Acta Mineralogica-Petrographica, Szeged 2005, Vol. **46**, pp. 47-52

ACTA
Mineralogica
Petrographica

THE ROLE OF GROUNDWATER FLOW IN CONTROLLING THE ARSENIC CONCENTRATION IN THE SOUTHERN PART OF THE GREAT HUNGARIAN PLAIN

IRÉN VARSÁNYI[1], LAJOS Ó. KOVÁCS[2]

[1] Department of Mineralogy, Geochemistry and Petrology, University of Szeged, H-6701 Szeged, P.O.Box 651, Hungary
[2] Hungarian Geological Survey, H-1440 Budapest, P.O.Box 17, Hungary
e-mail: varsanyi@geo.u-szeged.hu

ABSTRACT

Concentrations of main and microelements and humic substances were determined in 456 subsurface water samples in the Great Hungarian Plain (central part of the Pannonian Basin). The lack of correlation between arsenic and other chemical components in the bulk of the samples, and the geographical and depth distributions of arsenic suggest that processes influencing the arsenic content should be studied in separate water flow systems. It was established that in the different parts of the groundwater flow line different factors play a role in controlling the arsenic content of waters. In the discharge regions of the water flow systems humic substances are the main controlling factors of mobilization of arsenic. In the recharge area association of arsenic and iron indicates adsorption or co-precipitation of arsenic on ferric oxides and hydroxides.

Key words: arsenic, groundwater, recharge, discharge, humic substances, iron

INTRODUCTION

Certain elements have a great importance in the diet of humans and animals, because they are essential to the health of organisms. Toxicity of high concentrations of these and other elements has also been recognized. For the last decades, the attention has been directed towards the possible relationship between the As content in drinking water and food, and the health of humans and animals (Xu and Thornton 1985, Adriano 1986, Varsányi et al. 1991). Standards have been established in many countries for a maximum allowable As level. In Hungary it is 10 mg·dm^{-3} for the drinking water.

Many authors have reported the distribution of arsenic in the porewater of lacustrine sediments (Farmer and Lovell 1986), in estuarine (Belzile 1988, Belzile and Tessier 1990), geothermal (Stauffer and Thompson 1984) coastal and ground water (Bottomley 1984). The amount of As dissolved in water is attributed to geochemical processes, like dissolution-precipitation, oxidation-reduction, adsorption, and biologically mediated reactions (Welch et al. 1988, Ferguson and Gavis 1972). The mobility of As in surface and ground waters is closely tied to the behavior of iron. During the weathering of As-containing minerals As enters the surficial cycle mainly as soluble arsenate in which As is present in pentavalent state. This form is quite mobile, however, it coexists and coprecipitates with ferric oxide (Wilson and Hawkins 1978). In a reducing environment As is released. The latter is attributed to modification of redox conditions, i.e. pyrite formation and degradation of organic matter (Belzile 1988, Peterson and Carpenter 1986).

In certain regions of Hungary the arsenic content of groundwater is higher than the acceptable limit for drinking water. About half a million consumers are affected by drinking water containing arsenic above the health limit. Investigations have been carried out to outline the prevalence of arsenic in groundwater and to establish the geological and/or geochemical processes controlling its mobility (Csanádi et al. 1985, Csalagovits 1999, Erdélyi 1991), however, the exact mechanism of its mobilization is not yet known. The aim of the present work is to determine the main factors influencing the amount of As dissolved in the subsurface water in the central part of the Pannonian Basin.

GEOLOGICAL BACKGROUND

The study region, located in the southeastern part of Hungary, represents the central part of the Pannonian Basin (Fig. 1). Its geological evolution is summarized in Varsányi et al. (1997), therefore only a short description is given here. The Pannonian Basin, having a Paleozoic-Mesozoic basement, is filled with Neogene-Quaternary sediments. The initial formation of deep basins and uplifted highs was related to Early Miocene tectonics. In the Late Miocene to Pliocene, thermal subsidence over the entire region was accompanied by rapid sedimentation leading to a complete filling-up by the end of Pliocene. The Late Pliocene and Pleistocene tectonic events seem to follow SW-NE tectonic

