Groundwater residence time and movement in the Maltese islands – a geochemical approach

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Abstract

The Maltese Islands are composed of two limestone aquifers, the Upper and Lower Coralline Limestone separated by an aquitard, the 'Blue Clay'. The Lower Coralline Limestone is overlain in part by the poorly permeable Globigerina Limestone. The upper perched aquifers are discontinuous and have very limited saturated thickness and a short water level response time to rainfall. Frequent detections of coliforms suggest a rapid route to groundwater. However, the unsaturated zone has a considerable thickness in places and the primary porosity of the Upper Coralline Limestone is high, so there is likely to be older recharge by slow matrix flow as well as rapid recharge from fractures. Measurement of SF_6 from a pumping station in a deep part of one of the perched aquifers indicated a mean saturated zone age of about 15 years. The Main Sea Level aquifers (MSL) on both Malta and Gozo have a large unsaturated thickness as water levels are close to sea level. On Malta, parts of the aquifer are capped by the perched aquifers and more extensively by the Globigerina Limestone. The limited detection of coliform bacteria suggests only some rapid recharge from the surface via fractures or karst features. Transmissivity is low and tritium and CFC/SF_6 data indicate that saturated zone travel times are in the range 15-40 years. On Gozo the aquifer is similar but is more-extensively capped by impermeable Blue Clay. CFC data show the saturated zone travel time is from 25 years to possibly more than 60 years. Groundwater age is clearly related to the extent of low-permeability cover. The $\delta^{13}C$ signature of groundwater is related to the geochemical processes which occur along the flowpath and is consistent with residence time ages in the sequence; perched aquifers<Malta MSL<Gozo MSL. The ^{18}O and ^{2}H enriched isotopic signature of post 1983 desalinated water can be seen in more-modern groundwater, particularly the urbanised areas of the

perched and Malta MSL aquifers. In all aquifers, movement of solutes from the surface travelling slowly through the matrix provide a long term source of groundwater contaminants such as nitrate.

1 Introduction

Groundwater can have a wide range of residence times and knowing the range that occurs within an aquifer is important for understanding both contaminant transport and the sustainability of groundwater abstraction (Cook and Herczeg, 1999). Groundwater residence times on islands can be very short because the recharge area and areal extent of aquifers are limited (Chilton et al., 2000; Hahn et al., 1997; Jones and Banner, 2003; Vacher et al., 1990). Island aquifers, which are often critical for sustaining island water supplies, have limited resources, which can be seriously affected by seasonal variability in recharge (Jones and Banner, 2003; Robins et al., 2002) and are often vulnerable to pollution (Green et al., 1998; Kent et al., 1994; Koh et al., 2005; Leung et al., 2005). On the island of Malta water resources are extremely limited due to the high population density and low recharge, and the aquifers are affected by seawater intrusion and by high nitrate concentrations.

The Maltese islands have been described by the European Environment Agency as having the most widespread groundwater nitrate problem among the EU member states (EEA, 2008). Nitrate-N concentrations in the main aquifer on Malta average 14 mg/L as N, exceeding the 11.3 mg/L limit imposed by the Nitrate and Water Framework Directives (EC, 1991; EU, 2000). Groundwater nitrate appears to be largely due to agricultural activities and animal husbandry. Nitrate concentrations in recharge are assumed to have increased over time and estimating these is important for predicting future changes. Tesoriero et al. (2007) attempted to estimate historical recharge concentrations using current concentrations, groundwater age and excess nitrogen resulting from past denitrification and found that two- to five-fold increases had occurred in four US aquifers since the 1960s.

The timescale of remedial measures to reduce nitrate concentrations in groundwater depends on the residence time of the groundwater in the aquifer. Therefore the results of this study will be key to assessing likely future trends in nitrate concentrations following implementation of management measures by the regulatory authorities on Malta with a view to reducing the input of nitrate into aquifers.

Limestones consist of accretions of microscopic marine organism fossils and mineral precipitation; and coralline limestones, such as those forming the Maltese Islands, are composed of coralline algae (Bosence, 1983; Pedley, 1979). The limestone matrix porosity and the pore structure are dependent on the nature of this source material and subsequent alteration. The matrix is often intersected by fractures. There are two types of fracture porosity: primary or unmodified fractures and secondary porosity associated with karstic carbonate dissolution (Siemers and Dreybrodt, 1998). Development of such karst features in island aquifers can be focused in the saline-freshwater mixing zone and influenced by sea-level changes (Mylroie and Mylroie, 2007). Limestones can act as dual porosity aquifers where there is often both slow groundwater movement through the pores of the matrix and fast movement through fractures and solution features (Barker, 1993; Greswell et al., 1998; Renken et al., 2008). The proportion of slow and fast groundwater flow depends on the nature of the matrix porosity and the size of the pore throats relative to the density and continuity of fracturing or solution features.

Water and soluble pollutants, such as nitrate, can move by both routes, depending on the relative permeability. Where pore throats are very small, some colloidal material or large microbiological cysts are excluded and may move preferentially through fractures. Long travel times may be anticipated in the matrix of both the unsaturated and saturated zones if the porosity is high. Diffusive exchange may also occur as solutes move into or out of slow-moving matrix water from the more rapidly moving fracture water (Barker, 1981).

The water resources of the Maltese islands have been studied over a long period (Tricker, 1977). Water levels in the aquifers respond rapidly to rainfall and the system has been considered to be composed of karstic coralline limestone aquifers (De Ketelaere, 1996), with similarities to those of the Caribbean. However, many Caribbean islands differ from Malta because they have high rainfall, low relief, and a limited volume of storage (Chilton et al., 2000; Farrell and Boyce, 2007). Sapiano et al. (2006) note that in the Maltese islands there is large storage in the sea level aquifers.

On Malta the conventional hydrochemical indices (such as Mg, Sr or Li relative to Ca) for evaluating groundwater residence time in the main aquifers are compromised by seawater contamination (Schiavo et al., 2006). However they still provide useful information and there are a number of other tools that can be applied.

Tritium concentrations in groundwater can be used to indicate aquifer residence time (Plummer et al., 2001; Rademacher et al., 2003; Shevenell and Goff, 1995). Recent work in

Malta by Bakalowicz and Mangion (2003) using tritium has suggested that residence times in the aquifer may be several decades.

Anthropogenic industrial processes have released low but measureable concentrations of CFCs and SF_6 into the atmosphere which can be used as indicators of residence times in the saturated zone (Gooddy et al., 2006; Katz, 2004; Zuber et al., 2005). These tracers are generally well-mixed in the atmosphere, except in some urban areas (Darling and Gooddy, 2007). The technique assumes that exchange between water in the unsaturated zone and the atmosphere is rapid causing equilibrium between CFC and SF_6 concentrations but that once in the saturated zone no further exchange takes place. CFC and SF_6 measurements in groundwater therefore give an indication of the residence time in the saturated zone only and groundwater travel times in the unsaturated zone are additional.

The application of ^{14}C dating to residence time estimation is compromised by carbonate dissolution. Here we use the carbon stable isotopic ratios, $^{13}C/^{12}C$, as a qualitative indicator of this dissolution process along the flowpath (Gonfiantini and Zuppi, 2003; Kloppmann et al., 1998; Schiavo et al., 2006). These ratios in groundwater carbonate can be valuable in combination with other indicators. Emblanch et al. (2003) use $\delta^{13}C$ and $\delta^{18}O$ data for hydrograph separation of spring outflows in a karst aquifer.

In this study existing data providing an indication of groundwater residence times and new data (measurements of CFCs, SF_6, carbon isotopes and coliform bacteria) are combined to develop a conceptual model of the timescale of groundwater flow in the Maltese aquifers.

2 Hydrogeological setting

2.1 Geology and hydrogeology

The Maltese islands are composed of two porous and fractured limestones (Pedley et al., 1976); the Miocene Upper Coralline Limestone (UCL) and the Oligocene Globerigina-Lower Coralline Limestone (GL-LCL) (Figure 1). Both are porous and massive formations, the GL-LCL being particularly uniform over the Maltese islands. The UCL crops out mainly in the north and west of the islands (Figure 1) and varies in thickness from about 30 m on the ridge and plateau areas to 60-90 m in the faulted valleys. The LCL formation is generally up to 210 m thick.

Separating the two limestones is a layer of clayey and marly material known as the Blue Clay Formation, which in places also has the thin Greensand Formation above it. The Blue Clay Formation is 20 to 65 m thick (Pedley et al., 1976), and sufficiently impermeable that the UCL and LCL aquifers are considered to function independently, with the former perched above the latter (Figure 2). However, some groundwater stored in the perched aquifers of the UCL does 'leak' to the underlying Main Sea Level (MSL) aquifer in the LCL (Sapiano et al., 2006).

