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Geochemistry and arsenic mobilisation in groundwaters of the Pannonian Basin (Hungary and Romania).

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The geochemistry of groundwaters from the Pannonian Basin (Hungary and Romania) were analysed to elucidate the general geochemistry and processes controlling elevated levels of arsenic. Using cluster analysis 4 main groups were identified. Group 4, influenced by geothermal and saline inputs (Na-HCO_3 to Na-Cl type, high Li, Si, NH_4 and B, low δ^7Li values) with low As levels (mean 33.1 µg/L, range <0.5 to 240 µg/L). Group 3 waters, sampling only dug wells with geochemistry influenced by rain water and surface contamination (Ca-Mg-HCO_3 type, elevated K, NO_3, S(tot) and Cl) and also with low As (mean 1 µg/L, range <0.5 to 2.1 µg/L).

Groups 1 and 2 represented general reducing groundwaters of the area (Mg/Ca-HCO_3 to Na-HCO_3). Despite such similarities, both groups had different redox characteristics, (i) group 1 indicative of waters dominated by methanogenesis (high CH_4, low to absent S(tot)), (ii) group 2 indicative of waters dominated by SO_4-reduction (low CH_4, moderate S(tot)), and (iii) both group 1 and 2 having similar ranges of Fe concentrations indicating that Fe-reduction is occurring equally in both groups. Arsenic levels in group 1 (methanogenesis) were high, ranging from 23.4 to 208 µg/L (mean 123 µg/L) and predominantly as As(III). Levels in group 2 (SO_4-reducing) were much lower, ranging from <0.5 to 58 µg/L (mean 11.5 µg/L), again predominantly as As(III). Typically low levels of As in group 4 waters (geothermal), combined with positive correlations between δ^7Li and As(tot) indicate that elevated As is not from an external input, but is released due to an in-aquifer process.

Geochemical reasoning implies As mobilisation is controlled by redox-processes, most likely reductive dissolution of As bearing Fe-oxides, known to occur in sediments from the area. More important however is an overlying retention mechanism determined by the presence or absence of SO_4.. Ongoing SO_4-reduction will release S^{2-}, removing As from solution either by the formation of As-sulphides, or from sorption onto Fe-sulphide phases (group 2). In the group dominated by methanogenesis (group 1), any As released by reductive dissolution is not removed from solution and can rise to the high levels observed. Levels of organic carbon are thought to be the ultimate control on the redox conditions in these 2 groups. High levels of organic carbon (as found in group 1) would quickly exhaust any SO_4 present in the waters, driving the system to methanogenesis and subsequent high levels of As. Group 2 has much lower concentrations and so SO_4 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 SO_4 in the waters.

Keywords : Arsenic, Romania, Hungary, Pannonian Basin, Iron, Sulphate reduction, Reductive dissolution, Methane, Groundwater, Lithium isotopes.

1. Introduction

The presence of naturally occurring arsenic 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), and the US (Welch et al., 2000, Warner 2001, Saunders et al., 2005).

The problem is by no means limited to these regions. 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 2006a), 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 (Figure 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, Ćavar 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), making it the most severely affected region in Europe (Table 1), though this number is only liable to increase as more research is undertaken in the area. 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.

Despite the high numbers of people worldwide affected by As related contamination in reducing aquifers, modes of release are yet to be fully understood. However, it is commonly thought that 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., 2009) and the presence of sulphate also playing an important role (Kirk et al., 2004, Quicksall et al., 2008, Buschmann and Berg 2009). It has been suggested for Hungary, based on groundwater geochemical investigations, that a similar process is also the primary cause of As release (Csalgovitis 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, dependant on the hydrogeology of the area, 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). To our knowledge, As 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 Csalgovitis (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, Aiuppa et al., 2006) and Greece (Tyrovola 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 arsenic 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 arsenic in waters on the population of Hungary, Romania and Slovakia has shown associations between arsenic and increased cases of cancers in the skin, bladder and kidney (Fletcher et al., 2008). The ASHRAM project also found correlations between the level of arsenic in drinking water and urine in the same countries (Lindberg et al., 2006).

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, an understanding of the modes of arsenic release and subsequent predictions of its distribution within the natural aquifer systems is important to help local water

management to find water sources with As levels below the drinking water limit. If this is not possible, detailed knowledge of the geochemistry of the groundwaters is also required to provide information to develop remediation solutions for the area.

Therefore the aim of this work was to elucidate the dominant influences on geochemical and isotopic characteristics of a variety of wells and groundwater types in an area spanning the Western Romanian Plain, and Eastern Hungary (Figure 1), a region known to contain elevated arsenic in its groundwaters (Csalgovitis 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 arsenic release will then be examined.

2. Pannonian basin

2.1. General palaeogeography and geological development

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 outwith 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, Juhász et al., 2004, Juhász et al., 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 are shown in Figure 2.

2.2. 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 (Viczian 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 (Viczian 2002), with the uplift of the Pannonian basin, at approximately 2.4 Ma, initiating more fluvial sedimentation in the Quaternary (Viczian 2002, Gábris and Nádor 2007). In addition, evidence of swamp and wetland deposits are found throughout the Pliocene and Quaternary deposits is some areas (Koros basin) (Viczian 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 kyr 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 Micoene (Vicizian 2002).

Studies of Hungarian sediments (reviewed by Viczian 2002, typically detected by XRD) show a variety of Fe minerals, including goethite, limonite, pyrite and siderite. Fe-oxyhydroxides have also been identified by chemical extraction in 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 iron(III) oxides (goethite and limonite) (Vicizian 2002). In the Lower Pliocene of the Maros fan, these are replaced by iron 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).

2.3. Ground water system of the field area

Groundwater type and geochemical composition is strongly controlled by the sedimentary and palaeogeographical history of the region (Figure 2). Within the Lower Pannonian (Pannonian s.s.) sediments, groundwaters are typically stagnant with Na-Cl to Na-HCO_3 geochemistry (Varsányi and Kovács 1997). Na-HCO_3 waters are then present within the Upper Pannonian (Pontian) sediments. Younger Quaternary sediments, dependant on the dominant size fraction, contain Na-HCO_3 dominated waters within finer sediments and Ca/Mg-HCO_3 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). 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 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 of 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 km^2, 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 ^{o}C, are Na-HCO_3/Cl type with dissolved gases (especially CH_4) 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, found 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 CH_4 (Korim 1972). Waters in this area are less dominated by Cl, being predominantly Na-HCO_3 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).

3. Methodology

3.1. Sample location and collection

Samples were collected in December 2007 and May/June 2008 from a region covering the Western Romanian Plain and Eastern Hungary, bounded to the east by the Tisza River and the foothills of the Apunsi mountains to the west. This area is known to contain elevated levels of arsenic in its groundwaters (Csalagovitis et al., 1999, Gurzau and Gurzau 1991, Varsányi and Kovács 2006)

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 years for artesian wells, 1 to 50 years for hand pump wells and 25 to 79 years 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 minutes 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 hours or more). All water samples and water characterisation were undertaken from an open PVC container which was rinsed three 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 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 supapure, Merck, into 60 ml of sample). Samples for anion, TOC and δ^7Li analysis were also filtered with 0.45 µm nylon filters (Cronus, Sigma-Aldrich) into transparent acid washed polypropylene bottles. Waters for δD and $\delta^{18}O$ analysis were collected without filtering and stored in brown borosilicate bottles with no head space. Samples for CH_4, $\delta^{13}C_{CH4}$, 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 ^oC), and then stored at 4 ^oC until analysis, except during transit from Romania to Switzerland (typically 1 day).

3.2. 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. Aqueous major and trace elements concentrations were measured after dilution of acidified groundwater samples with 1% HNO_3 supapure (Merck). 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 (Tot(S)), Ca, Mg, Na, Si, K, Ca, Mn, Fe and Li being measured 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 µg/L and ICP-OES of 0.1 mg/L.

As(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 analysed after the addition of a reducing solution (2.5 g KI and 0.5 g ascorbic acid in 5 ml of H_2O) 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 AsH_3 under these pH conditions (Yamamoto et al., 1981). Analytical accuracy for ICP-MS, AFS and ICP-AES 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.

H_2S (detection limit 85 µg/L), NH_4 (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 H_2S analysis was undertaken within 8 hours of sampling, with analysis for alkalinity undertaken within 3 days of sampling. Total organic carbon (TOC) was measured with a TOC 5000 A analyzer (Shimadzu, Switzerland), with a detection limit of 0.5 mgC/L. Cl (detection limit 0.5 mg/L), SO_4 (detection limit 5 mg/L) and NO_3 (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-Aldritch, UK) and detection limits were 50 µg/L. $\delta^{13}C_{CH4}$ in a select 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 methane 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 minutes, raised to 230°C at 10°C/min and then held constant for 7 minutes. The GC had a 500 µl sample loop. Scotty Transportable gas standards were used for calibration (Scott Specialty Gases, US).