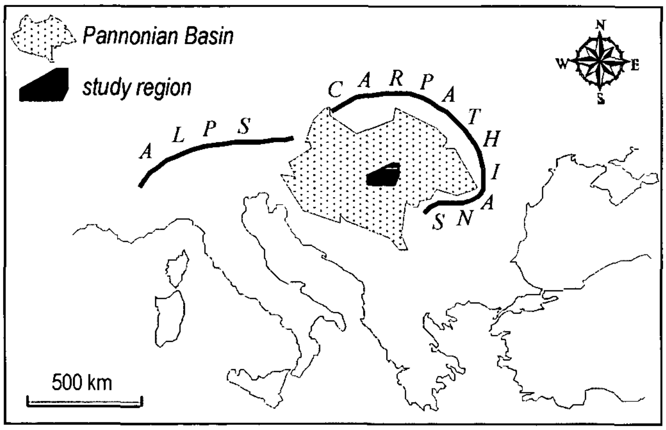

Fig. 1. Location of the study area.

lines developed during the Miocene. The subsidence and uplift occurred at different rates over the Pannonian Basin (Horváth et al. 1988, Juhász et al. 2002) which resulted in a strongly variable thickness of the sedimentary cover ranging from several hundred to several thousand meters. In the Miocene, 1000-3000 m of marine sediments were covered by 1000-3000 m of lake sediments. The Lower to Middle Miocene pre-Pannonian sediments formed in a marine to brackish environment. The Late Miocene Pannonian was characterized by lake deposits, followed by Pontian lacustrine and deltaic sedimentations. The Pliocene is characterized by interbedded lacustrine and fluvial sediments (Rónai 1985). In the Pontian and Pliocene, repeated subsidence caused cyclic features of sediments (Molnár 1973) and diachronous commencement of fluvial sedimentation. The latter started already at the end of Pliocene in the Duna-Tisza Interfluve and South Tisza region, while in the Körös Basin the lacustrine-marshy sedimentation prevailed until the Early Pleistocene, and only later was it replaced by a fluvial one. As a result, the overall thickness of the fluvial sediments varies from 100 to 700 m, often having a cyclic character (Rónai 1983). After the Pleistocene, eolian sedimentation deposited windblown sand and loess over the region.

RESULTS AND DISCUSSION

Subsurface water samples from wells of 30-2500 m depth were collected and analyzed. Major and minor chemical components: Na^+, Ca^{2+}, Mg^{2+}, K^+, total Fe, total Mn, Sr^{2+}, Li^+, Ba^{2+}, alkalinity, Cl^-, SO_4^{2-}, PO_4^{3-} and humic substances, were determined. The wellhead sampling, sample preservation procedures, and methods of analysis are described in Varsányi et al. (1997).

The arsenic concentration varies from practically 0 to 4.53 μmol·l^{-1} with a mean value of 0.68 μmol·l^{-1}. Spatial distribution of arsenic is not homogeneous over the study area. The frequency distribution of the arsenic concentration is bimodal indicating at least two main factors controlling the arsenic content of groundwater (Fig. 2). The most frequent arsenic concentrations are between 0.2 and 0.4 μmol·l^{-1}, and between 1.2 and 1.4 μmol·l^{-1}; and there are samples with higher arsenic contents up to 4.53 μmol·l^{-1}. In several regions and depth intervals arsenic seems to be concentrated in the water. Three groups of waters were separated and locations of these groups were studied. The separation was performed on the basis of the frequency distribution: the two maximums indicate two populations, and the outstanding As values compose a third group. The groups are as follows: the first one contains arsenic below 1.0 μmol·l^{-1}, the second one between 1.0 and 1.8. μmol·l^{-1}, and the third one above 1.8 μmol·l^{-1}. Fig. 3 indicates the location of the groups.

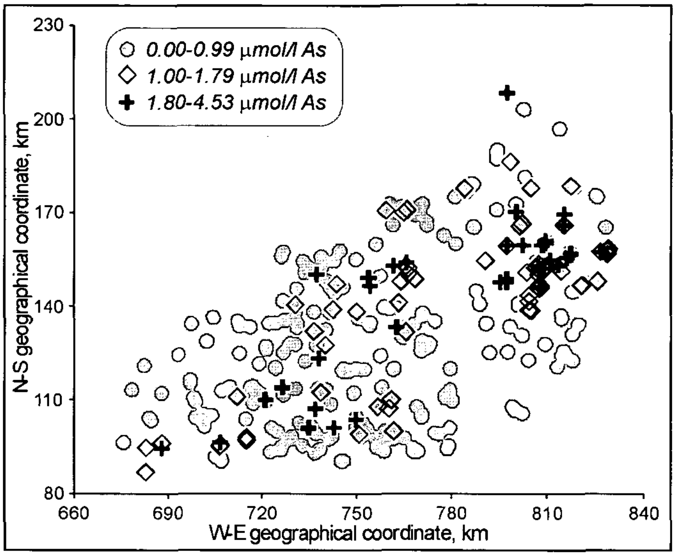

Fig. 3. Geographical distribution of As.