From a structural point of view, the main island of Malta can be divided into the northern and the central/southern regions separated by the barrier of the Victoria Fault. Thus to the south of this fault, the UCL aquifer is perched vertically above the LCL aquifer separated by the Blue Clay aquiclude. The lower aquifer is in direct contact with sea water resulting in the development of a classic 'Ghyben-Herzberg' lens. The potentiometric head is fixed close to sea level by abstraction from the large public supply gallery network.

The northern part of the island is divided by faulting into a succession of horst and graben-like structures, producing hydraulically distinct aquifer blocks. Such small, broken blocks of aquifer allow little scope for groundwater development and groundwater is mainly used for agriculture and for secondary purposes from small private abstraction sites. At some locations, where the perched blocks are tilted, the Blue Clay formation dips below sea level and the perched groundwater body is in contact with the sea at the coast. More importantly in these areas the UCL is thrust downwards due to faulting. Faulting, sinkholes and local patch reefs partially penetrate the impermeable formation.

The Globerigina Limestone is only locally important as a productive aquifer where it is sufficiently fractured. In some areas it serves to partly confine the underlying LCL but still allowing some downwards flow to the lower aquifer. Fractures are thought to play an important role in groundwater movement; particularly within the marly middle formation, given that this formation has quite a high fracture density where exposed (Sapiano et al., 2006).

On the island of Gozo, the LCL aquifer sustains a 'Ghyben-Herzberg' groundwater system over the whole island, except for a small area in the south-east. Here the Blue Clay formation occurs at sea level because of the effects of local faulting. The UCL crops out in separate areas, producing aquifer blocks sustaining distinct groundwater bodies, which are exclusively used for irrigation. The potentiometric head in the lower aquifer is controlled by abstraction from the public supply network.

The climate of the Maltese Islands is typically semi-arid Mediterranean, with hot, dry summers and mild, wet winters. There is considerable variation in both inter-annual and intra-annual rainfall with a frequent occurrence of low rainfall years and a seasonal scarcity of rainfall in the main tourist season when water demand is greatest. The potential evapotranspiration is high and estimates of effective rainfall vary between 95 and 200 mm/yr (Sapiano et al., 2006). The estimated water balance is shown in Table 1.

Malta is dependent on groundwater for both public supply and irrigation as there is very limited surface water. Public supply sources include both boreholes and ‘pumping stations’. These pumping stations consist of horizontal radiating galleries dug into bedrock at the water table level. In the Malta MSL aquifer the galleries are slightly above sea level and designed to skim freshwater from the top of the lens. Springs in the perched aquifer are not now used for public supply due to poor water quality, but continue to be used for irrigation. Abstraction from a number of sources in the sea-level aquifers has also been discontinued due to high chloride concentrations, predominantly in the northern and southeastern regions of Malta. The available resources cannot meet the current demand and over 50% of water for public supply is provided by desalination (Sapiano et al., 2006). Desalination of seawater by reverse osmosis for public supply was implemented in Malta in 1983 and reached a peak in 1994/95.

2.2 Aquifer properties

The UCL and GL have relatively high primary porosity (Table 2). The primary porosity of the LCL is lower and more variable (Bakalowicz and Mangion, 2003). There are few data on matrix permeability although Bakalowicz and Mangion (2003) suggest that it is generally low. BRGM (1991) report that permeability is higher in unfractured samples from the UCL than the LCL. Flow in the matrix in all three limestones will therefore be slow. Diffusional exchange of solutes between the porous low permeability matrix and faster flowing water in the fracture/fissure aquifer components is likely to have the effect of initially slowing down the rate of contaminant transport through the aquifer, but will also prolong contaminant residence times.

There is very little published hydraulic conductivity or transmissivity data for the Maltese limestones. Values for the LCL are low compared to other carbonate aquifers, although this needs to be offset against the likely thinness of the effective aquifer (Table 2). The UK Chalk is a mildly karstic carbonate aquifer which has similar hydrogeological characteristics to the Maltese coralline limestones. Transmissivity for the Chalk is considerably higher than for the Maltese limestones, although the Chalk aquifer thickness is much greater (Allen et al., 1997). In the UK, higher transmissivity for both the Chalk and the Jurassic limestones is associated with solutional enlargement of fractures. It is therefore likely that in the Maltese limestones transmissivities exceeding 1000 m^2/d will also occur locally where primary fractures have been modified by dissolution. This is likely in both the UCL and LCL where small-scale solutional features have been observed. There are also a small number of currently hydrologically inactive large caves.

Although there are no pumping test data reported for the UCL, the springs are reported to be characterised by high turbidity and bacteriological contamination BRGM (1991). A rapid response to rainfall indicates high transmissivity and suggests that the aquifer is karstic and that rapid groundwater flow is common. The low transmissivities observed in the LCL suggests that it may be less karstic and have lower permeability. However large scale fossil cave development in the LCL at Ghar Dalam indicates that the aquifer is susceptible to dissolution, and the lack of karstic indicators (turbidity, bacteriological contamination etc.) may be a function of attenuation and slow travel times in the overlying GL.

Localised solutional enlargement of vertical fractures is observed in the GL in quarry faces, but with limited horizontal extent. The GL otherwise has low transmissivity. The Middle Globigerina Member is a marly limestone which is likely to have lower permeability than the Upper and Lower. Where the Upper or Middle Globigerina outcrop at the surface, recharge through to the underlying Lower Coralline limestone is therefore likely to be limited by the low permeability Middle Globigerina.

The BRGM survey of private boreholes carried out in 1990 (BRGM, 1991) found that contaminant concentrations, in particular nitrate, varied spatially over quite short distances in some areas. This was ascribed to low pollutant mobility, presumably as a result of the low transmissivity.

2.3 Residence time estimates

Bakalowicz and Mangion (2003) found that the tritium content in rainfall was in the range 2.6 to 11 TU. In the perched aquifer, tritium ranged between 1.9 and 7.4 TU and in the Malta MSL aquifer between 0.2 and 3.1 TU, mainly being below 1.5 TU. These concentrations indicate that the residence time in the MSL aquifer is probably >40 years. Tritium measured at the Fiddien borehole (GW 232 of the present study) suggested that groundwater was recharged to the MSL aquifer around the Dingli-Rabat plateau, possibly through fractures in the intervening largely impermeable beds.

The amount of water stored in the Maltese sea level aquifers is of the order of 1.5×10^9 m^3 (BRGM, 1991). The estimated water balance shown in Table 1 for 2002 indicates that annual replenishment from recharge was low (57×10^6 m^3) compared to the storage, resulting in likely residence times in the order of 26 years. The geological complexity of Malta with its vertically divided sequence of aquifers may limit the amount of recharge to parts of the lower sea level aquifer and help to increase residence times. This is consistent with tritium measurements (Bakalowicz and Mangion, 2003).

Water levels in the perched aquifers and spring flow are reported to respond within a few hours to rainfall events and this may indicate rapid recharge. Water levels in some parts of the MSL aquifers can also respond rapidly. Whilst this may be evidence of rapid recharge it may also be a pressure wave rather than a transfer of water. There is also the possibility that the limited areal extent of these responses indicates that perhaps a few boreholes are providing a conduit for rapid water movement, for example by connecting fractures. Surface water disappears quickly after intense rainfall on LCL outcrops and some rapid infiltration routes are visible, for examples a sink hole in the Wied il-Ghasel valley system.

3 Methods

Fifty groundwater samples were collected from the MSL aquifers on Malta and Gozo and the more important of the perched aquifers on Malta (Figure 1). Samples from the perched aquifers came mainly from springs around the edges of the plateaux and 4 were from pumping stations. In the Malta MSL aquifer samples were from a mixture of pumping stations (taking water from adits or galleries) and boreholes. Boreholes generally terminate well above the base of the freshwater lens. Most had raw water sampling taps from which a sample which had not been in contact with the air could be collected. All samples on Gozo were from boreholes.

At boreholes where chlorination disinfection is used the chlorine was switched off before sampling and field testing of residual chlorine was undertaken to ensure that none was present in the samples. Boreholes not in use for public supply were flushed by pumping before sampling. Unstable parameters (dissolved oxygen and redox potential, pH, temperature, conductivity and alkalinity) were measured at the time of sample collection, and a series of samples were collected for later analysis for coliforms, CFCs, SF_6, stable isotopes, and major, minor and trace ions. Sampling for CFCs and SF_6 required an air tight connection at the sampling point and so excluded springs and boreholes with open discharges and pumping stations with water flow in galleries where groundwater is exposed to the atmosphere. Only one sample was obtained for CFCs and SF_6 from the perched aquifers due to a lack of suitable sampling points.

Currently 13% of the total sewage generated is treated to tertiary standard, disinfected and made available for reuse by agriculture and industry. Samples of treated sewage effluent (TSE) were collected from the main agricultural irrigation storage reservoirs and processed similarly to groundwater. Raw sewage samples were collected from a representative range of urban areas and included community cesspits serving outlying villages. Unstable parameters were not measured on these samples.