Waters for δD and $\delta^{18}O$ were determined by laser spectroscopy with a liquid-water isotope analyzer (Los Gatos Research DT-100). The resulting δD and $\delta^{18}O$ values were normalized using internal standards which were calibrated against VSMOW. δD and $\delta^{18}O$ in waters collected in December 2007 were also calibrated against VSMOW and analysed by the method outlined by Berg et al., (2008). δD and $\delta^{18}O$ mean monthly rainfall estimates and subsequent LMWL were taken from Bowen (2009) for Bekescaba (latitude 46.684458, longitude 21.086989, altitude 84 m). The LMWL as calculated by Deak et al., (1987) of $\delta D = 8\delta^{18}O + 6.4$, plus values taken from geothermal waters sourced 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). $^7Li/^6Li$ 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 δ^7Li is about 0.1-0.2‰ ($2\sigma_m$).

3.3. Cluster analysis

From the original data set of 91 samples, 73 samples were used during statistical analysis, with samples rejected due to repeat sampling or missing data. 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 dendogram 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 (Guler et al., 2002), so the cophenetic correlation coefficient was used as validity measurement with values of 0.8 or more usually taken as a point of acceptability that the dendogram produced provided an acceptable two-dimensional representation of the multi-dimensional relationships within the original data (Rao and Srinivas 2006).

A total of 23 geochemical variables was used during the hierarchical cluster analysis; pH, temperature, conductivity, total organic carbon (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 ($\delta^{18}O$, δD, $\delta^{13}C_{CH4}$ and $\delta^{7}Li$) 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 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 dendogram that a distinct group of As-rich samples were observed (Figure 4). Cophenetic correlation coefficient measured for the hierarchical cluster analysis used in this study was 0.7, which is slightly lower than the 0.8 cut-off usually used. However, from discussions as outlined below robust geochemical reasons for their distribution could still be explained and so this was not considered an issue.

4. 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 µg/L) to 240 µg/L, and found predominantly as As(III) (Table 3). As(tot) was found at levels above the EU limit of 10 µg/L in all groups, apart from the dug wells of group 3 (Figure 4). However, waters in group 1 had consistently higher As levels (mean average 123 µg/L, range 23 to 210 µg/L As(tot)). 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. 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 (Table 2). Geochemical reasoning for these groupings is discussed, followed by a more detailed look at the potential mechanisms of As release within these waters.

4.1. Group 4 – thermal and saline influences

Group 4 contained all thermal wells sampled with several distinct geochemical characteristics (Table 2). Thermal waters in this study are classified as waters with surface temperatures above 35 ^{o}C (Korim 1971). Waters within both groups included Na-Cl, Na-HCO_3 and Mg/Ca-HCO_3 types (Figure 5), with high levels of a variety of constituents including NH_4, Li, Sr, Fe, B, Na, Cl, alkalinity and conductivity (Table 3) and low δ^7Li isotope values (Figure 6). The group is widely geographically separated throughout the area (Figure 3).

Li, Si, NH_4 and B are all common constituents in 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 groups 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-HCO_3 type) associated with geothermal waters from Upper Pannonian sediments (Korim 1972, Antics 2000, Antics and Rosca 2003) (Figure 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 sedimentalogical regions.

Not all samples in these groups are 'thermal' (i.e. above 35 ^{o}C at the surface), and in addition a small number have Ca/Mg-HCO_3 type, which is in contrast to the dominant geothermal characteristics in the area. Despite this, even these samples show elevated Li, Si, NH_4 and B. This can be more clearly seen

when comparing Li contents with temperature (Figure 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 Andrésdóttir 1995), or from the breakdown of organic matter causing elevated NH_4 (Appelo and Postma 2005). However, further evidence of geothermal influence can be investigated from the lithium isotopic compositions (δ^7Li) 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. It has been shown that Li isotope fractionation during water-rock interaction is a function of temperature with more extensive fractionation at lower temperatures (Millot et al., 2007a, b, 2009). Therefore geothermal waters, or waters that have mixed with geothermal waters will typically have lower δ^7Li values than those who have had no interaction with such systems. Analysis of samples within group 4 shows lower δ^7Li values in comparison with the other groups, which is characteristic of greater water/rock interaction as would be seen in geothermal waters (Figure 6). High levels of CH_4 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, CH_4 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 methane known to occur in the region (Veto et al., 2004). δC^{13}_{CH4} 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 CH_4 (Clark and Fritz 1997).

A small number of samples have Na-Cl type waters of 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 are seen from the piper plot (Figure 5), and have Na/Cl ratios of 0.55, similar to seawater (data not shown) (Nordstrum et al., 1989). Other indicators in this small group include high B, Li and NH_4 concentrations that can occur in waters that circulate marine sediments (Duchi et al., 1992), which occur within this region (Figure 2).

δD and $\delta^{18}O$ values for these groups are variable (Figure 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 Figure 8). Such a trend is not observed within the geothermal, geothermally influenced and saline waters within our sample set, as all plot close to the LMWL. However, samples from these groups cover a wide geographical area (Figure 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.

4.2. Group 3 – dug wells

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-HCO_3 type (Figure 5), have positive Eh values and are the only group containing significant NO_3 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 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 (Figure 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 taping the surface aquifers with strong rain water influences.

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 (Figure 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 and SO_4 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 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.

4.3. Group 1 and 2 – general groundwaters

4.3.1. General characteristics

In contrast to wells in groups 3 (dug wells) and 4 (thermal/saline) waters in groups 1 and 2 have much more neutral characteristics and form the bulk of waters sampled (Table 2). Waters in group 2 vary from Mg/Ca-HCO_3 to Na-HCO_3 dominated, with group 1 being dominated by Na-HCO_3 type water (Figure 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 $\delta^{18}O$ values that plot close to both the dug well (group 3) and rainwater values (Figure 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 which have similar δD and $\delta^{18}O$ values, but much lower NO_3, Cl, K and Na contents than those of group 3 (Figure 8). This suggests that all dug wells are strongly influenced by infiltration of modern rainwater, 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-HCO_3 type) also having depleted values (Figure 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, Deak and Stute 1989), with infiltration thought to occur between 70,000 and 12,000 yrs 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-HCO_3 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 and K. 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 Na-HCO_3 geochemistry) forming the end

members, with a small number of Ca/Mg-HCO_3 waters having a slightly depleted δD and $\delta^{18}O$ values that plot close to the dug wells (Figure 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).

4.3.2. Redox characteristics

Although the geochemistry of groups 1 and 2 are similar, there are some striking differences, most notably in more redox sensitive parameters (Table 2, Table 3). Although SO_4 was measured in all samples, values were often below the detection limit (5 mg/L, data not shown). Comparison of SO_4 and S(tot) measured found that the majority of S(tot) was SO_4, with H_2S forming only a minor component (Table 3), therefore S(tot) is taken as a proxy for SO_4. 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 greater abundances of CH_4 and low to negligible S(tot) concentrations in comparison to group 2 which contains lower CH_4 and higher S(tot) concentrations (Table 3). Trace levels of H_2S were found in both group 1 (2 out of 13 samples) and 2 (3 out of 27 samples) waters, but levels were close to detection limit (Table 3). $\delta^{13}C_{CH4}$ measured in a selection of samples from both groups showed values < -40 ‰ with those in group 1 being more depleted than group 2 (Figure 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 CH_4 or S(tot) (Figure 10).

The $\delta^{13}C$ signature in CH_4 can be used to identify the source, with samples depleted in $\delta^{13}C$ (< -40 ‰) indicative of a microbial source. Although CH_4 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-reducing community within sediments can be detected either by a reduction in SO_4 content or the presence of S^{2-} (Christensen et al., 2000). Levels of H_2S detected in both groups are low or absent which would indicate that SO_4 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 as a single measurement is not an indicator of a active SO_4-reduction, but it has been suggested that the minimum concentrations of SO_4 required for SO_4-reduction is 2.8 mg/L (Lovley and Klug 1986), which

is the case in most samples from group 2 (Table 3). Sulphate-reduction and methanogenesis tend to be mutually exclusive as active SO_4-reducers and methanogens often compete for the same substrates. For example, active SO_4-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-reducers in environments low in SO_4 (Lovley and Klug 1986). This can explain the negative covariance observed between S(tot) and CH_4 (Figure 9). Fe(III) reduction can occur in mixed metabolic zones with SO_4-reduction or methanogenesis, when Fe(III) concentrations are low (Lovley and Goodwin 1988), as seen here (Fe < 1 mg/L), and explains why Fe levels are similar in both groups with no relationship observed with CH_4 and SO_4 (Figure 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-reduction and (iii) Fe reduction occurs in both sets of waters in equal measure.