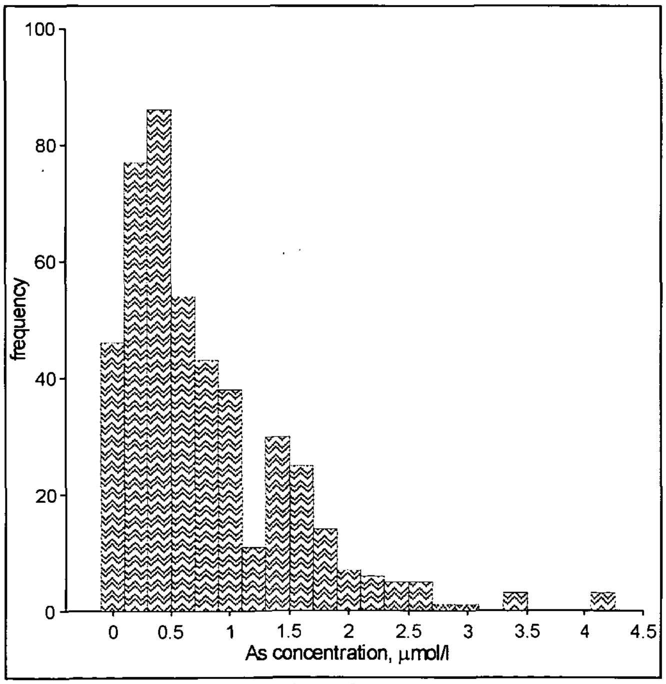

Fig. 2. Frequency distribution of As.

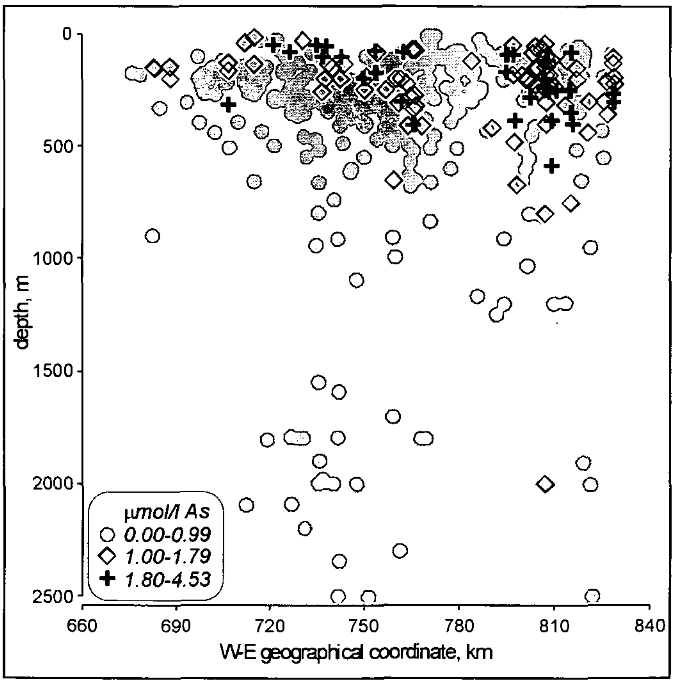

Fig 4. Depth dependence of As.

The highest concentrations were measured in the northeastern part of the studied area. In that region there are the greatest number of wells with high arsenic contents. The depth dependence of concentration is shown in Fig. 4. In general, the concentration is decreasing with depth. The western and eastern parts of the study area are different: in the western part enrichment of arsenic was found mostly in the upper 200 m, in the eastern region in the upper 500 m. The distribution is in connection with the surface elevation (Fig. 5). Water samples with the highest arsenic concentrations are located in the lowest regions indicating that the arsenic content of water is influenced by hydrogeological factors, as well.

Although many authors emphasize the importance of iron and organic matter in controlling the mobility of arsenic, in the studied 456 water samples no correlation has been found between arsenic and iron, or organic matter. To reveal the effect of organic matter on the concentration of dissolved arsenic, chemical oxygen demand (COD) and dissolved humic substances were considered. The pattern of geographical distribution of arsenic and the lack of general relationship between arsenic and other chemical components in the samples suggest the need of splitting the whole study area into sub-regions.

