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EFFECT OF THE GROUNDWATER FLOW ON TRACE ELEMENT DISTRIBUTION IN THE RIVER DANUBE DEPOSITS IN THE SOUTHERN PART OF THE PANNONIAN BASIN (HUNGARY)

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ABSTRACT

Processes controlling the groundwater trace element composition were studied in the River Danube deposits. Cluster analysis based on trace element concentration was used to separate the different aquifer systems. Separation resulted two groups, which correspond to the midline and to the discharge area of the same water flow. Principal component and correlation analyis were used to determine the geochemical processes, which control the trace element distribution of the groundwater in these hydrological regions. Geochemical computer models helped to simulate the possible chemical processes. PHREEQE was used to model the chemical composition of the average midline water, and PHREEQM to simulate the processes taking place along the flow path of groundwater. In the midline area, the main processes controlling the trace element content are dissolution of calcite, dolomite, and Fe- Mn-oxides, aluminosilicate weathering, and As adsorption. In the discharge area, cation exchange, As desorption and organic matter decomposition play an important role in water chemistry.

Key words: hydrology, principal component- and cluster analysis, ion exchange, adsorption, weathering, dissolution, organic matter decomposition.

INTRODUCTION

Previous studies of the distribution of trace metals in natural waters have emphasised the importance of different geochemical processes controlling the trace element content such as dissolution and precipitation of carbonate minerals, feldspar weathering (Paces, 1973; Chou, Wollast 1984; Berner, 1981; Murphy, Helgeson, 1987) redox reactions, oxidation of organic materials, sorption and cation exchange (Chapelle, Knobel, 1983; Appelo et al., 1989; Hrabovszki, 1998).

According to Tóth (1990) in the recharge and in the discharge area of the same water flow system, different chemical processes can play an important role in the groundwater chemistry. The main chemical processes modifying the chemical composition of the groundwater are dissolution of minerals and oxidation in the recharge area, precipitation, reduction or water mixing in the discharge area. Groundwater flow influences hydrochemical patterns. In the direction of the water flow ion exchange has fundamental importance in water-rock interaction (Appelo, Postma, 1993). Along the flow path the distribution of some components may follow a chromatographic pattern because of the differences in the retardation for the various cations.

From tne hydrological point of view, the Pannon basin is a large (1000,000 km^2), non-uniform multilayer flow-system formed mainly during the late Tertiary and Quaternary periods (Erdélyi et al., 1972; Erdélyi, 1979). The system is composed of two flow regions: an intermediate flow regime in the Pleistocene sediments and a regional one in the deeper zone (2500 m). In the Pleistocene sediments of the Great Hungarian Plain two water types exist (Erdélyi, 1979). The coarser sediments contain a calcium- and magnesium-bicarbonate water type and in the finer grained sediments sodium-bicarbonate water is characteristic. In the Ca-Mg-HCO_3 type waters the concentration of the dissolved solids is lower than in the Na-HCO_3 type waters.

Geochemical computer models have been developed to calculate the distribution of species when minerals dissolve, different types of waters mix or ion exchange takes place in the system. In the present study PHREEQE (Parkhurst et al., 1990) was used to model the composition of the avarage water type, and PHREEQM (Nienhuis et al., 1993) to simulate ion exchange.

In an earlier study (Hrabovszki, Varsányi 1998), processes which controll the trace element concentrations of groundwaters in the Great Hungarian Plain were determined. These processes are: dissolution of carbonate minerals, ion exchange, oxidation, reduction, albite weathering and formation of secondary minerals. On the basis of the trace metal content (As, Fe, Mn, Zn^{2+}, Ba^{2+}, Sr^{2+}, Li^+, Si) the study area was divided into three units, which correspond to different hydrogeological regions: the River Körös basin, the River Maros alluvial fan and the River Danube deposits. The aim of the present work is to separate the aquifer system in the intermediate flow regions of the River Danube deposits on the basis of the trace chemical components of the groundwater, to establish the main processes controlling the chemical features of these elements in the groundwater of the different aquifers and to present the trace element pattern in the water flow direction.

GEOLOGICAL SETTINGS

The location of the studied area can be seen in Fig. 1. The geology of the River Danube deposits was described earlier (Hrabovszki, Varsányi, 1998).

MATERIALS AND METHODS

In situ measurements and laboratory major and trace element analyses were used to establish the geochemical evolution of the groundwater in the studied aquifers. Groundwater samples from 52 water wells of different depths (174-605 m) from the River Danube deposits were collected, cooled and analyzed within 24 hours. Alkalinity, pH, Ca^{2+}, Mg^{2+}, Na^+, As, Fe, Mn, Zn^{2+}, Ba^{2+}, Sr^{2+}, Li^+, Si, Cl^- and chemical oxygen demand (COD) were determined (Hrabovszki, Varsányi, 1998).

22 core samples of 61-468 m depth were subjected to XRD analysis using a DRON-UM 1 X-ray diffractometer. X-ray studies show that sediments over the study area contain quartz, plagioclase, feldspar (mainly albite), calcite, dolomite, illite, chlorite and muscovite (Varsányi, Ó. Kovács, 1994).

