

**GEOCHEMICAL FINGERPRINTS OF CLIMATIC CHANGES IN CENTRAL
AND EASTERN HUNGARY**

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The arsenic concentration of conduit water was successfully pressed down under 50 µg/l in every settlement of Hungary. These concentrations are of natural origin: in the Pleistocene the Carpathian Basin acted as a kind of a regional geochemical trap, then – with the changes in climate — this trap “opened” and the included arsenic content was discharged. A determinant factor of this process is the change in the redox conditions. Another geochemical consequence of the dry and cold climate is that wind blew dolomite dust from the Transdanubian Range to the Danube–Tisza Interfluve. Thus, here the salinisation is accompanied by lime accumulation, while in the Trans-Tisza area, to where no dolomite dust was transported, it does not occur. The reduction process is not over; the soluble arsenic supply is continuous.

Arsenic drinking water in Hungary

In April 1981 it was detected that the arsenic content of the confined waters, utilised as drinking water, may be the multiple of the valid health limit value (50 µg/l) of that time in several settlements of Hungary — mainly in the southern and eastern parts of the Great Plain. Some 600,000 people consumed such water. During several decades, partly by means of arsenic release processes, partly by means of adding conduit water from arsenic-free areas the arsenic content of drinking water practically everywhere has been successfully decreased below the Hungarian limit value. However, in May 2004 we joined the European Union and thus we are obliged to set the limit of the maximum arsenic content of drinking water at 10 µg/l. In order to improve the chances of discovering arsenic-free water areas and to include that water in the production, it is fundamental to understand the genetics of arsenic enrichment. In the meantime, the investigations proved that the regional enrichment is of natural origin, but the time and

mechanism of its formations were outlined in different ways by the authors, dealing with the question.

The public health experts, describing first the phenomenon (Csanády et al. 1985), thought that arsenic gets into the water from the ore-bearing rocks of the Transylvanian Ore Mountains that had been eroded and transported into the basin, but they could not explain why it is dissolved in some places and not at others.

According to Erdélyi (1990, 1991), the main sources of arsenic are the (Eocene and Miocene, respectively) andesites of island arc type, spreading at several places at the margin of the basin and in the Hungarian Mid-Mountains. He thought that the more andesites had been in the removal areas of certain part basins of the Pannonian Basin, the higher is the arsenic content in the confined waters of these part basins now. He also held possible that a part of arsenic is washed out by the infiltrating waters in the Transylvanian Ore Mountains.

Szederkényi (1990) originated the arsenic content of the confined waters from the metamorphosis of the carbonate rocks of the basin basement and thought that it upwells along the deep fractures. This hypothesis on upwelling were refuted by Tóth et al. (1985) when they pointed out (Fig. 1) that arsenic is enriched in two horizons in the confined waters of the young sediments: partly immediately above the basement (this may be metamorphogenic), partly near the surface. Between these two horizons, in a medium depth, the water is (mainly) practically arsenic-free.