Earlier, based on chemical and isotope data, a hydrogeological model had been established (Varsányi et al. 1999, Varsányi et al. 2000). This model separates water bodies with different water flow directions and velocities from the surface down to about 2500 m (Fig. 6). The term 'water flow system' is used for a homogeneous water body in which the concentrations of the main chemical components are controlled by similar factors all over the water body. Seven water bodies were distinguished in the studied area (Fig. 6). Two of them, two water flow systems, are located in the Pleistocene layers, one in the Duna-Tisza Interfluve and South Tisza region, and another in the River Maros alluvial fan. Recharge and discharge areas of these flow systems are considered separately in this study. Another water flow system is in the Pleistocene and Pliocene layers of the Duna-Tisza Interfluve and South Tisza region. Two sub-regions of the studied area represent the discharge parts of water flow systems, one bringing up waters from deep layers in the South Tisza region, and the other facing upward in the Pleistocene layers in the Körös Basin. There are two deep water bodies, one with an unknown flow direction in the Pontian layers of the Duna-Tisza Interfluve and South Tisza region, and the other at the Pannonian-Pontian boundary, where water from the Pontian is mixing with upward seeping deep Pannonian waters. In the Körös Basin this deep water flows from the Pannonian-Pontian boundary up to the Pliocene layers.

The water samples were separated according to these water flow systems. In Pleistocene flow system of the Duna-Tisza Interfluve and South Tisza region the average arsenic concentration in the recharge area is 0.60 $\mu mol \cdot l^{-1}$, in the discharge area 0.62 $\mu mol \cdot l^{-1}$. In the southern part of the recharge area arsenic concentrations are elevated, the average is 1.17 $\mu mol \cdot l^{-1}$. In the River Maros alluvial fan the average in the recharge area is 0.49 $\mu mol \cdot l^{-1}$, while in the discharge area it is 1.32 $\mu mol \cdot l^{-1}$. In the Pliocene and Pleistocene flow systems of the Duna-Tisza Interfluve and South Tisza region the mean value is 0.48 $\mu mol \cdot l^{-1}$, whereas in the adjoining discharge area 0.17 $\mu mol \cdot l^{-1}$. The water samples from Pleistocene layers of the Körös Basin contain 0.90 $\mu mol \cdot l^{-1}$ of As as an average. The water in the Pontian layers is the most depleted in arsenic, the mean value is 0.09 $\mu mol \cdot l^{-1}$. The deepest studied zone, the Pannonian-Pontian boundary, has 0.47 $\mu mol \cdot l^{-1}$ on average. These differences are caused by different availability of arsenic in the sediments and by different processes mobilizing it.

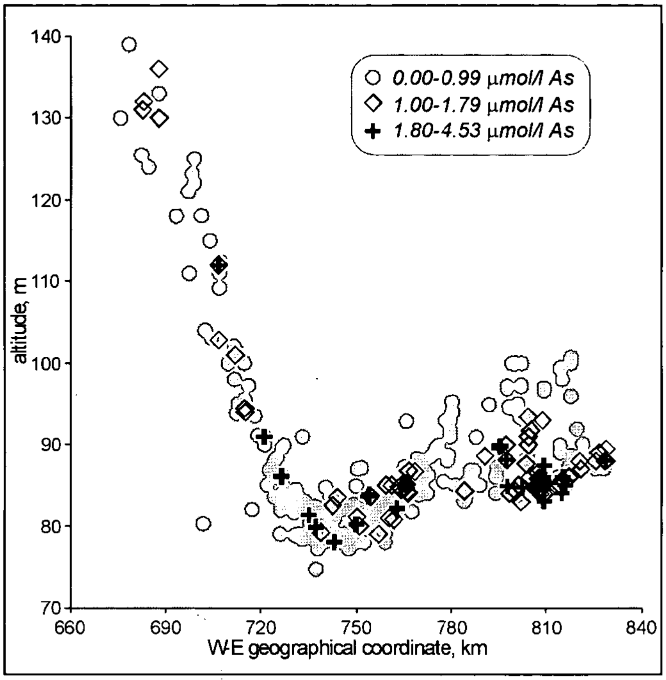

Fig. 5. Relationship of As and the surface elevation.

