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Geochemistry and arsenic behaviour in groundwater resources of the Pannonian Basin (Hungary and Romania)

Helen A.L. Rowland ^{a,d,*}, Enoma Omoregie ^b, Romain Millot ^c, Cristina Jimenez ^{a,d},
Jasmin Mertens ^{d,e}, Calin Baciu ^d, Stephan J. Hug ^a, Michael Berg ^{a,*}

^a Eawag, Swiss Federal Institute of Aquatic Science and Technology, 8600 Dübendorf, Switzerland.

^b School of Earth, Atmospheric and Environmental Sciences and Williamson Research Centre for Molecular Environmental Sciences, The University of Manchester, Manchester, United Kingdom.

^c BRGM, Metrology Monitoring Analysis Department, Orleans, France.

^d Faculty of Environmental Sciences, University of Babes-Bolyai, Cluj Napoca, Romania.

^e Institute of Biogeochemistry and Pollutant Dynamics (IBP), ETH Zurich, 8092 Zurich, Switzerland.

* Corresponding authors,

E-mail addresses: helen.rowland@aquatrain.eu (H.A.L. Rowland), michael.berg@eawag.ch (M. Berg)

Abstract

Groundwater resources in the Pannonian Basin (Hungary, Romania, Croatia and Serbia) are known to contain elevated naturally occurring As. Published estimates suggest nearly 500,000 people are exposed to levels greater than the EU maximum admissible concentration of 10 µg/L in their drinking water, making it the largest area so affected in Europe. In this study, a variety of groundwaters were collected from Romania and Hungary to elucidate the general geochemistry and identify processes controlling As behaviour. Concentrations ranged from <0.5 to 240 µg/L As(tot), with As predominantly in the reduced As(III) form. Using cluster analysis, 4 main groups of water were identified. Two groups (1 and 2) showed characteristics of water originating from reducing aquifers of the area with both groups having similar ranges of Fe concentrations, indicating that Fe-reduction occurs in both groups. However, As levels and other redox characteristics were very different. Group 1, indicative of waters dominated by methanogenesis contained high As levels (23 to 208 µg/L, mean 123 µg/L), with group 2 indicative of waters dominated by SO₄²⁻-reduction containing low As levels (<0.5 to 58 µg/L, mean 11.5 µg/L). The remaining two groups were influenced either by (i) geothermal and saline or (ii) surface contamination and rain water inputs. Near absence of As in these groups, combined with positive correlations between δ⁷Li (an indicator of geothermal inputs) and As(tot) in geothermal/saline influenced waters indicate that elevated As is not from an external input, but is released due to an in-aquifer process. Geochemical reasoning, therefore, implies As mobilisation is controlled by redox-processes, most likely microbially mediated reductive dissolution of As bearing Fe-oxides, known to occur in sediments from the area. More important is an overlying retention mechanism determined by the presence or absence of SO₄²⁻. Ongoing SO₄²⁻-reduction will release S²⁻, removing As from solution either by the formation of As-sulfides, or from sorption onto Fe-sulfide phases. In methanogenic waters, As released by reductive dissolution is not removed from solution and can rise to the high levels observed. Levels of organic C are thought to be the ultimate control on the redox conditions in these 2 groups. High levels of organic C (as found in group 1) would quickly exhaust any SO₄²⁻ present in the waters, driving the system to methanogenesis and subsequent high levels of As. Group 2 has much lower concentrations and so SO₄²⁻ is not exhausted. Therefore, As levels in waters of the Pannonian Basin are controlled not by release but by retention mechanisms, ultimately controlled by levels of TOC and SO₄²⁻ in the waters.

δD and δ¹⁸O analysis showed that groundwaters containing elevated As dated mostly from the last ice-age, and are sourced from Late Pliocene to Quaternary aquifers. The importance of TOC and retention capabilities of SO₄²⁻-reduction have only previously been suggested for recent (Holocene) sediments and groundwater, most notably those in SE Asia as these are the most likely to contain the right combination of factors to drive the system to the correct redox situation. In contrast, it is shown here that a much older system containing As bearing Fe-oxides, also has the potential to produce elevated levels of As if the TOC is suitable for the microbial population to drive the system to the correct redox situation and SO₄²⁻ is either absent or wholly consumed.

1. Introduction

1.1. Occurrence of arsenic in groundwater

The presence of naturally occurring As in shallow reducing aquifers used for irrigation and drinking water is a major health issue for millions of people worldwide. Research on mobilisation processes has commonly focused on SE Asia, in aquifers within the Ganges-Brahmaputra-Meghna, Mekong and Red River deltas (Smith et al., 2000; BGS and DPHE, 2001; Berg et al., 2001; Chakraborti et al., 2003; Charlet and Polya, 2006; Buschmann et al., 2007; Winkel et al., 2008), and the US (Welch et al., 2000; Warner, 2001; Saunders et al., 2005).

Within Europe, many countries have reducing aquifers with levels of As above the EU drinking water limit of 10 µg/L, requiring some form of remediation before waters reach consumers. Countries include Greece (Katsoyiannis and Katsoyiannis, 2006), Belgium (Coetsiers and Walraevens, 2006), Netherlands (Frapporti et al., 1996), Spain (Garcia-Sanchez et al., 2005; Gomez et al., 2006) and the UK (Smedley and Edmunds, 2002). For the most part As is geographically restricted affecting only small numbers of people. However, within Eastern Europe, the Pannonian Basin, spanning Hungary, Romania, Serbia, Slovakia and Croatia (Fig. 1), naturally occurring As in aquifers utilised for drinking waters is known to affect far larger populations. Estimates suggest that nearly 1 million people are exposed to naturally occurring As in drinking waters at levels greater than the 10 µg/L WHO and EU standards (Csalagovitis, 1999; Gurzau and Gurzau, 2001; Čavar et al., 2005; Varsányi and Kovács, 2006; Vidovic et al., 2006; Lindberg et al., 2006; Habuda-Stanić et al., 2007; Stauder, 2007; Djuric and Jevtic, 2008; Jimenez et al., 2009; Rowland et al., 2009b; Ujević et al., 2010), making it the most severely affected region in Europe (Table 1). The geology in the region is complex, with interactions between thermal, glacial palaeo-, fossil marine, surface and rain waters giving rise to a complex aquifer system, with a wide range of hydrogeological conditions.

It is commonly thought that As release is controlled by microbial processes via the dissolution of As bearing Fe-oxides due to the onset of reductive conditions during sediment burial and diagenesis (Nickson et al., 1998; McArthur et al., 2001; Harvey et al., 2002; Islam et al., 2004) with the presence and type of organic matter (Rowland et al., 2009a) and the presence of SO_4^{2-} also playing an important role (Kirk et al., 2004; Quicksall et al., 2008; Buschmann and Berg, 2009). For Hungary, based on groundwater geochemical investigations, similar process were suggested to be the primary cause of As release (Csalagovitis, 1999). Mineralogical and aqueous geochemical investigations by Varsányi and Kovács (2006) showed that As was correlated with both extractable organic matter and Fe-oxides within sediments of SE Hungary. However, they suggested that two processes were responsible for As release, (i) dissolution of As bearing Fe-minerals (as previously suggested) occurring in regions of low pH (~7.6) in areas of groundwater recharge, and (ii) high concentrations of organic ligands promoting mobilisation in areas of groundwater discharge with longer residence times (Varsányi and Kovács, 2006). A recent study conducted in Eastern Croatia showed that the spatial distribution of As in the groundwater is linked with geological, geomorphological and hydrogeological development of the alluvial basin, and that reductive dissolution of Fe oxides, desorption of As from Fe oxides and/or clay minerals as well as competition for the sorption sites with organic matter and PO_4^{3-} could be the principal mechanisms that control As mobilization (Ujević et al. 2010). Arsenic release mechanisms within other parts of the Pannonian basin have not been discussed in great detail within the literature, but elevated As levels in conjunction with higher Fe and organic matter concentrations in waters from the Vojvodina Province in northern Serbia (Vidovic et al., 2006;

Stauder, 2007; Djuric and Jevtic, 2008), imply that processes suggested by Varsányi and Kovács (2006) and Csalagovits (1999) could be occurring over a more widespread area.

The region is also known for its geothermal waters (Korim, 1972; Cohut and Bendea, 1999; Antics, 2000; Antics and Rosca, 2003). Natural waters associated with these systems commonly contain high As concentrations ranging from 0.1 to nearly 50 mg/L (Henley and Ellis, 1983; Ballantyne and Moore, 1988). In Europe, high levels of As within groundwaters due to hydrothermal activity have been found within Italy (Aiuppa et al., 2003, 2006) and Greece (Tyrovolas et al., 2006) and within Hungary, high levels of As have been reported from geothermal waters (Csalagovits, 1999). Arsenic in such geothermal waters can be sourced either from the thermal reservoir by fluid-rock interactions of As bearing minerals such as pyrite, or by scavenging of the aquifer rocks as hot fluids move through the subsurface (Ballantyne and Moore, 1988). Therefore, in a region known to contain thermal waters, elevated concentrations of As could be due to an 'external input' from geothermal waters, with variations in concentrations due to dilution with non-As bearing waters.

The health impact of As in drinking water on the population in the Pannonian Basin has shown predominantly negative results. Dermatological studies of populations in SE Hungary found cases of arsenical hyperkeratosis and hyperpigmentation, as well as elevated levels of As in hair occurring in people who drank water with levels above 50 µg/L, in comparison to a control population from the same region (Borzsinyi et al., 1992). Work by Varsányi et al. (1991) showed mixed results with no increase in mortality due to the consumption of waters above 50 µg/L when all causes of death were taken into account, but potential increases in mortality observed when the data-set was separated into males and females, and with certain diseases examined. In Croatia, positive correlations between As in drinking water and hair have been shown (Ćavar et al., 2005; Habuda-Stanic et al., 2007). Research as part of the EU project ASHRAM (Arsenic Health Risk Assessment and Molecular Epidemiology), looking at the impact of As in waters on the population of Hungary, Romania and Slovakia has shown associations between As and increased cases of cancers in the skin, bladder and kidney (Fletcher et al., 2008). The ASHRAM project also found, for the same countries, that there were correlations between the level of As in drinking water and urine (Lindberg et al., 2006).

1.2. General palaeogeography and geological development of the Pannonian Basin

The sediments of the Pannonian Basin are heterogeneous, thick and complex. The average thickness of Neogene and Quaternary sediments in the basin is 2 – 3 km, but in the deep troughs the thickness of sediments can reach 7 - 8 km (Lenkey et al., 2002). To help understand the groundwater geochemistry, knowledge of the palaeogeographic setting of the former Lake Pannon that formed the sedimentary deposits now containing the aquifers of interest is required. The tectonic setting for the basin was formed as the Tethys sea, being closed by the northward drift of Africa into Europe, was split into 2 parts, the Mediterranean Tethys in the south, and the Paratethys ('besides Tethys') during the middle Cenozoic (Rögl, 1999). The Paratethys consisted of a series of elongated, epicontinental basins stretching in its entirety from the Western Alps to the Transcaspian Basin (east of the Caspian sea), of which the Pannonian is situated in the central part (Rögl, 1999; Geary et al., 2002). However, a full description of the sedimentation history of the entire basin is outside the scope of this study, and readers are directed to the following for more detail (Rögl, 1999; Magyar et al., 1999; Juhász et al., 1999, 2004, 2007; Gábris and Nádor 2007) However, the sedimentation history from Late Miocene,

Pliocene to Quaternary can be highly simplified (oldest to youngest) as the following (i) shallow marine (Sarmatian), (ii) brackish – fresh water lacustrine (Lower Pannonian/Pannonian s.s.), (iii) lacustrine/deltaic/fluvial (Upper Pannonian/Pontian), and (iv) fluvial channel and flood plain (Quaternary). Terrestrial deposits from the Upper Miocene to the Pliocene sequence (as discussed above) are commonly referred to as the Pannonian *sensu lato* (Pannonian s.l.) and subdivided into the Pannonian *sensu stricto* (s.s.) and Pontian, with both stages also informally referred to as 'Lower Pannonian' and 'Upper Pannonian' respectively (Sacchi and Horvath, 2002). A cross section of the Pannonian basin showing these dominant sediment types is shown in Figure 2.

1.3. Geology and mineralogy

The facies development of the Pannonian Basin is extremely complex and variable throughout the region. Therefore, a more detailed overview of the region of study is given. In the field area, the boundary between the Quaternary and Pliocene (Upper Pannonian) deposits are closely related and so difficult to define (Vicizian, 2002). In the area, variegated clays of the Vésztő and Nagyalföld Formations make up the Quaternary and Pliocene (Upper Pannonian) sediments, respectively, with both units having similar facies development, dominated by siltstone and clay with interbedded sandy river deposits. However, the Pliocene (Upper Pannonian) is more marshy and lacustrine in nature, reflected by the greater abundance of clay in these deposits (Vicizian, 2002), with the uplift of the Pannonian basin, at approximately 2.4 Ma, initiating more fluvial sedimentation in the Quaternary (Vicizian, 2002; Gábris and Nádor, 2007). In addition, evidence of swamp and wetland deposits are found throughout the Pliocene and Quaternary deposits in some areas (Körös basin) (Vicizian, 2002; Juhász et al., 2004).

The Quaternary sediments, reaching up to 600m in thickness, consist of gravel, fine grained sand with silt and clay (20 to 50 m bed thickness) sourced from weathering of the Apuseni Mountains to the east and the redistribution of tertiary sediments from the same region (Juhász et al., 2004; Vicizian, 2002; Nádor et al., 2003). Patterns and type of fluvial sediments (including grain size) deposited during the Quaternary were controlled by (i) large scale Milankovitch orbital cycles of 40 and 100 ka cyclicity, with sediment load into the basin controlled by the alternating glacials (decreased sediment supply, finer grained sediments) and interglacials (greater transport capacity of rivers leading to higher sediment flux and coarser grain size) (Varsányi and Kovács, 1997; Juhász et al., 1999; Nádor et al., 2003) and (ii) subsidence of the basin, which impacted on the sediment accumulation rates in the area (Varsányi and Kovács, 1997; Juhász et al., 1999; Nádor et al., 2007; Gábris and Nádor, 2007). Sediments in the Upper and Middle Pleistocene contain thicker and more abundant sand layers than the Lower Pleistocene (Varsányi and Kovács, 1997), with mineralogical homogeneity throughout the Quaternary (and Pliocene) in the area implying that the sediment source remained the same, and it is thought to have been so since the Late Miocene (Vicizian, 2002).

Studies of Hungarian sediments (reviewed by Vicizian, 2002, typically detected by XRD) show a variety of Fe minerals, including goethite, limonite, pyrite and siderite. Iron-oxyhydroxides have also been identified by chemical extraction of sediments from the Quaternary (Varsányi and Kovács, 2006), with magnetite also identified within sediments of the same age (Nádor et al., 2003). Generally, upper horizons (Quaternary and Upper Pliocene), still retain poorly crystallised/amorphous Fe(III) oxides (goethite and limonite) (Vicizian, 2002). In the Lower Pliocene of the Maros fan, these are replaced by

Fe carbonates, though they can be present in small quantities in the Quaternary also (Vicizian, 2002). In addition, pyrite can be found in more organic-rich deposits, indicative of marshy environments (Vicizian, 2002).

1.4. Ground water system of the field area

Groundwater type and geochemical composition is strongly controlled by the sedimentary and palaeogeographical history of the region (Fig. 2). Within the Lower Pannonian (Pannonian s.s.) sediments, groundwaters are typically stagnant with Na-Cl to Na-HCO₃ geochemistry (Varsányi and Kovács, 1997). Sodium-HCO₃ waters are then present within the Upper Pannonian (Pontian) sediments. Younger Quaternary sediments, dependant on the dominant size fraction, contain Na-HCO₃ dominated waters within finer sediments and Ca/Mg-HCO₃ waters in the coarser layers (Varsányi and Kovács 1997). There are 3 defined groundwater flow systems in the basin (i) regional flow around the deeper Lower Pannonian (Pannonian s.s.) and Upper Pannonian (Pontian) boundary, (ii) a local flow within the upper layers of the basin and (iii) an intermediate flow that connects the regional and local flow (Varsányi et al., 1999). The δD and $\delta^{18}O$ isotope signatures of waters from the Upper Pannonian (Pontian) to Quaternary sediments in the area show a strong palaeometeoric signature with a depletion in δD and $\delta^{18}O$ due to the lower temperatures of the last ice-age (Rozanski, 1985; Deak et al., 1987; Stute and Deak, 1989; Varsányi et al., 1997, 1999; Varsányi and Kovács, 2009). With infiltration of these waters thought to have occurred due to tectonic and paleoclimatic events occurring at the end of the Pleistocene (Varsányi et al., 1997, 1999). Deeper waters, from the Lower Pannonian (Pannonian s.s.) show δD and $\delta^{18}O$ signatures enriched in heavy isotopes with respect to the Local Meteoric Water Line (LMWL), thought to be due to the influence of deeper oil field waters being squeezed from the underlying fine-grained sediments (Varsányi et al., 1997, 1999; Varsányi and Kovács, 2009). Connectivity between the different bodies of groundwater can also be seen from geochemical and petrographic studies of fracture and pore filling minerals showing meteoric water has had a 'longstanding (late Miocene to recent)' hydraulic connection throughout the sedimentary column from the basement to recent sediments (Juhász et al., 2002).

Artesian waters are common in the region, with overpressures of 15% found below the Lower Pannonian (Pannonian s.s.) sediments (Varsányi and Kovács, 1997). Dewatering, uneven compaction and rapid subsidence of thick units of shaly Pannonian sediments (deposited at rates of up to 200-1000 m/Ma) are thought cause these high levels of overpressure (Juhász et al., 2002). This can also lead to a complex distribution of pressure, with evidence of alternation of overpressured pools with hydrostatic pools in a single vertical section (Juhász et al., 2002).

The region is also known for its geothermal waters. The Pannonian geothermal aquifer in Romania is multilayered and confined at the base of the Upper Pannonian in an area of ~2500 km², following the Western border of Romania from Satu Mare (north) to Timisoara (south) (Cohut and Bendea, 1999; Antics and Rosca, 2003). The main geothermal systems in Romania are found in porous permeable formations such as sandstones and siltstones (Western Plain) or in fractured carbonate formations (near Oradea) (Cohut and Bendea, 1999). Geothermal waters are found at a depth of 0.8 to ~ 2 km depth, with surface temperatures of 50 – 90 °C, are Na-HCO₃/Cl type with dissolved gases (especially CH₄) and total dissolved solids of 4 - 6 g/L, with little variation in composition with time, implying hydrologic unity over the entire region (Antics, 2000; Antics and

Rosca, 2003). Geothermal waters are also found in shallow groundwater in the Vojvodina Province in Northern Serbia, in aquifers from Quaternary, Upper and Lower Pannonian sediments (Mrazovac and Basic, 2009). Across the border in South Eastern Hungary, geothermal waters are also sourced from Upper Pannonian sediments (sandstones, clays and clayey marls), found at a depth of 0.8 to 2.4 km and contain CH₄ (Korim, 1972). Waters in this area are less dominated by Cl⁻, being predominantly Na-HCO₃ type (Korim, 1972). The presence of geothermal waters in the region, are thought to be due to high heat flow occurring after Middle Miocene extension which caused thinning of the lithosphere, as shown by the thin crust, thin lithosphere and normal faults in the basement of Neogene sediments (Lenkey et al., 2002).