The great number of the samples and parameters to be processed require a statistical approach. Classification of the water samples on the basis of the trace elements is one of the classical tasks of multivariate statistics (Marriott, 1974; Mardia et al., 1979). Cluster analysis (Le Maitre, 1982) was used to divide the water samples into groups. All variables were brought into the same range by scaling the values for each constituent. The similarity measure was the correlation coefficients. The groups of highest similarity were connected by the unweighted pair group average method. This algorithm results in clusters containing samples with close values. Principal component analysis and correlation analysis (Sváb, 1979) were applied to determine what chemical processes play important roles in the trace element distribution of the ground water in each cluster.

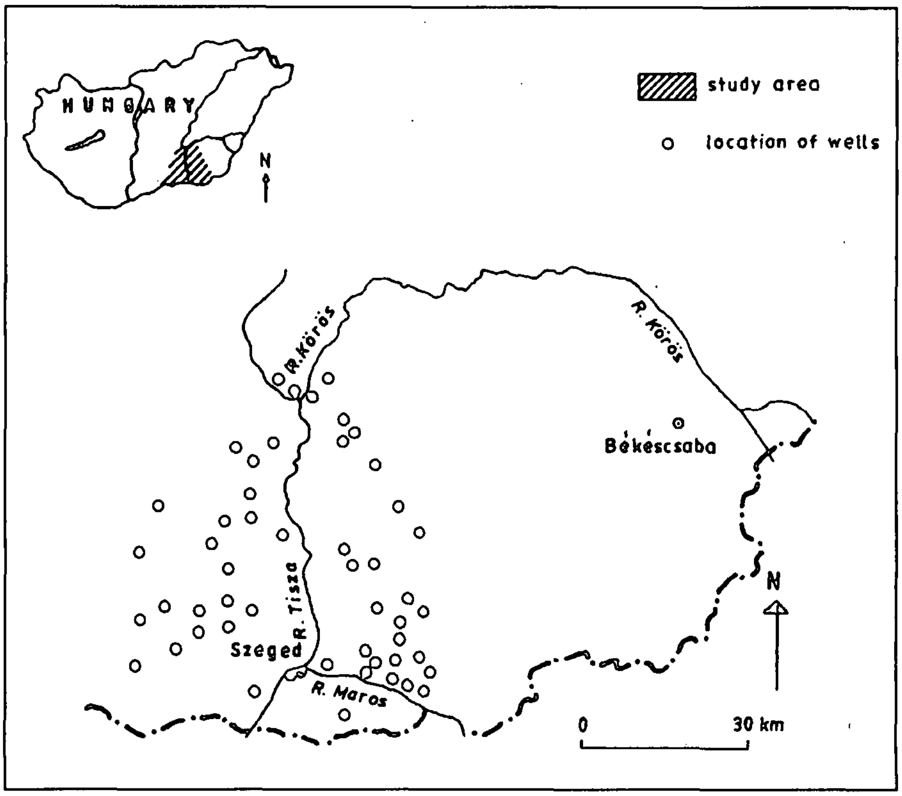

Fig. 1. Location of the water samples in the study area.

RESULTS AND DISCUSSION

On the basis of the frequency distributions of the trace components (As, Fe, Mn, Zn^{2+}, Ba^{2+}, Sr^{2+}, Li^+, Si), it was established that the groundwater quality is not uniform throughout the study area. Samples represent more than one population. This possibly means that different processes can influence the distribution and mobility of the trace element composition in the groundwater from different depths or locations. In order to investigate geochemical processes which may influence the trace element distribution in groundwater of the study area, the first task was to separate the different aquifer systems from each other.

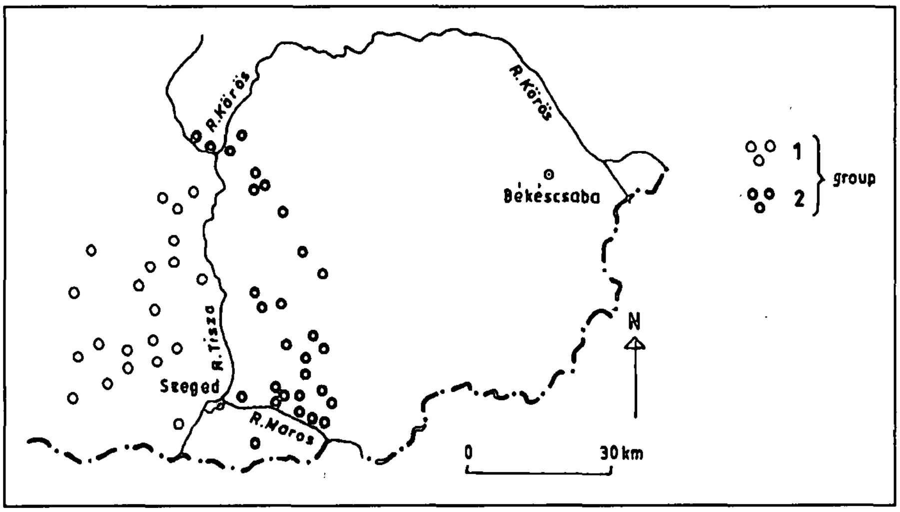

Fig. 2. Location of the groundwaters characterized by different water quality on the basis of the trace element content.