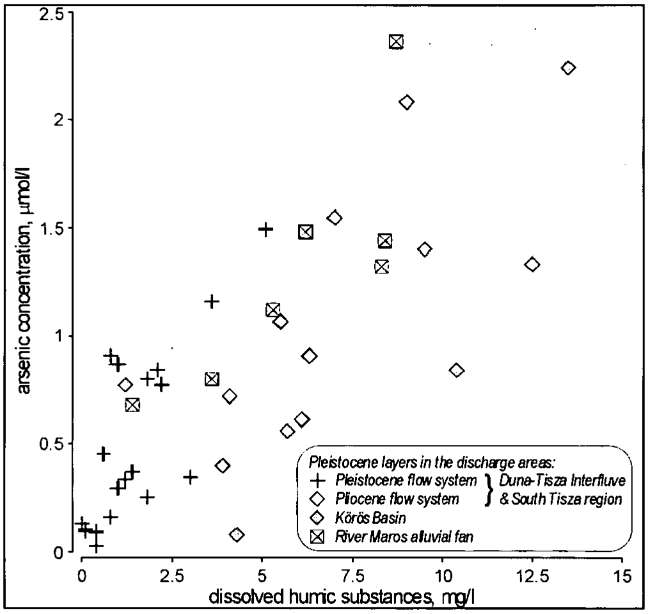

Fig. 7. As vs. dissolved humic substances in the discharge areas.

The processes controlling the mobilization of arsenic may be revealed by comparing arsenic data with other chemical components. In the discharge areas of the water flow systems (except one), an association was observed between arsenic and dissolved humic substances (Fig. 7). High concentrations of humic substances cause high arsenic concentrations in groundwater with no accompanying high iron level.