1.5. Aims of this study

EU countries within the Pannonian Basin (Hungary, Croatia and Romania) have to comply with the Drinking Water Directive (98/83/EC), in which levels of As in waters intended for human consumption must be below 10 µg/L. Therefore, groundwater quality assessments and an understanding of the modes of As release and subsequent predictions of its distribution within the natural aquifer systems are urgently needed. Such knowledge is important as it can aid local government and water management to locate new water sources with As levels below the EU limits. A complete and detailed knowledge of geochemical processes within groundwater requires extensive data sets, based on water and sediment composition, as well as analysis of microbial communities present. Such data is not always readily available. For example the collection of sediment for geochemical and microbial analysis from the levels of interest can be both very expensive and time consuming. In contrast, ground water samples from existing wells can be collected within reasonable time and at much less cost. Since the mobilization (and retention) of As is largely controlled by the redox conditions of the groundwater, but only to a lesser degree related to the chemical composition of the sediments, groundwater can provide much of the required information about As in different types of groundwater and the underlying geochemical processes.

Therefore, the aim of this work was to elucidate the occurrence of As and the dominant geochemical processes based on the chemistry and isotopic characteristics of groundwater samples collected from a variety of existing wells in the area spanning the Western Romanian Plain, and Eastern Hungary (Fig. 1), a region known to contain elevated As in its groundwaters (Csalagovitis, 1999; Varsányi and Kovács, 2006; Gurzau and Gurzau, 2001). Based on this evidence and work by others in the region and elsewhere, possible modes of As release will then be examined.

2. Methodology

2.1. Sample location and collection

The study area is located between 20.1–22.6° N and 45.8–47.5° E (Fig. 1). A total set of 73 groundwater samples was collected in December 2007 and May/June 2008 from a region covering ~7,500 km² of the Western Romanian Plain and ~8,000 km² of Eastern Hungary, bounded to the east by the Tisza River and the foothills of the Apuseni mountains to the west. This area is known to contain elevated levels of As in its groundwaters (Csalagovitis et al., 1999; Gurzau and Gurzau, 2001; Varsányi and Kovács, 2006; Jimenez et al., 2009; Rowland et al., 2009b). Although preferable to have

an even distribution of wells throughout this region, sample distribution relied on the availability and access to public wells and so is spatially uneven (Fig. 3).

To sample the broadest range of aquifers, a variety of well types tapping different depths were sampled including artesian (depth 50 to 800 m), hand pump (depth 70 to 200 m), open dug (depth to water table ~ 2 to 4 m), and thermal wells which were typically artesian (depth 400 to 3000 m). Well age information was also collected and ranged from <1 to 200 a for artesian wells, 1 to 50 a for hand pump wells and 25 to 79 a for thermal wells. However, depth and age information was not always available, and when obtained, independent verification was not always possible, so this information can only be used as an indication. To ensure that the water sampled was as representative to that at depth, hand-pump wells were pumped for at least 10 min to remove standing water from within the borehole with samples taken only after redox and pH readings stabilised. Artesian and thermal artesian wells were sampled directly from the well head as it was presumed that the water emerging was a direct comparison to that at depth. Water from open dug wells was lifted from depth using the water receptacle used by local users, and deep thermal wells when not artesian were sampled only after they had been pumped for a considerable time period (4 h or more). All water samples and water characterisation were undertaken from an open PVC container which was rinsed 3 times with sample water prior to use, and sporadically emptied and refilled as samples and data was collected.

On site water data was obtained using a handheld unit (WTW Multi 340i) with daily calibrated probes for the following parameters; pH and temperature (WTW SenTix 41-3), conductivity (WTW TetraCon) and Eh (WTW SenTix ORP). Probes were calibrated daily using standard reagents prior to use. Samples for cation and NH_4 analysis were filtered using a 0.45 μm nylon filters (Cronus, Sigma-Aldrich) into opaque acid washed poly-propylene bottles and were preserved by the addition of HNO_3 (1 mL, 1 M HNO_3 suprapure, Merck, into 60 mL of sample). Samples for anion, TOC and $\delta^7\text{Li}$ analysis were also filtered with 0.45 μm nylon filters (Cronus, Sigma-Aldrich) into transparent acid washed polypropylene bottles. Waters for δD and $\delta^{18}\text{O}$ analysis were collected without filtering and stored in brown borosilicate bottles with no head space. Samples for CH_4 , $\delta^{13}\text{C}_{\text{CH}_4}$, ethane and propane measurements were preserved with NaOH (6 mL of sample, 3 mL of 20% NaOH) in glass vials, sealed with rubber stoppers, crimped and stored in the dark. All samples were kept cool on the day of sampling by storage in a freezer box (typically <10 °C), and then stored at 4 °C until analysis, except during transit from Romania to Switzerland (typically 1 day) to minimise microbial activity and sample quality degradation.

2.2. Aqueous phase analytical methods

Water samples for analysis of total cation and anion analysis were measured within 4 weeks of collection, with the majority of samples analysed well within this time frame. Each parameter was analysed in triplicate. Aqueous major and trace elements concentrations were measured after dilution of acidified groundwater samples with 1% HNO_3 supapure (Merck). Arsenic, Na, Mg, Si, K, Ca, Mn, Fe, B, V, Mo, Li, Sr and U were determined by inductively coupled plasma-mass spectrometry (ICP-MS; Agilent 7500cx, Agilent US) with total S (S_{tot}) being quantified with inductively coupled plasma optical emission spectroscopy (ICP-OES; Spectro Ciros CCD, Kleve, Germany). Standards for both ICP-MS and ICP-OES were prepared from dilution of single element standards (Merck) with a detection limit for the ICP-MS of 0.5 $\mu\text{g/L}$ and ICP-OES of 0.1 mg/L .

Arsenic(III) from samples collected in December 2007 were determined by hydride generation atomic fluorescence spectrometer (AFS) (PS Analytical Ltd, Kent, UK., Millenium Merlin/Millenium Excalibur System), with those collected in May 2008 determined by infield separation using an As speciation cartridge (for details see Roberts et al., 2007). Total As (As(tot)) in samples from December were determined after the addition of a reducing solution (2.5 g KI and 0.5 g ascorbic acid in 5 mL of H₂O) prior to analysis by AFS, with samples from May 2008 measured by ICP-MS (as described previously). During AFS analysis (both As(III) and As(tot) after reduction) a pH 4.8 disodium citrate buffer (0.5 M) was used as only As(III) is converted to AsH₃ under these pH conditions (Yamamoto et al., 1981). The detection limit for the AFS was 0.7 µg/L. Analytical accuracy for ICP-MS, AFS and ICP-OES was ensured by the use of certified reference materials (Nist 1643e, TM28.3 Lake Ontario, and Merck X CertiPUR Lot no. HC626403 and reference standards from interlaboratory quality evaluations ARS 21-28, Berg and Stengel (2008)) and by cross analysis using different techniques.

Hydrogen sulfide (detection limit 85 µg/L), NH₄ (detection limit 0.05 mgN/L) and alkalinity (detection limit 1 mM) were measured using photometric methods as described by Gilboa-Barber (1971), Berg et al. (2008) and Sarazin et al. (1999), respectively. Analysis for H₂S was undertaken within 8 h of sampling, with analysis for alkalinity undertaken within 3 days of sampling. A select number of samples for alkalinity measurements were double checked using filtered chilled samples on return to the laboratory by Gran Titration, with result variations not greater than 5%. Total organic C (TOC) was measured with a TOC 5000 A analyzer (Shimadzu, Switzerland), with a detection limit of 0.5 mgC/L. Chloride (detection limit 0.5 mg/L), SO₄²⁻ (detection limit 5 mg/L) and NO₃⁻ (detection limit 0.25 mg/L) were measured by ion-chromatography (Metrohm 761 Compact IC, Switzerland).

Methane was determined by gas-chromatography (GC). Concentrations were determined by injecting 50 to 100 µL of headspace into an Agilent 7890A GC (Agilent Technologies UK), equipped with a HP-PLOT-Q column and an Agilent 5975C mass spectrometer detector. Analytical accuracy was ensured by the use of certified standards (Sigma-Aldrich, UK) and detection limits were 50 µg/L. $\delta^{13}\text{C}_{\text{CH}_4}$ in a selected number of samples was also determined in a method similar to Sansome et al. (1997). Measurements were done using an IsoPrime mass spectrometer coupled to a TraceGas preconcentrator (GV Instruments, UK). The amount of injected gas depended on the CH₄ concentration in the sample, ranging from a few µL to several mL with all samples measured twice. Results are noted in the standard δ -notation relative to Vienna PeeDee Belemnite (VPDB).

Ethane and propane were measured using an Agilent GC with a Carboxen 1010 Plot column (Supelco) with flame ionization detection (FID). The temperature was kept constant at 100°C for 4 min, raised to 230°C at 10°C/min and then held constant for 7 min. The GC had a 500 µL sample loop. Scotty Transportable gas standards were used for calibration (Scott Specialty Gases, US).

In waters δD and $\delta^{18}\text{O}$ were determined by laser spectroscopy with a liquid-water isotope analyzer (Los Gatos Research DT-100). The resulting δD and $\delta^{18}\text{O}$ values were normalized using internal standards which were calibrated against VSMOW. δD and $\delta^{18}\text{O}$ in waters collected in December 2007 were also calibrated against VSMOW and analysed by the method outlined by Berg et al., (2008). δD and $\delta^{18}\text{O}$ mean monthly rainfall estimates and subsequent Local Meteoric Water Line (LMWL) were taken from Bowen (2009) for Bekescaba (latitude 46.6845, longitude 21.0870, altitude 84 m). The LMWL as calculated by Deak et al. (1987) of $\delta\text{D} = 8\delta^{18}\text{O} + 6.4$, and values from

geothermal waters from Pliocene aquifers from Hungary $\delta D = 5.7\delta^{18}O - 16$, and $\delta D = 5.6\delta^{18}O - 30$ were also used.

Lithium isotopic compositions were measured using a Neptune Multi-Collector ICP-MS (Millot et al., 2004). $^7\text{Li}/^6\text{Li}$ ratios were normalized to the L-SVEC standard solution (NIST SRM 8545, Flesch et al., 1973) following the standard-sample bracketing method. Typical in-run precision on the determination of $\delta^7\text{Li}$ is about 0.1-0.2‰ ($2\sigma_m$).

2.3. Cluster analysis

Samples were collected from a range of well types (dug, artesian, drilled, thermal), with hierarchical cluster analysis used to divide the data set into groups. From the dendrogram produced, groups can be identified which are created based on their 'similarity', which in turn can identify key parameters that can help explain the geochemical variation (Güler et al., 2002). Hierarchical cluster analysis was done with R (open source statistical program), using Euclidean distance as a similarity measurement combined with Wards method for linkage, after the data was scaled and centred to minimise variations due to differing units. The combination of Ward and Euclidean distance typically produces the most distinctive groups, and is commonly used for analysis of geochemical data sets (see for example Güler et al., 2002; Rao and Srinivas, 2006). Hierarchical cluster analysis does not however provide a statistical test of the different groupings, nor gives reasons for the groupings (Güler et al., 2002), so the cophenetic correlation coefficient (a value between 0 and 1) was used as a validity measurement of the data set as a whole (Rao and Srinivas, 2006).

A total of 23 geochemical variables was used during the hierarchical cluster analysis; pH, temperature, conductivity, total organic C (TOC), Cl^- , NO_3^- , PO_4 , NH_4 , Alkalinity, As(tot), Na, Mg, Si, K, Ca, U, Mn, Fe, B, Mo, Li, Sr and S(tot). These particular parameters were selected as variances between them should define major influences on groundwater geochemistry such as mineral dissolution (i.e. Mg, Ca, Cl^- , Na, Alkalinity, Si), surface pollution (i.e. NO_3^-), redox indicators (i.e. Fe, Mn, U, NH_4 , NO_3^-), inputs from thermal activity (i.e. B, Cl^- , Li) and marine influences (i.e. NH_4 , Na, Cl^- , Sr, B). Other key parameters such as isotopic analysis ($\delta^{18}\text{O}$, δD , $\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta^7\text{Li}$) and CH_4 were not included as these were not measured in all samples. Although hierarchical cluster analysis is a useful tool to identify groups of samples with similar characteristics, it cannot inform on why these groups are similar. Therefore care was taken not to split the data set into too many small groups. As the main focus of this work was to identify modes of As release, the different groups were taken at the point within the cluster dendrogram that a distinct group of As-rich samples were observed (Fig. 4). The cophenetic correlation coefficient measured in this study was 0.703.

3. Results and discussion

Cluster analysis revealed 4 major groups. Distinctive geochemical characteristics are shown in Table 2, with all data shown in Table 3. Geographical distribution of the wells is shown in Figure 3. Arsenic within the waters sampled ranged from below detection limits ($<0.5 \mu\text{g/L}$) to $240 \mu\text{g/L}$, and was predominantly As(III) with geochemical parameters indicative of reducing conditions (Table 3). Arsenic (tot) was found at levels above the EU limit of $10 \mu\text{g/L}$ in all groups, apart from the dug wells of group 3 (Fig. 4). Despite the initial range in geochemical parameters, the groups fall into 3 main categories, (i) group 4, which contained all waters with unusual characteristics, including all thermal

wells sampled (ii) group 3, which contained most (7 out of 10) dug wells sampled, and (iii) groups 1 and 2, representing general groundwaters with reducing conditions in all but 3 wells, which were dug wells and consequently showed oxidising conditions (Table 2 and 3). However, waters in group 1 had consistently higher As levels (mean 123 $\mu\text{g/L}$ As(tot), range 23 to 210 $\mu\text{g/L}$). Therefore, identification of the geochemical characteristics that dominate these groups, especially those that separate groups 1 and 2 is important, to determine why certain waters contain elevated As. Geochemical reasoning for these groupings is discussed, followed by a more detailed look at the potential mechanisms of As release within these waters.

3.1. Group 4 – thermal and saline influences (<0.5–240 $\mu\text{g/L}$ As, mean 33 $\mu\text{g/L}$)

Group 4 contained all thermal wells sampled with several distinct and highly variable geochemical characteristics (Table 2). Thermal waters in this study are classified as waters with surface temperatures above 35 °C (Korim, 1972). Waters within this group included Na-Cl, Na-HCO₃ and Mg/Ca-HCO₃ types (Fig. 5), with high levels of a variety of constituents including NH₄, Li, Sr, Fe, B, Na, Cl⁻, alkalinity and conductivity (Table 3) and low $\delta^7\text{Li}$ isotope values (Fig. 6). The group is widely geographically separated throughout the area (Fig. 3).

Lithium, Si, NH₄ and B are all common constituents of geothermal waters being easily leached from the surrounding rock by circulating warm waters (Fouillac and Michard, 1981; Henley and Ellis, 1983) and are all found in higher concentrations within the thermal waters of group 4 as would be expected. Bulk geochemistry of the majority of group 4 matches that of other geothermal waters sampled in the same region (as discussed in section 2.3.), with waters (Na-HCO₃ type) associated with geothermal waters from Upper Pannonian sediments (Korim, 1972, Antics, 2000, Antics and Rosca, 2003) (Fig. 2). Well depths are variable, but are typically deeper than those of groups 1 and 2. However, lack of independent verification of this information makes it difficult to accurately place waters in specific sedimentary regions.

Not all samples in these groups are 'thermal' (i.e. above 35 °C at the surface), and in addition a small number have Ca/Mg-HCO₃ type, which is in contrast to the dominant geothermal characteristics in the area. Despite this, even these samples show elevated Li, Si, NH₄ and B. This can be more clearly seen when comparing Li contents with temperature (Fig. 7) which shows good positive correlation between high temperature and high Li waters. However, some samples from group 4 have high Li contents but low temperatures common to non-thermal waters. It could then be argued that the presence of these geothermal indicators are due to other processes such as the dissolution of mineral phases and rocks rich in these constituents (Arnórsson and Andriessdóttir, 1995), or from the breakdown of organic matter causing elevated NH₄ (Appelo and Postma, 2005). However, further evidence of geothermal influence can be investigated from the Li isotopic compositions ($\delta^7\text{Li}$) measured in a select number of samples. Recent studies have shown that the extent of fractionation of Li isotopes in waters is controlled by temperature and the intensity of water/rock interaction. Hence, Li isotope fractionation during water-rock interaction is a function of temperature with more extensive fractionation at lower temperatures (Millet and Négrel, 2007; Millet et al., 2007, 2010). Therefore geothermal waters, or waters that have mixed with geothermal waters will typically have lower $\delta^7\text{Li}$ values than those which have had no interaction with such systems. Analysis of samples within group 4 shows lower $\delta^7\text{Li}$ values in comparison with the other groups, which is characteristic of greater

water/rock interaction as would be seen in geothermal waters (Fig. 6). High levels of CH₄ in most samples from these groups are also expected as this is the dominant gas present in geothermal waters from the area (Korim, 1972; Antics, 2000; Antics and Rosca, 2003; Veto et al., 2004). Within the subsurface, CH₄ can be produced from a variety of sources including biogenic (generated from microbial activity), thermocatalytic (generated from the cracking of hydrocarbons), abiogenic (generated by minerals acting as reductants) or mantle (produced from mantle gases) sources (Clark and Fritz, 1997), with both thermogenic and biogenic CH₄ known to occur in the region (Veto et al., 2004). $\delta C^{13}_{CH_4}$ for a select number of samples analysed are all less than -40 ‰, with only trace levels of propane and ethane (Table 3) indicative of biogenic CH₄ (Clark and Fritz, 1997).

A small number of samples have Na-Cl type waters which are a mix of thermal and cooler temperatures. Geothermal waters of Na-Cl type are found in Romania (Antics, 2000; Antics and Rosca, 2004). These waters show brackish/marine influences from these sediments as seen from the piper plot (Fig. 5), and have Na/Cl ratios of 0.55, similar to seawater (data not shown) (Nordstrom et al., 1989). Other indicators in this small group include high B, Li and NH₄ concentrations that can occur in waters that circulate in marine sediments (Duchi et al., 1992), which occur within this region (Fig. 2).