Cluster analysis of 52 water samples based on trace elements (As, Fe, Mn, Zn^{2+}, Ba^{2+}, Sr^{2+}, Li^+, Si) resulted in two groups, which are shown in Fig 2. Separation based on the distribution of major elements (Na^{2+}, Ca^{2+}, Mg^{2+}) gives very similar location of groups (Hrabovszki, Varsányi, 1998) to Group 1 and Group 2. Group 1 belongs to the throughflow (midline) area, Group 2 to the discharge area of the same groundwater flow system (Fig. 3). Comparing the mean valus of the major and trace element concentrations of the groups (Table 1), the throughflow area can be characterized by higher Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+}, Fe, Mn, Si content, and lower Na^+, As, Li^+ concentration. Erdélyi (1979) determined the potentiometric contours of the Pleistocene aquifers to the depth of 200-400 m. The potentiometric

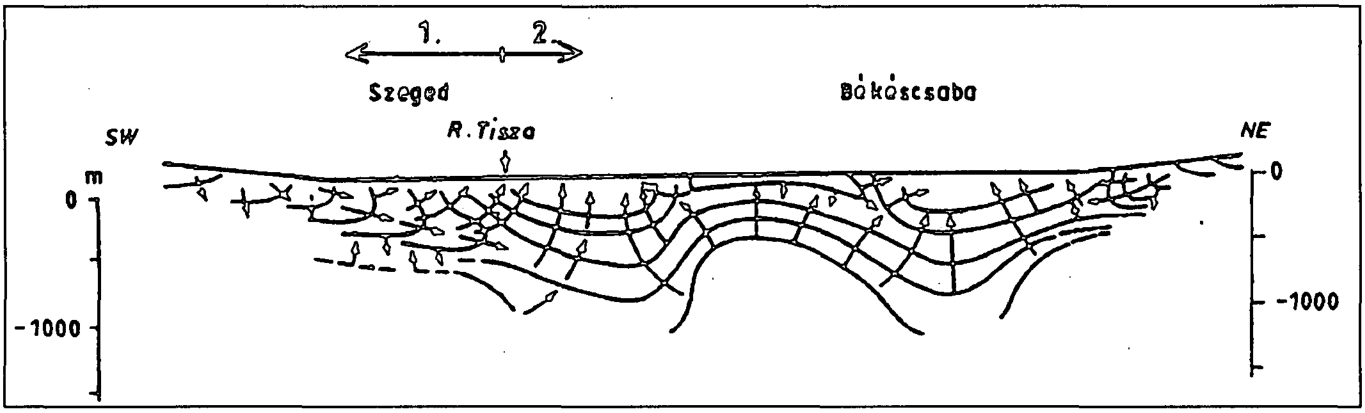

Fig. 3. The piezometric contours and water flow directions by Erdélyi (1976) with the location of the groups separated by cluster analysis.

contours indicate that in the generally flows from west to east in the RiverDanube deposits. In the study area from West to East – in the West-East water flow direction - Ba^{2+}, Sr^{2+}, Fe, Mn, Si content decreases, while As, Zn^{2+} and Li^+ increase.

In order to determine what reactions occure between groundwater and sediments in each aquifer, principal component analysis was used. Only those chemical parameters can be used up for the calculation which distribution in each group is normal, therefore the second step was to study the normality of pH and alkalinity, COD, Ca^{2+}, Mg^{2+}, Na^+, As, Fe, Mn, Zn^{2+}, Ba^{2+}, Sr^{2+}, Li^+, Si concentration distribution in groups with Kolmogorov-test (Füst, 1997). According to the result of the Kolmogorov-test, the frequency distribution of pH and alkalinity, COD, Ca^{2+}, Mg^{2+}, Fe, Ba^{2+}, Sr^{2+}, Li^+, Si can be described as lognormal in Group 1. In Group 2. distribution of pH and COD, Ca^{2+}, Mg^{2+}, Na^+, As, Fe, Mn, Zn^{2+}, Ba^{2+}, Sr^{2+}, Li^+, Si concentration can be approached with lognormal distribution.

GEOCHEMISTRY OF THE TRACE ELEMENTS IN THE THROUGHFLOW AREA

In the Group 1. principal component analysis was carried out with the logarithmic value of pH and logarithmic transformed concentration of, Ca^{2+}, Mg^{2+}, Fe, Ba^{2+}, Sr^{2+}, Li^+, Si, alkalinity and COD. Results of the calculation are summarized in Table 2. In the first factor alkalinity, Mg^{2+}, Sr^{2+}, Ba^{2+} show the highest value. This factor also has some influence on Li^+ content of the groundwater. On the basis of the correlation matrix (Table 3) Sr^{2+} displays good correlation with Na^+, Ba^{2+} and Mg^{2+}. Correlation between Mg^{2+} and Na^+ is tighter ($r_{Mg^{2+}-Na^+} = 0,53$) than between Mg^{2+} and Ca^{2+} ($r_{Mg^{2+}-Ca^{2+}} = 0,28$). Ba^{2+} has positive correlation with Mg^{2+} and Na^+ concentration. Correlation of Li^+ content with Na^+ and Ba^{2+} is moderate, but it is also positive.