Differences in the dominant microbial behaviour between the two groups could be due either to the availability of SO_4, or from the availability and suitability of the TOC present. Sources of SO_4 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 4.1) have S(tot) levels below detection limits, implying that SO_4 has already been depleted, preventing it from being a more wide-scale source of SO_4 within the system. Absence of SO_4 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, 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 within the subsurface cannot satisfactorily explain the differences between the two groups, then the availability of organic carbon 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 S(tot) (Figure 11). Such high levels of TOC within group 1 (methanogenic) would quickly exhaust any SO_4 that had been present, driving the system to methanogenesis. Within group 2 (SO_4-reducing) waters, the lower concentrations of TOC does not allow the flux of SO_4 within the system to be exhausted as quickly, and so SO_4-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 supplies have been exhausted, with the lower TOC in group 2 allowing active SO_4-reduction to be maintained.

4.4. Arsenic, source and mobilisation mechanisms

4.4.1. 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, and As/Cl relationships are not always seen due to the scavenging of As into mineralogical phases (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 (Figure 4), though some individual samples do contain appreciable concentrations (Table 3). As previously discussed (Figure 6, section 4.1) Li isotopes (δ^7Li) have been used as a tracer for geothermal input with waters containing the lowest δ^7Li values (group 4, thermal/marine) being those strongly influenced by geothermal waters. Comparison of the δ^7Li with As(tot) values show a positive correlation, with heaviest δ^7Li values being found in waters with the highest As(tot) content (Figure 12), implying that waters with higher As(tot) contents are those with little geothermal influence. The presence of individual samples in groups 4 with high As is therefore contradictory, but these samples have heavier δ^7Li signatures more typical of general groundwaters (groups 1 and 2) (Figure 12). The presence of notable As in select general groundwaters (group 1) implies that these samples are more likely a combination of geothermal waters and general groundwaters, with As present an overprint from the latter. Dug wells (group 3) have negligible As(tot) values (Figure 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.

4.4.2. Redox processes

The reducing nature of the waters in group 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 (Vizican 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 our samples. The lack of correlation between As(tot) and Fe (Figure 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).

Sulphate reducing waters (group 2)

Despite similarities with regards to general characteristics (groundwater type, Figure 5; δD and $\delta^{18}O$, Figure 8), there are major differences dependant on the key microbial processes occurring as indicated by certain redox indicators (see section 4.3). Group 1 is dominated by methanogenesis (high CH_4, low S(tot), lighter $\delta^{13}C_{CH4}$), group 2 is undergoing SO_{4-}-reduction which would limit methanogenesis (low CH_4, presence of S(tot)), with Fe-reduction occurring in both (Table 2). The reduction of SO_4 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 sulphide 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-sulphides such as realgar (AsS) and orpiment (As_2S_3) or (ii) adsorption and/or coprecipitation onto other sulphide phases, most notably Fe-sulphide (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-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) observed (Figure 13).

Work by O'Day et al., (2004) showed that Fe rich sediments favour the adsorption of As onto surfaces of Fe-sulphides as a retention mechanism (as opposed to precipitation of As-sulphides), as any free S^{2-} present is likely to form Fe-sulphide phases such as pyrite. Under these high Fe conditions, precipitation of As-sulphides will only occur if aqueous As levels are high (75 to 7500 µg/L). Therefore the precipitation of As-sulphides is more likely to occur when Fe sediment levels are low, as levels of S^{2-} can then build up to levels high enough to stabilise As-sulphide phases. Although sedimentalogical 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-sulphide, 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 µg/L and 341 ug/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 coupled to the reduction of As(V) (Newman et al., 1997).

Methanogenic waters (group 1)

Under the dominantly methanogenic conditions prevailing within group 1, SO_4-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 can build up over time to the high concentrations as observed within the groundwater. Indeed a positive correlation between As and CH_4 is observed (Figure 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 (Kirk et al., 2004, Quicksall et al., 2008, Buschmann and Berg 2009).

The role of organic carbon

The presence of SO_4 appears to be controlled by TOC, which would in turn have a direct consequence on the presence or absence of As. Group 1 contains high levels, which would rapidly exhaust any SO_4 present driving the system to methanogenesis. Conversely, group 2 has much lower TOC levels allowing the uptake of SO_4 during microbial reduction to keep up with the flux of SO_4 through the system. There is no clear correlation between As and TOC observed (Figure 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 As concentrations.

4.4.3. Implications for remediation

Arsenic removal from natural waters is an important option for water supplies in affected regions, with a variety of removal mechanisms available. Established procedures are typically based on (i) sorption in ion exchange resins, (ii) adsorption onto activated alumina or iron based sorbents such as granular ferric oxide and iron oxide coated sand, (iii) precipitation with Fe(III) and Al(III) salts followed by coagulation and filtration, coagulation and membrane filtration, oxidation and filtration, (iv) reverse osmosis, and (v) lime softening (EPA 2003, Katsoyiannis and Zouboulis 2006b). An in-depth review of all potential remediation technologies for the region is outside the scope of this study. Here we provide a brief outline of the most important geochemical characteristics that impact the choice of the

optimal remediation technology for the investigated groundwaters in the Pannonian Basin (group 1), which are affected by elevated As in the range of 23 to 210 µg/L (mean 123 µg/L). These are (i) As speciation dominated by As(III) (64-100 % of total As, mean 92 %), (ii) neutral pH (7.7 to 9.1, mean 8.1), (iii) high levels of TOC (0.5 to 34 mgC/L mean 7.7 mgC/L) and (iv) low levels of Fe (0.01 to 0.78 mg/L, mean 0.3 mg/L).

Under the reducing conditions of the Pannonian waters, As is found predominantly as uncharged As(III) (H_3AsO_3) at circumneutral pH which is poorly removed by the conventional methods (mentioned above) designed to sorb, adsorb or precipitate As out of the aqueous phase (Katsoyiannis and Zouboulis 2006b). Therefore, pre-oxidation of As(III) to As(V) ($H_2AsO_4^-/HAsO_4^{2-}$ with negative charge of -1 to -2), would be required for these waters, adding to the cost and complexity of the overall treatment. One of the cheapest oxidants is chlorine, which is also commonly used at the end of the water treatment process as a disinfectant prior to entry into the distribution network. However, chlorine can react with organic matter to form a variety of undesired chlorinated by-products such as trihalomethanes and halocetic acids and can cause taste and odour problems. In reducing waters, chlorine can additionally react with ammonia, Fe(II), and reduced moieties of organic carbon, so requiring higher overall doses (Singer 1999, Stauder 2007). Therefore, the use of alternative oxidants, such as permanganate, ozone or H_2O_2, prior to arsenic removal should be considered (EPA 2003). Even after oxidation, high levels of phosphate and TOC can have a negative impact on removal due to competition for sorption/adsorption sites (Grafe et al., 2001, Hug et al., 2008), such that more sorbent is required. Application of reverse osmosis is possible, but produces large volumes of reject water (20-50% of input) which strains resources in regions where water is scarce, as well as disposal issues, leading to expensive set up and maintenance costs (AWWA 2003).

The use of zero valent iron (ZVI) or the biological oxidation of arsenic are both newer technologies that have the potential to remove As(III) without the need for pre-oxidation and so requiring lower setup and running costs (Katsoyiannis and Zouboulis 2006b). Biological oxidation still relies on the adsorption or co-precipitation of As onto Fe-oxides, but As(III) is oxidised prior to removal, together with Fe(II) and Mn(II) in a microbial oxidation step, causing a much greater removal efficiency (Katsoyiannis and Zouboulis 2006b). For waters with unsufficient natural Fe concentrations (such as in the As-rich waters of group 1) Al(III) or Fe(II,III) is added after biological oxidation, an approach which has been successfully used, for example in a community water treatment plant in Northern Greece (Katsoyiannis et al 2008b). Application of ZVI, typically in sand columns, is a promising option for removal of As(III) without pre-oxidation (Nikolaidis et al., 2000, Su and Puls 2001). Under reducing conditions, arsenic is removed by sorption and surface precipitation on ZVI, on not yet fully specified corrosion products and/or in As- and Fe-sulfides formed by biotically mediated sulfate reduction (Nikolaidis et al., 2000). ZVI corrosion in aerated water leads to oxidation of As(III) and sorption of As(V) and As(III) on forming Fe(III)(hydr)oxides (Hug and Leupin 2003, Katsoyiannis et al 2008a). In Bangladesh, tens of thousands of household arsenic removal units based on ZVI are

already in operation (Hussam et al. 2007). However, the suitability of this method in larger treatment units that would be required in Eastern Europe has to be investigated in more detail.