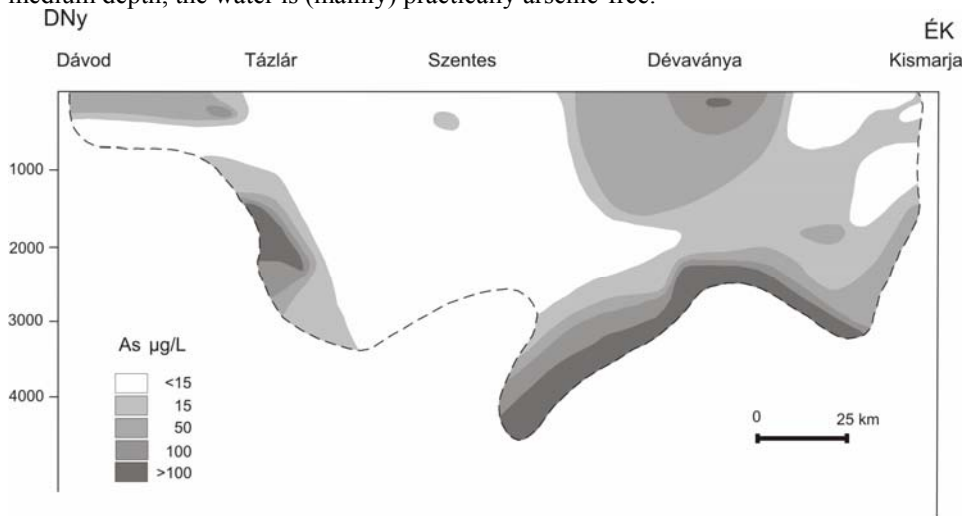


Fig. 1. Arsenic content ($\mu\text{g/l}$) of artesian waters in the Dávod – Kismarja section of the Great Hungarian Plain (after Tóth et al. 1985)

According to Csalagovits (1996), arsenic was trapped on the surface of FeOOH in the marsh–swamp sediments of the young Holocene–Pleistocene fluvial sequences and it is discharged because they got under ground water level, that is under reductive conditions due to the overlying young sediments. He took notice of the connection between the distribution of the glacial sediments and arsenic waters: the latter ones can be expected mainly where the thickness of the Pleistocene layers is more than 50 m (Fig. 2).



Fig. 2. Pleistocene layer thickness and arsenic water (after Csalagovits, 1996)

According to Varsányi and Kovács (2002), arsenic is mobilised in metal organic complexes. They detected that there are no regional rules of the co-movement of arsenic and the other components dissolved in water valid for the whole basin; element association is different in the different current systems.

As a spectacular example of it, the arsenic content of water in the Pleistocene sediments in the environs of the Gödöllő hill country is normal (Fig. 2): excess water, flowing down from the chain of the hills and infiltrating at the margin, has already washed out arsenic from these sediments. Similar but smaller “washouts” can be observed at other hill margins as well.

Arsenic in young sediments

While compiling the geochemical atlas of Hungary (Ódor et al. 1997), we took notice of the phenomenon, confirming the hypothesis of Csalagovits (1999), that the concentration of arsenic is much higher in the soil and the near surface loose sediments in several hundred km² of these adjoining areas than it is usual in Europe – not only in the environs of the ore deposits but even in the very middle of the basin (Fig. 3). A similar result was obtained by the researchers of the Research Institute for Soil Science and Agricultural Chemistry of the Hungarian Academy of Sciences (MTA TAKI) and the Budapest Capital Plant Health and Soil Protection Service (BFNTÁ; Németh et al. 1997, Várallyai et al. 2003). The bulk of the surface enrichments can be found in the southern part of the Danube–Tisza Interfluve. For assessing their environmental hazard, first of all the mobility of near surface arsenic has to be determined. Based on the principle of analogy, this may help to clarify the formation of the enrichments in deeper positions as well.