The X-ray diffraction analysis showed the presence of albite, muscovite, illite, calcite and dolomite in the sediment. Albite dissolution and ion exchange on clay minerals are

Table 1. Mean chemical compositions and standard deviations in the groups.

		River Danube deposits							
		Group 1.				Group 2.			
		mean	s. d.	minimum	maximum	mean	s. d.	minimum	maximum
Alkalinity	mequ./l	5,23	0,45	4,50	6,10	6,42	2,06	5,00	13,90
COD	mg/l	1,79	0,66	0,80	3,50	2,56	0,90	1,30	4,60
pH		7,59	0,13	7,30	7,80	7,80	0,18	7,40	8,10
Cl^-	mmol/l	0,09	0,03	0,06	0,17	0,16	0,17	0,08	0,87
Na^+	mmol/l	0,95	0,22	0,60	1,38	3,55	3,50	1,17	6,58
Ca^{2+}	mmol/l	1,41	0,15	1,13	1,70	0,70	0,35	0,12	1,39
Mg^{2+}	mmol/l	0,94	0,11	0,79	1,15	0,53	0,28	0,08	1,13
Ba^{2+}	mmol/l	0,00110	0,00025	0,00051	0,00145	0,00082	0,00034	0,00020	0,00174
Sr^{2+}	mmol/l	0,00400	0,00070	0,00250	0,00540	0,00350	0,00170	0,00040	0,00600
As	mmol/l	0,00010	0,00010	0,00000	0,00035	0,00050	0,00040	0,00003	0,00173
Fe	mmol/l	0,00480	0,00200	0,00170	0,00106	0,00250	0,00180	0,00040	0,00830
Zn^{2+}	mmol/l	0,00014	0,00010	0,00000	0,00044	0,00018	0,00010	0,00006	0,00040
Mn	mmol/l	0,00080	0,00020	0,00052	0,00113	0,00065	0,00020	0,00015	0,00094
Li^+	mmol/l	0,00050	0,00020	0,00020	0,00130	0,00084	0,00040	0,00030	0,00210
Si	mmol/l	0,450	0,042	0,380	0,545	0,354	0,042	0,264	0,439
Al^{3+}	mmol/l	0,00				0,00			
T	^0C	20,5	2,5	16,0	26,0	24,1	3,5	18,0	30,0
$logP_{co2}$		-2,14	0,13	-2,38	-1,89	-2,28	0,16	-2,56	-1,91
depth	m	313,8	80,0	200,0	500,0	354,4	104,0	174,0	605,0
No of sample		21				31			

Table 2. Result of the principal component analysis for Group 1 (λ is Eigenvalue)

	I.	II.	III.	IV.
alkalinity	0,868	-0,007	0,200	0,050
pH	-0,118	0,316	-0,550	-0,580
COD	0,091	0,348	0,721	0,214
Ca^{2+}	0242	0,869	-0,284	0,189
Mg^{2+}	0,938	0,029	0,104	0,167
Fe	-0,302	-0,357	-0,063	0,640
Ba^{2+}	0,903	-0,123	-0,132	-0,130
Sr^{2+}	0,825	-0,435	0,212	0,083
Li^+	0,644	-0,183	0,336	-0,364
Si	0,223	0,890	-0,273	0,138
λ	3,766	2,135	1,209	1,034
λ%	46,26	26,22	14,82	12,70

Table 3. Correlation matrix of the chemical components of Group 1

	alk.	pH	COD	Na^+	Ca^{2+}	Mg^{2+}	As	Fe	Zn^{2+}	Mn	Ba^{2+}	Sr^{2+}	Li^+	Si
alk.	1,00													
pH	0,07	1,00												
COD	0,05	0,37	1,00											
Na^+	0,41	-0,39	-0,12	1,00										
Ca^{2+}	0,19	0,01	0,14	-0,32	1,00									
Mg^{2+}	0,87	-0,13	0,09	0,53	0,28	1,00								
As	0,12	0,09	-0,16	0,41	-0,71	-0,09	1,00							
Fe	-0,17	-0,13	-0,01	-0,08	-0,10	-0,23	0,07	1,00						
Zn^{2+}	-0,16	-0,23	0,20	-0,03	0,43	0,01	-0,35	0,26	1,00					
Mn	-0,46	-0,12	0,06	-0,55	0,49	-0,26	-0,74	0,16	0,31	1,00				
Ba^{2+}	0,66	-0,15	0,03	0,68	0,21	0,73	0,09	-0,33	0,12	-0,52	1,00			
Sr^{2+}	0,67	-0,17	0,10	0,86	-0,25	0,74	0,27	-0,18	-0,16	-0,51	0,71	1,00		
Li^+	0,08	-0,08	-0,36	0,33	0,33	0,12	0,22	-0,03	0,25	-0,24	0,40	0,1	1,00	
Si	0,18	0,02	0,18	-0,38	0,87	0,27	-0,73	-0,22	0,37	0,41	0,15	-0,25	0,08	1,00