δD and $\delta^{18}O$ values for these groups are variable (Fig. 8). Previous studies have shown that Na-Cl waters in SE Hungary are sourced from trapped marine/brackish water (Varsányi and Kovács, 2009), and thermal waters sourced from the Pliocene (Deak et al., 1987) with δD and $\delta^{18}O$ isotope values controlled by evaporative processes which cause them to plot to the right of the LMWL (as indicated in Fig. 8). Such a trend is not observed within the geothermal, geothermally influenced and saline waters of group 4 within the present sample set, as all plot close to the LMWL. However, samples from these groups cover a wide geographical area (Fig. 3) and in the absence of detailed hydrogeological information especially due to the lack of accurate depth data explaining the connectivity within the subsurface, the relatively small data set makes it difficult to make any definitive conclusions.

3.2. Group 3 – dug wells (<0.5–2.1 µg/L As, mean 1.0 µg/L)

Wells in group 3 are all dug-wells. These wells are open pits, varying from 40 to 100 cm in diameter which tap the surface aquifer, and all show certain geochemical traits (Table 2). Waters are Ca/Mg-HCO₃ type (Fig. 5), have positive Eh values and are the only group containing significant NO₃⁻ and U (Table 3). Ignoring group 4 (thermal/saline), the dug wells also contain elevated Cl⁻, S(tot), K and conductivity in comparison to groups 1 and 2 (general groundwaters). In the area of study, dug-wells are typically found in gardens and courtyards of individual houses, with the land around them commonly being used for raising livestock and growing food. Although most dug-wells sampled had some form of protective covering to prevent physical contamination, they were not sealed and sometimes used as waste receptacles.

High Ca/Mg contents imply waters dominated by calcite dissolution and are indicative of young fresh groundwaters (Appelo and Postma, 2005). δD and $\delta^{18}O$ isotopes values of these waters are typically enriched and plot within the range of rainwater values calculated for the area (Fig. 8) (Bowen, 2009). The presence of U, which under reducing conditions is found in the highly insoluble U(IV) form but, under oxygenated conditions is found in the soluble U(VI) form (Appelo and Postma, 2005),

coupled with positive Eh values both indicate oxygenated conditions. These characteristics all would be expected from wells tapping the surface aquifers with strong rain water influence.

Despite this, Cl^- contents are very high in comparison to general groundwaters (groups 1 and 2) (Table 3). This can indicate contamination from a variety of sources including agricultural chemicals, animal and human waste, sea water, basin brines, road de-icers and municipal landfill leachate (Panno et al., 2006). The dug wells are sampled over a wide geographical area (Fig. 3) so contamination from a single point source such as landfill leachate is unlikely. Basin brines and sea water could also be the cause, as seen in the wells of groups 4 (thermal/saline), but the dug wells do not have the other characteristics such as elevated Li, NH_4 and B which would be indicative of such contamination. Although the use of salt as a road de-icer cannot be discounted as a possible contaminant, especially as the dug wells were sampled during the winter (Table 3), the proximity of the dug wells to small holdings means that the most likely source of the elevated Cl^- is anthropogenic activities from agriculture and waste disposal. Studies have shown elevated K, NH_4 , Cl^- , Na, PO_4^{3-} and SO_4^{2-} are all indicators of contamination by animal waste (Krapac, et al., 2002; Panno et al., 2006), K, NO_3^- and Cl^- can indicate contamination by fertilizers and from agricultural run off (Marie and Vengosh, 2001; Panno et al., 2006), and high SO_4^{2-} and NO_3^- can indicate domestic waste (Marie and Vengosh, 2001). Therefore, the geochemistry of group 3 is indicative of fresh groundwater, contaminated by surface human and animal wastes.

3.3. Group 1 and 2 – general groundwaters (<0.5–208 $\mu\text{g/L As}$)

3.3.1. General characteristics

Waters in groups 1 and 2 form the bulk of waters sampled, have much more neutral characteristics and have no obvious geochemical overprints from processes such as surface pollution (group 3, dug wells) and thermal activity (group 4) (see Table 2). Because of this, they can be used to represent the background geochemistry of waters in the region, and therefore are termed 'general groundwaters'. Waters in group 2 (<0.5–58 $\mu\text{g/L As}$, mean 11.5 $\mu\text{g/L}$) vary from Mg/Ca- HCO_3 to Na- HCO_3 dominated, with group 1 (23–208 $\mu\text{g/L As}$, mean 123 $\mu\text{g/L}$) being dominated by Na- HCO_3 type water (Fig. 5). This range in geochemistry is observed in waters sourced from Late Pliocene to Quaternary sediments in the area, with Mg/Ca- HCO_3 dominated waters shown to occur within coarser parts of the aquifer, and Na- HCO_3 dominated waters associated with finer grained sediments (Varsányi et al., 1997). Quaternary sediments in the area exceed 500 m in depth (Varsányi and Kovács, 1997; Nádor et al., 2003; Juhász et al., 2004), and although depth data collected could not be independently verified, most wells fit up to and below this depth (Table 2).

Within group 2, the fresher Ca/Mg dominated waters have more enriched δD and $\delta^{18}\text{O}$ values that plot close to both the dug well (group 3) and rainwater values (Fig. 8). This is to be expected as waters with higher Ca and Mg are indicative of groundwater with shorter residence times (Appelo and Postma, 2005). Group 2 also contains a small number of dug wells (3) which show geochemistry that is a mix between those of group 3 (contaminated dug wells) and group 2. Most clear is the lower NO_3^- , Cl^- , K and Na contents in comparison to those of group 3, despite similar redox and δD and $\delta^{18}\text{O}$ values (Fig., 8). This suggests that all dug wells are strongly influenced by infiltration of modern rainwater and exposure to the atmosphere, but those contained within group 2 are less contaminated by anthropogenic activities.

Waters in group 2 with more depleted δD and $\delta^{18}O$ values in comparison to modern rainwaters have Na as their dominant cation, with group 1 waters (all Na-HCO₃ type) also having depleted values (Fig. 8). Throughout Europe during the last ice-age, lower temperatures led to a depletion in δD and $\delta^{18}O$ being observed between Pleistocene and Holocene natural groundwaters (Rozanski, 1985). Within the Upper Pannonian and Quaternary sediments of the Pannonian Basin, palaeowaters dating from the last ice-age are well known (Rozanski, 1985; Stute and Deak, 1989), with infiltration thought to occur between 70 and 12 ka BP at the end of the Pleistocene (Varsányi et al., 1997, 1999). Over time as water moves through the subsurface, cationic exchange and the dissolution of minerals such as mica and feldspars (known to occur within these aquifer sediments, eg. Viczian, 2002; Juhász et al., 2002) causes groundwater to become more dominated by Na and K (Appelo and Postma, 2005). These Na-HCO₃ waters are also thought to be characteristic of waters held within finer grained sediments (Varsányi et al., 1997), so it makes sense that these waters have been present for a long time within the aquifer with time for the cationic composition to be dominated by Na. It would, therefore, seem that waters within group 2 plot on a mixing line, with infiltration waters containing $\delta^{18}O$ and δD signatures typical of modern meteoric waters occurring in dug wells and waters of a palaeometeoric origin (depleted $\delta^{18}O$ and δD and with Na-HCO₃ geochemistry) forming the end members, with a small number of Ca/Mg-HCO₃ waters having a slightly depleted δD and $\delta^{18}O$ values that plot close to the dug wells (Fig. 8). Although such a theory would require further evidence from hydrogeological investigations, evidence of the long term infiltration of meteoric waters (late Miocene to present) and mixing between palaeometeoric and present day meteoric waters have been observed within Hungary (Varsányi et al., 1997, 1999; Juhász et al., 2002; Veto et al., 2004).

3.3.2. Redox characteristics

Although the geochemistry of groups 1 and 2 are similar, there are some striking differences, most notably in more redox sensitive parameters (Tables 2 and 3). Although SO₄²⁻ was measured in all samples, values were often below the detection limit (5 mg/L, data not shown). Comparison of measured SO₄²⁻ and S(tot) found that the majority of S(tot) was SO₄²⁻, with H₂S forming only a minor component (Table 3), therefore S(tot) is taken as a proxy for SO₄²⁻. Reliance on groundwater geochemistry to determine redox conditions can be problematic, and it is better to couple such information with solid phase sediment analysis and identification of the microbial community present. However, as long as such limitations are understood, and in the absence of additional information, groundwater geochemistry can provide good evidence pertaining to the dominant processes occurring at depth.

Group 1 contains consistently higher concentrations of CH₄ and low to negligible S(tot) concentrations in comparison to group 2 which contains lower CH₄ and higher S(tot) concentrations (Table 3). Trace levels of H₂S were found in both group 1 (2 out of 13 samples) and 2 (3 out of 27 samples) waters, but levels were close to the detection limit. $\delta^{13}C_{CH_4}$ measured in a selection of samples from both groups showed values < -40 ‰ with those in group 1 being more depleted than group 2 (Fig. 8) and only trace levels of ethane and propane (Table 3). All samples show a similar range of Fe concentrations (Table 3) which shows no correlation with either CH₄ or S(tot).

The $\delta^{13}C$ signature of CH₄ can be used to identify the source, with samples depleted in $\delta^{13}C$ (< -40 ‰) indicative of a microbial source. Although CH₄ is known to migrate within the subsurface

(Christensen et al., 2000; Appelo and Postma, 2005), the presence of such high concentrations in group 1, coupled with the more depleted signatures (in comparison to group 2) indicate that methanogenesis is a dominant process in these waters. An active SO_4^{2-} -reducing community within sediments can be detected either by a reduction in SO_4^{2-} content or the presence of S^{2-} (Christensen et al., 2000). As mentioned, levels of H_2S detected in both groups are low or absent which would indicate that SO_4^{2-} reduction is not a dominant process. However measurement of S^{2-} (as H_2S) can be problematic due to its volatile nature, and in the presence of Fe it has a very low solubility, so values are liable to be an underestimation and its absence is not surprising (Christensen et al., 2000). The presence of SO_4^{2-} as a single measurement is not an indicator of an active SO_4^{2-} -reduction, but it has been suggested that the minimum concentrations of SO_4^{2-} required for SO_4^{2-} -reduction is 2.8 mg/L (Lovley and Klug, 1986), which is the case in most samples from group 2 (Table 3). Sulfate-reduction and methanogenesis tend to be mutually exclusive as active SO_4^{2-} -reducers and methanogens often compete for the same substrates. For example, active SO_4^{2-} -reducing populations have been shown to maintain acetate concentrations at levels inhibiting the activity of methanogens, with consumption of acetate by methanogens then outcompeting SO_4^{2-} -reducers in environments low in SO_4^{2-} (Lovley and Klug, 1986). This could explain the negative covariance observed between $\text{S}(\text{tot})$ and CH_4 (Fig. 9). Iron(III) reduction can occur in mixed metabolic zones with SO_4^{2-} -reduction or methanogenesis, when Fe(III) concentrations are low (Lovley and Goodwin, 1988), as seen here ($\text{Fe} < 1 \text{ mg/L}$), and explains why Fe levels are similar in both groups with no relationship observed with CH_4 and SO_4^{2-} (Fig. 10). Evidence then suggests that (i) waters in group 1 are dominated by methanogenesis, (ii) those in group 2 more likely to be undergoing active SO_4^{2-} -reduction and (iii) Fe reduction occurs in both sets of waters.

Differences in the dominant microbial behaviour between the two groups could be due either to the availability of SO_4^{2-} , or from the availability and suitability of the TOC present. Sources of SO_4^{2-} within the subsurface can be from the dissolution of gypsum, oxidation of pyrite and from mixing with seawater (Appelo and Postma, 2005). The presence of fossil seawater is known to occur within the Pannonian Basin (see for example Deak et al., 1987), but samples with Na-Cl geochemistry observed in this study (see section 3.1) have $\text{S}(\text{tot})$ levels below detection limits, implying that SO_4^{2-} has already been depleted, preventing it from being a more wide-scale source of SO_4^{2-} within the system. Absence of SO_4^{2-} in fossil seawater has also been observed in other parts of the Pannonian Basin (Deak et al., 1987). Variation in mineralogy, such as pyrite, known to occur in the region (Vicizian, 2002), could be a reason for the difference in the availability of SO_4^{2-} , but previous work has suggested mineralogical homogeneity in the Quaternary and Pliocene sediments of the region (Vicizian, 2002), though fine-scale mineralogical variations cannot be discounted.

If variations in the availability and flux of SO_4^{2-} within the subsurface cannot satisfactorily explain the differences between the two groups, then the availability of organic C to drive the process could be to blame (Appelo and Postma, 2005). Comparison of the TOC between both groups shows much greater concentrations in group 1 than group 2, with a positive correlation between TOC and CH_4 and a negative covariance between TOC and $\text{S}(\text{tot})$ (Fig. 11). Higher levels of TOC within group 1 (methanogenic) would quickly exhaust any SO_4^{2-} that had been present, driving the system to methanogenesis. Within group 2 (SO_4^{2-} -reducing) waters, the lower concentrations of TOC does not allow the flux of SO_4^{2-} within the system to be exhausted as quickly, and so SO_4^{2-} -reduction can

dominate. Therefore, the difference between the behaviour of these two groups of waters is likely to be due to the very high TOC within group 1 driving the system to methanogenesis after SO_4^{2-} supplies have been exhausted, with the lower TOC in group 2 allowing active SO_4^{2-} -reduction to be maintained.

3.4. Arsenic, source and mobilisation mechanisms

3.4.1. Geothermal and anthropogenic sources?

Correlation between Cl^- and As has been used to show the relationship between the mixing of As-rich hydrothermal fluids and As-depleted meteoric waters (Aiuppa et al., 2006) but this is not observed in waters sampled here (data not shown). However, this presumes that both Cl^- and As are behaving conservatively within the system. Arsenic does not behave conservatively in groundwater systems, and As/Cl relationships are not always seen due to the scavenging of As into mineralogical phases, redox processes (Ballantyne and Moore, 1988). Indeed comparison of the total abundance of As(tot) shows group 4 (thermal/saline) to have predominantly low As(tot) concentrations (Fig. 4), though some individual samples do contain appreciable concentrations (Table 3). As discussed in section 3.1 (Fig. 6) Li isotopes ($\delta^7\text{Li}$) have been used as a tracer for geothermal input with waters containing the lowest $\delta^7\text{Li}$ values (group 4, thermal/marine) being those strongly influenced by geothermal waters. Comparison of the $\delta^7\text{Li}$ with As(tot) values show a positive correlation, with heaviest $\delta^7\text{Li}$ values being found in waters with the highest As(tot) content (Fig. 12), implying that waters with higher As(tot) contents are those with little geothermal influence. The presence of individual samples in group 4 with high As is, therefore, contradictory, but these samples have heavier $\delta^7\text{Li}$ signatures more typical of general groundwaters (groups 1 and 2). The presence of notable As in group 4 implies that these samples are more likely a combination of geothermal waters and general groundwaters, with As present as an overprint from the latter. Dug wells (group 3) have negligible As(tot) values (Fig. 4), as would be expected with As strongly sorbing to minerals under neutral, oxidising conditions, but also suggest that As is not entering the system via surface run-off. Therefore, elevated As within the Pannonian Basin is not due to an external input (geothermal or anthropogenic), but from an in-aquifer process.

3.4.2. Redox processes

The reducing nature of the waters in groups 1 and 2 (general groundwaters) and the predominance of As in the reduced form (Table 3), coupled with the knowledge that in the area Fe-oxides are (i) known to occur (Viczián, 2002), and (ii) found associated with As in aquifer sediments (Varsányi and Kovács, 2006), suggests that reductive dissolution of As-bearing oxides also plays an important role in the present samples. The lack of correlation between As(tot) and Fe (Fig. 13), has been seen in other similar situations as Fe can be highly reactive in the subsurface, removed from solution due to the formation of Fe-phases such as siderite, previously suggested within the Pannonian Basin (Varsányi and Kovács, 2006), or from the sorption of Fe onto Fe-oxides not already reduced (Appelo et al., 2002), as observed in groundwaters of Bangladesh (Horneman et al., 2004). However, this does not explain why waters in group 1 have much higher As(tot) levels than in group 2, especially as both sets have very similar ranges in aqueous Fe concentrations (Table 3).

3.4.2.1. Sulfate reducing waters (group 2)

Despite similarities with regard to general characteristics (groundwater type, Fig. 5; δD and $\delta^{18}O$, Fig. 8), there are major differences dependant on the key microbial processes occurring as indicated by certain redox indicators (see section 3.3). Group 1 is dominated by methanogenesis (higher CH_4 , lower $S(tot)$, lighter $\delta^{13}C_{CH_4}$ in comparison to group 2), group 2 seem to be undergoing SO_4^{2-} -reduction which would limit methanogenesis (indicated by lower CH_4 and higher $S(tot)$ in comparison to group 1), with Fe-reduction occurring in both (Table 3). The reduction of SO_4^{2-} by microbial communities leads to the production of S^{2-} , which can in turn react with other components such as Fe and trace metals to form sulfide precipitates, removing them from the aqueous phase (Aggett and O'Brian, 1985; Moore et al., 1988; Huerta-Diaz et al., 1998). This process has been shown to ameliorate As levels within waters in both laboratory (Jong and Parry, 2003; O'Day et al., 2004) and field scale studies (Aggett and O'Brien, 1985; Moore et al., 1988; Huerta-Diaz et al., 1998; Kirk et al., 2004; Quicksall et al., 2008; Buschmann and Berg, 2009). Arsenic is removed from solution under these conditions either by (i) precipitation to form As-sulfides such as realgar (AsS) and orpiment (As_2S_3) or (ii) adsorption by and/or coprecipitation with other sulfide phases, most notably Fe-sulfide (Jong and Parry, 2003; O'Day et al., 2004; Kirk et al., 2004). Removal of As released into solution by dissolution of Fe-oxides in the presence of SO_4^{2-} -reduction and subsequent S^{2-} production could occur in the waters of group 2, and explains the negative correlation observed between As and $S(tot)$ (Fig. 13).

