Journal of Hydrology 414–415 (2012) 244–254

Contents lists available at SciVerse ScienceDirect

Journal of Hydrology

journal homepage: www.elsevier.com/locate/jhydrol

An isotope study of the sources of nitrate in Malta's groundwater

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ARTICLE INFO

Article history:
Received 29 September 2010
Received in revised form 23 August 2011
Accepted 29 October 2011
Available online 7 November 2011
This manuscript was handled by Laurent Charlet, Editor-in-Chief, with the assistance of Eric C. Gaucher, Associate Editor

Keywords:
Groundwater
Nitrate
Isotope
Soil
Sewage
Manure

SUMMARY

Levels of nitrate in Malta's groundwater are high. Median concentrations in the main sea-level aquifers of Malta and Gozo are 14 and 10 mg NO_3–N L^{-1}, respectively, and even higher in the younger groundwaters of the perched aquifers on Malta (37 mg NO_3–N L^{-1}). The wide variations in groundwater nitrate concentration are not due to denitrification, as $^{15}N/^{14}N$ and $^{18}O/^{16}O$ analyses of 47 samples from the three aquifer types found clear evidence for this process in only one sample. 90% of the groundwater nitrate samples had $\delta^{18}O$ values in the range +3.1 to +6.1‰, which correspond exactly to those expected for nitrate formed by microbial processes in the presence of Maltese surficial waters ($\delta^{18}O$ of H_2O typically −5.3 to −4.3‰). The $\delta^{15}N$ values of these groundwater nitrate samples, +7.7 to +11.7‰, were compared with those of a wide variety of potential nitrate sources in Malta (fertilizers, sewage, manure and soils). The closest correspondence was found for the organic N in cultivated soils (+6.0 to +11.2‰). These relatively high $\delta^{15}N$ values for soils may reflect greater fluxes of N from soils with a low C/N ratio and a long history of cultivation. While the isotope data support soil nitrification as the source for nitrate in the groundwaters, they do not rule out direct leaching of manure-derived nitrate as a source.

1. Introduction

The Republic of Malta is largely comprised of two islands, Malta (246 km^2) and Gozo (67 km^2), and with a population of 412,000 is one of the most densely populated countries in the world (DOIM, 2009). 23% of the land is built upon, and 60% of the remaining area is used for agriculture (NSO, 2006). The combined domestic, tourist, industrial and farming activities place strong demands on water supplies, with Malta having one of the world's highest Water Competition Indexes (population per unit of available water; Mangion et al., 2005). The demand is met predominantly by groundwater abstraction (56%) and seawater desalinization (34%), with more limited use of harvested rainwater runoff and treated sewage effluent (Sapiano et al., 2006). Over half of the water put into public supply is desalinated seawater. But whilst this provides a reliable supply of good quality water, the high cost of desalinization, and its dependence on imported oil, means that groundwater continues to be a vital resource.

The utility of this groundwater resource, however, is being compromised by poor chemical quality: especially seawater intrusion (some parts of aquifers having chloride levels above WHO limits) and high levels of nitrate (MEPA, 2006). Average nitrate concentrations in the main aquifers sampled as part of the present study exceed the 11.3 mg NO_3–N L^{-1} limit imposed by the European Union's (EU) Nitrate Directive and Water Framework Directive, with nitrate levels in some of the minor groundwater bodies reaching levels more than six times the EU quality standard (EC, 1991; EU, 2000; EEA, 2008). As part of Malta's programme to address this problem, the British Geological Survey and the Malta Resources Authority conducted a preliminary study on the identification of the sources of nitrate contamination in groundwater in Malta. Geochemical aspects of groundwater movement are reported elsewhere (Stuart et al., 2010); the present work reports on the results of the isotope study of nitrate.

2. Malta's groundwater

2.1. Hydrogeology

A schematic section of the main island of Malta is shown in Fig. 1, and illustrates features of the geohydrology relevant to both Malta and Gozo. The Tertiary geology is essentially made up of two limestone sequences separated by an impermeable clay-marl: the Blue Clay (Pedley et al., 1976; Fig. 1).

2.1.1. Perched aquifers

Above the Blue Clay, the top of the succession is formed by the Upper Coralline Limestone, mainly present on the west side of

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doi:10.1016/j.jhydrol.2011.10.037