A study by Stauder (2007) reviewed potential remediation solutions for As (up to 210 µg/L) and TOC (6 to 12 mg/L) removal from groundwaters in northern Serbia. A complex treatment was recommended involving aeration, flocculation and sedimentation (using Fe(III)-salts to remove As(V) and organic matter), ozonation, multilayer filtration and disinfection. Installing such complex technologies at small and medium sized plants would be expensive as the region does not have major centralised treatment facilities, so the use of alternative water sources is suggested, including the use of bank filtrate extraction of the Tisza River (Stauder 2007). Again in Serbia, aquifers held within the Danube alluvion with water sourced from the Danube, have also been suggested as an alternative water source to deeper As rich aquifers (Djuric and Jevtic 2008). Levels of elevated As (18 µg/L) have been detected in these aquifers, but remediation would be cheap and simple, requiring only aeration, filtration and disinfection (Djuric and Jevtic 2008). Finding safe alternate water sources can be problematic, not least of all due to the expense of accurately measuring low levels of As in natural waters. The inverse relationship observed between As and SO_4 as observed here could provide an alternative, as SO_4 is much easier and cheaper to detect, and could be used to identify low As concentrations in reducing waters in Late Pliocene and Quaternary aquifers of the Pannonian Basin (Kirk et al., 2004).

4.4.4. Worldwide implications

Holocene deltaic sediments, i.e. deposited in the last 10 ka BP, have been shown in recent studies to be key in predicting the presence of elevated arsenic in groundwaters of South East 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 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 taping older Pleistocene sediments then contain much lower As levels (BGS and DPHE 2001).

By contrast, we show here that much older aquifer systems with sediments from the Late Pliocene/Quaternary and containing palaeowaters dating from the last ice-age (70,000 and 12,000 yrs BP) are also capable of mobilising arsenic under similar conditions. As-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 the two arsenic bearing aquifers in the 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 pre-requisite. What is of greater importance is the type and abundance of TOC and its relatively suitability as an energy source to the microbes present within the aquifer in question. This suggests reducing aquifers containing As-bearing Fe-oxides, regardless of age, all have the potential to produce elevated levels of As if TOC levels are high enough and SO_4 is totally consumed, or absent to begin with. Therefore concentrations of SO_4 and TOC should be taken into account, especially with regards to older aquifer systems, in future developments of groundwater prediction models determining As contamination due to reductive dissolution.

5. Conclusions

From a dataset of 73 groundwater samples from the Pannonian Basin (Western Romania and Eastern Hungary), cluster analysis was used to identify dominant groundwater types and elucidate potential arsenic release mechanisms. Four major groups where identified which were divided into three main categories (i) group 4 with strong geothermal and saline influences with low levels of As (mean average 33.1 µg/L, range <0.5 to 240 µg/L), (ii) group 3 containing only dug wells with very low As (mean average 1 µg/L, range <0.5 to 2.1 µg/L) and (iii) group 1 and 2 representing general groundwaters, with group 1 containing the highest levels of As (mean average 123 µg/L, range 23.4 to 208 µg/L) in contrast to group 2 (mean average 11.5 µg/L, range <0.5 to 58.0 µg/L).

High levels of Li, Si, NH_4 and B in waters from groups 4, coupled with low δ^7Li values are all indicative of the influence of geothermal activity, despite not all samples having elevated (+ 35 ^{o}C) temperatures. 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.

Waters from dug wells in group 3 were all Ca/Mg-HCO_3 type, with δD and δ^{18}O characteristic of local rain water and the presence of U, all to be expected from wells tapping surface aquifers which are exposed to the atmosphere with strong rain water influences. These background characteristics are

then overprinted by geochemical influences from contamination by surface and animal waste (elevated K, NO_3, S(tot) and Cl).

Waters within group 2 had a range of geochemical parameters. A small number of Ca/Mg-HCO_3 type waters with δD and $\delta^{18}O$ values similar to the dug wells of group 3 indicative of young fresh groundwaters with strong influences from modern meteoric waters. Also included within this group were some dug wells, again similar to those of group 3, but with lower levels of Cl, NO_3 and K levels indicating these wells had much lower levels of anthropogenic contamination from surface and human waste. The remainder of group 2 and all of group 1 waters had Na-HCO_3 type water with depleted δD and $\delta^{18}O$ values in comparison to modern meteoric water, indicative of palaeowaters from the last ice-age (Rozanski 1985, Deak et al., 1987, Stute and Deak 1989). Despite the similarities between the Na-HCO_3 waters of both groups, they each showed distinctive redox characteristics with (i) group 1 indicative of waters dominated by methanogenesis (high CH_4, low to absent S(tot)), (ii) group 2 indicative of waters dominated by SO_4-reduction (low CH_4, moderate S(tot)), and (iii) similar range in Fe concentrations indicating that Fe-reduction was occurring in both groups. Much higher levels of TOC in group 1 is thought to be the reason for these differences as high levels leading to rapid exhaustion of any SO_4 present, driving the system to methanogenesis.

Arsenic levels varied between the 4 groups. Typically low concentrations in group 4 combined with positive correlations between δ^7Li and As(tot) indicate that As is not sourced from geothermal activities in the area. Very low As(tot) (mean average 1.0, range <0.4 to 2.1 µg/L) was observed in the dug wells of group 3, indicating that As is not sourced from surface run off contamination. The reducing nature of group 1 and 2 waters, coupled with knowledge that Fe-oxides are known to occur in these aquifers and 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. In group 2, ongoing SO_4-reduction releases S^{2-} which can then remove As from solution, either by the formation of As-sulphides, or from sorption of As onto Fe-sulphide phases formed from the concurrent release of Fe. This leads to the low As(tot) concentrations found within this group (mean average 11.5, range <0.5 to 58 µg/L) . By contrast, group 1 waters that are dominated by methanogenesis, 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 average 123, range 23.4 to 208 µg/L). High TOC levels in group 1 could also further exacerbate As levels by competitive sorption for surface sites and also by binding onto TOC. Therefore, As levels within waters of the Pannonian basin as studied here are controlled not by mobilisation but by retention processes. Levels of SO_4 within groundwaters appear to be governed by the amount of organic carbon present, leading to low As concentrations in the presence of SO_4, but high As levels in waters to which SO_4 levels have been exhausted.

High levels of TOC coupled with As present predominantly in the reduced, As(III) form complicates potential remediation solutions, and requiring pre-oxidation if conventional methods are to be used. This would add to the overall cost and complexity of any treatment required. Therefore, novel treatment methods such as the use of ZVI, thought to unaffected by the speciation of As could be suitable. The use of alternative sources such as shallower low As aquifers, or bank filtrate from river sources could be a cheaper alternative. In areas were this is not possible, identification of low As waters from Late Pliocene/Quaternary aquifers could be done by measuring levels of SO_4, taking advantage of the inverse relationship observed between SO_4 and As.

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Figure 1 : Location map of field area

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, Juhász et al., 2007, Gábris and Nádor 2007).

Figure 3 : Location map of wells in study area

Figure 4 : Arsenic box-plot of different groups. Although levels of As above the EU limit of 10 µg/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). Sample 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/K-HCO_3) groundwaters.

Figure 6 : Comparison between Li concentrations and δ^7Li values (‰). Group 4 display the lowest δ^7L 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 ^oC) typically have higher Li contents, with concentrations increasing with temperature. Presence of high Li but low temperature (< 35 ^oC) waters (circled area) indicates water with strong geothermal influences despite cool surface temperatures.

Figure 8 : Comparison of δD and $\delta^{18}O$ 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. Waters with Na-HCO_3 waters plot within the range of palaeowaters from the previous ice-age.

Figure 9 : Comparison of CH_4 with $\delta^{13}C_{CH4}$ and S(tot) of waters from groups 1 and 2 (general groundwaters). Waters of group 1 show a more depleted $\delta^{13}C_{CH4}$ signature than group 2. Levels of S(tot) are higher in group 2, with CH_4 higher in group 1, with a negative covariance observed between CH_4 and S(tot).

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

Figure 11 : Comparison of TOC with CH_4 and S(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 S(tot), with waters in group 2 containing low concentrations of TOC but with higher concentrations of S(tot).

Figure 12 : Comparison between As(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 As(tot) with CH_4, S(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 S(tot). Range in Fe concentrations is similar in both groups.