Work by O'Day et al., (2004) has shown that Fe-rich sediments favour the adsorption of As onto surfaces of Fe-sulfides as a retention mechanism (as opposed to precipitation of As-sulfides), as any free S^{2-} present is likely to form Fe-sulfide phases such as pyrite. Although sedimentological data was not collected as part of this study, the relatively low concentrations of Fe found within these waters (<1 mg/L) implies an Fe-limited environment, suggesting that the formation of As-sulfide, typically orpiment, is the dominant retention mechanism in these waters (O'Day et al., 2004). Even so, the precipitation of any mineral is dependant on the aqueous concentrations of each component exceeding its solubility product. Batch experiments have shown the abiotic precipitation of orpiment requires concentrations of As and S^{2-} in excess of 750 $\mu g/L$ and 341 $\mu g/L$, respectively (Newman et al., 1997) which are not observed in the waters of group 1 and 2. However, these results are based on bulk groundwater characterisations and it is well known that microbes can create supersaturated microenvironments favourable for mineralization (Beveridge, 1988). Microbes have also been shown to directly precipitate As_2S_3 , by the reduction of SO_4^{2-} coupled to the reduction of As(V) (Newman et al., 1997).

3.4.2.2. Methanogenic waters (group 1)

Under the dominantly methanogenic conditions prevailing within group 1, SO_4^{2-} -reduction is absent or occurring only at minimal levels. Arsenic released from the reduction and dissolution of Fe-oxides is then not subjected to removal by precipitation with S^{2-} , allowing levels to build up over time to the high concentrations as observed within the groundwater. Indeed a positive correlation between As and CH_4 is observed (Fig. 13). Therefore, the presence of As in the groundwaters of the Pannonian Basin is not controlled by mobilisation processes, but by subsequent retention mechanisms determined by the presence or absence of SO_4^{2-} (Kirk et al., 2004; Quicksall et al., 2008; Buschmann and Berg, 2009).

3.4.2.3. The role of organic carbon

There is no clear correlation observed between As and TOC (Fig. 13), but the presence of such high levels of TOC in group 1 waters (up to 33.6 mgC/L, mean average 7.73 mgC/L) could also enhance As levels in the water by competitive sorption for surface sites between organic matter and As (Grafe et al., 2001). This process was suggested by Varsányi and Kovács (2006) as an additional As release mechanism observed in the discharge area of their study. Within Hungary, TOC of waters are dominated by humic acids of a terrestrial source (Varsányi et al., 1997, 2002). Studies by Buschmann et al. (2006) have shown that terrestrially sourced humics have a higher affinity for binding with As than those of an aquatic source, with potential for up to 10% of As(V) to be attracted. However, the dominant form of As in the waters studied here is As(III) which binds to humic acids only at very high humic acid concentrations (Buschmann et al., 2006). In waters of group 1 with much higher TOC concentrations, binding of As(III) could be possible, and would have implications for the retention in the aqueous phase, again enhancing aqueous As concentrations.

4. Conclusions

The studied groundwaters of the Pannonian Basin showed a wide range of chemical composition. The major types of groundwater are classified as follows:

- (i) Generally reducing groundwaters (group 1 and 2), with group 1 containing the highest levels of As (mean 123 $\mu\text{g/L}$, range 23.4 to 208 $\mu\text{g/L}$) in contrast to group 2 (mean 11.5 $\mu\text{g/L}$, range <0.5 to 58 $\mu\text{g/L}$),
- (ii) Dug wells with very low As (group 3, mean 1 $\mu\text{g/L}$, range <0.5 to 2.1 $\mu\text{g/L}$), and,
- (iii) Wells characterized by strong geothermal and saline influences with low levels of As (group 4, mean 33.1 $\mu\text{g/L}$, range <0.5 to 240 $\mu\text{g/L}$).

High levels of Li, Si, NH_4 and B occur in geothermal and saline waters, which have low $\delta^7\text{Li}$ values. General water characteristics (Na-HCO_3) and the presence of CH_4 of biogenic origin suggest that these waters are likely to be sourced from Upper Pannonian sediments. A small number of samples from this group were Na-Cl type, with elevated B, NH_4 and Li, indicative of marine and/or brackish influences. These waters are likely to be sourced from Lower Pannonian sediments in the region.

The nature of reducing waters, coupled with knowledge that Fe-oxides are known to occur in these aquifers and are found in association with As, suggest that reductive dissolution of As bearing Fe-oxides is responsible for releasing As into groundwaters within the Pannonian Basin. More important however is the presence or absence of SO_4^{2-} . In waters of group 2, ongoing SO_4^{2-} -reduction is supposed to release S^{2-} which can then remove As from solution, either by the formation of As-sulfides, or from sorption of As onto Fe-sulfide phases formed from the concurrent release of Fe. This leads to the low As(tot) concentrations found within this group (mean 11.5 $\mu\text{g/L}$).

By contrast, in waters that are dominated by methanogenesis (group 1), As released by the reduction of Fe-oxides would not be exposed to any retention mechanisms, and so can build up to the high levels as observed in the groundwater (mean 123 $\mu\text{g/L}$). High TOC levels could also further exacerbate As levels by competitive sorption for surface sites and also by binding onto TOC. Therefore, the magnitude of As levels within waters of the Pannonian basin as studied here are controlled largely by retention processes. Levels of SO_4^{2-} within groundwaters appear to be in part governed by the

amount of organic C present, leading to low As concentrations in the presence of SO_4^{2-} , but high As levels for waters in which SO_4^{2-} levels have been exhausted.

δD and $\delta^{18}\text{O}$ analysis showed that the reducing groundwaters containing elevated As dated mostly from the last ice-age (palaeowaters), and well depths when obtained suggest all are sourced from Late Pliocene to Quaternary aquifers. Holocene deltaic sediments, i.e. deposited in the last 10–15 ka BP, have been shown in recent studies to be key in predicting the presence of elevated As in groundwaters of South and SE Asia due to reductive dissolution of As bearing Fe-oxides (Charlet and Polya, 2006; Winkel et al., 2008). Waters within these aquifers typically have low flushing rates (half lives of tens of thousands of years or more, Charlet and Polya, 2006), but in essence are relatively young, and influenced strongly by surface inputs (Harvey et al., 2002). The importance of the young sediment and groundwater age in aquifers of SE Asia is assigned to the fact that these sediments contain abundant organic matter at levels capable of driving the system to reducing conditions required for mobilisation. As a broad simplification, As-rich aquifers then tend to be limited to younger Holocene sediments at shallower depths typically up to 150 m depth, with deeper wells tapping older Pleistocene sediments then contain much lower As levels (BGS and DPHE, 2001).

However, it is shown here that much older aquifer systems with sediments from the Late Pliocene/Quaternary and containing palaeowaters dating from the last ice-age (70 and 12 ka BP) are also capable of mobilising As under similar conditions. Arsenic-rich waters are found up to ~ 600 m at depth, which is much greater than those observed in SE Asia. Although the age and facies development of these two regions is different (taking the West Bengal delta as a proxy for other SE Asian aquifers) both could be said as a broad generalisation to be similar consisting of a complex terrestrial system of alternating sand, mud and silt layers, interbedded with organic rich deposits (Umitsu, 1993; McArthur et al., 2004; Juhász et al., 2004). Evidence from the geochemistry of the groundwater studied in this work suggests that in aquifers containing As bearing Fe-oxides, As mobilisation is controlled only by redox conditions, regardless of age of the groundwater or aquifer sediments. The implications of these findings suggest that although the combination of young groundwaters and young aquifer sediments are more likely to provide the correct combination of factors, i.e. high enough levels of TOC to drive a system to the correct redox state, it is not a prerequisite. What is of greater importance is the type and abundance of TOC and its relative suitability as an energy source to the microbes present within the aquifer in question. This suggests that any reducing aquifer containing As-bearing Fe-oxides, regardless of age, has the potential to produce elevated levels of As if TOC levels are high enough and SO_4^{2-} is totally consumed, or absent to begin with. Therefore concentrations of SO_4^{2-} and TOC should be taken into account, especially with regards to older aquifer systems, in future developments of groundwater prediction models determining As enrichment due to reductive dissolution.

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References

- Aggett, J., O'Brien, G. A., 1985. Detailed model for the mobility of arsenic in lacustrine sediments based on measurements in Lake Ohakuri. *Environ. Sci. Technol.* 19, 231-244.
- Aiuppa, A., D'Alessandro, W., Federico, C., Palumbo, B., Valenza, M., 2003. The aquatic geochemistry of arsenic in volcanic groundwaters from Southern Italy. *Appl. Geochem.* 18, 1283-1296.
- Aiuppa, A., Avino, R., Brusca, L., Caliro, S., Chiodini, G., Alessandro W. D', Favara, R., Federico, C., Ginevra, W., Inguaggiato, S., Longo, M., Pecoraino, G., Valenza, M., 2006. Mineral control of arsenic content in thermal waters from volcano-hosted hydrothermal systems: Insights from island of Ischia and Phlegrean Fields (Campanian Volcanic Province, Italy). *Chem. Geol.* 229, 313-330.
- Antics, M., 2000. Computer simulation of geothermal reservoirs in the Pannonian Basin, Eastern Europe. *Proc. World Geothermal Congress, 2000, Kyushu - Tohoku, Japan, May 28- June 10, 2000*
- Antics, M., Rosca, M., 2003. Geothermal development in Romania. *Geothermics.* 32, 361-370.
- Appelo, C. A. J., Postma, D., 2005. *Geochemistry, groundwater and pollution*. A. A. Balkema Publishers.
- Appelo, C. A. J., Van der Weiden, M. J. J., Tournassat, C., Charlet, L., 2002. Surface complexation of ferrous iron and carbonate on ferrihydrite and the mobilisation of arsenic. *Environ. Sci. Technol.* 36, 3096-3103.
- Arnórsson, S., Andrésdóttir, A., 1995. Processes controlling the distribution of boron and chlorine in natural waters in Iceland. *Geochim. Cosmochim. Acta.* 59, 4125-4146.
- Ballantyne, J. M., Moore, J. N., 1988. Arsenic geochemistry in geothermal systems. *Geochim. Cosmochim. Acta.* 42, 475-483
- Berg, M., Stengel, C., 2008. ARS 25-28 Arsenic Reference Samples, Interlaboratory Quality Evaluation (IQE). Report to participants, Eawag, Swiss Federal Institute of Aquatic Science and Technology, March 2008, Dübendorf, Switzerland.
- Berg, M., Tran, H. C., Nguyen, T. C., Pham, H. V., Schertenleib, R., Giger, W., 2001. Arsenic contamination of groundwater and drinking water in Vietnam: A human health threat. *Environ. Sci. Technol.* 35, 2621-2626.
- Berg, M., Trang, P. T. K., Stengel, C., Buschmann, J., Viet, P. H., Dan, N. V., Giger, W., Stuben, D., 2008. Hydrological and sedimentary controls leading to arsenic contamination of groundwater in the Hanoi area, Vietnam: The impact of iron-arsenic ratios, peat, river bank deposits and excessive groundwater abstraction. *Chem. Geol.* 249, 91-112.
- Beveridge, T. J., 1988. Role of cellular design in bacterial metal accumulation and mineralization. *Annual Rev. Microbiol.* 43, 141-171.
- BGS and DPHE, 2001. Arsenic contamination of groundwater in Bangladesh. Kinniburgh, D. G., Smedley, P. L., (Eds.), vol 2: Final report. British Geological Survey Report WC/00/19, British Geological Survey, Keyworth. UK.
- Borzsonyi, M., Bereczky, A., Rudnai, P., Csanady, M., Horvath, A., 1992. Epidemiological studies on human subjects to arsenic in drinking water in Southeast Hungary. *Arch. Toxicol.* 66, 77-78.
- Bowen, G. J., 2009. The Online Isotopes in Precipitation Calculator, version 2.2(07/2008) <http://www.waterisotopes.org>.
- Buschmann, J., Berg, M., 2009. Impact of sulfate reduction on the scale of arsenic contamination in groundwater of the Mekong, Bengal and Red River deltas. *Appl. Geochem.* 24, 1278-1286.
- Buschmann, J., Berg, M., Stengel, C., Sampson, M. L., 2007. Arsenic and manganese contamination of drinking water resources in Cambodia: coincidence of risk areas with low relief topography. *Environ. Sci. Technol.* 41, 2146-2152.
- Buschmann, J., Kappeler, A., Lindauer, U., Kistler, D., Berg, M., Sigg, L., 2006. Arsenite and arsenate binding to dissolved humic acids: Influence of pH, type of humic acid and aluminum. *Environ. Sci. Technol.* 40, 6015-6020.
- Čavar, S., Klapac, T., Grubešić, R. J., Valek, M., 2005. High exposure to arsenic from drinking water at several localities in eastern Croatia. *Sci. Total Environ.* 339, 277-282.
- Chakraborti, D., Mukerjee, S. C., Pati, S., Sengupta, M. K., Rahman, M. M., Chowdhury, U. K., Lodh, D., Chanda, C. R., Chakraborti, A. K., Basu, G. K., 2003. Arsenic groundwater contamination in Middle Ganga Plain, Bihar, India: A future danger? *Environ. Health Perspect.* 111, 1194-1201.

- Charlet, L., Poly, D. A., 2006. Arsenic in shallow reducing groundwaters in Southern Asia: an environmental health disaster. *Elements* 2, 91-96.
- Christensen, T. H., Bjerg, P. L., Banwart, S. A., Jakobsen, R., Heron, G., Alrechtsen, H-J., 2000. Characterization of redox conditions in groundwater contaminant plumes. *J. Contam. Hydrol.* 45, 165-241.
- Clark, I. D., Fritz, P., 1997. *Environmental Isotopes in Hydrogeology*. Lewis Publishers, CRC Press LLC.
- Coetsiers, M., Walraevens, K., 2006. Chemical characterization of the Neogene Aquifer, Belgium. *Hydrol. J.* 14, 1556-1568.
- Cohut, I., Bendea, C., 1999. Geothermal Development Opportunities in Romania. *Geothermische Energie*, 24/25, 7 Jahrgang/Heft ½, Geothermische Vereinigung, Geeste, Marz/September S. 8-13.
- Csalagovitis, I., 1999. Arsenic-bearing artesian waters of Hungary. *Ann. Rep. Geological Institute of Hungary*, 1992-1993/II: 85-92.
- Deak, J., Stute, M., Rudolph, J., Sonntag, C., 1987. Determination of the flow regime of Quaternary and Pliocene layers in the Great Hungarian Plain (Hungary) by D, ^{18}O , ^{14}C and Noble Gas Measurements. In *Isotope techniques in Water Resources Development. Proc. IAEA Symp., Vienna, IAEA Proc. Series STI/PUB/757*, 335-350.
- Djuric, D., Jevtic, G., 2008. Solutions for groundwater management in areas affected by high arsenic content - Vojvodina case study. *Proc. 2nd Internat. Congress on "Arsenic in the Environment"*, 21-23 May 2008, Valencia, Spain, 159-160.
- Duchi, V., Minissale, A., Paolieri, M., Prati, F., Valori, A., 1992. Chemical relationships between discharging fluids in the Siena-Radicofani graben and the deep fluids produced by the geothermal fields of Mt Amiata, Torre Alfina and Latera (Central Italy). *Geothermics* 21, 401-413.
- Flesch, G. D., Anderson, A. R., Svec, H. J., 1973. A secondary isotopic standard for $^6\text{Li}/^7\text{Li}$ determinations. *Internat. J. Mass Spectrom. Ion Phys.* 12, 265-272.
- Fletcher, T., Leonardi, G., Goessler, W., Gurzau, E., Koppova, K., Kumar, R., Rudnai, P., Vahter, M., 2008. Arsenic in residential drinking water and cancer in Central Europe – the ASHRAM study. The 3rd Central and Eastern European Conf. Health and the Environment (CEECH), Cluj-Napoca, Romania, 19-22nd November 2008.
- Fouillac, C., Michard, G., 1981. Sodium/Lithium ratio in water applied to geothermometry of geothermal reservoirs. *Geothermics* 10, 55-70.
- Frapporti, G., Vriend, S. P., van Gaans, P. F. M., 1996. Trace elements in the shallow groundwater water of the Netherlands. A geochemical and statistical interpretation of the National Monitoring Network data. *Aquat. Geochem.* 2, 51-80.
- Gábris, G., Nádor, A., 2007. Long-term fluvial archives in Hungary: response of the Danube and Tisza rivers to tectonic movements and climatic changes during the Quaternary: A review and new synthesis. *Quatern. Sci. Rev.* 26, 2758-2782.
- Garcia-Sanchez, A., Moyano, A., Mayorga, P., 2005. High arsenic contents in groundwater of central Spain. *Environ. Geol.* 47, 847-854.
- Geary, D. H., Staley, A. W., Muller, P., Magyar, I., 2002. Iterative changes in Lake Pannon *Melanopsis* reflect a recurrent theme in gastropod morphological evolution. *Paleobiol.* 28, 208-221.
- Gilboa-Garber, N., 1971. Direct spectrophotometric determination of inorganic sulphide in biological materials and in other complex mixtures. *Anal. Biochem.* 43, 129-133.
- Gomez, J. J., Lillo, J., Sahun, B., 2006. Naturally occurring arsenic in groundwater and identification of the geochemical sources in the Duero Cenozoic Basin, Spain. *Environ. Geol.* 50, 1151-1170.
- Grafe, M., Eick, M. J., Grossl, P. R., 2001. Adsorption of arsenate (V) and arsenite (III) on goethite in the presence and absence of dissolved organic carbon. *Soil Sci. Soc. Am. J.* 65, 1680-1687.
- Güler, C., Thyne, G. D., McCray, J. E., Turner, A. K., 2002. Evaluation of graphical and multivariate statistical methods for classification of water chemistry data. *Hydrogeol. J.* 18, 455-474.
- Gurzau, E. S., Gurzau, A. E., 2001. Arsenic in drinking water from groundwater in Transylvania, Romania: an overview. In: Chappell, W. R., Abernathy, C. O., Calderon, R. L. (Eds), *Arsenic Exposure and Health Effects IV*. Elsevier, 181-184.
- Habuda-Stanić, M., Kuleš, M., Kalajdžić, B., Romić K., 2007. Quality of groundwater in eastern Croatia. The problem of arsenic pollution. *Desalination* 210, 157-162.
- Harvey, C. F., Swartz, C. H., Badruzzaman, A. B. M., Keon-Blute, N., Yu, W., Ali, M. A., Jay, J., Beckie, R., Niedan, V., Brabander, D., Oates, P. M., Ashfaq, K. N., Islam, S., Hemond, H. F., Ahmed, M. F., 2002. Arsenic mobility and groundwater extraction in Bangladesh. *Science* 298, 1602-1606.
- Henley, R. W., Ellis, A. J., 1983. Geothermal systems ancient and modern: A geochemical review. *Earth Sci. Rev.* 19, 1-50.