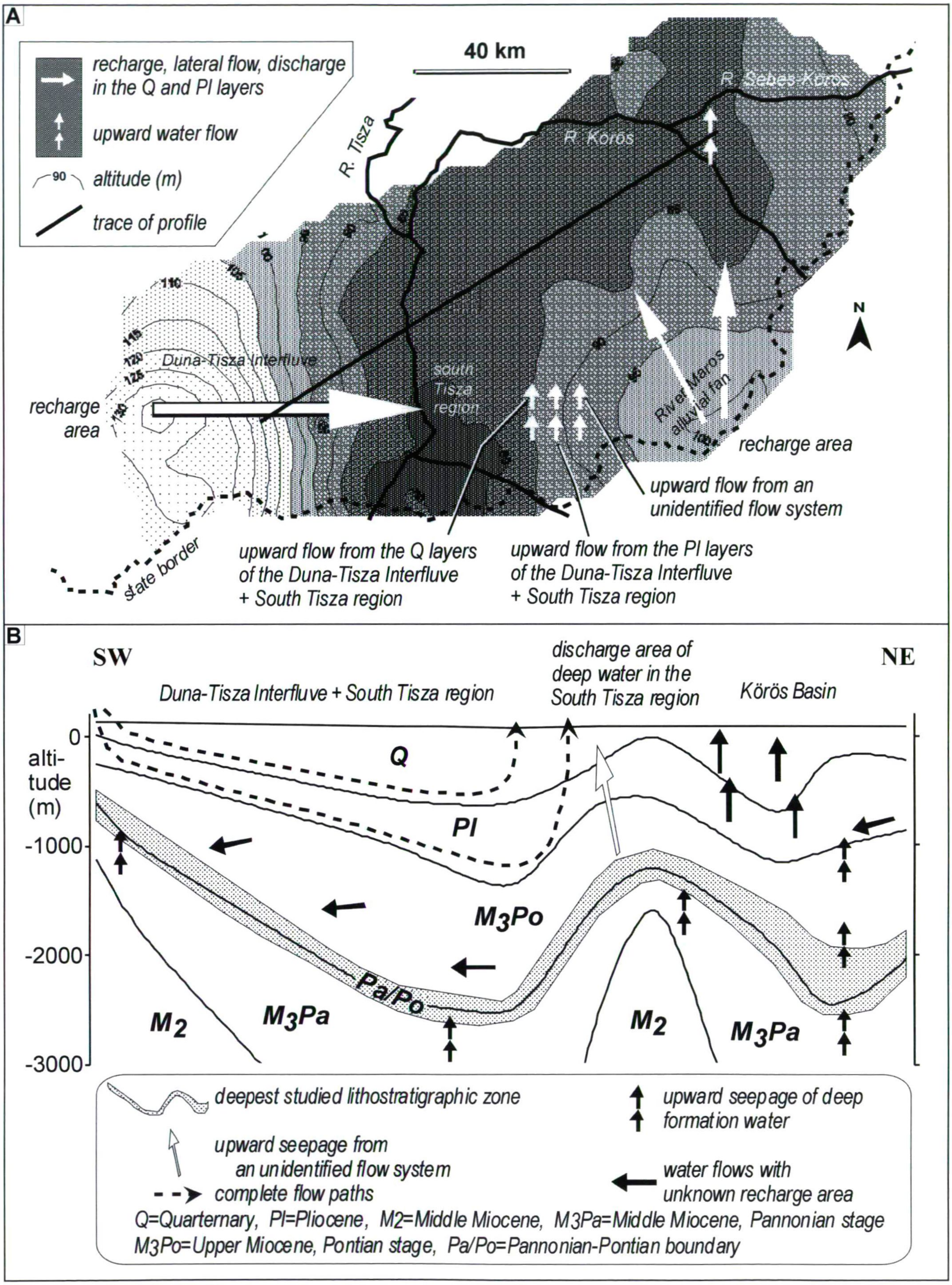

Fig. 6. Separation of water flow systems.

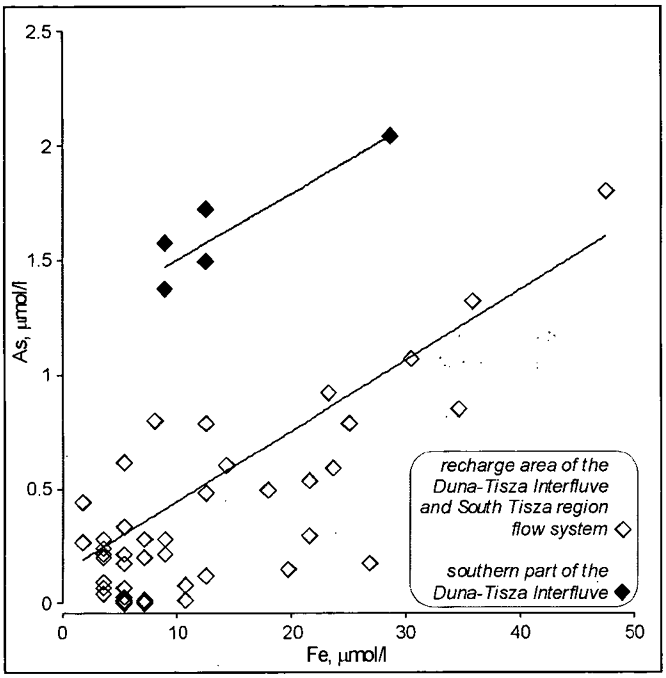

Fig. 8. As vs. Fe in the recharge area of the Duna-Tisza interfluve and south Tisza region.

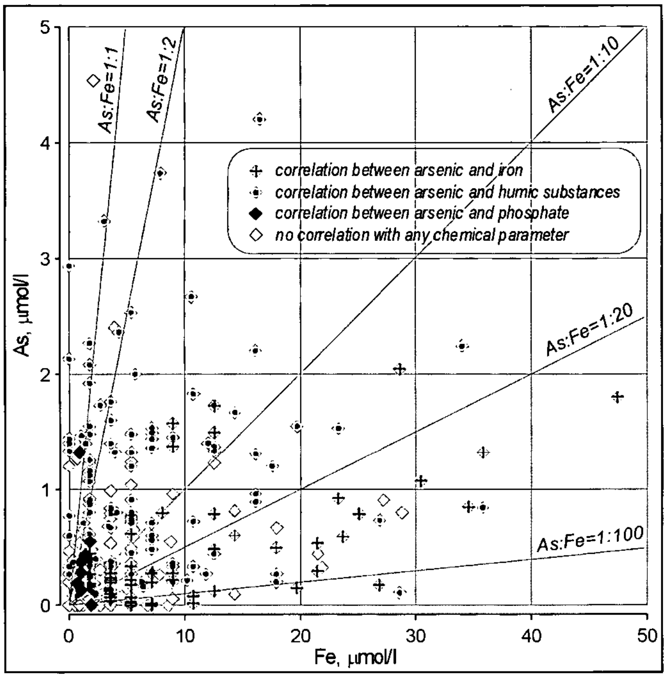

Fig. 9. As vs. Fe with ratios of As to Fe.