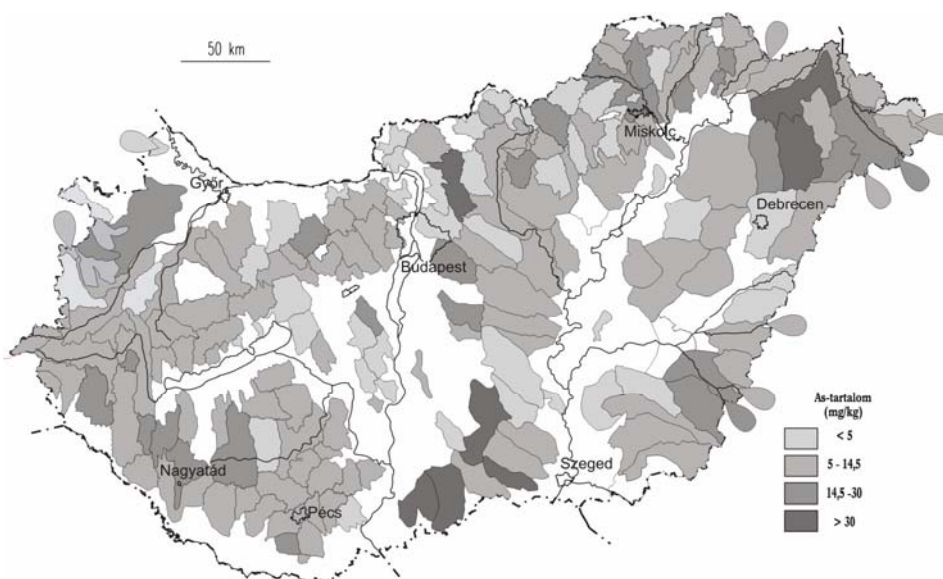


Fig. 3. Arsenic in the overbank sediments of Hungary (after Ódor et al. 1998)

Samples were collected at the margin of the anomaly, in the southern part of the Great Plain, in Szeged. To the north of the Makkosházi boulevard, young fluvial sediments, reworked from the Danube–Tisza Interfluvial ridge, are deposited on the surface (Fig. 4). Out of these samples arsenic concentrations above the intervention limit value can be dissolved by nitrohydrochloric acid and nitric acid, however by distilled water only a small part of these quantities can be mobilised (Table 1). So, in the sampling area arsenic occurs in the soil and beneath in oxidised, mineral bound form: it is not mobile (Table 2) and does not endanger its environment.

Table 1 Arsenic content of the soil samples from the Szeged area

Number and depth of soil sample	As concentration, dissolution by nitrohydrochloric acid (mg/kg)	Number and depth of the control sample	As concentration, dissolution by nitric acid (mg/kg)	As concentration, dissolution by 1:10 distilled water (mg/kg)
2 F; 2.0–3.0	55	2 AF; 2.0–3.0	16.4	< 0.01
3 F; 2.0–3.0	55	3 AF; 2.0–3.0	27.7	< 0.01

Table 2 Arsenic content of the groundwater samples from the Szeged area

Number of the groundwater sample	As concentration (µg/l)
1F	4
3F	3,5
5F	3,5

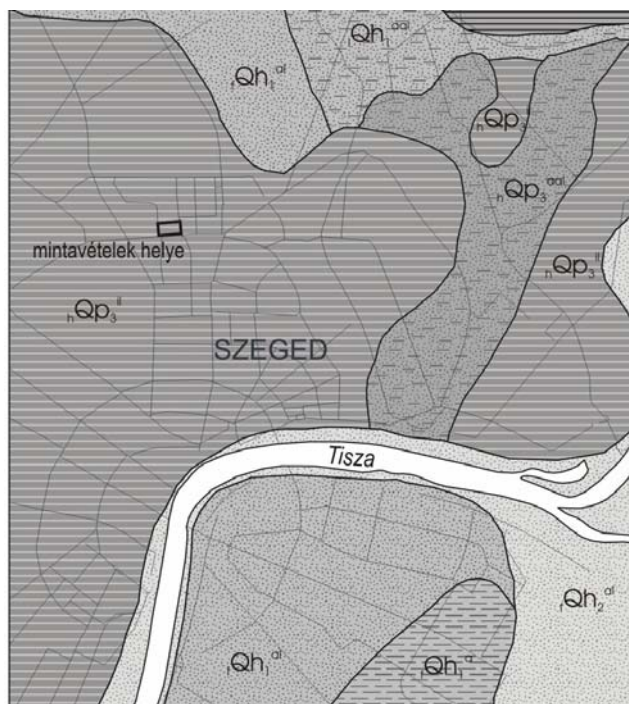


Fig. 4. Area of investigations in Szeged ${}_{f}Qh_2^{al}$ = fluvial siltstone, ${}_{l}Qh_1^{aal}$ = lacustrine argillaceous siltstone, ${}_{f}Qh_1^a$ = alluvial clay, ${}_{f}Qh_1^{al}$ = fluvial siltstone, ${}_{h}Qp_3^{aal}$ = argillaceous siltstone (argillaceous loess), ${}_{h}Qp_3^{il}$ = infusion loess