- Horneman, A., van Gee, A., Kent, D. V., Mathe, P. E., Zheng, Y., Dhar, R. K., O'Connell, S., Hoque, M. A., Aziz, Z., Shamsudduha, M., Seddique, A. A., Ahmed, K. M., 2004. Decoupling of As and Fe release to Bangladesh groundwater under reducing conditions. Part I: Evidence from sediment profiles. *Geochim. Cosmochim. Acta*. 68, 3459-3473.
- Huerta-Diaz, M. A., Tessier, A., Carignan, R., 1998. Geochemistry of trace metals associated with reduced sulphur in freshwater sediments. *Appl. Geochem.* 13, 213-233.
- Islam, F. S., Gault, A. G., Boothman, C., Polya, D. A., Charnock, J. M., Chatterjee, D., Lloyd, J. R., 2004. Role of metal-reducing bacteria in arsenic release from Bengal delta sediments. *Nature* 430, 68-71.
- Jimenez, C., Mertens, J., Rowland, H. A., Baciú, C., Berg, M., Furrer, G., Hug, S., Cordos, E., 2009. Groundwater geochemistry and As content in the Eastern Pannonian Basin (Romania) - PCA analysis. *Geochim. Cosmochim. Acta* 73, A596.
- Jong, T., Parry, D. L., 2003. Removal of sulphate and heavy metals by sulphate reducing bacteria in short-term bench scale upflow anaerobic packed bed reactor runs. *Water Res.* 37, 3370-3389.
- Juhász, A., Tóth, T. M., Ramseyer, K., Matter, A., 2002. Connected fluid evolution in fractured crystalline basement and overlying sediments, Pannonian Basin, SE Hungary. *Chem. Geol.* 182, 91-120.
- Juhász, E., Phillips, L., Müller, P., Ricketts, B., Toth-Makk, Á., Lantos, M., Kovács, L. Ó., 1999. Late Neogene sedimentary facies and sequences in the Pannonian Basin, Hungary. In: Durand, B., Jolivet, L., Horváth, F., Séranne, M. (Eds), *The Mediterranean Basins: Tertiary Extension within the Alpine Orogen*. *Geol. Soc. London Special Publication* 156, 335-356.
- Juhász, G., Müller, P., Toth-Makk, Á., 2004. Alluvial architecture and fluvial cycles in Quaternary deposits in a continental interior basin, E Hungary. *Geologica Croatica*. 57, 171-190.
- Juhász, G., Pogácsás, G., Magyar, I., Vakarcz, G., 2007. Tectonic versus climatic control on the evolution of fluvio-deltaic systems in a lake basin, Eastern Pannonian Basin. *Sed. Geol.* 202, 72-95.
- Katsoyiannis, I. A., Katsoyiannis, A. A., 2006. Arsenic and other metal contamination of groundwater in the industrial area of Thessaloniki Northern Greece. *Environ. Monitor. Assess.* 123, 393-406.
- Kirk, M. F., Holm, T. R., Park, J., Jin, Q., Sanford, R. A., Fouke, B. W., Bethke, C. M., 2004. Bacterial sulfate reduction limits natural arsenic contamination in groundwater. *Geology* 32, 953-956.
- Korim, K., 1972. Geological aspects of thermal water occurrences in Hungary. *Geothermics*. 1, 96-102.
- Krapac, I. G., Dey, W. S., Roy, W. R., Smyth, C. A., Stormont, E., Sargent, S. L., Steele, J. D., 2002. Impacts of swine manure pits on groundwater quality. *Environ. Pollut.* 120, 475-492.
- Lenkey, L., Dövényi, P., Horváth, F., Cloetingh, S. A. P. L., 2002. Geothermics of the Pannonian basin, and its bearing on the neotectonics. *EGU Stephan Mueller Special Publication Series* 3, 29-40.
- Lindberg, A.-L., Goessler, W., Gurzau, E., Koppova, K., Rudnai, P., Kumar, R., Fletcher, T., Leonardi, G., Slotova, K., Gheorghiu, E., Vahter, M., 2006. Arsenic exposure in Hungary, Romania and Slovakia. *J. Environ. Monitor.* 8, 203-208.
- Lovley, D. R., Goodwin, S., 1988. Hydrogen concentrations as an indicator of the predominant terminal electron-accepting reactions in aquatic sediments. *Geochim. Cosmochim. Acta*. 52, 2993-3003.
- Lovley, D. R., Klug, M. J., 1986. Model for the distribution of sulphate reduction and methanogenesis in freshwater sediments. *Geochim. Cosmochim. Acta*. 50, 11-18.
- Magyar, I., Geary, D. H., Müller, P., 1999. Paleogeographic evolution of the Late Miocene Lake Pannon in Central Europe. *Palaeogeog. Palaeoclimatol. Palaeoecol.* 147, 151-167.
- Marie, A., Vengosh, A., 2001. Sources of salinity in ground water from Jericho Area, Jordan Valley. *Groundwater* 39, 240-248.
- McArthur, J. M., Banerjee, D. M., Hudson-Edwards, K. A., Mishra, R., Purohit, R., Ravenscroft, P., Cronin, A., Howarth, R. J., Chatterjee, A., Talukder, T., Lowry, D., Houghton, S., Chadha, D. K., 2004. Natural organic matter in sedimentary basins and its relation to arsenic in anoxic groundwater: the example of West Bengal and its worldwide implications. *Appl. Geochem.* 19, 1255-1293.
- McArthur, J.M., Ravenscroft, P., Safiulla, S., Thirlwall, M.F., 2001. Arsenic in groundwater: testing pollution mechanisms for sedimentary aquifers in Bangladesh. *Water Resour. Res.* 37, 109-117.
- Millot, R., Négrel, P., 2007. Multi-isotopic tracing ($\delta^7\text{Li}$, $\delta^{11}\text{B}$, $^{87}\text{Sr}/^{86}\text{Sr}$) and chemical geothermometry: evidence from hydro-geothermal systems in France. *Chem. Geol.* 244, 664-678.
- Millot R., Guerrot C., Vigier N., 2004. Accurate and high precision measurement of lithium isotopes in two reference materials by MC-ICP-MS. *Geostand. Geoanal. Res.* 28, 53-159.

- Millot, R., Négrel, Ph., Petelet-Giraud, E., 2007. Multi-isotopic (Li, B, Sr, Nd) approach for geothermal reservoir characterization in the Limagne Basin (massif Central, France). *Appl. Geochem.* 22, 2307-2325.
- Millot R., Scaillet B. Sanjuan B., 2010. Lithium isotopes in island arc geothermal systems: Guadeloupe, Martinique (French West Indies) and experimental approach. *Geochim. Cosmochim. Acta* 74, 1852-1871.
- Moore, J. N., Fickin, W. H., Johns, C., 1988. Partitioning of arsenic and metals in reducing sulfidic sediments. *Environ. Sci. Technol.* 22, 432-437.
- Mrazovac, S., Basic, D., 2009. Methane-rich geothermal waters in the Pannonian Basin of Vojvodina (northern Serbia). *Geothermics*. 38, 303-312.
- Nádor, A., Lantos, M., Tóth-Makk, Á., Thamó-Bozsó, E., 2003. Milankovitch-scale multi-proxy records from fluvial sediments of the last 2.6 Ma, Pannonian Basin, Hungary. *Quatern. Sci. Rev.* 22, 2157-2175.
- Nádor, A., Thamó-Bozsó, E., Magyair, Á., Babinszki, E., 2007. Fluvial responses to tectonics and climate change during the Late Weichselian in the eastern part of the Pannonian Basin (Hungary). *Sed. Geol.* 202, 174-192.
- Newman, D. K., Beveridge, T. J., Morel, F. M. M., 1997. Precipitation of arsenic trisulfide by *Desulfotomaculum auripigmentum*. *Appl. Environ. Microbiol.* 63, 2022-2028.
- Nickson, R., McArthur, J., Burgess, W., Matin Ahmed, K., Ravenscroft, P., Rahman, M., 1998. Arsenic poisoning of Bangladesh groundwater. *Nature* 395, 338.
- Nordstrom, D. K., Ball, J. W., Donahoe, R. J., Whittemore, D., 1989. Groundwater chemistry and water-rock interactions at Stripa. *Geochim. Cosmochim. Acta*. 53, 1727-1740.
- O'Day, P. A., Vlassopoulos, D., Root, R., Rivera, N., 2004. The influence of sulphur and iron on dissolved arsenic concentrations in the shallow subsurface under changing redox conditions. *Proc. Nat. Acad. Sci.* 101, 13703-13708.
- Panno, S. V., Hackley, K. C., Hwang, H. H., Greenberg, S. E., Krapac, I. G., Landsberger, S., O'Kelly, D. J., 2006. Characterization and identification of Na-Cl sources in groundwater. *Groundwater* 44, 176-187.
- Quicksall, A. N., Bostick, B. C., Sampson M. L., 2008. Linking organic matter deposition and iron mineral transformations to groundwater arsenic levels in the Mekong delta, Cambodia. *Appl. Geochem.* 23, 3088-3098.
- Rao, A. R., Srinivas, V. V., 2006. Regionalization of watersheds by hybrid-cluster analysis. *J. Hydrol.* 318, 37-56.
- Rögl, F., 1999. Mediterranean and Paratethys. Facts and hypotheses of an Oligocene to Miocene Paleogeography (short overview). *Geological Carpathica* 50, 339-349.
- Roberts, L. C., Hug, S. J., Dittmar, J., Voegelin, A., Saha, G. C., Ali, M. A., Badruzzaman, A. B. M., Kretzschmar, R., 2007. Spatial distribution and temporal variability of arsenic in irrigated rice fields in Bangladesh. 1. Irrigation water. *Environ. Sci. Technol.* 41, 5960-5966.
- Rowland, H. A. L., Boothman, C., Pancost, R., Gault, A. G., Polya, D. A., Lloyd J. R., 2009a. The role of indigenous microorganisms in the biodegradation of naturally occurring petroleum, the reduction of iron, and the mobilization of arsenite from West Bengal aquifer sediments. *J. Environ. Qual.* 38, 1598-1607.
- Rowland, H. A. L., Jimenez, C., Omoregie, E., Mertens, J., Berg, M., Baci, C., Hug, S. J., 2009b. Controls on groundwater geochemistry and arsenic mobilisation processes in aquifers of Eastern Europe (Pannonian Basin). *Geochim. Cosmochim. Acta*. 73, A1126.
- Rozanski, K., 1985. Deuterium and oxygen-18 in European groundwaters – links to atmospheric circulation in the past. *Chem. Geol.* 52, 349-363.
- Sacchi, M., Horváth, F., 2002. Towards a new time scale for the Upper Miocene continental series of the Pannonian basin (Central Paratethys) EGU Stephan Mueller Special Publication Series 3, 79–94.
- Sansone, F. J., Popp, B. N., Rust, T. M., 1997. Stable carbon isotopic analysis of low-level methane in water and gas. *Anal. Chem.* 69, 40-44.
- Sarazin, G., Michard, G., Prevot, F., 1999. A rapid and accurate spectroscopic method for alkalinity measurements in sea water samples. *Water Res.* 33, 290-294.
- Saunders, J. A., Lee, M.-K., Uddin, A., Mohammad, S., Wilkin, R. T., Fayek, M., Korte, N. E., 2005. Natural arsenic contamination of Holocene alluvial aquifers by linked tectonic, weathering and microbial processes. *Geochem. Geophys. Geosyst.* 6, Q04006.
- Smedley, P. L., Edmunds, W. M., 2002. Redox patterns and trace-element behaviour in the East Midlands Triassic Sandstone Aquifer, UK. *Groundwater* 40, 44-58.

- Smith, A. H., Lingas, E. O., Rahman, M., 2000. Contamination of drinking-water by arsenic in Bangladesh: a public health emergency. *Bull. WHO* 78, 1093-1103.
- Stauder, S., 2007. Chemistry and treatment of groundwater in the Vojvodina. *Water Sci. Technol.* 7, 93-101.
- Stute, M., Deak, J., 1989. Environmental isotope study (^{14}C , ^{13}C , ^{18}O , D, Noble gases) on deep groundwater circulation systems in Hungary with reference to Palaeoclimate. *Radiocarbon* 31, 902-918.
- Tyrovola, K., Nikolaidis, N. P., Veranis, N., Kallithrakas-Kontos, N., Koulouridakis, P. E., 2006. Arsenic removal from geothermal waters with zero-valent iron – effect of temperature, phosphate and nitrate. *Water Res.* 40, 2375-2386.
- Ujević, M., Duić, Ž., Casiot, C., Sipos L., Santo, V., Dadić, Ž., J. Halamić, J., 2010. Occurrence and geochemistry of arsenic in the groundwater of Eastern Croatia. *Appl. Geochem.* 25, 1017-1029.
- Umitsu, M., 1993. Late Quaternary sedimentary environments and landforms in the Ganges Delta. *Sed. Geol.* 83, 177-186.
- Varsányi, I., Kovács, L. Ó., 1997. Chemical evolution of groundwater in the River Danube deposits in the southern part of the Pannonian Basin (Hungary). *Appl. Geochem.* 12, 625-636.
- Varsányi, I., Kovács, L. Ó., 2006. Arsenic, iron and organic matter in sediments and groundwater in the Pannonian Basin, Hungary. *Appl. Geochem.* 21, 49-963.
- Varsányi, I., Kovács, L. Ó., 2009. Origin, chemical and isotopic evolution of formation water in geopressed zones in the Pannonian Basin, Hungary. *Chem. Geol.* 264, 187-196.
- Varsányi, I., Fodre, Z., Bartha, A., 1991. Arsenic in drinking water and mortality in the Southern Great Plain, Hungary. *Environ. Geochem. Health* 13, 14-22.
- Varsányi, I., Kovács, L. Ó., Karpáti, Z., Matray, J. M., 2002. Carbon forms in formation waters from the Pannonian Basin, Hungary. *Chem. Geol.* 189, 165-182.
- Varsányi, I., Matray, J-M., Kovács, L. Ó., 1997. Geochemistry of formation waters in the Pannonian Basin (southeast Hungary). *Chem. Geol.* 140, 89-106.
- Varsányi, I., Matray, J-M., Kovács, L. Ó., 1999. Hydrogeochemistry in two adjacent areas in the Pannonian Basin (South-east Hungary). *Chem. Geol.* 156, 25-39.
- Veto, I., Futo, I., Horvath, I., Szanto, S., 2004. Late and deep fermentative methanogenesis as reflected in the H-C-O-S isotopy of the methane-water system in deep aquifers of the Pannonian Basin (SE Hungary). *Org. Geochem.* 35, 713-723.
- Viczian, I., 2002. Mineralogy of Pliocene to Pleistocene pelitic sediments of the Great Hungarian Plain. *Acta Mineralogica-Petrographica* 43, 39-53.
- Vidovic, M., Nikic, Z., Milovanovic, B., 2006. Water quality of the North Banat basal aquifer system. *Geographica Pannonica* 10, 43-46.
- Warner, K. L., 2001. Arsenic in glacial drift aquifers and the implication for drinking water – Lower Illinois River Basin. *Ground Water* 39, 433-442.
- Welch, A. H., Wetjohn, D. B., Helsel, D. R., Wanty, R. B., 2000. Arsenic in groundwater of the United State: Occurrence and geochemistry. *Ground Water* 38, 589-604.
- Winkel, L., Berg, M., Amini, M., Hug, S. J., Johnson, C. A., 2008. Predicting groundwater arsenic contamination in Southeast Asia from surface parameters. *Nature Geosci.* 1, 536-542.
- Winston, R.B., 2000. Graphical User Interface for MODFLOW, Version 4: U.S. Geological Survey Open-File Report 00-315, 27 p. http://water.usgs.gov/nrp/gwsoftware/GW_Chart/GW_Chart.html Version 1.21.0.0.
- Yamamoto, M., Urata, K., Murashige, K., Yamamoto, Y., 1981. Differential determination of arsenic(III) and arsenic(V), and antimony(III) and antimony(V) by hydride generation-atomic absorption spectrophotometry, and its application to the determination of these species in sea water. *Spectrochim. Acta* 36B, 671-677.

Figure 1 : Topographical map of Europe (A) showing location of field area and important topological features (B).

Figure 2 : Simplified cross section of the Pannonian Basin (not to scale) with dominant sediment and groundwater types (Magyar et al., 1999; Varsányi et al., 1997; Juhász et al., 1999; Juhász et al., 2004, 2007; Gábris and Nádor, 2007).

Figure 3 : Location map of studied wells in the Pannonian Basin. The altitude of the study area is 100 ± 25 m above sea level.

Figure 4 : Arsenic box-plot of different groups. Although levels of As above the EU limit of $10 \mu\text{g/L}$ are found in all groups apart from group 3, group 1 is the only one with consistently high concentrations.

Figure 5 : Piper plot of groundwaters (Winston, 2000). Samples display a wide variation in dominant group types including saline waters (Na-Cl), typical groundwater gradients representing cation exchange from freshest (Mg/Ca- HCO_3) and to older (Na- HCO_3) groundwaters.

Figure 6 : Comparison between Li concentrations and $\delta^7\text{Li}$ values (‰). Group 4 display the lowest $\delta^7\text{Li}$ signatures, with groups 1 and 2 the highest, indicating that waters with the highest Li contents also show the highest levels of water/rock interaction.

Figure 7 : Comparison between Li concentrations and temperature. Thermal waters of group 4 ($+ 35^\circ\text{C}$) typically have higher Li contents, with concentrations increasing with temperature. Presence of high Li but low temperature ($< 35^\circ\text{C}$) waters (circled area) indicates water with strong geothermal influences despite cool surface temperatures.

Figure 8 : Comparison of δD and $\delta^{18}\text{O}$ values of waters with LMWL, thermal and rainfall values from the area (Rozanski et al., 1986, Deak et al., 1987, Bowen 2009). All samples plot on or close to the LMWL for the area, with dug wells and those with Ca/Mg- HCO_3 plotting in the range for infiltration waters. Sodium- HCO_3 waters plot within the range of palaeowaters from the previous ice-age.

Figure 9 : Comparison of CH_4 with $\delta^{13}\text{C}_{\text{CH}_4}$ and $\text{S}(\text{tot})$ of waters from groups 1 and 2 (general groundwaters). Waters of group 1 show a more depleted $\delta^{13}\text{C}_{\text{CH}_4}$ signature than group 2. Levels of $\text{S}(\text{tot})$ are higher in group 2, with CH_4 higher in group 1, with a negative covariance observed between CH_4 and $\text{S}(\text{tot})$.

Figure 10 : Comparison of Fe with CH_4 and $\text{S}(\text{tot})$ of waters from groups 1 and 2 (general groundwaters). No correlation is observed between Fe, $\text{S}(\text{tot})$ or CH_4 in waters from either group.