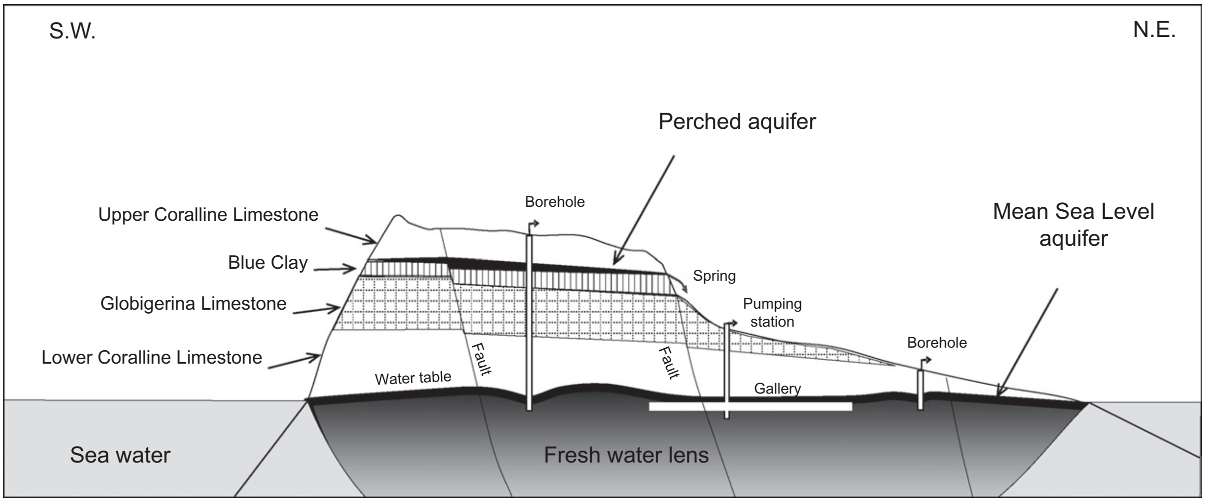

Fig. 1. Schematic cross-section through Malta (main island), showing the 'Perched' aquifer above the low permeability Blue Clay, and the 'Mean Sea Level' aquifer – a Ghyben–Herzberg lens of fresh water floating on sea-water.

Malta and the east side of Gozo. The impermeabililty of the clay supports perched groundwater within the overlying limestone. Faulting and erosion means that this groundwater is present as several hydrologically separate perched aquifers. These provide water for agricultural use from shallow boreholes or natural springs.

2.1.2. Mean sea level (MSL) aquifers

Stratigraphically below the Blue Clay, Globigerina and Lower Coralline limestones constitute the major rock formations of the islands. Over most parts of both Malta and Gozo the Lower Coralline Limestone supports a classic 'Ghyben-Herzberg' lens of fresh water floating on sea-water (Fig. 1). The fresh water is abstracted from boreholes and, in particular, from long galleries which take water from the top of the lens and maintain its water table at just a few metres above mean sea level (Fig. 1). These two 'Mean Sea Level' aquifers ('Malta MSL' and 'Gozo MSL') supply over 80% of Malta's groundwater, for both potable and agricultural use, with the Malta MSL aquifer being by far the most important (Bakalowicz and Mangion, 2003; Sapiano et al., 2006).

2.2. Groundwater residence time and chemistry

2.2.1. Perched aquifers

In agreement with the hydrological settings, tritium and SF_6 data suggest that the perched aquifers contain relatively young groundwater (Bakalowicz and Mangion, 2003; Stuart et al., 2010). This was confirmed for 10 of the 12 perched aquifer sources sampled in this study by the presence of often high concentrations of *Escherichia Coli*, a bacterium excreted by mammals which usually survives only a few days in the sub-surface environment (Stuart et al., 2010). The major ion chemistry is predominantly Ca + Mg bicarbonate, but also with high concentrations of Na and Cl (median ca. 250 mg Cl L^{-1}) in ratios close to that of seawater (Table 1). This is presumed to derive mainly from sea salts in rainfall concentrated by evaporation (Stuart et al., 2010), or by minor sea water contamination where perched aquifers are close to sea level (Sapiano et al., 2006).

2.2.2. Mean sea level (MSL) aquifers

Since the islands rise to a maximum altitude of 239 m above sea level, the MSL aquifers are overlain by a thick unsaturated zone, typically from 40 to 120 m for boreholes sampled in this study (Stuart et al., 2010). In western parts of Malta, and over a large area of Gozo this zone is capped by the Blue Clay and Upper Coralline Limestone. Estimates of groundwater age based on rock properties, tritium, CFC and SF6 data are variable, with maximum residence times in the unsaturated plus saturated zones of a 100 years or more, and the probability that water in the Gozo MSL aquifer is older due to the greater extent of low permeability Blue Clay cover on Gozo (Bakalowicz and Mangion, 2003; Stuart et al., 2010). In contrast to the perched aquifers, 75% of the boreholes tapping MSL aquifers had no detectable *E. Coli.* (Stuart et al., 2010). Waters in the MSL aquifers have bicarbonate concentrations comparable to the perched aquifers, but with higher $\delta^{13}C$ values and Mg/Ca and Sr/Ca ratios than in the perched aquifers, suggesting more evolved incongruent solution of carbonate (Stuart et al., 2010). Na and Cl concentrations are substantially higher than in the perched aquifers (median ca. 420 and 900 mg Cl L^{-1} in Malta MSL and Gozo MSL, respectively, Table 1), reflecting intrusion of seawater into the fresh water lens, largely in response to intensive abstraction (Sapiano et al., 2006).

2.3. Nitrate

In 2004 two-thirds of Malta's Water Services abstraction boreholes had nitrate concentrations exceeding EU limits for drinking water (MEPA, 2006). Agricultural and/or sewage disposal practices are regarded as the most likely cause.

About half of Malta's land area is taken up by intensive agriculture (BRGM, 1991; Meli, 1993; Mangion, 2001). Potatoes and other vegetables constitute the major crops, but much of the cultivated area goes towards growing forage for livestock (NSO, 2008). With limited land available, this livestock production is intensive, with cattle, pigs, poultry and rabbits kept in stockyards or cages most of the time (Meli, 1993). A recent estimate of nitrogen balances (NSO, 2008) suggests that the arable production is supported by addition of an estimated 60 kg N ha^{-1} a^{-1} applied as mineral fertilizer, and an additional 95 kg N ha^{-1} a^{-1} applied as animal manure fertilizer, usually in the late summer. This manure fertilizer, however, is mainly the solid animal waste, and only constitutes about 60% of the total production of animal waste nitrogen. The remainder, chiefly pig slurry, being disposed as sewage (NSO, 2008).

Disposal of animal and human sewage is by networks of mains sewers draining the densely populated parts of the islands, and septic tanks and cesspits serving smaller or more isolated communities. Inadequacies in capacity or the sealing of these systems