Calcareous–dolomitic soils in Mid-Hungary

Turning over the pages of the geochemical atlas of Hungary (Ódor et al. 1998), we can see that the main geochemical characteristics of the middle part of the country is not the accumulation of arsenic but the high content of lime in the soils. This phenomenon is remarkably presented also by the analyses of the soil protection information monitoring system (TIM; Németh et al. 1997). The distribution of the “calcareous” soils (Geochemical Province 2) is continuous from Komárom to Szeged. This egg-shaped formation (Fig. 5) – the longitudinal axis of which is markedly near to the predominant NW wind direction – is characterised by the fact that out of the cations Ca (and with it Sr) and Mg (with it Ba), while out of the anions carbonate (with it sulphate and phosphate) are intensely accumulated in the near surface loose sediments. In these soils, no other ions can accumulate; their nutritive microelement supply is outstandingly poor.

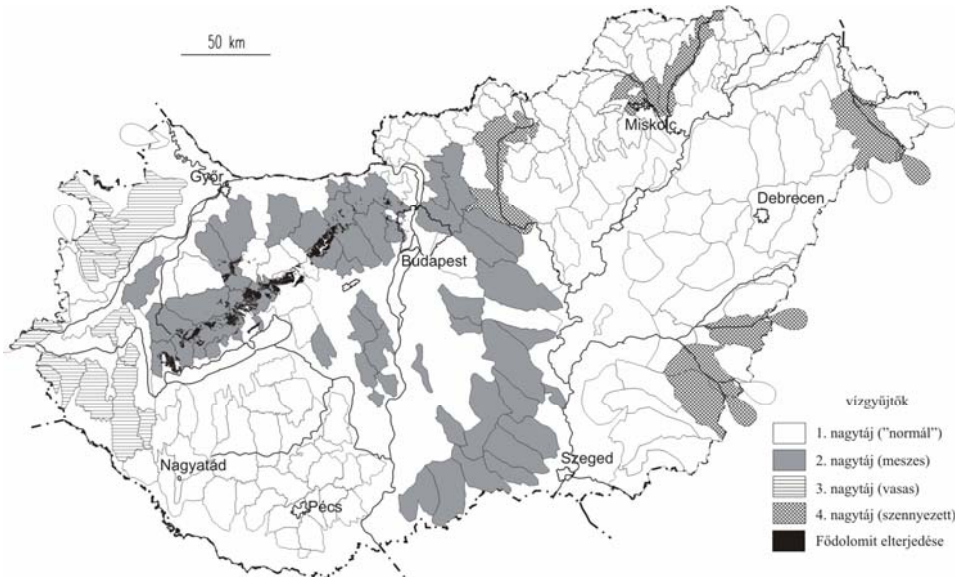


Fig. 5. Geochemical provinces of Hungary and the spreading area of the Hauptdolomit.
 1 – province (“normal”), 2 – province (“carbonatic”), 3 – province (“ironic”), 4 –
 province (“polluted”), Black rectangle: spreading area of the Hauptdolomit

Different authors derive sands, deposited in the middle of the Danube–Tisza Interfluve, from different geological processes: some of them from the alluvium of the Danube branches, meandering here at one time, others from eolian sources. According to the latter view, wind picked up and blew here flood-plain sediments, deposited in the present-day valley of the Danube. Apparently, none of the theories gives explanation to the origin of the calcareous material, although several authors (Kreybig, 1944; Pécsi, 1967, 1969) called attention to the fact that carbonate grains are regularly found in the sediments of Danube, but not in those of Tisza. Molnár (1980) established that there is a considerable amount of carbonates not only in sand but also in loess (not rarely 20–30 %) in the Danube–Tisza Interfluve. As a source of them, he designated (without clarifying the reworking mechanism) the limestone and dolomite pebbles, occurring regularly in the Danube sand, as well as the fossils (Nummulites, Foraminifera) – however, the carbonate content of these sands is altogether 5–10%. Kuti et al. (2003) made unambiguous that the calcium and magnesium, necessary for the lime accumulation, accompanying the salinisation in the ground water fluctuation zone, are dissolved from clastic lime and dolomite grains on the Danube–Tisza Interfluve ridge.