Figure 11 : Comparison of TOC with CH_4 and $\text{S}(\text{tot})$ of waters from groups 1 and 2 (general groundwaters). Positive correlation between TOC and CH_4 is observed within waters of group 1. Group 1 waters contain much higher concentrations of TOC with little $\text{S}(\text{tot})$, with waters in group 2 containing low concentrations of TOC but with higher concentrations of $\text{S}(\text{tot})$.

Figure 12 : Comparison between $\text{As}(\text{tot})$ and Li isotopes. Positive correlation implies waters with lowest As contents are those that have undergone the highest levels of water/rock interaction as associated with geothermal waters.

Figure 13 : Comparison of $\text{As}(\text{tot})$ with CH_4 , $\text{S}(\text{tot})$, TOC and Fe of waters from groups 1 and 2 (general groundwaters). Arsenic, CH_4 and TOC concentrations are much higher in group 1, with group 2 waters having much higher abundances of $\text{S}(\text{tot})$. Range in Fe concentrations is similar in both groups.

Table 1: Values of As in drinking water, and estimates of people affected in countries of the Pannonian Basin. For locations see Figure 1.

Country	Arsenic ($\mu\text{g L}^{-1}$)	Population affected	References
Hungary - Great Hungarian Plain	0 - 220	400,000 to 500,000	Csalagovitis, 1999; Varsányi and Kovács, 2006
Romania - Bihor and Arad counties (Western Romanian Plain)	0 - 176	50,000	Gurzau and Gurzau, 2001
Croatia - Osijek-Baranja and Vukovar- Syrmia counties (Eastern Croatia)	<1 - 610	200,000 and/or 3% of population	Habuda-Stanic et al., 2007, Čavar et al., 2005, Ujević et al., 2010
Serbia - Northern Banat (Vojvodina province)	11 - 222	200,000	Vidovic et al., 2006; Stauder, 2007; Djuric and Jevtic, 2008
Slovakia - Banska Bystrica and Nitra counties	37 - 39	Not reported	Lindberg et al., 2006

Table 2 : Distinguishing characteristics and As concentrations of the main groups of groundwaters

Group name	n	Predominant characteristics	As(tot) µg/L Mean average and range
Group 1 – General groundwaters – Methanogenic	15	<p>⇒ Consistent elevated As(tot) in all samples</p> <p>⇒ Elevated CH₄, TOC</p> <p>⇒ Low Fe and S(tot)</p> <p>Redox characteristics and Eh indicate reducing conditions</p> <p>Na -HCO₃ groundwater types</p> <p>Lighter δ⁷Li isotopic characteristics</p> <p>δD and δ¹⁸O values similar to palaeowaters</p>	<p>123</p> <p>23.4 to 208</p>
Group 2 – General groundwaters – Sulfate-reducing	35	<p>⇒ Range of As(tot) values</p> <p>⇒ Moderate S(tot)</p> <p>⇒ Low Fe</p> <p>Redox characteristics and Eh indicate predominantly reducing conditions</p> <p>Mg/Ca-HCO₃ to Na -HCO₃ groundwater types</p> <p>Lighter δ⁷Li isotopic characteristics</p> <p>Range of δD and δ¹⁸O values from rainwater to palaeowaters</p>	<p>11.5</p> <p><0.5 to 58.0</p>
Group 3 – Dug wells	7	<p>⇒ Redox characteristics and Eh indicate oxidising conditions</p> <p>⇒ Elevated SO₄²⁻, NO₃⁻, U, Cl⁻, K and conductivity</p> <p>⇒ As(tot) below detection limit</p> <p>Mg/Ca-HCO₃ groundwater type</p> <p>δD and δ¹⁸O values similar to rain water</p>	<p>1.0</p> <p><0.5 to 2.1</p>
Group 4 – Thermal and saline waters	16	<p>⇒ Redox characteristics and Eh indicate reducing conditions</p> <p>⇒ Highly variable geochemistry</p> <p>⇒ Elevated levels of NH₄⁺, Li, Cl⁻, Na, Sr, Fe, B, alkalinity</p> <p>⇒ Group contained all thermal wells (+35 °C)</p> <p>Na-Cl, Na-HCO₃ and Mg/Ca-HCO₃ groundwater types</p> <p>Heavier δ⁷Li isotopic characteristics</p> <p>Variable δD and δ¹⁸O values</p>	<p>33.1</p> <p><0.5 to 240</p>

Table 3 : Geochemical parameters for Pannonian Basin groundwaters

Grp ^a	Name ^b	Well ^c	Depth (m)	Age (yrs)	δD ‰ VSMOW	d18O ‰ VSMOW	δ ⁷ Li ‰ VL-SVEC	δ ¹³ C _{org} ‰ VPDB	pH	Temp °C	eH mV	Cond mS/cm	TOC mgC/L	Cl ⁻ mg/L	NO ₃ ⁻ mgN/L	S(tot) ^d mg/L	H ₂ S μg/L	CH ₄ mg/L	C ₂ H ₆ μg/L	C ₃ H ₈ μg/L	PO ₄ mgP/L	NH ₄ mgN/L	Alk mM	As(III) μg/L	As(tot) ^e μg/L	Na ⁺ mg/L	Mg ⁺ mg/L	Si ⁺ mg/L	K ⁺ mg/L	Ca ⁺ mg/L	Fe ⁺ mg/L	Mn ⁺ μg/L	U ⁺ μg/L	Mo ⁺ μg/L	B ⁺ mg/L	Li ⁺ μg/L	Sr ⁺ μg/L
1	M_R108	A	300	66	-79.78	-11.14	-	-	8.29	20.8	121	0.9	1.1	72.6	<0.25	0.3	<85	<0.05	-	-	0.1	0.3	9.4	20.6	23.4	196	1.8	7.3	0.9	9.5	0.01	31.3	<0.5	73.0	0.1	5.7	90.6
1	M_H204	A	582	88	-81.43	-10.81	-	-91.7	8.17	27.6	-56	1.3	13.1	49.8	<0.25	1.2	<85	9.4	0.7	0.0	0.3	1.0	11.5	70.8	110.4	294	3.1	14.7	2.0	9.9	0.30	24.0	<0.5	120	1.1	19.5	102
1	M_R112	A	230	100	-84.12	-11.63	14.2	-	8	21.4	-153	1.1	2.7	107	<0.25	0.4	<85	<0.05	-	0.6	0.5	8.7	76.1	79.5	221	3.1	13.0	0.8	16.2	0.11	52.4	<0.5	113	0.1	9.6	126	
1	M_H215	P	-	-	-95.81	-12.64	-	-92.3	8.02	15.4	-169	0.9	7.2	3.3	<0.25	0.5	<85	5.9	0.1	0.0	1.4	0.7	9.6	111	125	203	5.5	9.7	0.5	8.6	0.29	52.9	<0.5	2.4	1.2	3.1	85.4
1	M_H203	A	-	-	-81.28	-10.83	-	-91.9	8.03	21.8	-133	1.3	28.7	10.0	<0.25	1.0	<85	10.0	1.2	0.0	0.4	1.6	14.2	101	113	299	3.9	9.7	1.6	16.1	0.43	17.9	<0.5	24.0	0.4	13.3	139
1	M_R164	A	290	38	-78.18	-10.75	-	-87.3	7.71	18.7	-97	1.6	0.5	159	<0.25	0.2	-	0.40	-	-	0.3	0.3	12.3	77.6	80.1	326	13.8	10.7	1.2	30.9	0.46	151.2	<0.5	14.0	0.1	9.1	340
1	M_R111	A	200	10	-	-	-	-98.4	8.2	21	-193	-	3.1	25.2	<0.25	<0.1	149	0.40	-	-	0.7	0.5	5.8	48.4	48.3	125	2.7	12.8	0.6	10.1	0.05	49.6	<0.5	16.2	0.4	3.5	74.9
1	M_H206	A	-	0.08	-99.82	-13.59	-	-95.0	8.12	18.9	-130	0.5	4.6	16.1	<0.25	<0.1	162	3.6	0.0	0.0	0.6	1.8	4.9	93.7	96.7	92.4	4.0	12.1	0.7	19.5	0.17	44.8	<0.5	3.2	0.2	4.0	140
1	M_H208	A	-	-	-89.49	-12.45	-	-	9.08	26.6	-169	0.6	3.2	15.8	<0.25	2.0	<85	<0.05	0.0	0.1	0.8	0.5	6.0	80.7	85.2	136	0.8	8.0	1.5	4.2	0.04	15.9	<0.5	26.7	0.5	6.5	41.7
1	M_H201	A	-	-	-82.14	-11.23	-	-	7.7	15.3	-123	0.4	0.3	2.1	<0.25	1.9	<85	-	-	-	0.4	0.1	3.6	194	195	42.2	6.1	9.8	1.0	33.7	0.78	501.4	0.7	0.9	0.2	4.9	208
1	M_H202	A	-	-	-77.54	-10.59	-	-94.6	7.85	20.4	-134	1.4	33.6	46.6	<0.25	1.2	<85	19.7	14.2	2.4	0.5	1.8	13.3	202	210	282	8.9	12.4	1.5	28.0	0.58	18.3	<0.5	17.5	0.3	11.5	214
1	M_R165	A	120	30	-78.32	-10.86	-	-78.3	7.84	17	-40	0.8	2.0	20.5	<0.25	0.4	-	35.2	-	-	0.3	0.5	9.2	190	208	190	6.5	9.4	1.2	16.9	0.20	87.3	<0.5	10.7	0.2	10.9	178
1	M_H210	A	-	-	-88.89	-11.97	-	-	8.45	22.7	-148	0.6	3.8	21.8	<0.25	1.1	<85	0.07	0.0	0.0	0.5	0.5	6.5	92.8	99.1	141	0.7	7.9	0.7	5.5	0.09	12.9	<0.5	60.7	0.5	6.3	50.3
1	M_R113	A	300	38	-81.27	-11.15	-	-	8.13	18.9	-63	1.0	6.1	32.7	<0.25	0.2	<85	11.2	-	-	0.3	1.4	10.2	168	182	220	4.6	8.3	1.6	18.2	0.13	41.7	<0.5	60.6	0.1	6.8	127
1	D_R10	A	-	-	-77.70	-10.80	-	-	8.19	15.9	-	1.0	6.0	24.3	<0.25	<0.1	<85	4.1	-	-	0.5	1.3	10.5	160	183	207	4.1	7.6	1.5	19.1	0.23	55.3	1.0	53.1	0.1	5.5	113
2	M_R106	P	89	12	-69.11	-10.03	-	-92.7	7.82	14.8	-189	0.5	1.1	10.6	<0.25	<0.1	<85	0.59	-	-	0.4	1.2	4.3	3.9	4.1	25.7	9.9	9.8	1.2	54.0	0.09	173.9	<0.5	0.5	0.0	1.1	298
2	M_H214	P	80/90	-	-91.95	-12.26	-	-85.9	8.03	14.5	-179	1.3	8.0	14.2	<0.25	0.1	<85	10.9	0.4	0.0	0.4	0.3	13.1	10.8	12.6	288	6.7	9.2	0.8	12.3	1.50	62.0	<0.5	4.3	1.5	8.3	144
2	M_R115	A	250	10	-86.37	-12.19	13.2	-	8.12	18.4	-186	0.8	0.8	10.8	<0.25	0.2	<85	1.3	-	-	0.1	0.3	9.0	57.3	58.0	181	2.2	6.2	1.0	8.6	0.24	46.4	<0.5	4.8	0.9	8.9	54.7
2	M_R139	A	230	-	-	-	-	-70.1	8.79	16.7	-60	0.9	1.0	33.2	<0.25	0.2	<85	8.6	-	-	0.1	3.8	8.1	1.0	1.1	193	0.7	8.3	2.2	2.1	0.05	0.7	<0.5	0.2	1.0	43.0	131
2	M_R127	A	50	25	-87.44	-12.31	-	-67.5	8.7	15.9	-85	0.4	0.3	3.9	<0.25	0.2	140	9.9	169	0.2	0.1	0.4	4.5	1.4	1.5	95.1	2.2	7.7	1.1	7.3	0.02	16.4	<0.5	<0.5	0.1	18.0	17.6
2	M_R105	P	70	1	-68.86	-9.86	-	-96.3	7.81	14.4	-179	0.6	1.5	13.2	<0.25	0.3	<85	1.5	-	-	0.7	1.8	6.1	29.5	32.9	31.0	14.8	9.1	1.1	60.9	0.36	335.5	<0.5	0.6	0.1	1.6	389
2	M_R109	A	300	100	-83.25	-11.72	-	-69.4	7.9	19.5	-169	0.8	0.6	57.7	<0.25	0.5	<85	0.09	-	-	0.1	0.2	9.0	40.9	45.1	173	3.5	7.6	1.1	10.7	0.32	72.1	<0.5	14.1	0.9	8.5	80.5
2	M_R129	A	700	11	-83.58	-11.75	-	-	8.09	31.5	-143	1.0	2.3	3.9	<0.25	0.6	<85	-	-	-	0.1	4.0	11.6	1.7	1.9	234	2.1	9.6	2.7	4.6	0.10	12.2	<0.5	1.9	0.5	50.7	53.8
2	M_R102	P	70	30	-70.71	-9.93	-	-	7.8	14.3	-24	0.4	0.6	9.1	<0.25	0.6	<85	<0.05	-	-	0.1	0.2	4.1	<0.5	0.7	18.4	9.4	10.2	1.8	49.6	0.05	170.4	<0.5	0.5	0.0	2.1	225
2	M_R118	A	-	-	-87.30	-12.30	-	-76.5	8.64	21.7	-191	0.6	3.7	5.1	<0.25	0.7	740	<0.05	-	-	0.5	0.7	7.1	9.4	9.9	135	0.3	8.9	0.5	2.7	0.06	14.3	<0.5	1.7	0.3	10.5	5.3
2	M_213	P	-	-	-82.09	-11.27	-	-	7.69	14.8	-39	0.5	0.3	19.7	<0.25	2.2	<85	0.06	0.0	0.0	0.1	0.1	3.3	<0.5	2.8	33.5	14.9	9.1	1.5	34.9	0.13	98.6	<0.5	2.4	0.1	6.5	319
2	M_R120	A	150	150	-89.07	-12.51	-	-	8.33	23.5	-136	0.5	0.5	2.9	<0.25	2.3	<85	<0.05	-	-	0.1	0.4	4.6	11.5	12.0	102	0.9	6.5	0.7	3.5	0.08	16.7	<0.5	2.3	0.3	6.9	23.7
2	M_R116	A	260	46	-90.97	-12.75	13.7	-	8.33	20.7	-187	0.4	0.3	2.0	<0.25	2.5	<85	<0.05	-	-	0.1	0.2	3.2	3.5	4.7	54.1	2.6	9.9	0.9	23.4	0.44	89.4	2.3	2.8	0.1	5.1	168
2	M_R104	A	370	130	-90.14	-12.41	-	-	8.44	21.4	-246	0.3	0.9	15.9	<0.25	2.7	109	<0.05	-	-	0.1	0.4	2.7	8.1	8.9	63.4	1.2	9.3	0.6	15.7	0.03	28.4	<0.5	1.8	0.1	2.4	120
2	D_R08	A	-	-	-85.52	-11.90	-	-	8.34	12.9	-	0.4	2.2	5.9	<0.25	3.1	-	<0.05	-	-	0.2	0.1	4.3	-	3.9	76.5	3.7	9.6	1.0	12.2	0.07	36.8	1.3	8.3	0.2	17.4	99.2
2	M_R101	P	83	50	-70.35	-10.16	-	-37.2	7.72	14	-159	0.4	0.5	9.4	<0.25	3.3	<85	<0.05	0.0	0.0	0.1	0.2	3.5	<0.5	<0.5	20.8	10.1	11.2	1.8	46.4	0.21	247.7	<0.5	0.6	0.0	3.2	213.0
2	M_R122	A	-	-	-	-	-	-	8.22	26.4	-93	0.4	0.6	2.0	<0.25	3.3	<85	<0.05	-	-	0.1	0.3	3.4	23.0	23.9	79.5	1.1	7.1	0.8	6.0	0.02	32.9	<0.5	1.5	0.1	4.3	44.9
2	M_R123	A	135	-	-80.51	-11.04	-	-	7.21	18.7	-20	0.4	<0.5	2.0	<0.25	3.4	<85	<0.05	-	-	0.1	0.1	4.0	1.0	1.1	25.5	10.8	14.3	1.6	45.4	0.03	297.9	3.1	1.6	0.1	17.4	290
2	M_R117	A	350	55	-90.04	-12.57	-	-	8.15	23.6	-157	0.4	<0.5	2.1	<0.25	3.4	<85	<0.05	-	-	0.1	0.2	3.3	19.1	24.3	67.0	1.3	7.9	0.8	12.2	0.06	46.4	0.6	2.8	0.1	4.3	89.3
2	D_R26	A	-	-	-82.51	-12.00	-	-	8.21	17.8	-205	0.3	<0.5	2.8	<0.25	3.6	-	<0.05	-	-	0.1	0.2	8.0	20.2	20.6	63.2	0.9	7.6	1.0	11.9	0.20	40.8	1.7	2.8	0.2	3.8	86.1
2	D_R05	A	-	-	-92.14	-12.50	-	-	7.48	13.4	-85	0.7	<0.5	5.2	<0.25	3.6	-	0.11	-	-	0.3	0.7	9.3	-	3.5	85.2	18.2	14.6	2.1	38.7	0.42	231.2	1.6	3.1	0.1	33.3	327
2	M_R137	A	100	25	-88.90	-12.65	-	-	7.62	17.3	-30	0.4	<0.5	3.8	<0.25	3.7	<85	<0.05	-	-	0.1	0.2	4.7	11.7	12.3	57.1	8.4	7.9	1.5	24.1	0.10	27.1	<0.5	2.2	0.1	12.5	288
2	M_R110	A	130	26	-86.14	-12.49	-	-	7.88	17.9	-107	0.7	<0.5	25.4	<0.25	3.8	<85	<																			