In the discharge areas the grain size of the sediments is much finer than in the recharge areas, and the high COD values indicate a higher organic matter content. It is supposed that during the transformation of insoluble sediment organic matter, arsenic associated with it is released together with soluble humic substances formed during the organic decay. The depth dependence of arsenic and humic substances is similar: there are two depth intervals with high arsenic and humic concentrations; one is the upper 500 m, the other is around 2000 m. In the discharge areas of water flow systems, organic matter seems to be more important than iron in controlling the arsenic concentration.

Many authors established the central role of iron in the mobility of arsenic, although quantitative models linking dissolved As and Fe are supported mainly by laboratory experiments. In the study area, no general correlation between arsenic and iron was found in the subsurface water; however, connection was established between them in the recharge area of the water flow system of the Duna-Tisza Interfluve and South Tisza region (Fig. 8). In the southern part of this recharge area several samples contain elevated arsenic values the additional source for which was not identified in the present work. In the deeper, Pliocene and Pontian layers, waters contain less arsenic than in the overlying Pleistocene layers. In the deepest zone (at the Pannonian-Pontian boundary) and in the Pontian layers in the Körös area arsenic is in inverse relationship with PO_4^{3-}: 1.0 µmol·l^{-1} increase in the PO_4^{3-}concentration corresponds to approximately the same decrease in the arsenic content.

It was found that factors controlling the mobility of arsenic change with the ratio of dissolved arsenic to dissolved iron. Fig. 9 indicates that the ratio of As to Fe varies in a very wide range: from less then 1% to more then 100%. In those water samples where an association of arsenic and iron was established, the ratio is lower then 1:10. Waters with a ratio of 1:2 indicate a connection between arsenic and phosphate. Where the arsenic concentration depends on the humic substances the ratio is not relevant.

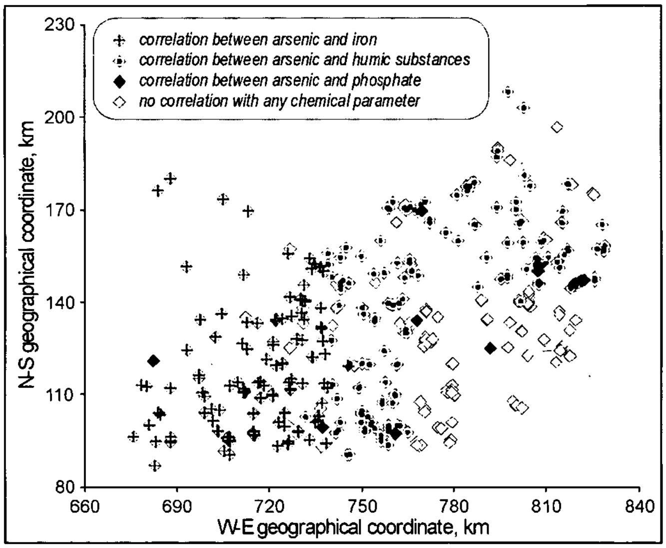

Fig. 10. Location of the factors controlling the arsenic concentration.

Geographical distribution of the factors controlling the arsenic concentration is shown in Fig. 10. Correlation between arsenic and iron is characteristic of the recharge area in the Duna-Tisza Interfluve, while correlation between arsenic and humic substances of the discharge areas: the South Tisza region and the Körös Basin.

CONCLUSIONS

The arsenic content is not uniform throughout the study area, indicating that diverse factors control its concentration in subsurface water. In most of the samples the arsenic content is above detection limit. It means a general availability of arsenic in the sediments; however, the amount may be different in certain regions and depth intervals. According to the hydrogeochemical model, the water samples can reasonably be grouped. These groups correspond to separate water flow systems. In the different flow systems different controlling factors play a dominant role. In the recharge area the adsorption or co-precipitation model is consistent with the correlation of arsenic and iron. In the discharge areas, transformation of sediment organic matter and dissolution of humic substances are the principal sources of arsenic. In the deepest zone where waters are depleted in arsenic, an association of arsenic with phosphorous was found.

ACKNOWLEDGEMENTS

This work has been supported by the Scientific Research Fund (Hungary), grant No is T 037269 and K 60751.

REFERENCES

ADRIANO, D. C. (1986): Trace element in the terrestrial environment, Springer Verlag, New York.

BELZILE, N. (1988): The fate of arsenic in sediments of the Laurentin Trough. Geochim. Cosmochim. Acta, **52**, 2293–2302.

BELZILE, N., TESSIER, A. (1990): Interaction between arsenic and iron oxyhydroxides in lacustrine sediments. Geochim. Cosmochim. Acta, **54**, 103–109.