Both the calcite and dolomite are crystalline; the grains corrode under surface conditions (Kuti et al. 1999). In the Trans-Tisza area, where no clastic carbonate grains were found, the salinisation is not accompanied by lime accumulation (Kuti et al. 2002) – however, the arsenic confined waters occur in both environments that geochemically seem to be so different.

The surface distribution of the Upper Triassic main dolomite (Fig. 5), building up a considerable part of the Transdanubian Range, is approximately coincides with the small axis of the potato shape of the calcareous soils. The main feature of this main dolomite is that its certain varieties are friable: the calcite, cementing the tiny dolomite crystals, weathers relatively easily, and the remnants of the rock crumble into rubble then dust. In the periods of glaciation, this rock dust was easily carried away by the wind in the lack of vegetation and thus soil and the dust became mixed into the depositing loess as well as sand (Scheuer, 1969). In the warmer periods (like now), the vegetation and precipitation, washing off the finer debris, prevents totally this kind of dusting off.

A speciality of the cold, dry climate is that the eolian carbonate and autochthonous limonitic phases may occur together near the surface: there is not enough water for the insolusion of carbonate minerals. Under the present climatic conditions, as it could be pointed out during our investigations in Bodrogköz (Bartha et al. 1987), they can occur alternatingly at most in the three-phase zone: in the more sandy layers, where the grains desiccate, the iron hydroxides, while in the finer-grained sediments, where the grains are almost always covered by capillary water, the carbonate minerals can precipitate.

Climate and EH

From the point of view of arsenic, the geochemical importance of glaciation is in the drastic transformation of the redox state. In the glacial periods, the water is usually frozen. The vegetation decreases and the physical weathering gains ground at the expense of the biological one, which is also helped by the frequent change in the phase state. In the pores between the ice crystals, air can be found everywhere. As organic matter is also less due to the poorer vegetation this environment is unambiguously oxidative.

The elements of varying valency are much less mobile in their oxidised state than in their reduced form. Under such circumstances, the most frequent one is iron (and with it manganese and cobalt) precipitates and – as it was detected by Csalagovits (1996) – the As (V) ions are bound and gradually accumulate on the oxi-hydroxides.

In the sandy sediments arsenic that is bound so in the three-phase zone above ground water level may be preserved after warming up — this can be seen on the arsenic map of the geochemical atlas of Hungary. This state makes it possible for us to draw conclusions from the recent processes of changing the redox conditions on the

transformations at deeper horizons. We investigated the effects of the formation of a reductive environment in the environs of Nagyatád.

Near surface reduction in our days

The background concentration of arsenic in the catchment area of Rinya is 30 g/t. The plains in deeper position become frequently swampy: if our assumption is valid, we have to find more arsenic than the background in the (reddish) layers, bearing the marks of the former oxidative state, and less in the reduced (grey) sediments. In our section (Fig. 6), the former reddish colour of the mud was preserved only in smaller lenses: the sequence is predominantly grey. As the sediment fades, arsenic disappears from it: in the red lens it occurs in a quantity above 50 g/t, in the grey mud below 10 g/t. The reduction influences considerably the composition of ground water as well: where the sequence still contains red sediment (that is not all the arsenic had been dissolved), the arsenic content of ground water is above 50 µg/l, while where already everything is grey it is below 2 µg/l.