Analyses for inorganic parameters, groundwater tracers and carbonate stable isotopes were carried out using the methods shown in Table 3.

4 Results and discussion

4.1 E Coli and inorganic chemistry

The concentrations of E Coli and selected inorganic determinands are shown in Table 4 which also includes a description of the sample sites in terms of source type, aquifer setting and unsaturated zone thickness.

The survival of coliforms in the subsurface is limited, with a half life of the order of 11 to 18 hours (Coombs et al., 1999). Their detection in groundwater is therefore an indication of the presence of a rapid connection between the source of pathogens and groundwater (Morris et al. 2005), This connection can be due to poor sanitary completion of boreholes, e.g. water moving down the outside of the casing, or to rapid groundwater movement through highly permeable media, such as gravels, or through fractures. BRGM (1991) ascribed the lack of coliforms detected to attenuation and slow travel times in the overlying GL.

The perched aquifers are most vulnerable to bacterial pollution. 10 of the 12 samples collected from these aquifers had detectable *E. Coli* and half had concentrations of >300 cfu/100 ml. One of the low results was from the spring (GW 256), in an area of natural vegetation. In contrast, for the MSL aquifer on Malta only 6 of the 24 samples had detectable coliforms. On Gozo the pattern is similar with only 3 out of 14 samples having coliforms. The lack of detection of *E. Coli* at the majority of sample sites suggests that there are few rapid connections between the surface and the main aquifer. An obvious deduction must be that few boreholes in the MSL aquifers intersect a fully connected network of larger solutional fractures between the surface and the sampling point, the water moving through smaller voids where it is stored for longer periods.

.The Na/Cl ratio in groundwater from both the perched and MSL aquifers is about 0.5, slightly lower than seawater (0.556). This suggests that the groundwater chemistry is dominated by the impact of seawater. In the perched aquifers Cl results from sea spray, irrigation with water from the lower aquifers and rainfall, concentrated by evapotranspiration. Sodium and Cl in rainfall are confirmed as being predominantly of marine origin in the region (Aiuppa et al., 2003). Chloride concentrations in the perched aquifers average 265 mg/l and reach 383 mg/l at a site impacted by cattle farming. This is much higher than concentrations observed in carbonate groundwater in Sicily where Cl concentrations averaged 43 mg/l (Fontana et al., 2009) and Barbados where concentrations were 30-50 mg/l (Chilton et al., 2000). The perched volcanic aquifers of the Azores also lower Cl concentrations with a mean of 35.6 mg/l (Cruz and Amaral, 2003). The proximity to the coast may be an important factor as most perched aquifers on Malta are within 2 km of the coast.

The major ion chemistry clearly demonstrates the effect of saline intrusion into the Gozo MSL and to a lesser extent into the Malta MSL. Chloride concentrations in the Malta MSL average 502 mg/l and reach a maximum of 1250 mg/l in the central pumping station. This is mainly ascribed to sea-water upconing. Monitoring wells in the vicinity show the hydraulic head to be less than 1 m and therefore water level drawdown and consequent upconing to be significant. On Gozo Cl concentrations average 870 mg/l and reach 1990 mg/l.

Other ions which could be largely ascribed to seawater include SO_4, Mg, K, Br, F, Sr, B, Li and Rb, and concentrations of these ions follow a similar distribution pattern to Na and Cl. This saline intrusion limits the usefulness of the major ions as signs of contamination as well as indicators of carbonate dissolution. Elements such as Mg, Sr and Li are enhanced relative to Ca during incongruent dissolution and calcite precipitation and can therefore often provide information on groundwater residence time. Data for Mg, Sr and Li are also presented in Table 4.

Calcium and HCO_3 behave differently and Figure 3 shows the relationship between Ca and HCO_3. Bicarbonate is enhanced relative to seawater particularly in the MSL aquifers whereas Ca declines from the perched to the Gozo MSL. The difference in bicarbonate content between the perched and MSL aquifers may be due to the flow conditions; the perched aquifers being largely represented by springs and pumping stations open to exchanges with the atmosphere and with depleted pCO_2 compared to the MSL aquifers mainly protected from atmospheric exchanges by impermeable cover and/or the absence of karst features. An exception to this is GW 241 in the perched aquifer which has the lowest pH in the dataset (6.6) and thus the highest pCO_2. It also has the highest nitrate-N concentration (92.7 mg/l) and these exteme values are ascribed to pollution from anaimal wastes.

4.2 CFC and SF_6 residence time indicators

Estimation of groundwater age and flow mechanisms using SF_6 and CFCs depends on relating these to changing recharge composition. This technique gives ages starting at the time of recharge to the saturated zone. The results of different mechanisms can be represented by a lumped model of SF_6 and CFC-12 concentrations (Figure 4). The dotted line represents piston (matrix) flow. The dashed line is an exponential function representing the accretion of water of different ages along a flowline. The solid line represents binary mixing between old water which does not contain tracers and modern rainfall.

All these models are simplifications of the flow mechanisms as the aquifer is not of uniform thickness, there will be zones of relatively higher permeability and the points of recharge may vary due to less permeable younger strata. In addition further complication is likely through mixing within the well if the screened abstraction area is large (combining flow lines of differing ages). None-the-less, such models can give an indication as to how old the groundwater is in terms of a mean concentration of an 'average' packet of water.

The results for CFCs and SF_6 for groundwater in Malta and Gozo are set out in Table 5 and also plotted on Figure 4. These show groundwaters in Malta and Gozo have quite different histories. For Malta, groundwater in the MSL aquifer is, on average, between 15 and 40 years old. The two sites in the Malta MSL which abstract from beneath the perched aquifer gave groundwater ages in the same range as the other sites in the aquifer. The value from under the perched aquifer on Gozo was towards the lower end of the range. Five of the 23 sites (all on Malta) had concentrations of CFCs in excess of modern rainfall, indicating that groundwater has been locally contaminated, e.g. by refrigerants and these data cannot be used for 'dating' purposes. Results for SF_6 tend to be much less affected by such problems and an age can be obtained.

Flow to boreholes appears to be by a number of mechanisms (Figure 4). Groundwater from the boreholes at GW 232 and GW 246 plots close to the piston flow line. Groundwater from the boreholes at GW 238, 239 and 244 plots along the exponential line. Groundwater at GW 239 was the youngest in the survey. Groundwater from GW 228 and 231, and possibly 240 plot in this area close to the binary mixing line. Results from Gozo show that the groundwater is generally much older (from 35 years old to pre-dating the introduction of CFCs in the 1940s). All but one of the data points, fall on the dashed exponential line.

The results can also be considered in terms of the proportion of mixing of old and modern water. This would suggest that groundwater in the perched aquifer (one sample only) is about 43% modern water, in the Malta MSL between 20 and 50% modern; whilst on Gozo groundwater is between 0 and 35% modern. There is no obvious correspondence between fraction of modern water and coliform concentration for the MSL aquifers.

4.3 Water stable isotopes

The δ^2H and δ^{18}O analyses of waters are shown in Table 5 and plotted in Figure 5. More than 90% of the groundwater samples (46 out of 50) have δ^2H and δ^{18}O values between -28 to -23‰ and -5.3 to -4.3‰, respectively; a range indistinguishable from that reported by Bakalowicz and Mangion (2003) for groundwaters not mixed with seawater. There is no obvious distinction between groundwaters from the MSL and perched aquifers on Malta. The Gozo MSL groundwaters all lie towards the bottom end of the range.

Several waters, however, have δ^2H and δ^{18}O values higher than the main range, and lie along a line extending towards the isotopic composition of seawater (Figure 5). These include a few urban groundwaters from the two Malta aquifers (GW 247, 281 and 285), but mainly the samples of sewage waters and TSE. Based on their chloride contents, none of these groundwater or sewage samples contain more than 5% seawater, and the TSE samples contain not more than 12% sea water (Turekian, 1968). These amounts are not sufficient to explain the elevated δ^2H and δ^{18}O values in terms of mixing between fresh groundwater and normally saline seawater. Instead this suggests the presence of non-saline water with an isotope composition similar to sea water. An analysis of tap water from a coastal hotel confirms that this is probably desalinated water produced by reverse osmosis of seawater (Figure 5). Thus the degree to which the δ^2H and δ^{18}O values of the sewage and TSE waters are higher than those of most groundwater probably reflects the proportion of desalinated water. From detecting desalinated water in the groundwater it is inferred that there has been recharge from the mains water distribution or sewerage systems over this period and that a fraction of the groundwater is less than 15 years old. Many studies have identified mains and sewer leakage as significant contributors to groundwater recharge in urban areas (Lerner, 1986; Garcia-Fresca and Sharp, 2005).