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

Country	Arsenic ($\mu g\ L^{-1}$)	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	10 – 610	200,000 and/or 3% of population	Habuda-Stanic et al., 2007, Ćavar et al., 2005
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 arsenic 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	⇒ Redox characteristics and Eh indicate reducing conditions ⇒ Consistent elevated As(tot) in all samples ⇒ Elevated CH_4, TOC ⇒ Low Fe and S(tot) Na/K-HCO_3 groundwater types Lighter δ^7Li isotopic characteristics δD and δ^{18}O values similar to palaeowaters	123 23.4 to 208
Group 2 – General groundwaters – Sulphate-reducing	35	⇒ Redox characteristics and Eh indicate reducing conditions ⇒ Range of As(tot) values ⇒ Moderate S(tot) ⇒ Low Fe Mg/Ca-HCO_3 to Na/K-HCO_3 groundwater types Lighter δ^7Li isotopic characteristics Range of δD and δ^{18}O values from rainwater to palaeowaters	11.5 <0.5 to 58.0
Group 3 – Dug wells	7	⇒ Redox characteristics and Eh indicate oxidising conditions ⇒ Elevated SO_4, NO_3, U, Cl, K and conductivity ⇒ As(tot) below detection limit Mg/Ca-HCO_3 groundwater type δD and δ^{18}O values similar to rain water	1.0 <0.5 to 2.1
Group 4 – Thermal and saline waters	16	⇒ Redox characteristics and Eh indicate reducing conditions ⇒ Highly variable geochemistry ⇒ Elevated levels of NH_4, Li, Cl, Na, Sr, Fe, B, alkalinity ⇒ Group contained all thermal wells (+35 °C) Na-Cl, Na-HCO_3 and Mg/Ca-HCO_3 groundwater types Heavier δ^7Li isotopic characteristics Variable δD and δ^{18}O values	33.1 <0.5 to 240

Table 3 : Geochemical parameters for Pannonian Basin groundwaters

Grp[a]	Name[b]	Well[c]	Depth	Age	δD	d18O	δ^7Li	$\delta^{13}C_{CH4}$	pH	Temp	eH	Cond	TOC	Cl	NO_3	S(tot)[d]	H_2S	CH_4	C_2H_6	C_3H_8	PO_4	NH_4	Alk	As(III)	As(tot)[e]	Na[f]	Mg[f]	Si[f]	K[f]	Ca[f]	Fe[f]	Mn[f]	U[f]	Mo[f]	B[f]	Li[f]	Sr[f]
			(m)	(yrs)	‰ VSMOW	‰ VSMOW	‰ VL-SVEC	‰ VPDB		°C	mV	mS/cm	mgC/L	mg/L	mgN/L	mg/L	µg/L	mg/L	µg/L	µg/L	mgP/L	mgN/L	mM	µg/L	µg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	µg/L	µg/L	µg/L	mg/L	µg/L	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	5.8	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	-82.7	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	0.4	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	<0.05	-	-	0.1	0.2	6.7	8.0	9.3	123.9	4.9	8.1	0.7	16.6	0.24	177.7	1.1	6.0	0.8	6.5	106
2	M_R132	A	130	79	-85.13	-11.84	-	-	8.34	15.4	0	0.5	<0.5	7.8	<0.25	4.2	<85	0.53	0.0	0.0	0.1	0.2	4.1	4.7	5.2	88.9	1.7	6.1	0.7	9.7	0.01	30.0	0.1	12.7	0.3	11.5	76.5
2	M_R133	A	150	1	-	-	-	-	8.14	17.1	45	0.4	<0.5	6.2	<0.25	4.3	<85	-	-	-	0.1	0.2	4.0	7.0	7.6	85.3	1.6	5.8	0.7	8.8	0.01	22.0	<0.5	11.1	0.2	10.1	70.5
2	M_R114	A	300	3	-87.30	-12.23	-	-	8.04	16.6	-184	0.5	<0.5	3.1	<0.25	4.3	<85	<0.05	-	-	0.3	0.1	5.3	3.3	5.1	107	1.3	7.7	0.6	9.2	0.49	62.2	2.3	15.9	0.2	4.7	55.8
2	M_R121	A	150	-	-87.77	-12.22	-	-	7.74	17.5	-236	0.6	<0.5	5.3	<0.25	4.7	<85	<0.05	-	-	0.1	0.5	7.4	5.8	6.5	124	3.7	10.2	1.0	16.3	0.77	183.8	1.6	20.7	0.2	25.6	164
2	M_R119	A	180	200	-89.69	-12.77	-	-	7.89	17.9	-147	0.5	0.5	4.1	<0.25	4.9	<85	<0.05	-	-	0.1	0.3	5.1	9.4	10.6	101	2.1	9.8	0.7	12.1	0.35	99.7	0.8	7.6	0.2	21.5	110
2	M_R134	A	100	100	-87.22	-12.54	-	-	8.45	16.1	-17	0.4	<0.5	5.4	<0.25	4.9	<85	-	-	-	0.1	0.2	3.6	6.3	6.8	79.0	1.6	6.2	0.6	8.6	0.02	35.1	<0.5	6.6	0.2	10.3	64.0
2	M_R136	P	200	-	-87.44	-12.19	-	-	8.81	15.2	-15	0.4	<0.5	5.1	<0.25	5.2	<85	<0.05	-	-	0.1	0.2	3.3	17.0	20.4	84.0	0.3	5.3	0.4	3.0	0.03	8.3	<0.5	3.2	0.2	5.6	19.7
2	M_R160	A	150	1	-81.83	-11.82	-	-	7.97	20.4	-120	0.7	<0.5	3.8	<0.25	5.5	-	0.08	-	-	0.1	1.8	7.5	39.6	42.9	117	7.2	7.7	4.6	14.4	0.08	3.8	<0.5	1.8	0.2	61.8	1264
2	M_R130	A	-	-	-65.65	-9.55	-	-	7.12	14.1	-62	0.9	0.7	4.1	<0.25	14.1	<85	<0.05	-	-	0.1	0.6	9.3	0.2	0.5	16.8	27.9	15.4	1.2	123	0.80	201	<0.5	<0.5	0.2	26.0	545
2	D_R32	Dg	-	-	-62.25	-8.20	-	-	7.5	9.2	-	1.0	2.1	23.8	18.3	20.8	-	-	-	-	0.0	0.2	7.7	0.2	1.1	50.0	41.3	8.6	1.5	102	0.02	11.5	3.8	<0.5	0.1	8.9	595
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	0.5	<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	0.6	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	<0.5	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	0.6	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-AES
[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 14