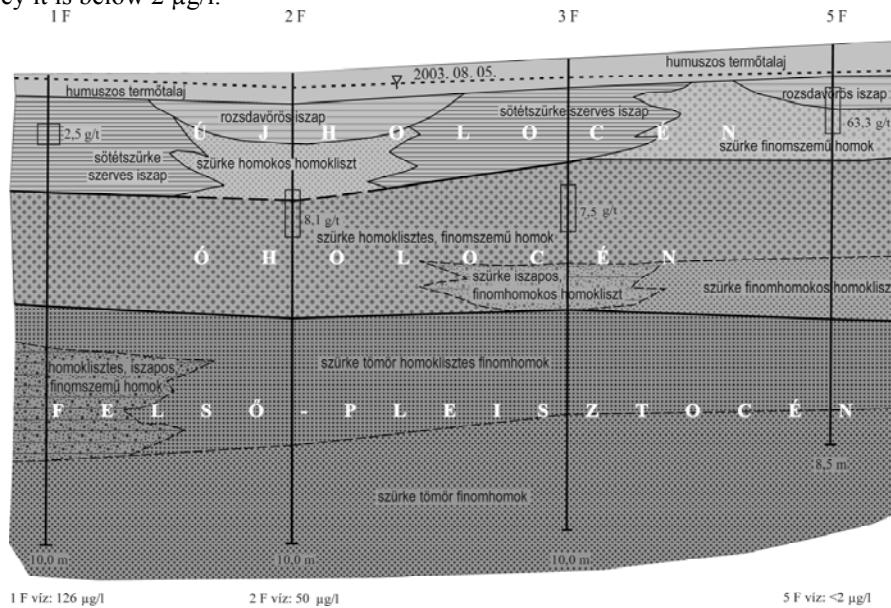


Fig. 6. Geological cross- section of the near surface sediments in a swampy model area at Nagyatád with the arsenic contents of the sediments (mg/kg) and the groundwater (µg/l)

Geochemical traces of climatic changes

It can be concluded that the climatic changes effect considerably the geological processes. The main result of the warming up of the temperate climate is the acidification of ground water: because of this, terra rossa, laterite, bauxite, etc. are formed. However, the dry cold shifts not so much the pH, but rather the redox conditions: strongly oxidative circumstances develop near the surface. If the climate becomes warmer again, the precipitated oxi-hydroxides break down and the elements bound on them, get mobilised. In the dry cold, the stable carbonate grains are dissolved and their material is reworked mainly into the ground water fluctuation zone.