4.4 Carbon stable isotopes

The two main sources of carbon determining the δ^{13}C value of dissolved inorganic carbon (DIC) in groundwater are soil-respired CO_2 and the soil or rock carbonate. For Malta we assume these have typical δ^{13}C values of about -23‰ (Clark and Fritz, 1997) and -1‰ (Knoerich and Mutti, 2006), respectively. Solution of the carbonate by dissolved CO_2 would produce HCO_3^- (the predominant species at near-neutral pH) with expected δ^{13}C values of between about -16 to -11‰ for equilibrium under 'open' or 'closed' conditions, respectively (Clark and Fritz, 1997).

δ^{13}C values for DIC in the range -16 to -11‰ are indeed common for many groundwaters, and a third of the Maltese samples fall within this range (Table 6). What is unusual about the Maltese groundwater, however, is the large proportion of samples having much higher δ^{13}C values, extending up to -3‰. These high values are thought to reflect a process of continued chemical and isotope exchange between DIC and the aquifer carbonate, so that DIC δ^{13}C values progressively increase from about -16 to -11‰ towards about -1‰. Figure 6 demonstrates a clear relationship of increasing δ^{13}C with increasing Sr/Ca ratios, suggesting that the DIC exchange with aquifer carbonate is linked with a process of incongruent dissolution.

We do not know what factors control the rate of this process, but must assume that waters with higher δ^{13}C or Sr/Ca are more evolved, and will therefore tend to be older. This appears to be born out by the relationship between δ^{13}C values and the ages of groundwaters derived from SF_6 analysis (Figure 7). However, in the study by Gonfiantini and Zuppi (2003) the half-lives of the isotope exchange processes in the carbonate aquifers of Cyrenaica, Libya were shown to be several thousands of years. Other studies where dated limestone groundwaters have elevated ^{13}C contents (e.g. Bishop and Lloyd 1990; Gunn et al. 2006) also find this to be a property of relatively old water. This is at variance with the comparatively very young average age of Maltese groundwater. Bearing in mind the complex dual porosity of the Maltese limestones, however, we must accept that the average groundwater age will reflect a mixture of waters of different age, The high Sr/Ca ratios and δ^{13}C values may reflect the presence of an old, highly evolved component of water - perhaps from the matrix porosity - mixed with much younger water.

4.5 Conceptual model of groundwater movement

In both the perched and MSL aquifers on Malta there is some evidence for rapid groundwater movement. In the perched aquifers there is a consistent pattern of detections of faecal indicator organisms and evidence from δ^2H and δ^{18}O of recharge by relatively modern desalinated seawater assumed to be derived from the public supply or sewerage system. In the MSL aquifer ingress of desalinated water is greatest in urban areas on the east side of the island where the unsaturated zone is thinner. Water levels and spring discharges are reported to respond very rapidly to rainfall events, particularly on the perched aquifers, surface water drains away rapidly and there are surface and quarry face solution features.

Evidence from other residence time indicators suggests that groundwater movement may be slow. Firstly there is a thick unsaturated zone in many places since the islands rise to a maximum elevation of 239 m. In the present study the maximum unsaturated zone thickness in the perched aquifers was 115 m and the minimum was effectively zero at springs. On Malta it varied between 35 m and 143 m and on Gozo from 55–125 m (Table 4).

The unsaturated flow rate can be calculated using the approach of Chilton and Foster (1991) using porosity values and effective precipitation. Since the method uses total rather than effective porosity, the calculated flow rates would be expected to be an underestimate, and travel times an overestimate, but the method did give some agreement with flow rates estimated using porewater tritium concentrations. For the UCL an effective precipitation of 142 mm/year (45×10^6 m^3/year (Table 1)) and a total porosity of 41–45 % would give a downwards rate of movement in the matrix of 0.32–0.34 m/year. For the LCL a porosity of 7–22 % would give a rate of between 0.7 and 2 m/year. Migration through the GL is reported to be primarily through fractures but a similar calculation would give 0.35–0.44 m/year for matrix movement. As an example, unsaturated travel time in the matrix for a borehole with

50 m of GL overlying 50 m of LCL (taking the upper values of porosity) could be 113 years in the GL and 25 years in the LCL assuming the upper range of migration.

Secondly for the saturated zone the results for CFCs and SF_6, present a consistent picture of groundwater being, on average, at least 10-15 years old, even in the perched aquifers, with one sample from the Gozo MSL aquifer contained no CFCs at all. These data are in agreement with relative age from $\delta^{13}C$ analysis. These data are consistent with the reported groundwater balance which suggests an average turnover of about 40 years.

The discrepancy between the total residence time for the Malta MSL aquifer indicated by tritium measurements (perhaps 40 years) and that indicated by the sum of the unsaturated zone travel time (decades) and the average saturated zone residence time (15-40 years) has been observed in other dual porosity aquifers, e.g. the Chalk of southern England (Gooddy et al., 2006). It is unclear why this discrepancy occurs.

Our conceptual model for the perched aquifers assumes that the saturated thickness is limited, response to rainfall events is rapid and the existence of rapid pathways is shown by the high detection rate of coliforms. However downwards movement in the matrix is slow and the travel time in the unsaturated zone could be long in the thicker parts of the aquifer and the limited SF_6 data indicates that some water in the saturated zone may be decades old.

The model of the MSL aquifers assumes that:

- the water table is controlled by abstraction and is presently up to only 3 m above sea level in places.
- downwards movement in the matrix is relatively slow, but faster than in the perched aquifers, particularly in the LCL and the travel time in the unsaturated zone is long in the thicker parts of the aquifer
- rapid transport from the surface to the aquifer is limited as indicated by the small number of coliforms detected.

Groundwater in the main aquifer from areas beneath the perched aquifers is of similar age to the rest of the aquifer so may not be static water as has been previously considered. Possible flow mechanisms are slow infiltration through the Blue Clay from the upper aquifer, enhanced recharge at the edge of the Blue Clay or the Middle Globigerina or rapid infiltration along faults or fractures.

Differences between the Malta and Gozo aquifers are due to the amount of Blue Clay, and also Middle Globigerina Limestone cover. In Malta residence times in the saturated zone are in the range 15-40 years from groundwater tracers and in Gozo these are 30-60 years. In this setting it is likely that solutes derived from surface activity, such as nitrate, are retained in porewater and are moving slowly through the matrix, providing a long-term source affecting the aquifer in both the unsaturated and saturated zones.

5 Conclusions

Groundwater in the perched aquifers in the Upper Coralline Limestone on Malta appears to be young, with consistently high concentrations of coliform bacteria. Water levels are reported to respond extremely quickly to rainfall events. However $\delta^{13}C$ and a single age calculated using SF_6 indicate that least a proportion of the water may be several decades old.

Water in the sea level aquifers has a wide range of ages as shown by different indicators. In Malta, tritium data residence time indicators and the recharge/storage ratio suggest an age of several decades. Aquifer porosity data indicate a possible unsaturated zone matrix travel time of over 100 years The proportion of sources without detectable coliforms suggests a limited number of rapid pathways. However, response to rainfall events and stable isotopic evidence for the presence of relatively modern desalinated water suggests that there are also some more rapid routes. This agrees with estimates of percentage modern water.

In Gozo the pattern is similar but the greater extent of lower permeability cover means that the average age is older. Carbonate stable isotopes are consistent with water in Gozo and the centre of Malta having the oldest relative age.

In all aquifers it is likely that solutes from the surface, such as nitrate, are retained in porewater and are moving slowly through the matrix, providing a long-term source and sustained concentrations of nitrate in groundwater. This study is key to understanding likely future trends in nitrate concentrations following implementation of management measures by the regulatory authorities on Malta with a view to reducing the input of nitrate into aquifers.

6 Acknowledgements

The authors are grateful to staff of the Malta Resources Authority without whose effort none of this would have been possible. The authors are also grateful to the technical staff of the Water Services Corporation for assistance and facilitation of sample collection and to private site owners for access for sampling. The authors would like to thank colleagues in the BGS laboratories at Wallingford and NIGL for their contribution, particularly Peter Williams for assistance in sample collection and processing. The project was funded by the Technical Assistance Programme under the Rural Development Programme for Malta 2004-2006. This paper is published by permission of the Executive Director of the British Geological Survey and the Director for Water Resources, Malta Resources Authority.