thought to be the source of Na^+ in groundwaters. Fresh water is dominated by Ca^{2+} and HCO_3^- (Appelo, Postma, 1993). Cation exchangers take up Ca^{2+} from the water and release Na^+ if the Ca^{2+} concentration in the groundwater is relatively high to the concentration of Na^+ in the exchange position of clay minerals (Robertson, 1991), which assumes that the sediment was flushed by salt water before the fresh water intrusion. The result of the cation exhange the water quality changes from $Ca(HCO_3)_2$ to $NaHCO_3$. Na^+ does not show strong negative correlation with Ca^{2+} (Table 3), which suggests that not the ion exchange of Ca^{2+} for Na^+ but albit dissolution is likely to be the main process supplying Na^+ in the study area. The first step of the irreversible albit dissolution is the exchange of the Na^+ content of albit for H^+. The necessary H^+ is supplied by the reaction of CO_2 origined by organic matter decomposition and water. In the lattice of albit Mg^{2+} and Ba^{2+} does not occure (Koch, Sztrókay, 1967). Mg^{2+} can be found in the lattice of muskovite and illite. In muscovite and illite lattice Sr^{2+}, Ba^{2+}, in some cases Li^+ can substitute K^+. The results of the calculations indicate that different mineral phases are likely to dissolute at the same time in the study area. Na^+ is produced by irreversible albite dissolution, Sr^{2+}, Ba^{2+}, Li^+ concentration of the groundwater is probably determined by the dissolution of muscovite and illit. In the first factor pH correlates negatively with Mg^{2+}, Ba^{2+}, Sr^{2+} and Li^+ content, which suggests that increase in H^+ concentration of the water influences the dissolution rate of the mineral phases and Mg^{2+}, Ba^{2+}, Sr^{2+}, Li^+ and Na^+ content of the groundwater increases with decreasing pH.

The second factor contains Ca^{2+} and Si with the highest values. Ca^{2+} can came from the dissolution of calcite. Calcite dissolution is an equilibrium process which is controlled by the dissolved CO_2 originated from organic matter transformation (Appelo, Postma, 1993). In the study area Ca^{2+} concentration increases in the direction of the water flow (Fig. 4). The strong correlation between Ca^{2+} and Si ($r_{Si\text{-}Ca^{2+}}$ = 0,87) can be explained with the fact that change in H^+ concentration modifies not only Ca^{2+}, but also Si content of the groundwater. Si can be originated from irreversible feldspar weathering and dissolution of amorphous quartz (Grasselly, 1988). Solubility of amouphous quartz increases with increasing pH (Grasselly, 1988; Appelo, Postma, 1993). Since Si and Ca^{2+} concentration increases with decreasing pH, therefore Si content is probably controlled by the feldspar weathering not by the dissolution of quartz. Correlation between Si content and the temperature of the water samples cannot be found, therefore the feldspar weathering is controlled by only H^+ concentration of the groundwater. On the basis of the correlation matrix (Table 3) not only Si but also As displays correlation with Ca^{2+}. In natural waters As exists as $HAsO_4^{2-}$, $H_2AsO_4^-$, H_3AsO_4.

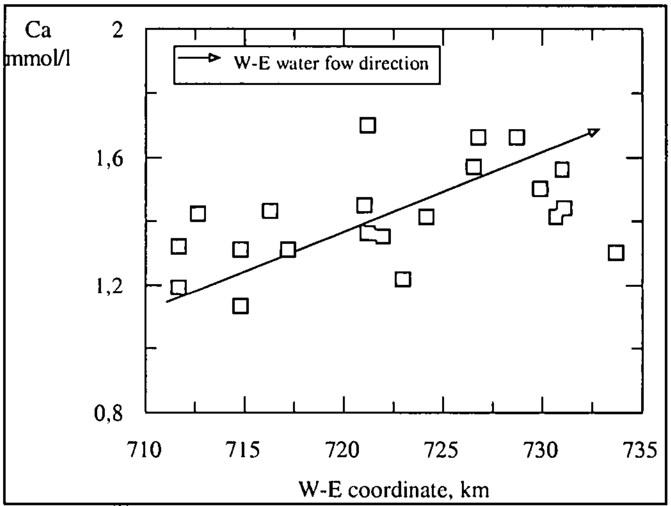

Fig. 4. Ca^{2+} concentration – distance graph.