BOTTOMLEY, D. J. (1984): Origins of some arseniferous groundwaters in Nova Scotia and New Brunswich, Canada. Journal of Hydrogeology, **69**, 223-257.

CSANÁDY, M., BOZSAI, G., DEÁK, ZS. (1985): Arsenic in the artesian waters in the Great Hungarian Plain. Egészségtudomány, **29**, 240-249. (in Hungarian)

CSALAGOVITS, I. (1999): Arsenic bearing artesian waters of Hungary. Annual Report of the Geological Institute of Hungary, 1992-1993/II. 85-92.

ERDÉLYI, M. (1991): Az arzéntartalom származása és alakulásának kérdései Békés megye vízmű kútjaiban (Hydrogeology of the artesian water containing arsenic in the Tiszántúl region). MTA SZAB Szeged. 71–86. (in Hungarian)

FARMER, J.,G., LOVELL, M.A. (1986): Natural enrichment of arsenic in Loch Lomond sediments. Geochim. Cosmochi. Acta, **30**, 2059–2067.

FERGUSON, H. F., GAVIS, J. (1972): A review of the arsenic cycle in natural waters. Water Research, **6**, 1259–1274.

HORVÁTH, F., DÖVÉNYI, P., SZALAY, Á., ROYDEN, L. H. (1988): Subsidence, thermal, and maturation history of the Great Hungarian Plain. In Royden, L. H., Horváth, F. (eds.) The Pannonian Basin: A study in basin evolution, Tulsa, OK. American Association of Petroleum Geologists, 355-372.

JUHÁSZ, A., M.TÓTH, T., RAMSEYER, K., MATTER, A. (2002): Connected fluid evolution in fractured crystalline basement and overlying sediments, the Pannonian Basin, SE Hungary. Chem. Geol., **182**, 91–120.

MOLNÁR, B. (1973): Az Alföld harmadidőszak végi és negyedkori feltöltődési ciklusai (Cyclicity of sedimentation during the Pleistocene and at the end of the Pliocene in the Great Plain). Földtani Közlöny, **103**, 294-310. (in Hungarian)

PETERSON, M. L., CARPENTER, R. (1986): Arsenic distribution in porewaters and sediments of Puget Sound, Lake Washington, the Washington coast and Saanlich Inlet B.C. Geochim. Cosmochim. Acta, **50**, 353–369.

RÓNAI, A. (1983): A Körös medence földtörténete a negyedkorban (Geological history of the Körös Basin during the Quaternary). Földtani Közlöny, **113/1**, 1–25. (in Hungarian)

RÓNAI, A. (1985): The Quaternary of the Great Hungarian Plain. Geologica Hungarica, **21**, Institutum Geologicum Hungaricum, Budapest, 426–436.

STAUFER, R. E., THOMPSON, J. M. (1984): Arsenic and antimony in geothermal waters of Yellowstone National Park, Wyoming, USA. Geochim. Cosmochim. Acta, **45**, 2501–2509.

VARSÁNYI, I., FODRÉ, ZS., BARTHA, A. (1991): Arsenic in drinking water and mortality in the Southern Great Plain, Hungary. Environmental Geochemistry and Health, **13**, 14–23.

VARSÁNYI, I., MATRAY, J. M., Ó.KOVÁCS, L. (1997): Geochemistry of formation waters in the Pannonian Basin (Southeast-Hungary). Chemical Geology, **140**, 89–106.

Varsányi, I., Matray, J. M., Ó.Kovács, L. (1999): Hydrogeochemistry in two adjacent areas in the Pannonian Basin (Southeast-Hungary). *Chemical Geology*, **156**, 25-39.

VARSÁNYI, I., Ó.KOVÁCS, L. (2000): Chemical tools for tracing subsurface water movements. Proceedings of the. 31st International Geological Congress, Rio de Janeiro, Brazil. Abstract Volume (CD).

WELCH, A. H., LICO, M. S., HUGHES, J. L. (1988): Arsenic in ground water of the Western United States. Ground Water, **26**, 333–347.

WILSON, F. H., HAWKINS, D. B. (1978): Arsenic in stream, stream sediments and ground water, Fairbanks area, Alaska. Environmental Geology, **2**, 195–202.

XU, J., THORNTON, I. (1985): Arsenic in garden soils and vegetable crops in Cornwall, England: implications for human health. Environmental Geochemistry and Health, **7**, 131–134.

Received: November 11, 2005; accepted: May 31, 2006