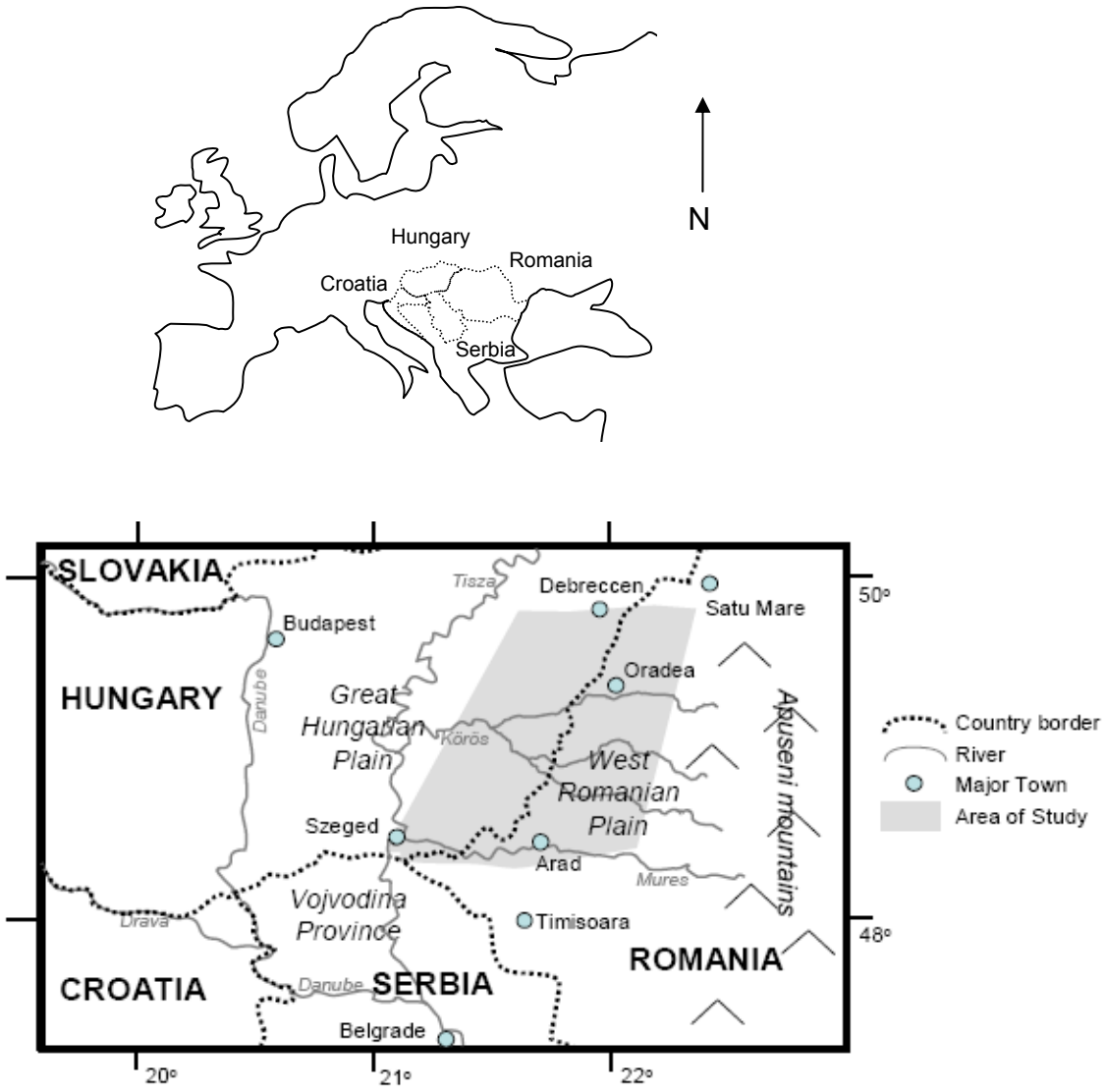

N
Hungary
Romania
Croatia
Serbia
SLOVAKIA
Budapest
HUNGARY
Danube
Tisza
Debreccen
Satu Mare
Oradea
Great Hungarian Plain
Körös
West Romanian Plain
Apuseni mountains
Szeged
Arad
Mures
Vojvodina Province
Drava
Timisoara
ROMANIA
CROATIA
Danube
SERBIA
Belgrade
20°
21°
22°
50°
48°
Country border
River
Major Town
Area of Study

Figure 15

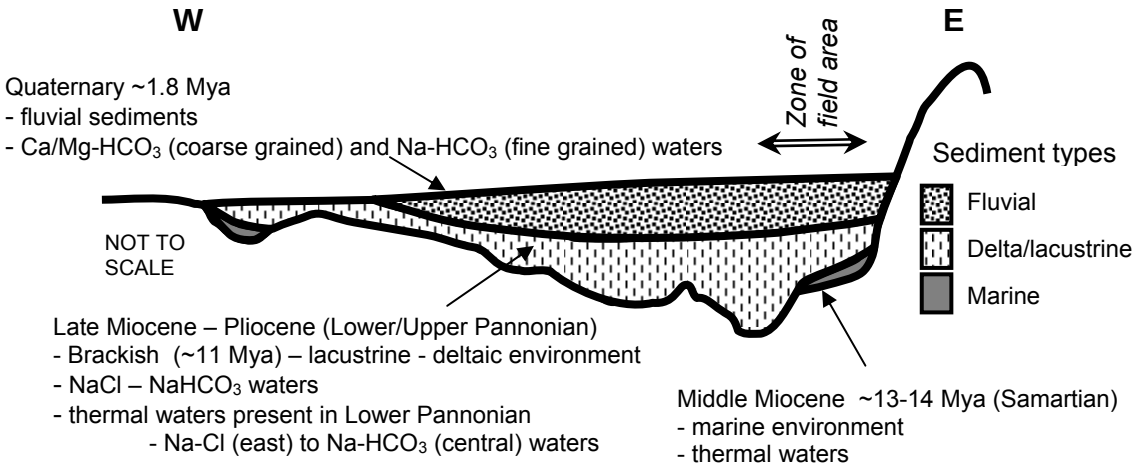

W
E
Zone of field area
Quaternary ~1.8 Mya
- fluvial sediments
- Ca/Mg-HCO3 (coarse grained) and Na-HCO3 (fine grained) waters
Sediment types
Fluvial
Delta/lacustrine
Marine
NOT TO SCALE
Late Miocene – Pliocene (Lower/Upper Pannonian)
- Brackish (~11 Mya) – lacustrine - deltaic environment
- NaCl – NaHCO3 waters
- thermal waters present in Lower Pannonian
- Na-Cl (east) to Na-HCO3 (central) waters
Middle Miocene ~13-14 Mya (Samartian)
- marine environment
- thermal waters

Figure 16 :

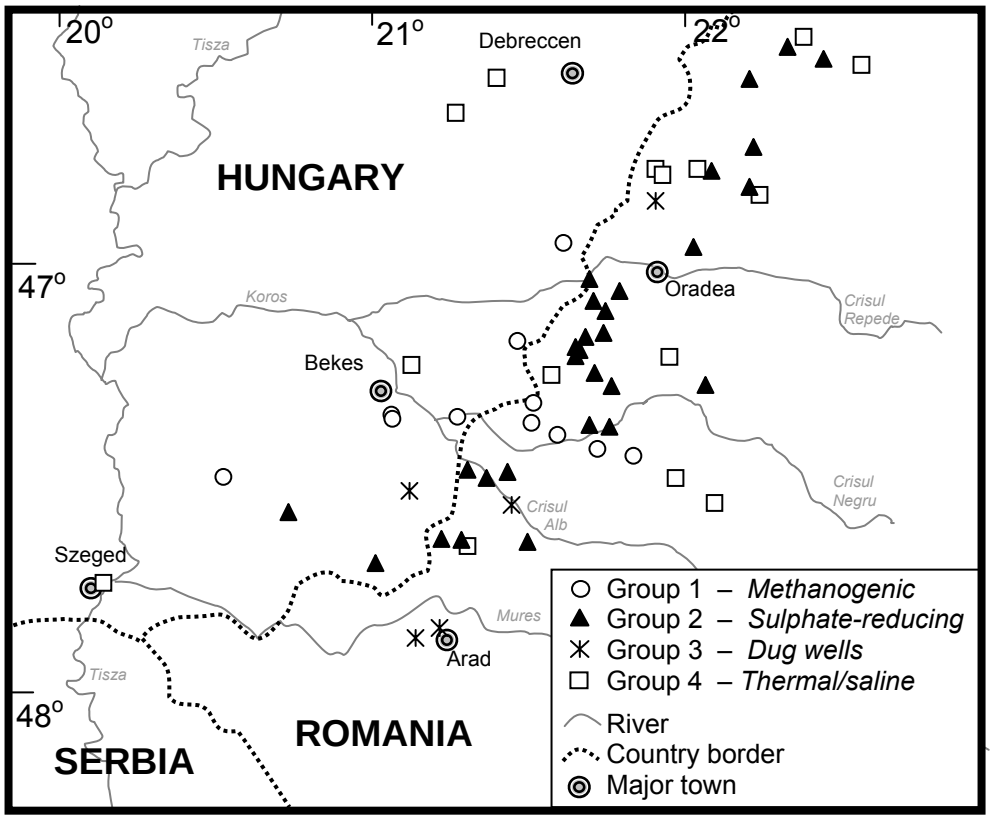

20°
21°
22°
47°
48°
Tisza
Debreccen
HUNGARY
Koros
Oradea
Crisul Repede
Bekes
Crisul Negru
Crisul Alb
Szeged
Mures
Arad
Tisza
ROMANIA
SERBIA
Group 1 – Methanogenic
Group 2 – Sulphate-reducing
Group 3 – Dug wells
Group 4 – Thermal/saline
River
Country border
Major town

Figure 17 : Arsenic box-plot of different groups. Although levels of As above the EU limit of 10 µg/L are found in all groups apart from group 3, group 1 is the only one with consistently high concentrations.