2	D_R04	Dg	-	-	-62.97	-8.50	-	-	7.57	10	138	1.0	2.3	41.4	1.14	21.6	-	<0.05	-	-	0.4	0.1	6.8	<0.7	<0.5	111	32.7	8.4	1.9	78.4	0.02	0.9	2.8	0.6	0.2	7.4	403
2	D_R35	Dg	-	-	-	-	-	-	7.26	12.5	-	1.5	2.3	58.7	49.5	32.0	-	-	-	-	0.1	0.2	9.2	<0.7	<0.5	75.4	44.9	11.5	35.6	160	0.01	6.2	2.3	<0.5	0.2	21.2	791
3	D_R27	Dg	-	-	-62.20	-8.20	-	-	7.31	11.8	180	1.9	2.5	129	62.4	69.0	-	<0.05	-	-	0.0	0.1	9.9	1.4	<0.5	59.9	85.1	10.4	5.3	237	0.00	<1.0	4.9	<0.5	0.1	7.2	815
3	D_R28	Dg	-	-	-58.90	-7.80	-	-	7.01	12.6	146	2.2	3.6	148	86.1	55.5	-	0.3	-	-	0.0	0.1	6.5	<0.7	2.1	114.2	86.4	10.5	2.8	246	0.02	12.3	5.2	<0.5	0.2	10.9	939
3	D_R29	Dg	-	-	-65.30	-9.50	-	-	7.33	11.1	149	1.9	1.6	93.2	103.1	38.9	-	<0.05	-	-	0.0	0.1	8.6	<0.7	1.2	45.5	89.1	9.7	1.8	223	0.00	0.3	5.7	<0.5	0.1	11.4	991
3	D_R06	Dg	-	-	-	-	-	-	7.65	10	-	1.7	3.3	105	24.5	77.7	-	-	-	-	0.8	0.1	9.9	<0.7	0.7	129	46.1	10.0	56.8	165	0.02	2.4	7.1	2.6	0.4	15.6	606
3	D_R09	Dg	-	-	-55.90	-7.80	-	-	7.46	11.5	-	2.3	6.6	147	48.9	77.8	-	-	-	-	0.3	0.1	14.6	-	0.8	194	124	9.1	56.4	121	0.02	208	10.1	2.5	0.3	8.4	988
3	D_R34	Dg	-	-	-60.10	-8.70	-	-	7.67	12.4	-	1.8	2.6	93.7	45.7	23.4	-	-	-	-	0.0	0.2	11.5	-	0.6	66	96.5	7.5	158.6	60.9	0.01	0.1	7.6	1.0	0.5	55.0	1044
3	D_R41	Dg	-	-	-60.75	-8.40	-	-	7.88	10.3	169	1.8	5.5	75.6	43.9	62.4	-	-	-	-	0.1	0.2	9.8	-	1.7	117	31.8	9.3	198.3	120	0.01	33.1	4.1	4.7	0.4	15.9	328
4	M_R128	A	-	-	-89.28	-12.37	-	-	6.26	15.7	-23	2.7	<0.5	0.5	<0.25	0.4	<85	<0.05	-	-	0.1	1.3	34.4	-	20.7	198	145	39.6	8.3	243	0.59	417	<0.5	<0.5	0.3	343	1637
4	M_R162	A	240	-	-74.68	-10.94	-	-	8.39	18.3	-86	1.5	4.6	138	<0.25	34.6	-	1.2	-	-	0.1	1.8	9.9	<0.5	<0.5	343	2.1	30.8	11.0	7.2	0.04	8.0	<0.5	6.8	2.8	60.7	94.9
4	M_R163	A	280	-	-81.50	-11.80	-	-	8.25	27	140	0.6	<0.5	17.5	<0.25	11.3	-	0.06	-	-	0.1	1.6	4.6	<0.5	<0.5	116	2.7	40.2	11.6	9.0	0.01	4.0	<0.5	14.8	0.3	30.6	106
4	M_R124	Th	3000	40	-68.22	-9.07	-	-68.2	7.66	55.3	-118	3.7	10.4	220	<0.25	1.0	197	8.9	15.6	1.4	0.5	8.4	35.7	<0.5	0.6	879	1.6	15.7	6.7	4.6	0.04	3.2	<0.5	0.6	4.9	179	292
4	M_R135	Th	400	40	-65.58	-9.15	9.9	-68.6	7.76	56.2	-170	3.6	15.0	172	<0.25	1.5	980	6.1	5.5	0.6	0.1	7.4	35.7	8.7	11.4	891	2.4	16.9	7.4	5.5	0.03	5.4	<0.5	4.5	8.3	197	246
4	M_H205	Th	-	-	-77.46	-10.27	12.3	-81.4	7.94	36.3	-153	1.9	55.7	51.8	<0.25	2.0	<85	15.2	2.2	0.0	0.1	2.9	18.5	47.0	55.0	434	5.2	14.4	3.5	14.6	0.38	14.4	<0.5	6.8	1.9	32.6	185
4	M_H211	Th	944	79	-90.59	-11.95	-	-76.7	8.01	46.8	-181	1.4	3.6	32.0	<0.25	0.4	85.4	6.40	-	-	0.1	1.3	14.2	6.4	7.5	328	2.1	12.1	2.2	3.9	0.14	11.2	<0.5	4.8	1.3	15.5	73.1
4	M_R103	Th	1800	25	-77.37	-10.17	11.6	-57.3	8.39	52.1	66	21.5	14.9	162	<0.25	0.3	<85	0.19	-	-	0.1	4.1	19.7	0.8	3.4	525	1.1	19.4	3.3	4.3	0.04	10.4	<0.5	1.7	2.9	53.0	98.9
4	D_R47	Th	-	-	-	-	-	-	8.09	56.6	39	5.2	18.6	1058	<0.25	1.1	-	-	-	-	0.0	7.8	28.0	-	<0.5	1046	2.5	18.3	15.0	8.4	0.01	1.6	1.2	<0.5	17.9	244	552.4
4	D_R49	Th	-	-	-	-	-	-	7.94	38	-179	8.5	16.9	2690	<0.25	<0.1	-	-	-	-	0.1	13.2	11.7	17.9	20.8	1341	16.8	12.5	12.8	35.5	0.14	8.3	1.2	<0.5	10.2	124	1096
4	D_R11	P	-	-	-64.80	-8.40	-	-	7.21	11.8	-	0.9	4.2	57.3	<0.25	0.4	-	2.07	-	-	1.4	5.4	8.4	14.9	14.2	40.2	21.7	16.8	2.7	117.1	10.54	1044	1.0	<0.5	0.1	2.5	440
4	D_R07	A	-	-	-69.00	-9.20	-	-68.2	6.92	13	-	5.5	267	0.5	<0.25	1.3	-	1.28	7.4	0.0	0.2	4.3	76.8	150	240	777	281	29.1	32.3	199	1.71	66.1	1.0	<0.5	0.4	1000	4732
4	D_R31	A	-	-	-	-	12.3	-73.2	6.75	16.2	-	4.7	108	0.5	<0.25	0.9	-	1.56	1.0	0.0	0.1	3.4	66.2	97.1	152.	622	240	28.6	31.8	177	1.95	80.9	1.0	<0.5	0.3	1191	3510
4	M_R138	Th	1200	32	-61.16	-8.04	8.93	-73.2	7.34	64.4	-137	14.8	9.8	4995	3.6	1.8	<85	10.1	23.2	2.6	0.1	21.6	21.6	<0.5	<0.5	3179	16.8	17.7	26.3	40.3	0.06	10.2	<0.5	<0.5	17.9	811	4230
4	M_R131	A	137	25	-72.98	-10.20	-	-60.4	6.93	16.3	-169	9.4	1.7	2642	<0.25	0.4	<85	20.5	4.6	0.0	0.1	12.4	13.5	1.7	2.0	1627	44.5	9.7	19.5	156	2.45	58.3	<0.5	<0.5	6.4	455	11847
4	M_R169	A	800	-	-69.54	-9.15	5.9	-64.6	6.43	16.4	38.7	2.7	1.2	270	<0.25	1.2	-	5.5	-	-	0.1	9.8	58.8	-	0.8	1100	73.9	32.3	51.1	158	1.29	20.0	<0.5	<0.5	4.2	1680	8320

^a Denotes group number (see text for details)

^b Denotes date of field work and location of sample; D = December 2007, M = May 2008, H = Hungary, R = Romania

^c Denotes well type; A = artesian, P = pump, Th = thermal, Dg = dug

^d Analysis by ICP-OES

^e Analysis by ICP-MS or AFS, dependant on date of collection, (see Methodology for details)

^f Analysis by ICP-MS

- Denotes analysis not undertaken

Figure 1

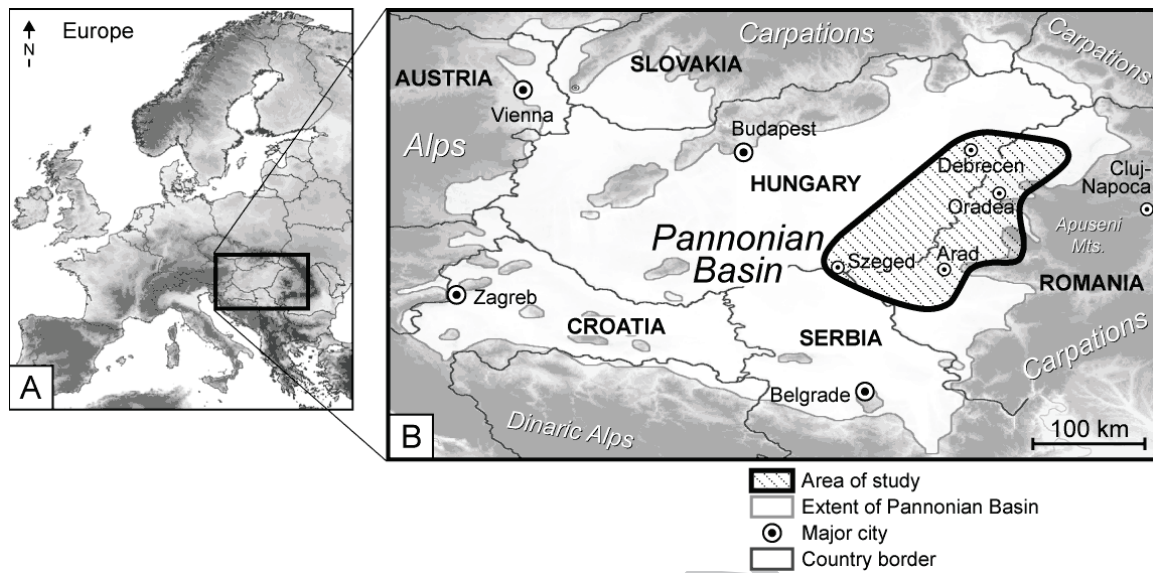


Figure 2

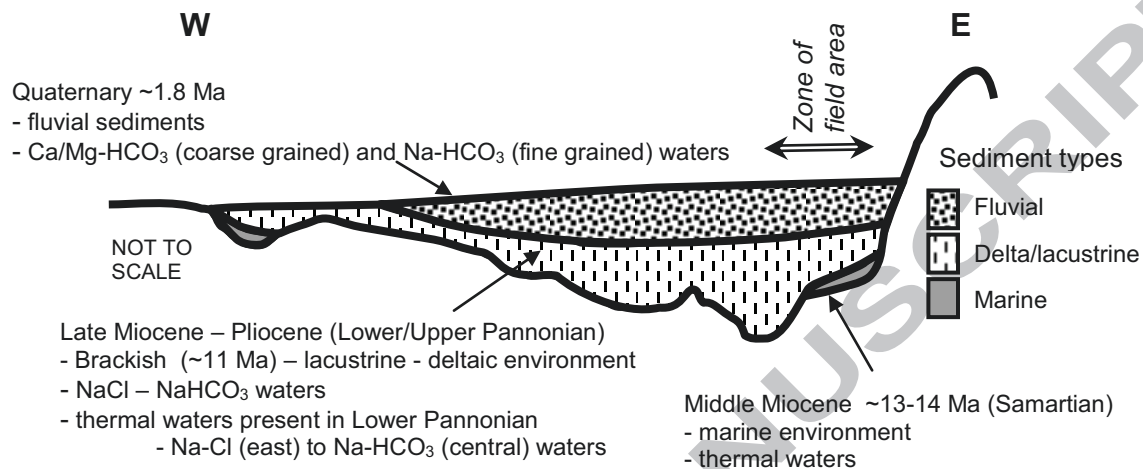


Figure 3 :

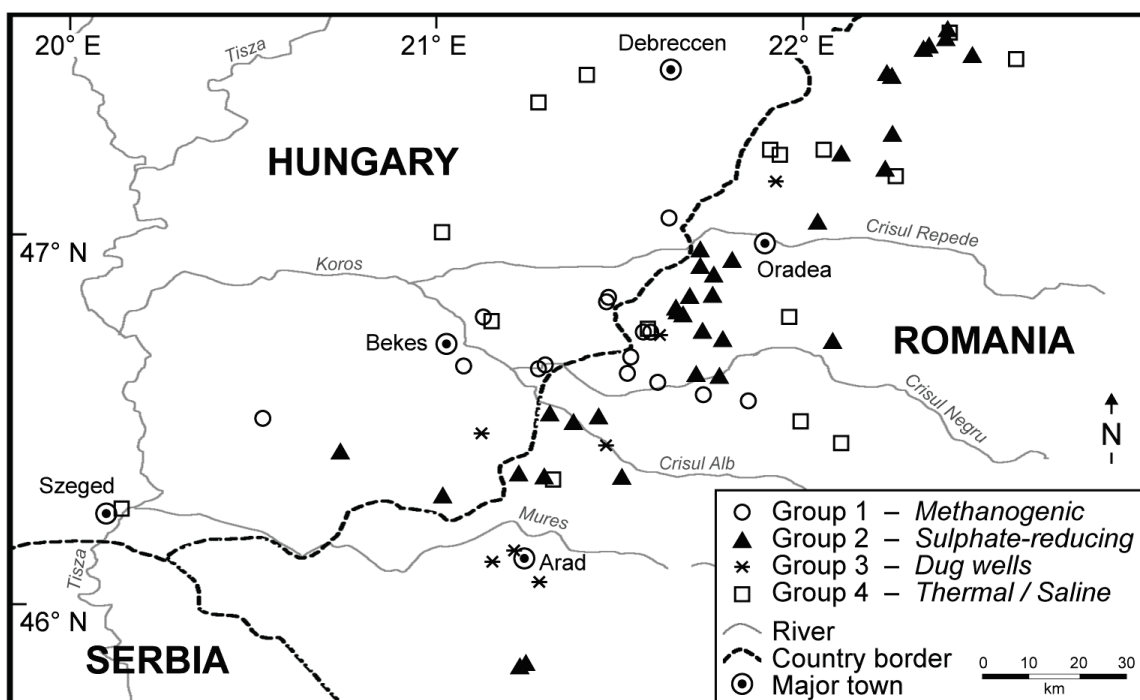


Figure 4

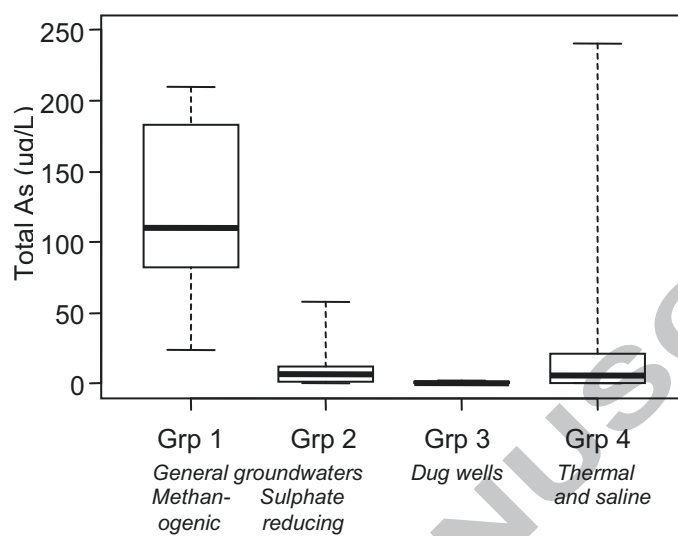


Figure 5 :

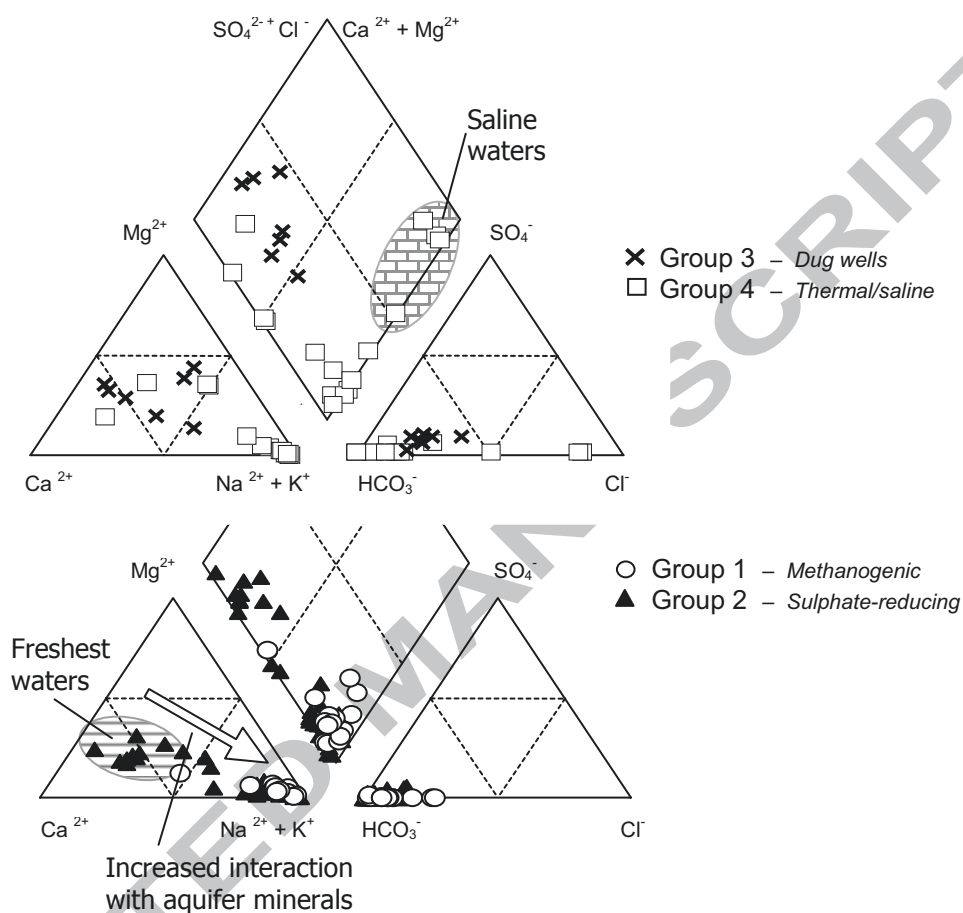


Figure 6 :