REFERENCES

- BARTHA A., FÜGEDI P.U., KUTI L. (1987) - *Mobile nutrient microelements in younger loose sedimentary rocks of the Bodrogek, N Hungary* (in Hungarian with English abstract). Annual Report of the Geological Institute of Hungary from 1985, pp. 165–186.
- CSALAGOVITS, I. (1996) - *Distribution of arsenic waters in Hungary, their geological and geochemical environment and formation*. Hungarian Geological Survey Annual Report, pp. 22–24.
- CSALAGOVITS, I. (1999) - *Arsenic-bearing artesian waters of Hungary*. Annual Report of the Geological Institute of Hungary from 1992–1993/II. pp. 85–92.
- CSANÁDY M., BOZSAI G., DEÁK ZS. (1985) - *Arsenic-bearing ground waters at the Great Hungarian Plain* (in Hungarian). *Egészségtudomány (Health Sciences)* 29: 240–249.
- ERDÉLYI M. (1990) - *Hydrogeology of arsenic-bearing groundwaters of the Trans-Tisza region* (in Hungarian). In: Szederkényi T. (red.) 1990: *Az arzéntartalom származása és alakulásának kérdései Békés megye vízmű kútjaiban*. Publications of the Szegedien Committee of the Hungarian Academy of Sciences, Szeged. p. 71–86.
- ERDÉLYI M. (1991) - *Hydrogeology of arsenic-bearing groundwaters of the Trans-Tisza region* (in Hungarian). *Földrajzi Értesítő* 1991 (3-4): 231–251.
- KUTI L., GEREI L., ZENTAY T., VATAI J. (1999) - *The role of mineral components in the sandy soils of the Bugac and Fülöp Model Areas* (in Hungarian). *Agrokémia és talajtan*, 45 (1999) No. 3-4. pp. 249–259.
- KUTI L., ZENTAY T., KERÉK B. (2002) - *The CaCO₃ content of the near-surface sediments at the Bugac and Fülöp model areas* (in Hungarian with English abstract). Annual Report of the Geological Institute of Hungary from 1997–1998 pp. 107–117.
- KUTI L., TÓTH T., KALMÁR J., KOVÁCS-PÁLFFY P. (2003) - *Mineral Composition of Salinized Alkaline Soils, and Recent Mineral Formation in the Neighborhood of Apajpuszta and Zabszék* (in Hungarian with English abstract.) *Agrokémia és talajtan*, 52 (2003) 3–4. pp. 275–292.
- MOLNÁR B. (1980) - *Hypersaline lacustrine dolomite formation in the Danube-Tisza Interfluve* (in Hungarian with English abstract). *Földtani Közlöny*, 10, pp. 45–64.
- NÉMETH T., SZABÓ J., PÁSZTOR L., BAKACSI ZS., ÓDOR L., HORVÁTH I., FÜGEDI U. MARTH P., SZALAI L. (1997) - *The base contamination level of Hungarian soils and the environmental background concentrations of the soils not affected by human activities* (manuscript, in Hungarian). Budapest, 46 p. <http://www.kvvm.hu/szakmai/karmentes/annotaciok/csop2/nemeth.htm>
- ÓDOR L., HORVÁTH I., FÜGEDI U. (1997) - *Low-density geochemical mapping in Hungary*. *Journal of Geochemical Exploration* 60 (1997) pp. 55–66.

- ÓDOR L., HORVÁTH I., FÜGEDI U. (1998) - *Geochemical Atlas of Hungary*.
<http://www.mafi.hu/microsites/geokem/Fomenu.htm>
- Pécsi M. (szerk.) (1967) - *Great Hungarian Plain, Aquifer of the Danube river* (in Hungarian). Hun. Acad. Sci. Budapest, p. 218.
- PÉCSI M. (szerk.) (1969) - *Great Hungarian Plain, Aquifer of the Tisza river* (in Hungarian). — Hun. Acad. Sci. Budapest, p. 248.
- SCHEUER GY., (1969) - *Talajfagyjelenségek dolomitfelszíneken*. Földrajzi Értesítő, 18 (2) p. 177–191.
- SZEDERKÉNYI T. (1990) - *On the deep base-inffloor origin of the arsenic at the drinking water on SE Hungary* (in Hungarian). In: Szederkényi T. (red.) 1990: The origin and variation of the arsenic content in the drinking water wells at Békés county, SE Hungary (in Hungarian). Publications of the Szegedien Committee of the Hungarian Academy of Sciences, Szeged. p. 59–69.
- TÓTH GY., EGERER F., NAMESÁNSZKY K. (1985) - *Hydrogeochemical Atlas of Hungary*, 1:1 000 000 (manuscript, in Hungarian). MÁFI.
- VÁRALLYAI L., KOVÁCS B., PROKISCH J., SZEGVÁRI I. (2003) - *Statistical analysis of the TIM samples* (in Hungarian). <http://www.date.hu/acta-agraria/2003-10/varallyai.pdf>
- VARSÁNYI I., Ó. KOVÁCS L. (2002) - *Factors influencing the As content of subsurface water in the Pannonian Basin, Hungary*. Proc. Groundwater and Human Development Congress 2002, Mar del Plata, Argentina, pp. 1533–1541. In: Groundwater and Human Development, Bocanegra, E. – Martínez, D. – Massone, H. (eds.), CD-ROM, ISBN 987-544-063-9.