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Table 1 Estimated water balance for the Maltese Islands for 2002 (from Sapiano et al. (2006))

	Element	***10^6 m^3 /yr***
Inflow	Precipitation	174
	Surface run off to sea	-24
	Evapotranspiration	-105
	Recharge from leaks	12
	Net inflow	**57**
Outflow	Public supply abstraction	16
	Private abstraction	15
	Subsurface outflow to sea	23
	Total outflow	**54**
Balance		**3**

Table 2 Hydraulic aquifer properties of Maltese and UK limestone aquifers (data from Allen et al. (1997); Bakalowicz and Mangion (2003); Cassar et al. (2008))

Parameter	**UCL**	**GL**	**LCL**	**UK Chalk**	**UK Jurassic Limestone**
Primary porosity (%)	41–45	32–40	7–20	34	14.5–19.1
Effective porosity (%)			10–15		
Matrix permeability (m/d)	9×10^{-4}	9×10^{-3} (v)	< UCL	6.3×10^{-4}	1×10^{-4}–0.018
Aquifer hydraulic conductivity (m/d)			35		
Transmissivity (m^2/d)			8–86	410–1800	139–318

(v) = vertical

Table 3 Summary of laboratory analytical methods

Parameter group	**Parameters**	**Method**
Carbonate stable isotopes	$\delta^{13}C$	Preparation as barium carbonate and analysis of acid-liberated CO_2 by dual-inlet IRMS
Water stable isotopes	$\delta^{2}H$, $\delta^{18}O$	Analysis by chromium reduction + EA-IRMS ($\delta^{2}H$) and by dual-inlet IRMS on equilibrated CO_2 ($\delta^{18}O$)
Chlorofluorocarbons	CFC-11, CFC-12	Gas chromatography
Sulphur hexafluoride	SF_6	Gas chromatography
Coliform bacteria	*E. Coli*	Membrane filtration
Alkalinity	HCO_3	Duplicate titrations at wellhead using Hach digital titrator with 1.6 N sulphuric acid and bromocresol green indicator
Major and minor ions	B, Ba, Ca, Fe, K, Mg, Na, total P, Si, SO_4, Sr,	Inductively coupled plasma-optical emission spectrometry (ICP-OES)
Trace elements	25 elements	Inductively coupled plasma-mass spectrometry (ICP-MS)
Anions and ammonia	NO_3, NO_2, NH_4, F, Cl, Br, I, PO_4	Ion chromatography and segmented flow colorimetry

Table 4 Groundwater site description, selected ion concentrations and E coli counts

Lab No	**Type**	**Aquifer**	**Unsat. Thick. (m)**	**Cl (mg/l)**	**Ca (mg/l)**	**Mg (mg/l)**	**Sr (mg/l)**	**Li (µg/l)**	**HCO_3 (mg/l)**	***E. Coli* (cfu/100 ml)**
GW 227	Spring	Perched	-	144	90	12.8	0.209	2.1	196	20
GW 234	Spring	Perched		296	126	18.9	0.402	5.6	191	>300
GW 236	PS	Perched	91	212	138	16	0.291	1.5	170	>300
GW 237	PS	Perched	115	227	130	19.7	0.443	3.5	197	0
GW 241	PS	Perched		383	258	31.3	0.741	2.6	192	>300
GW 242	Spring	Perched		298	170	21.5	0.379	2.1	139	>300
GW 256	Spring	Perched		94.8	81.2	8.77	0.143	1.3	190	0
GW 257	Spring	Perched		235	185	21.3	0.5	2.3	204	>300
GW 258	Spring	Perched		199	107	24.2	0.31	1.8	144	>300
GW 273	PS	Perched	57	414	92.6	29	0.354	4.2	213	2
GW 284	Spring	Perched		287	170	20.8	0.381	2.4	143	33
GW 285	Spring	Perched		304	116	19	0.319	3.2	151	61
GW 228	Borehole	Malta MSL	91	326	106	18.7	0.359	3.7	181	0
GW 229	Borehole	Malta MSL	123	250	93	39.1	1.22	14.3	271	0
GW 230	Borehole	Malta MSL*	112	234	102	41.8	1.69	17.4	319	24
GW 231	Borehole	Malta MSL*	84	351	92	44.4	1.34	13.7	268	14
GW 232	Borehole	Malta MSL*	143	469	83.8	58.1	2.64	17.0	297	0
GW 233	PS	Malta MSL	46	354	78.4	22.4	0.341	2.8	165	0
GW 238	Borehole	Malta MSL	98	535	116	33.1	0.487	4.5	150	0
GW 239	Borehole	Malta MSL	108	351	103	19.4	0.366	4.0	141	0
GW 240	Borehole	Malta MSL	64	396	110	17.8	0.291	2.9	243	0
GW 243	Borehole	Malta MSL	69	794	132	35.5	0.881	9.5	222	0
GW 244	Borehole	Malta MSL	82	236	93.3	14.3	0.269	2.0	208	0
GW 245	Borehole	Malta MSL	104	667	97.3	34	0.36	5.4	180	17
GW 246	Borehole	Malta MSL	68	1230	114	65.4	0.442	9.8	234	0
GW 247	Borehole	Malta MSL	74	415	94.6	19.5	0.319	4.2	184	0
GW 259	Borehole	Malta MSL	70	210	91.1	14.2	0.371	3.2	198	0
GW 260	Borehole	Malta MSL	92	221	105	15.4	0.349	4.0	169	>300
GW 261	Borehole	Malta MSL		677	164	44.7	0.635	6.7	213	35
GW 262	PS	Malta MSL		601	136	32.7	0.655	9.8	260	0
GW 263	Borehole	Malta MSL	103	195	75.1	25.7	1.19	8.5	198	5
GW 272	Borehole	Malta MSL	107	713	121	43.1	0.672	7.5	242	0
GW 274	PS	Malta MSL	93	1250	127	66	0.492	9.0	214	0
GW 281	Borehole	Malta MSL	48	710	130	34.2	0.359	4.4	229	0
GW 282	Borehole	Malta MSL	43	40.1	90.5	6.44	0.291	2.8	279	0
GW 283	Borehole	Malta MSL	35	650	142	38	0.835	14.2	282	0
GW 248	Borehole	Gozo MSL	78	469	92.8	52.1	1.84	11.9	235	0

Lab No	**Type**	**Aquifer**	**Unsat. Thick. (m)**	**Cl (mg/l)**	**Ca (mg/l)**	**Mg (mg/l)**	**Sr (mg/l)**	**Li (µg/l)**	**HCO_3 (mg/l)**	***E. Coli*** **(cfu/100 ml)**
GW 249	Borehole	Gozo MSL	75	438	99.4	33.4	0.876	6.1	202	19
GW 250	Borehole	Gozo MSL	102	1990	112	135	1.59	17.2	210	0
GW 251	Borehole	Gozo MSL	78	908	112	77.3	1.8	17.5		0
GW 252	Borehole	Gozo MSL	104	952	93.6	99.9	2.5	23.3	308	0
GW 253	Borehole	Gozo MSL	125	436	65.2	61.5	2.04	12.1	279	0
GW 254	Borehole	Gozo MSL	55	1490	132	102	1.02	24.9	256	>300
GW 255	Borehole	Gozo MSL	115	526	85.1	84.4	3.58	30.1	329	>300
GW 275	Borehole	Gozo MSL	70	323	95.8	18.4	0.452	4.0	206	0
GW 276	Borehole	Gozo MSL	86	1260	114	74.4	0.939	13.2	160	0
GW 277	Borehole	Gozo MSL		1220	123	107	2.5	25.5	293	0
GW 278	Borehole	Gozo MSL	82	1010	79.5	122	4.73	31.8	285	0
GW 279	Borehole	Gozo MSL*	85	267	52.9	49.3	1.7	11.7	251	0
GW 280	Borehole	Gozo MSL	78	898	120	81.2	1.9	20.3	266	0

* underlying a perched aquifer

Table 5 Interpreted results for groundwater tracers. Data in bold have concentrations of CFCs greater than atmospheric and indicate possible exposure to pollution

Lab No	**SF_6**		**CFC-12**		**CFC-11**	
	Fraction modern water	**Average year of recharge**	**Fraction modern water**	**Average year of recharge**	**Fraction modern water**	**Average year of recharge**
GW 228	0.40	1992	0.48	1977	0.43	1974
GW 231	0.27	1988	0.39	1974	0.25	1971
GW 232	0.23	1986	0.68	1983	0.69	1980
GW 238	0.28	1988	0.58	1980	0.52	1976
GW 239	0.48	1994	0.85	1988	0.51	1976
GW 240	0.35	1990	0.51	1978	0.44	1975
GW 243	**0.34**	**1990**	**1.51**	**>modern**	**2.80**	**>modern**
GW 244	0.26	1987	0.50	1977	0.64	1979
GW 245	**0.39**	**1992**	**48.86**	**>modern**	**11.68**	**>modern**
GW 246	0.27	1987	0.77	1986	0.59	1978
GW 248	0.06	1975	0.28	1971	0.29	1972
GW 249	0.18	1984	0.45	1976	0.34	1973
GW 252	0.15	1982	0.27	1971	0.27	1971
GW 254	0.28	1988	0.66	1982	0.43	1974
GW 261	**0.21**	**1985**	**1.43**	**>modern**	**2.34**	**>modern**
GW 273	**0.43**	**1993**	**1.71**	**>modern**	**2.09**	**>modern**
GW 275	0.24	1986	0.50	1977	0.58	1977
GW 276	0.24	1984	0.43	1975	0.34	1973
GW 277	0.19	1986	0.32	1973	0.46	1975
GW 278	0.00	<1971	0.00	<1944	0.00	<1949
GW 279	0.10	1979	0.19	1968	0.04	1960
GW 280	0.34	1990	0.63	1982	0.63	1979
GW 281	**0.23**	**1986**	**1.51**	**>modern**	**1.65**	**>modern**