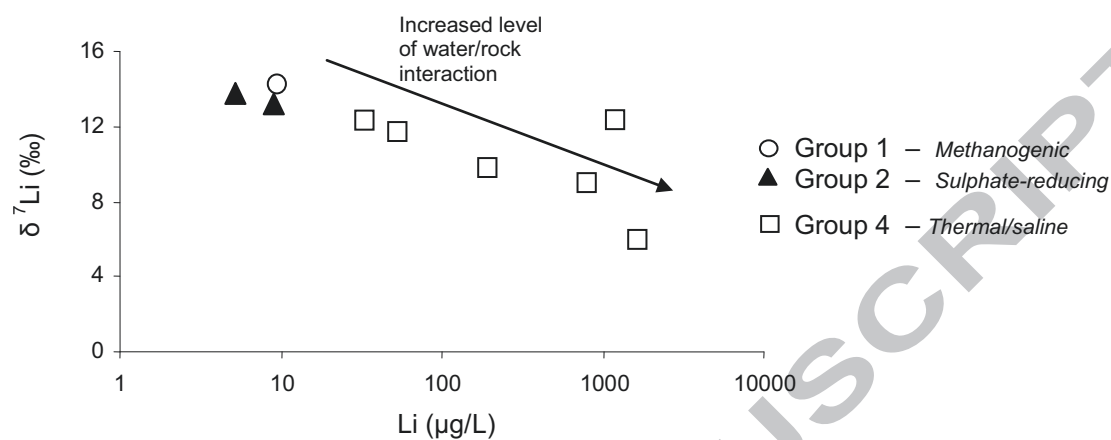


Figure 7 :

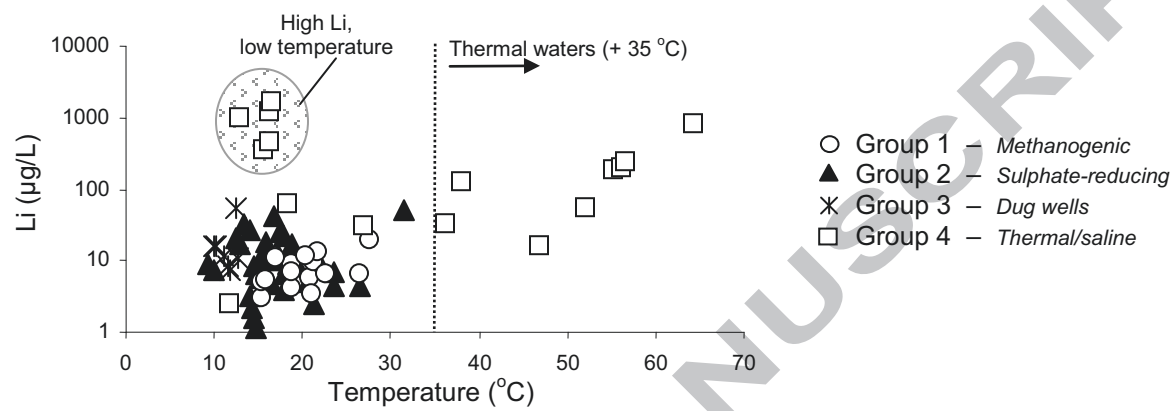


Figure 8 :

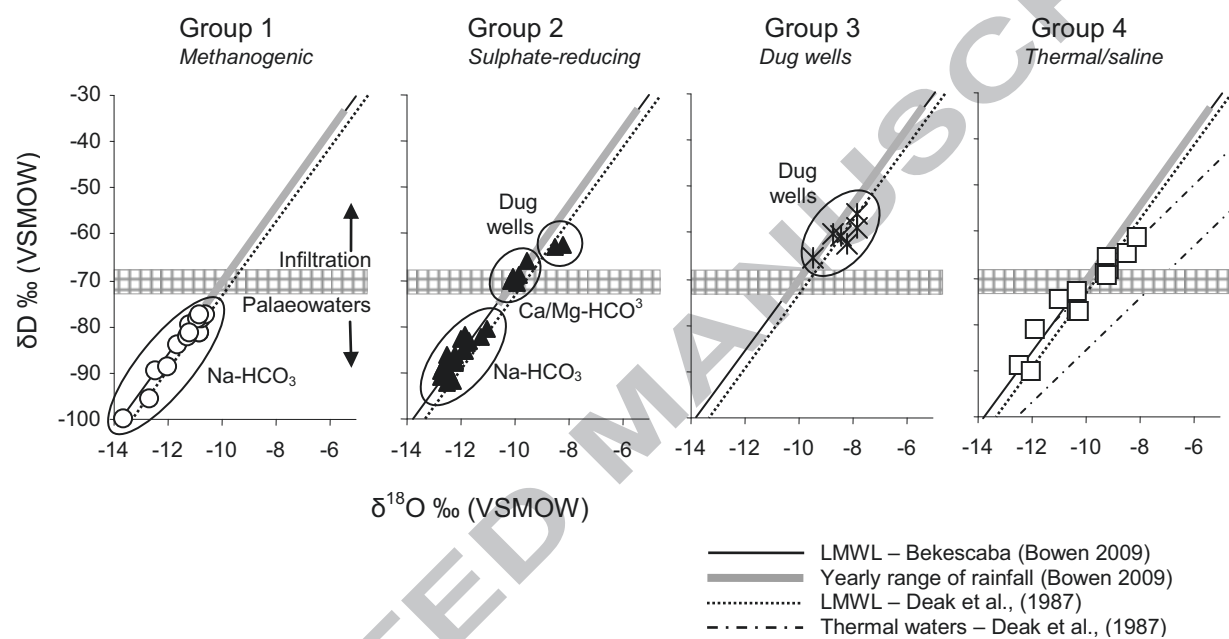


Figure 9 :

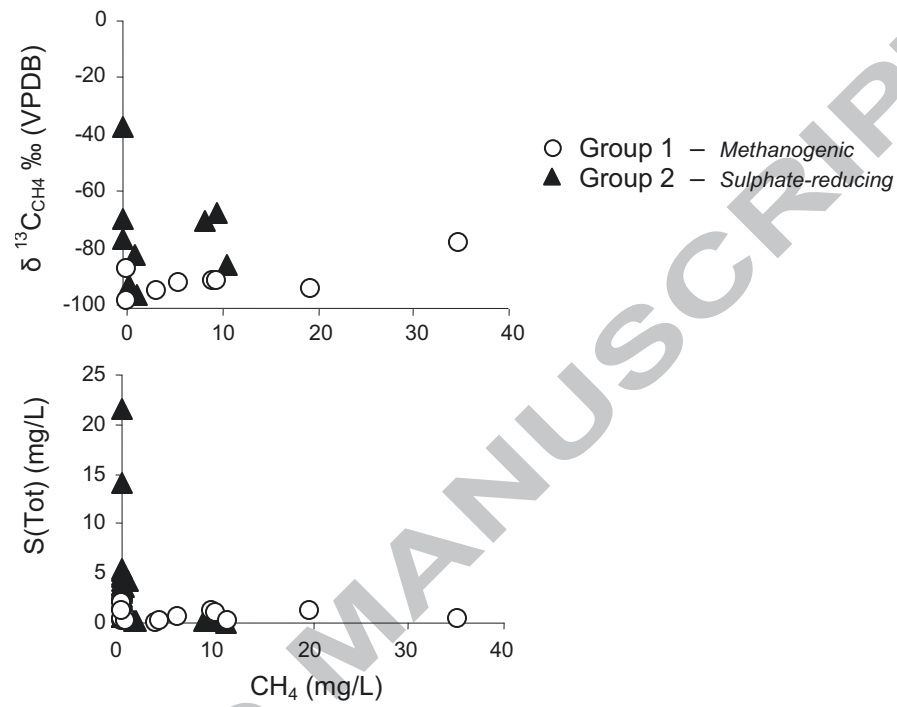


Figure 10 :

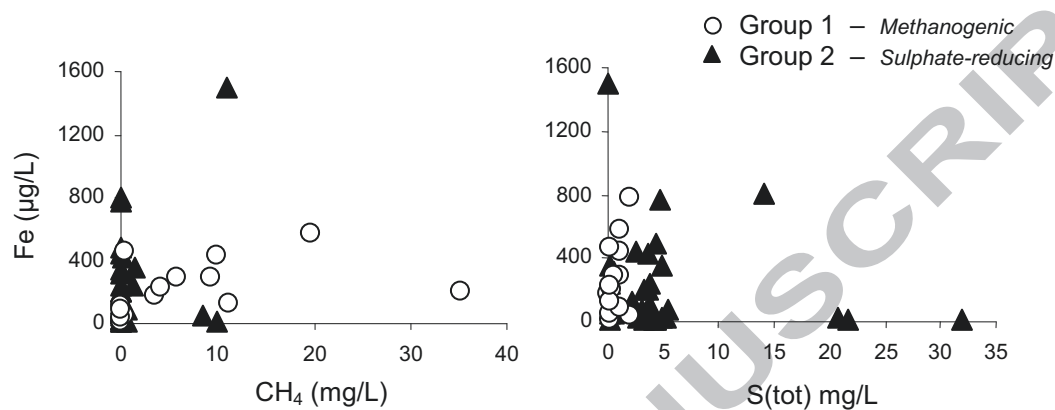


Figure 11 :

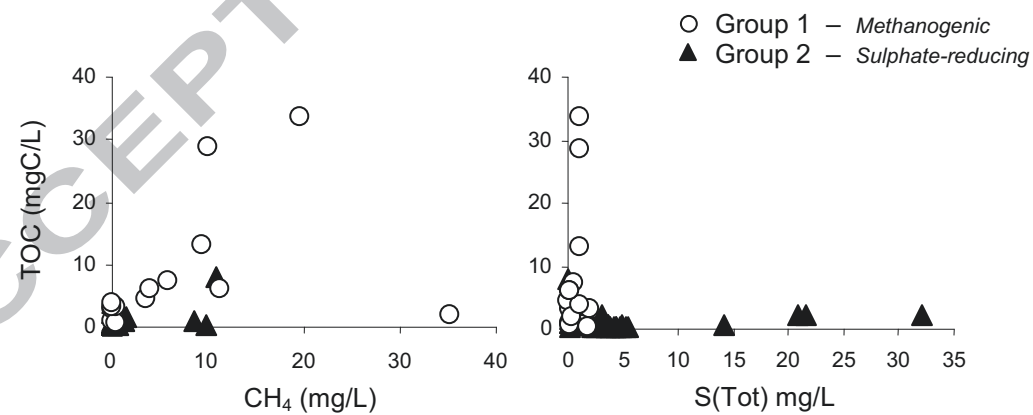


Figure 12 :

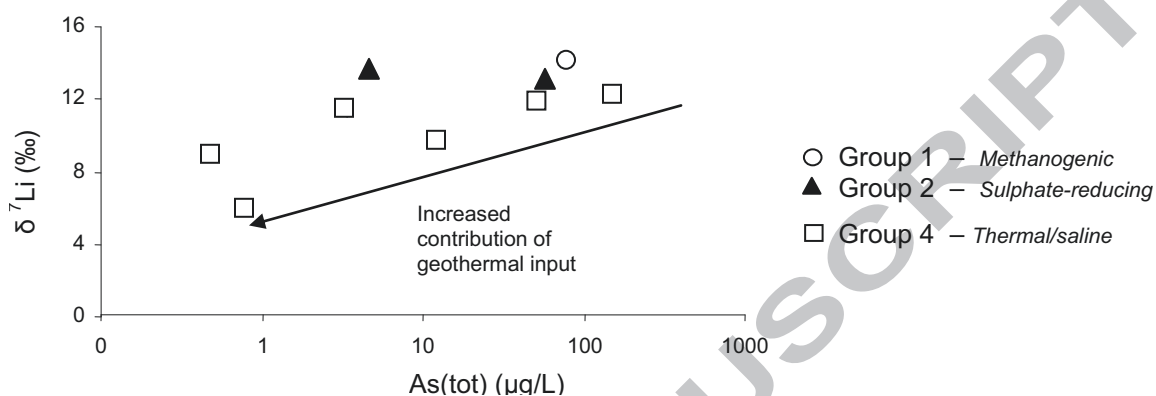
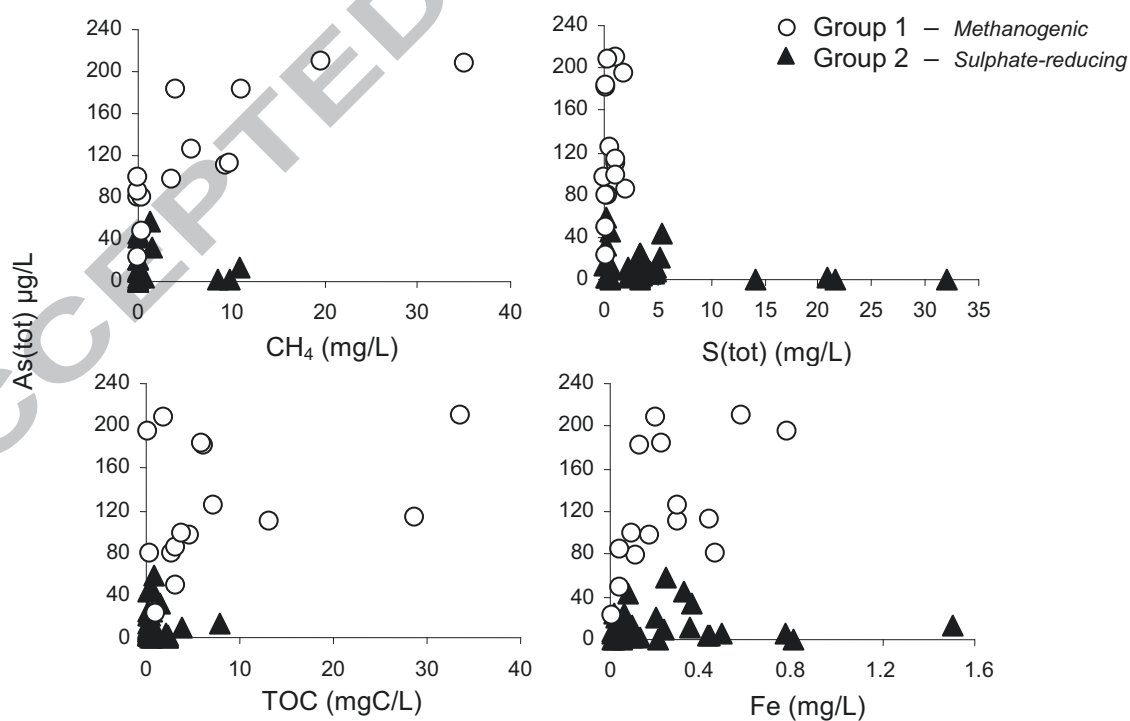
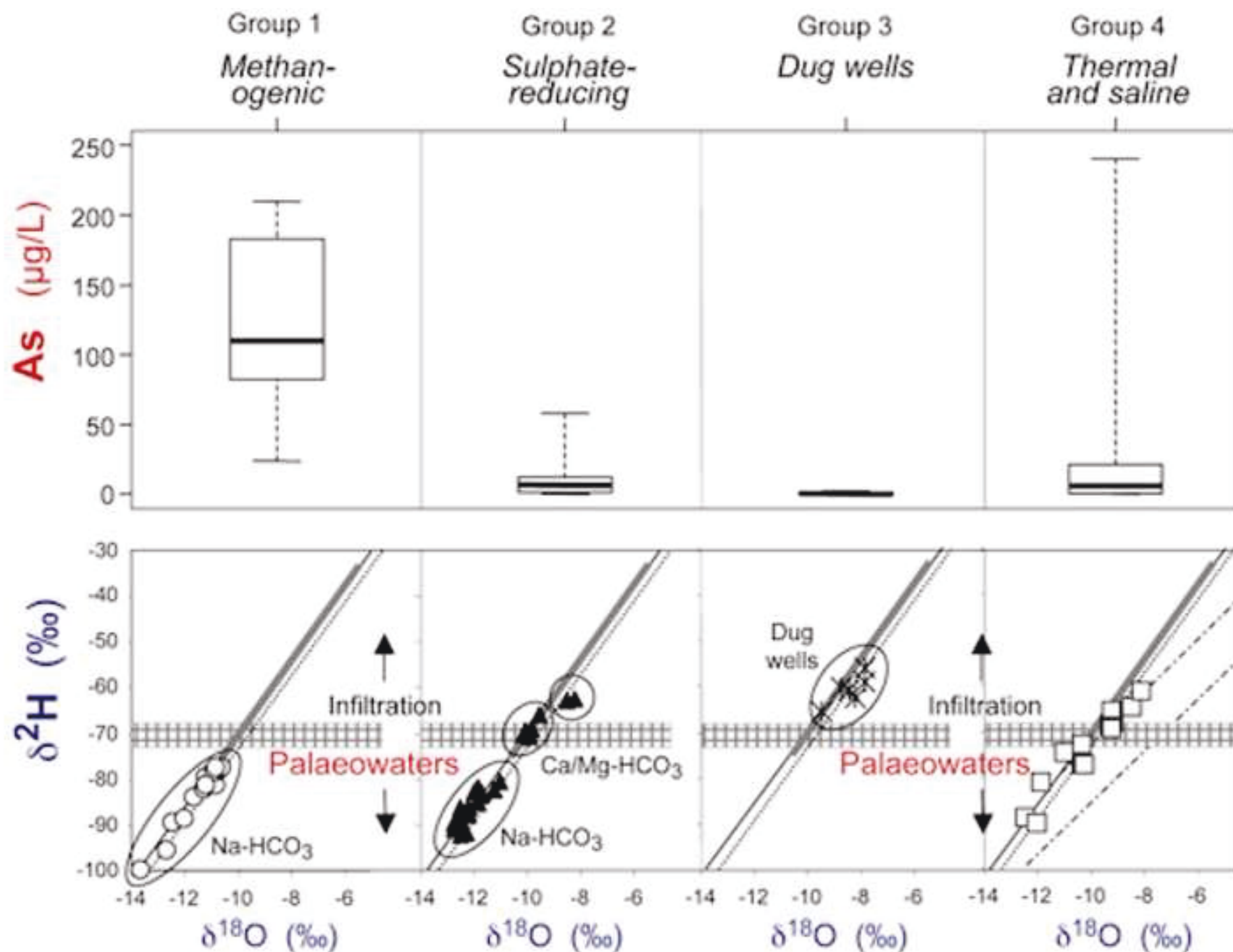


Figure 13 :





APGEO-D-09-00278R1 (Rowland et al.)

Research highlights

- Arsenic originates from Late Pliocene/Quaternary aquifers and some very old waters
- Arsenic levels are controlled by both mobilization and retention mechanisms
- Mobilization is caused by biogeochemical reductive dissolution
- Sufficient sulfate supply triggers arsenic retention in sulfide precipitates
- Nearly 500,000 people are exposed to elevated arsenic in their drinking water