Table 4. Result of the principal component analysis for Group 2. (λ is Eigenvalue)

	I.	II.	III.	IV.
pH	-0,497	0,050	0,278	0,595
COD	-0,623	0,029	0,372	-0,432
Na^+	-0,0844	0,164	0,040	0,077
Ca^{2+}	0,960	-0,161	0,049	-0,026
Mg^{2+}	0,968	-0,021	0,063	-0,036
As	-0,543	-0,601	-0,059	0,149
Fe	0,191	-0,127	0,810	-0,348
Mn	0,420	-0,689	0,029	0,300
Zn^{2+}	0,207	0,271	0,508	-0,480
Ba^{2+}	0,930	0,139	0,132	0,126
Sr^{2+}	0,967	0,095	0,031	0,030
Li^+	-0,085	0,470	-0,050	0,101
Si	0,680	0,213	-0,243	-0,090
λ	6,097	1,277	1,222	1,040
λ%	63,27	13,25	12,68	10,80

Arsenic can be adsorbed as an oxianion on the surface of the sediment (clay), Fe-, Mn-oxyhydroxides and organic matters (Onishi, Sandell, 1955; Laxen, 1985). Arsenic concentration does not show correlation with Fe and COD content of the water (Table 3), but there is a negative correlation between As and Mn, Si. Considering all these above the clay content of the sediment may play an important role in As adsorption. The negative correlation between Ca^{2+} and As ($r_{As-Ca}{}^{2+}$ = -0,71) can be explained with the change in pH of the groundwater. According to the experimets by Balistrieri, Murray (1982), arsenic adsorption on the surface of sediments increases with increasing H^+ concentration, the solubility of calcite increases with decreasing pH. The negative correlation between As and Mn shows the change in H^+ concentration. Mn exists in sediments as Mn-oxyhydroxides. Solubility of Mn-oxyhydroxides depends on H^+ concentration of the water (Grasselly, 1988). Because of decreasing pH Mn-oxides dissolute from the sediment producing higher Mn content in the water, while As adsorption on clay minerals increases with decreasing pH.

In the third factor COD and pH can be found with the highest value. The connection between these components is negative, therefore this factor can be connected with organic matter decomposition. Transformation of organic matters produces not only CO_2, but also water soluble organic components. The concentration of the organic components in water is proportional to COD (Varsányi, 1985).

Fe displays negative correlation with pH in the fourth factor. Fe exists as Fe-oxyhydroxides in sediments. Solubility of Fe-oxides depends on the H^+ content of the water, dissolution of Fe-oxyhydroxides increases - similarly to Mn - with decreasing pH (Grasselly, 1988).

GEOCHEMISTRY OF THE TRACE ELEMENTS IN THE DISCHARGE AREA

According to the result of Kolmogorov-test, principal component analysis was carried out with logarithmic value of pH and the logarithmic transformed concentration of COD, Ca^{2+}, Mg^{2+}, Na^+, As, Fe, Mn, Zn^{2+}, Ba^{2+}, Sr^{2+}, Li^+, Si, which resulted four factors above 1,000 (Table 4). In the first factor Na^+ shows good negative correlation with Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+}. On the basis of Fig. 5A-D concentration of Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+} decreases, Na^+ content increases along the flow path. The large increase in Na^+ and loss of Ca^{2+} and Mg^{2+} along the water flow show the typical pattern of cation exchange (Appelo, Postma, 1993). Taking all above into consideration, Sr^{2+} and Ba^{2+} content of the groundwater is likely to be controlled by ion exchange in the discharge area. In the same factor pH and COD can be found with the same sign, therefore this connection cannot be explained by the degradation of organic matters. According to the computer simulation of Varsányi (1994), in the study area H^+ concentration of water decreases along the flow path. On the basis of the correlation matrix (Table 5), pH correlates negatively with Ca^{2+}, Mg^{2+}, Sr^2, Ba^{2+} and positively with Na^+, which suggests that H^+ can also take part in ion exchange resulting increase in pH in the direction of water flow. Si concentration shows negative correlation with COD and pH in the first factor (Table 4). Silica distribution in groundwater cannot only be controlled by dissolution/precipiation processes of SiO_2 but also formation of secondary aluminosilicates (Grasselly, 1988). Solubility of SiO_2 increases with decreasing H^+. In the study area, Si content in the groundwater decreases with increasing pH, which means that Si concentration of the groundwater is mainly controlled by the formation of secondary silicates.

$$\underset{\text{(albite)}}{2NaAlSi_3O_8}+2H^++9H_2O = \underset{\text{(kaolinite)}}{Al_2Si_2O_5(OH)_4}+2Na^++4H_4SiO_4:$$

Table 5. Correlation matrix of the chemical components of Group 2

	alk.	pH	COD	Na^+	Ca^{2+}	Mg^{2+}	As	Fe	Zn^{2+}	Mn	Ba^{2+}	Sr^{2+}	Li^+	Si
alk.	1,00													
PH	0,09	1,00												
COD	0,59	0,09	1,00											
Na^+	0,42	0,43	0,55	1,00										
Ca^{2+}	-0,44	-0,56	-0,42	-0,92	1,00									
Mg^{2+}	-0,39	-0,49	-0,45	-0,93	0,96	1,00								
As	0,17	0,30	0,51	0,50	-0,41	-0,48	1,00							
Fe	-0,05	0,00	0,38	-0,08	0,18	0,13	0,25	1,00						
Zn^{2+}	-0,13	0,02	-0,02	-0,09	0,09	0,12	-0,17	0,08	1,00					
Mn	-0,55	-0,11	-0,20	-0,40	0,47	0,33	0,12	0,22	0,13	1,00				
Ba^{2+}	-0,31	-0,30	-0,53	-0,80	0,79	0,83	-0,59	0,09	0,23	0,33	1,00			
Sr^{2+}	-0,42	-0,45	-0,52	-0,94	0,89	0,94	-0,59	0,09	0,11	0,33	0,83	1,00		
Li^+	0,53	0,17	0,160	0,10	-0,21	-0,10	-0,20	-0,14	0,13	-0,47	0,06	0,03	1,00	
Si	-0,02	-0,46	-0,31	-0,69	0,76	0,78	-0,42	0,02	0,17	0,24	0,70	0,74	0,14	1,00