683 Table 6 Stable isotope results for water and sewage samples

Lab No	Sample type	δ^2H (‰ VSMOW)	δ^{18}O (‰ VSMOW)	δ^{13}C TDIC (‰ VPDB)
GW 227	Perched	-28.0	-5.26	-12.4
GW 234	Perched	-25.7	-4.75	-11.0
GW 236	Perched	-25.6	-4.89	-12.4
GW 237	Perched	-25.4	-4.76	-12.2
GW 241	Perched	-25.0	-4.74	-12.2
GW 242	Perched	-26.4	-5.04	-10.3
GW 256	Perched	-29.1	-5.54	-12.9
GW 257	Perched	-26.3	-5.07	-10.4
GW 258	Perched	-27.6	-5.15	-10.5
GW 273	Perched	-24.37	-4.57	-12.0
GW 284	Perched	-27.38	-5.20	-11.2
GW 285	Perched	-20.09	-3.89	-10.3
GW 228	Malta MSL	-27.7	-5.09	-11.7
GW 229	Malta MSL	-27.7	-5.08	-7.4
GW 230	Malta MSL	-26.9	-5.06	-5.9
GW 231	Malta MSL	-26.8	-4.94	-6.8
GW 232	Malta MSL	-26.6	-5.03	-4.5
GW 233	Malta MSL	-27.7	-5.19	-11.1
GW 238	Malta MSL	-25.8	-4.81	-11.3
GW 239	Malta MSL	-28.1	-5.14	-10.9
GW 240	Malta MSL	-25.9	-4.90	-12.0
GW 243	Malta MSL	-25.1	-4.61	-9.1
GW 244	Malta MSL	-26.8	-4.90	-10.7
GW 245	Malta MSL	-26.4	-4.88	
GW 246	Malta MSL	-26.0	-4.67	-13.0
GW 247	Malta MSL	-20.8	-4.02	-10.1
GW 259	Malta MSL	-28.0	-5.11	-12.0
GW 260	Malta MSL	-27.3	-5.12	-11.1
GW 261	Malta MSL	-25.4	-4.61	-11.3
GW 262	Malta MSL	-23.4	-4.38	-10.5
GW 263	Malta MSL	-26.3	-4.93	-3.9
GW 272	Malta MSL	-23.77	-4.46	-10.6
GW 274	Malta MSL	-25.26	-4.76	-11.2
GW 281	Malta MSL	-17.96	-3.41	-12.2
GW 282	Malta MSL	-28.34	-5.30	-14.4
GW 283	Malta MSL	-23.43	-4.39	-10.6
GW 248	Gozo MSL	-25.9	-4.90	-3.5
GW 249	Gozo MSL	-27.2	-5.06	-5.5

Lab No	**Sample type**	**δ^{2}H (‰ VSMOW)**	**δ^{18}O (‰ VSMOW)**	**δ^{13}C TDIC (‰ VPDB)**
GW 250	Gozo MSL	-25.4	-4.76	-4.3
GW 251	Gozo MSL	-26.4	-4.99	-5.2
GW 252	Gozo MSL	-25.5	-4.84	-3.7
GW 253	Gozo MSL	-27.3	-5.10	-2.8
GW 254	Gozo MSL	-25.4	-4.81	-10.4
GW 255	Gozo MSL	-27.1	-5.05	-2.9
GW 275	Gozo MSL	-28.33	-5.31	-9.6
GW 276	Gozo MSL	-26.48	-4.87	-7.3
GW 277	Gozo MSL	-25.28	-4.87	-5.2
GW 278	Gozo MSL	-25.03	-4.74	-3.0
GW 279	Gozo MSL	-26.22	-4.88	-3.1
GW 280	Gozo MSL	-26.28	-4.94	-25.6, -25.4
TW 001	Tap water	8.35	0.94	
TSE 264	TSE	-4.7	-1.18	-9.8
TSE 265	TSE	-6.8	-1.51	-11.9
SW 266	Sewage	-0.5	-0.36	
SW 267	Sewage	-13.2	-2.81	
SW 268	Sewage	-9.8	-2.09	
SW 269	Sewage	-8.3	-1.89	
SW 270	Sewage	-11.0	-2.29	
SW 271	Sewage	-14.3	-2.84	

List of Figures

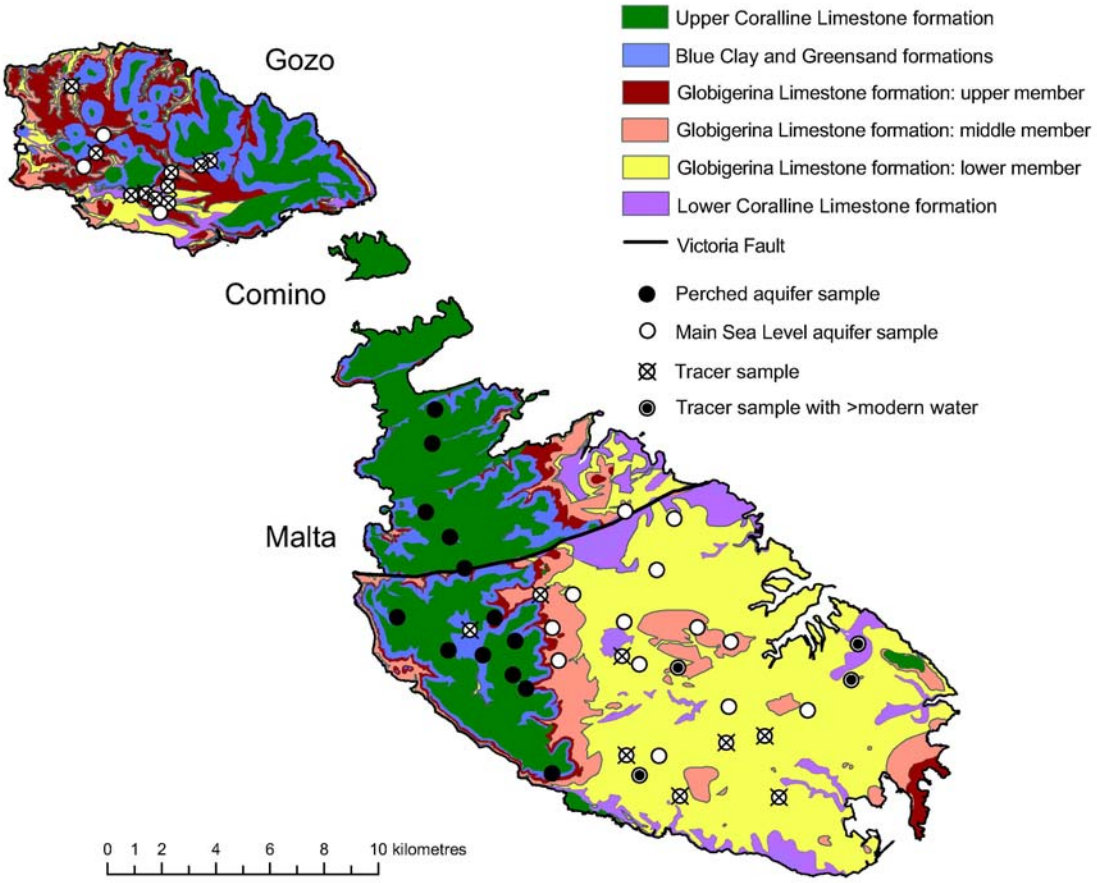

Figure 1 Simplified geology of the Maltese Islands showing the extent of the UCL perched aquifers, groundwater sampling sites and the subset where tracer samples were collected

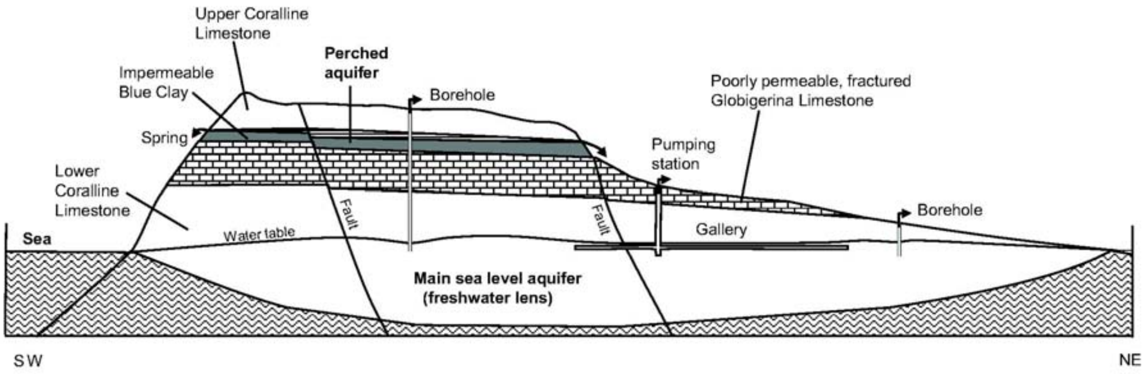

Figure 2 Conceptual cross-section of the MSL aquifer in the LCL and the perched aquifer in the UCL. Abstraction from pumping station galleries and boreholes

controls the water level of the MSL aquifer and also leads to saline water upconing.