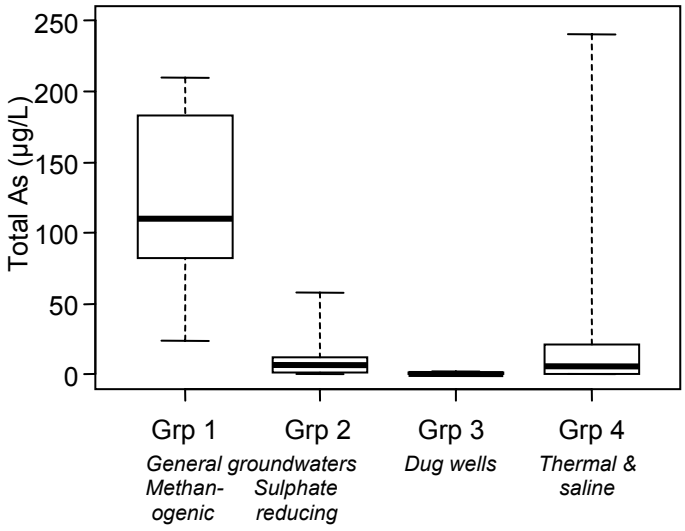


Figure 18 :

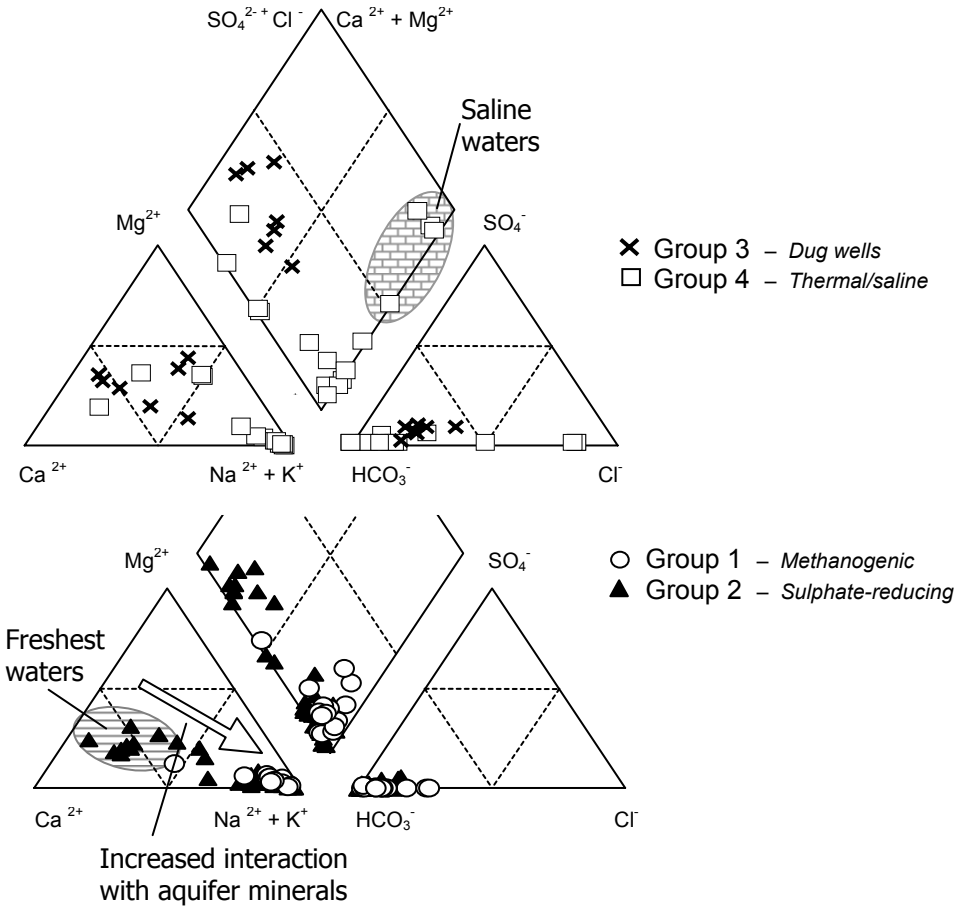

SO_4^{2-} + Cl^-
Ca^{2+} + Mg^{2+}
Saline waters
Mg^{2+}
SO_4^-
Ca^{2+}
Na^{2+} + K^+
HCO_3^-
Cl^-
Group 3 – Dug wells
Group 4 – Thermal/saline
Mg^{2+}
SO_4^-
Freshest waters
Ca^{2+}
Na^{2+} + K^+
HCO_3^-
Cl^-
Increased interaction with aquifer minerals
Group 1 – Methanogenic
Group 2 – Sulphate-reducing

Figure 19 :

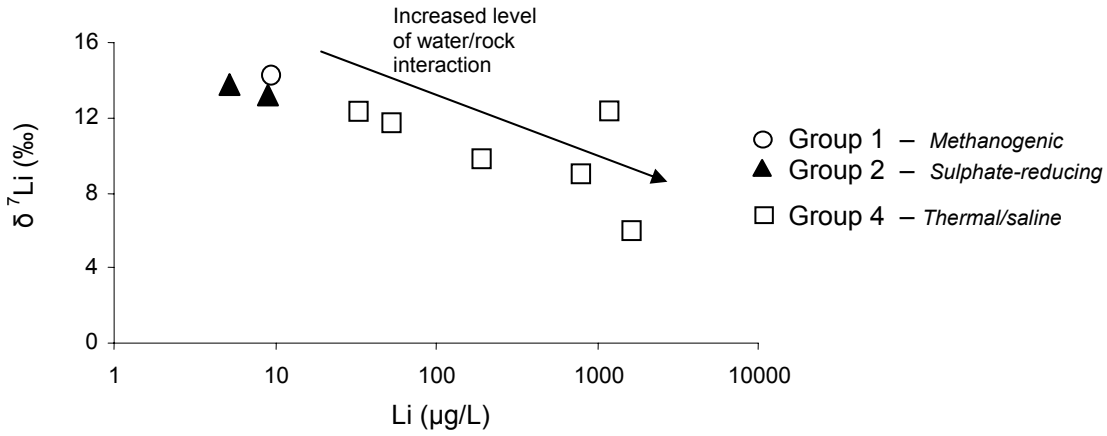

Increased level
of water/rock
interaction
16
12
8
4
0
δ 7Li (‰)
1
10
100
1000
10000
Li (µg/L)
Group 1 – Methanogenic
Group 2 – Sulphate-reducing
Group 4 – Thermal/saline

Figure 20 :

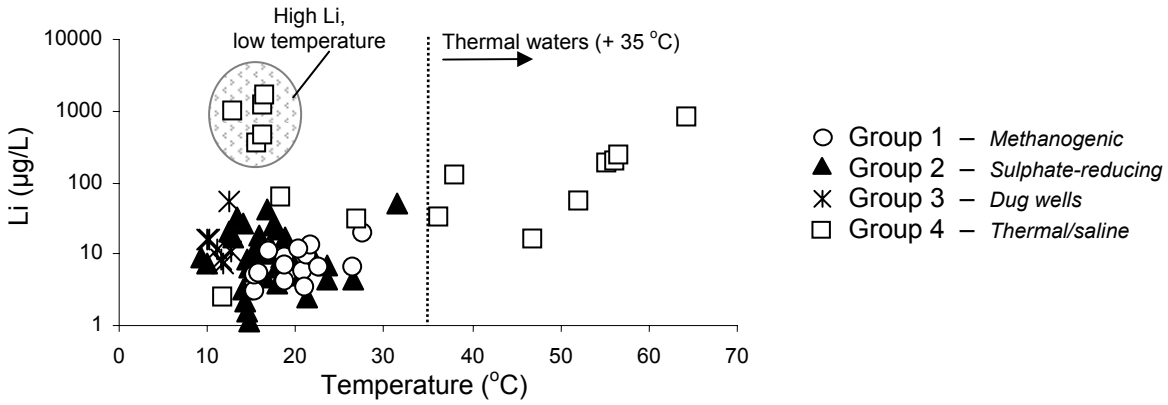

High Li,
low temperature
Thermal waters (+ 35 °C)
10000
1000
100
10
1
Li (µg/L)
0
10
20
30
40
50
60
70
Temperature (°C)
Group 1 – Methanogenic
Group 2 – Sulphate-reducing
Group 3 – Dug wells
Group 4 – Thermal/saline

Figure 21 :