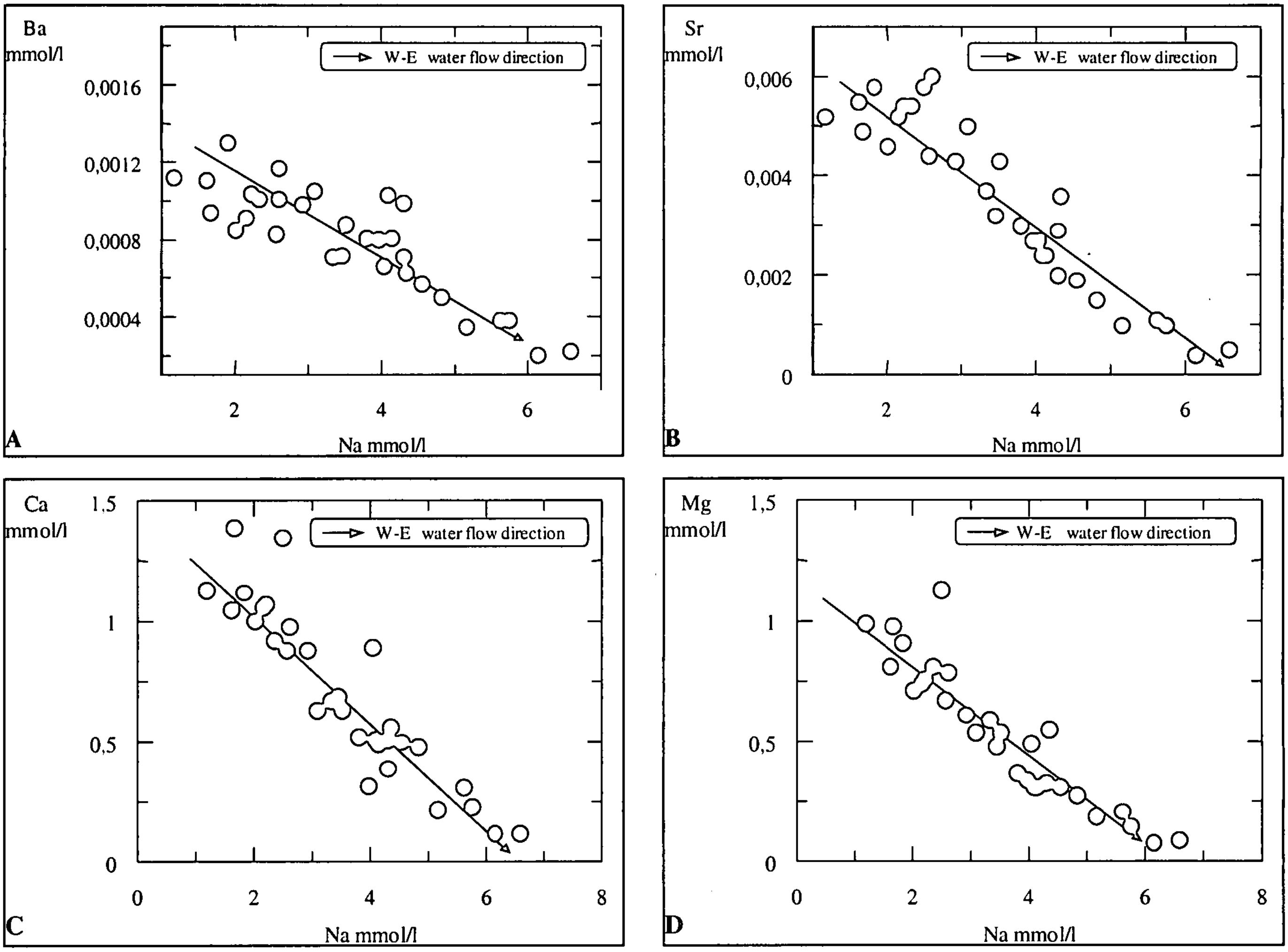

Fig. 5. Relationship between Na^+ concentration and **(A)** Ba^{2+}, **(B)** Sr^{2+}, **(C)** Ca^{2+}, **(D)** Mg^{2+}