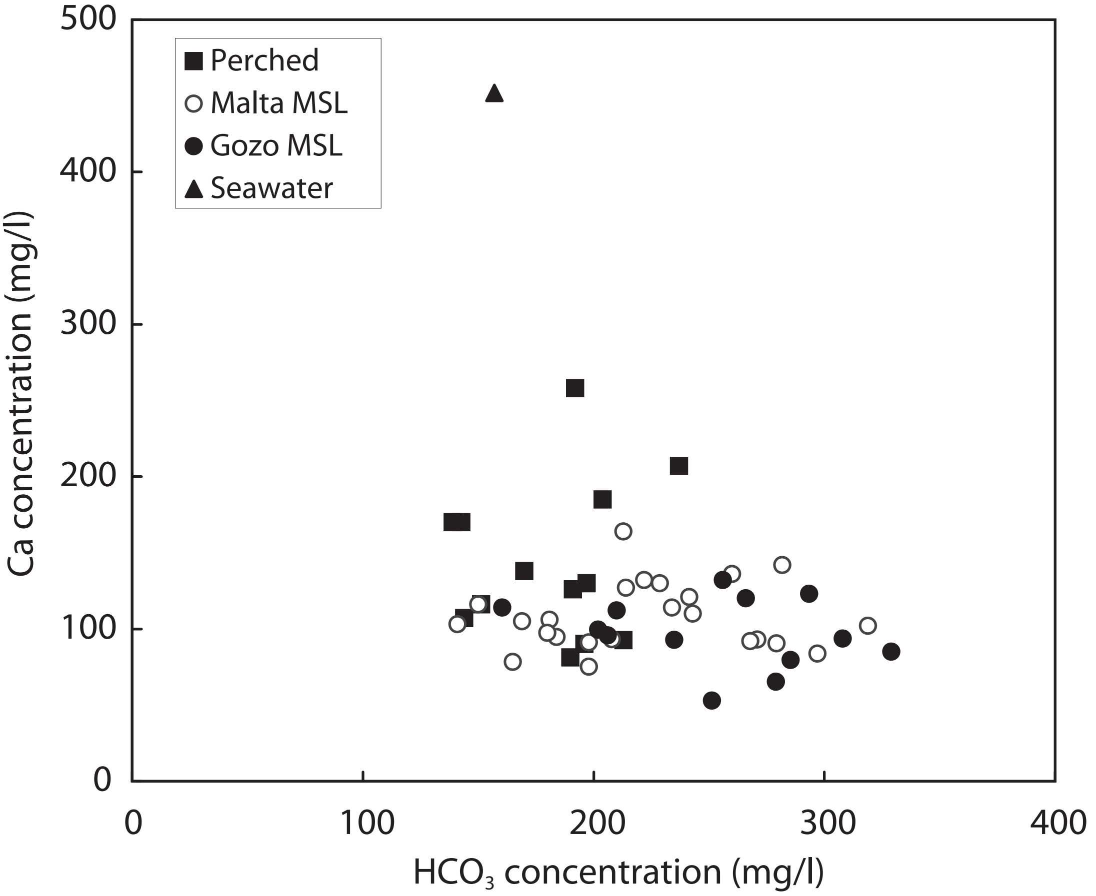

Figure 3 Crossplot of Ca and HCO_3 indicating a lack of simple correlation but higher concentrations in the perched aquifer where conditions may be are more open to the atmosphere than in the MSL aquifers

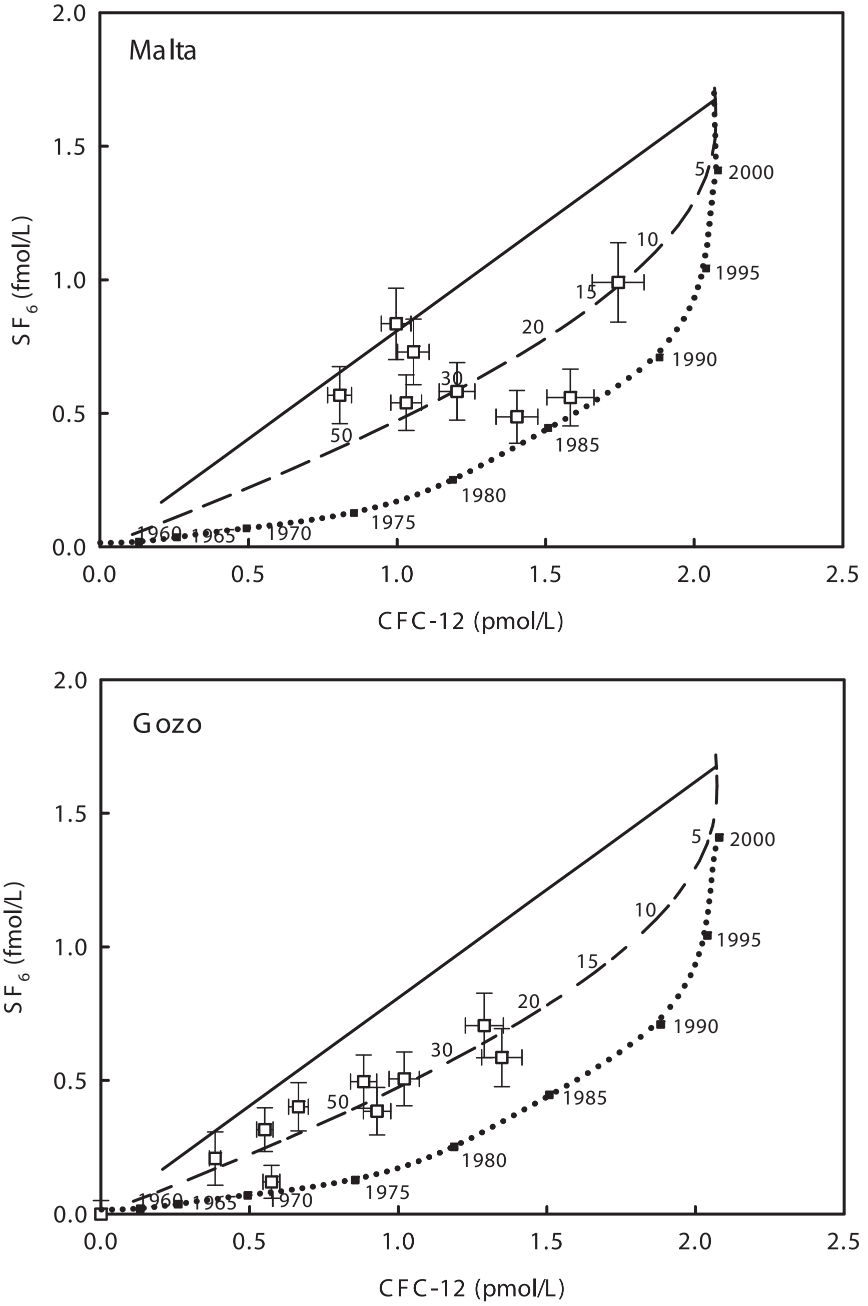

Figure 4 Estimation of groundwater age and flow mechanism using a lumped model of SF_6 and CFC-12 concentrations for Malta and Gozo. Solid line – simple mixing, dashed line – exponential mixing annotated with age in years, dotted line – piston flow annotated with year of recharge