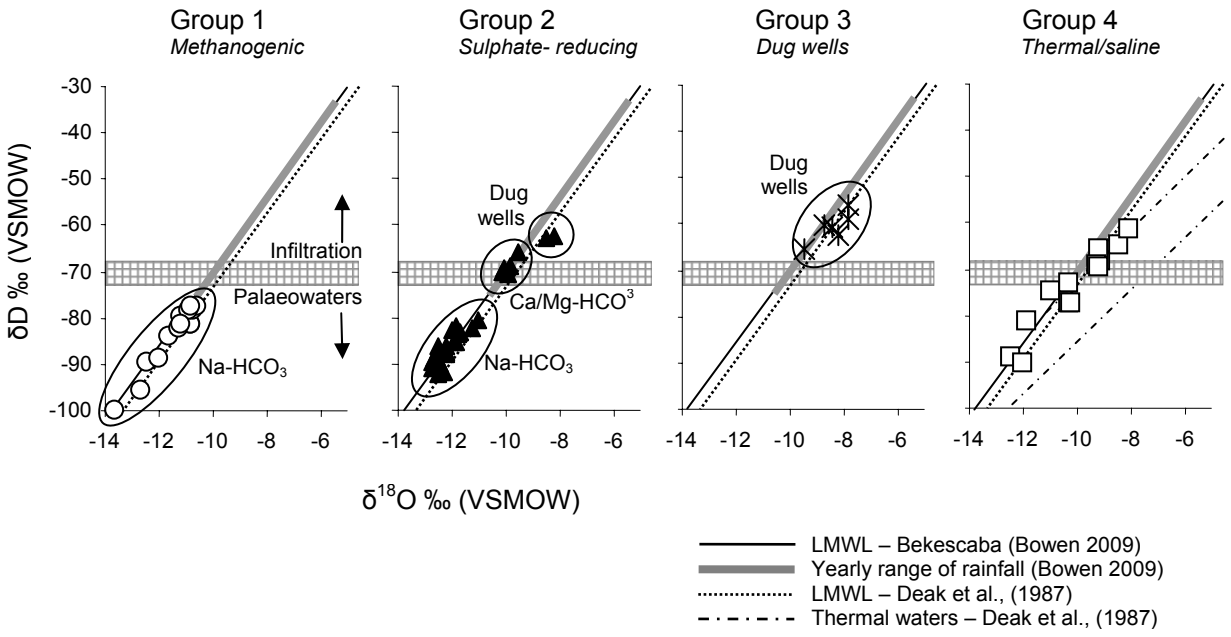

Group 1
Methanogenic
Group 2
Sulphate- reducing
Group 3
Dug wells
Group 4
Thermal/saline
δD ‰ (VSMOW)
-30
-40
-50
-60
-70
-80
-90
-100
Infiltration
Palaeowaters
Na-HCO3
Dug wells
Ca/Mg-HCO3
Na-HCO3
Dug wells
-14
-12
-10
-8
-6
δ18O ‰ (VSMOW)
LMWL – Bekescaba (Bowen 2009)
Yearly range of rainfall (Bowen 2009)
LMWL – Deak et al., (1987)
Thermal waters – Deak et al., (1987)

Figure 22 :

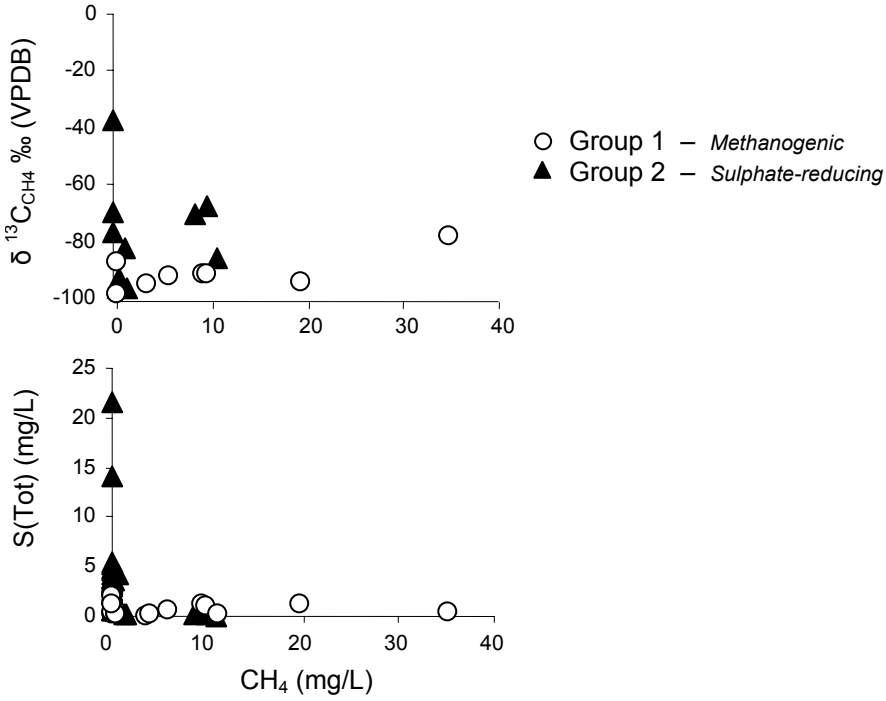

δ 13CCH4 ‰ (VPDB)
0
-20
-40
-60
-80
-100
0
10
20
30
40
S(Tot) (mg/L)
25
20
15
10
5
0
CH4 (mg/L)
Group 1 – Methanogenic
Group 2 – Sulphate-reducing

Figure 23 :

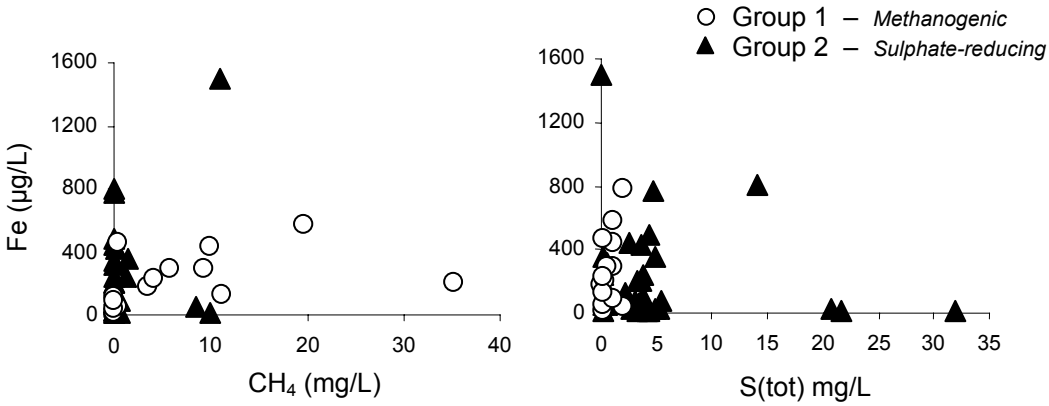


Figure 24 :

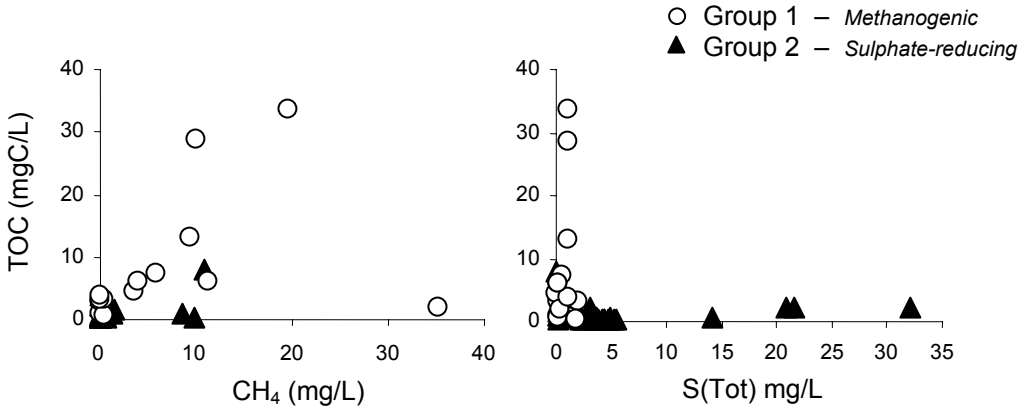


Figure 25 :

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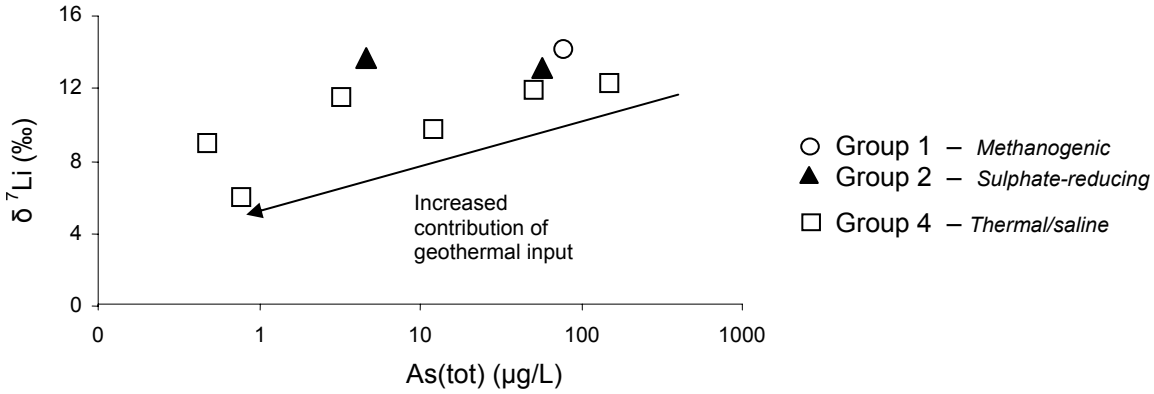


Figure 26 **:**

