al., 1999) (Bekins et al., 2001)
Sacramento, California	No info. available	8 data points 9–45 μequiv.g^{-1}	CDM bioassay kit	CDM – (Evans et al., 1999)
Sand Ridge State Forest, Illinois	Pristine aquifer	1 data point 374 μequiv.g^{-1}	Cr(II) reagent	(Barcelona and Holm, 1991)