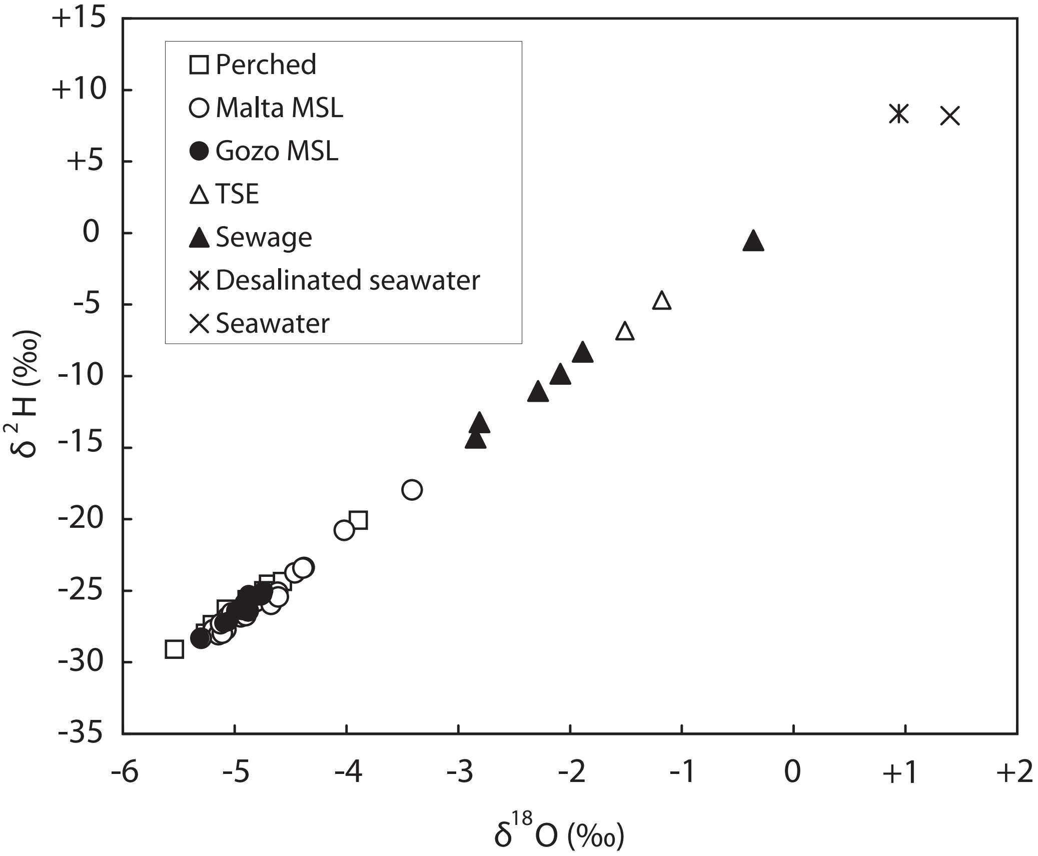

Figure 5 Crossplot of δ^2H vs δ^{18}O for waters in Malta showing desalinated water content of sewage

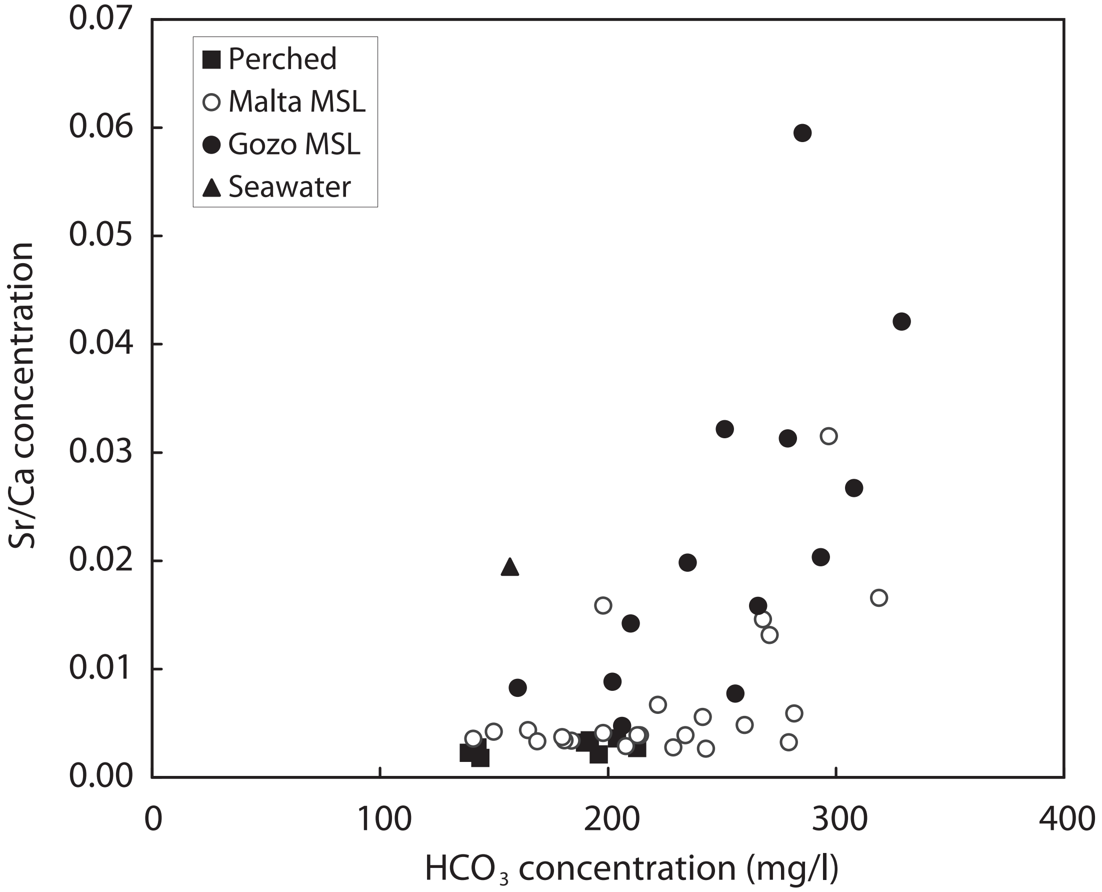

Figure 6 Crossplot of $\delta^{13}C$ against the Sr/Ca ratio showing enhancement of Sr relative to seawater with increasing $\delta^{13}C$

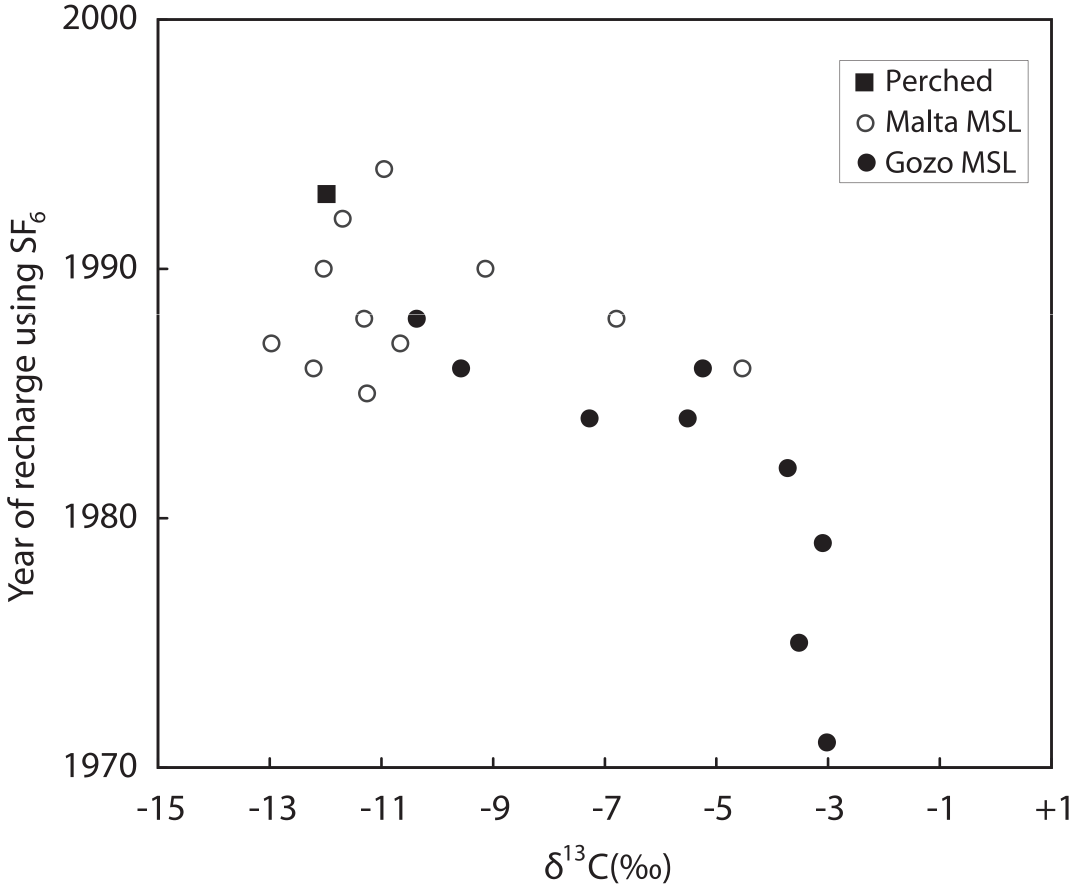

Figure 7 Crossplot of recharge year derived from SF_6 measurements against $\delta^{13}C$ indicating a relationship despite the difference in timescale of application