In the first factor (Table 4) arsenic and pH display the same, negative sign. This suggests that anion adsorption, which depends on H^+ concentration of the aquatic system, may play a role. The extent of arsenic adsorption on the sedimentary rocks decreases with increasing pH (James, Healy, 1972; Balistrieri, Murray, 1982). Sediments under South Plain of Hungary have a high arsenic adsorption potential. The factors controlling the extent of the arsenic adsorption in this area are pH and the composition of the sediments such as organic matter, Fe-oxyhydroxide content and the rate of the clay fraction (Hrabovszki, 1995). The positive correlation between As and COD ($r_{As\text{-}COD} = 0{,}51$) means that degradation of organic matters in sediments can also controll arsenic content in waters. Arsenic can be adsorbed on the surface of organic matters in sediments as an oxianion (Onishi, Sandell, 1955, Laxen, 1985), and it goes into solution with the oxidative transformation of organic matters. The positive connection between Mn and As in the second factor suggests that Mn-oxyhydroxides of sediments can play a role in arsenic distribution of the groundwater. Mn-oxides can adsorb As on their surface (Takamatsu et al., 1985; Newman et al., 1985; Baistrieri, Murrày, 1986). Oxidative deggradation of organic matters is carried out with O_2, NO_3^-, MnO_2, SO_4^{2-} in consecutive steps (Froehlich et al., 1979). Quantity of the burried organic matters can be brought in connection with the velocity of sedimentation (Wilson et al., 1985). At higher velocity of sedimentation the oxigen is consumed by organic matters and NO_3^-, MnO_2, and SO_4^{2-} become oxidizing substances. Mn-oxide is reduced and it goes into solution, which results the mobilization of arsenic. In the third factor Fe with Zn^{2+}, in the fourth factor Fe, Zn^{2+} and COD show positive correlation with each other and pH shows the highest value. Zn^{2+} adsorption on Fe-oxides plays an important role in Zn^{2+} distribution in natural waters (Johnson, 1986). Fe-oxyhydroxides can take part in the oxidative transformation of organic matters as oxidizing substances (Froechlich et al., 1979; Balistrieri, Murray, 1982). Fe^{3+} is reduced, Fe^{2+} goes into solution resulting mobilization of Zn^{2+}. Degradation of organic matters produces not only CO_2 but also water soluble organic components such as humic and fulvic acids (Varsányi, 1985). Concentration of these components corresponds to the increase in COD and decrease in pH.

COMPUTER SIMULATION OF PROCESSES

According to the results of the principal component analysis, different geochemical processes can control the trace metal distribution of groundwater in the midline and in the discharge area. Water quality is likely to be determined by dissolution of sediments in the midline area. The degree of dissolution depends on the quantity of the dissolved CO_2 in water, which is originated from the oxidative transformation of organic matters. In the discharge area, Sr^{2+} and Ba^{2+} concentration similarly to Ca^{2+} and Mg^{2+} content seems to be controlled by cation exchange. To test the above hypotheses, forward method of geochemical modelling (Plummer, 1984) was used to perform the calculation. The first step of the modelling was to assume geochemical reactions in the water-rock system, then water quality was calculated by geochemical computer programs and compared to the measured data. Since in the midline and in the discharge area different geochemical processes are likely to control the water quality, 2-stage model for evolution of groundwater is suggested.

The first stage of simulation dealt with modelling the water composition of the midline area. The partial pressure of CO_2 used for the calculation, was $10^{-1.95}$ atm, which corresponds to Pco_2 in the root zone. The dissolution of calcite was considered to be the source of Ca^{2+}, therefore under open system conditions ($Pco_2 = 10^{1.95}$ = constans) the clean water was brought into equilibrium with calcite first. Albite dissolution is thought to be the source of Na^+ in this area. Since albit dissolution is an irreversible process, modelling this process in a thermodynamic way is impossible, therefore the irreversible albit dissolution was represented by adding 1,0 mmol/l Na^+ into thre solution. Assuming that the trace elements (Sr^{2+}, Ba^{2+}, Li^+, Si, As, Fe, Mn, Zn^{2+}) and Mg^{2+} go into solution by irreversible dissolution in the study area, irreversible dissolution of these elements was carried out by adding Sr^{2+} (0,004 mmol/l), Ba^{2+} (0,001 mmol/l), Li^+ (0,0005 mmol/l), Si (0,45 mmol/l), As (0,0001 mmol/l), Fe (0,005 mmol/l), Mn (0,0008 mmol/), Zn^{2+} (0,0015 mmol/l), Mg^{2+} (1,00 mmol/l) into the solution on the same CO_2 partial pressure. PHREEQE was used to perform the simulation of the water composition. In Table 6 the measured and the computed composition of the water show good agreement.

Table 6. Calculated and measured average water chemistry for Group 1.

		measured	simulate
alk	mequ./l	5,31	5,70
pH		7,59	7,50
Na^+	mmol/l	1,09	1,00
Ca^{2+}	mmol/l	1,39	1,30
Mg^{2+}	mmol/l	0,94	1,00
Ba^{2+}	mmol/l	0,0011	0,0010
Sr^{2+}	mmol/l	0,0038	0,0040
As	mmol/l	0,0001	0,0001
Fe	mmol/l	0,0047	0,0050
Zn^{2+}	mmol/l	0,0020	0,0015
Mn	mmol/l	0,0008	0,0008
Li^+	mmol/l	0,0005	0,0005
Si	mmol/l	0,4467	0,4500

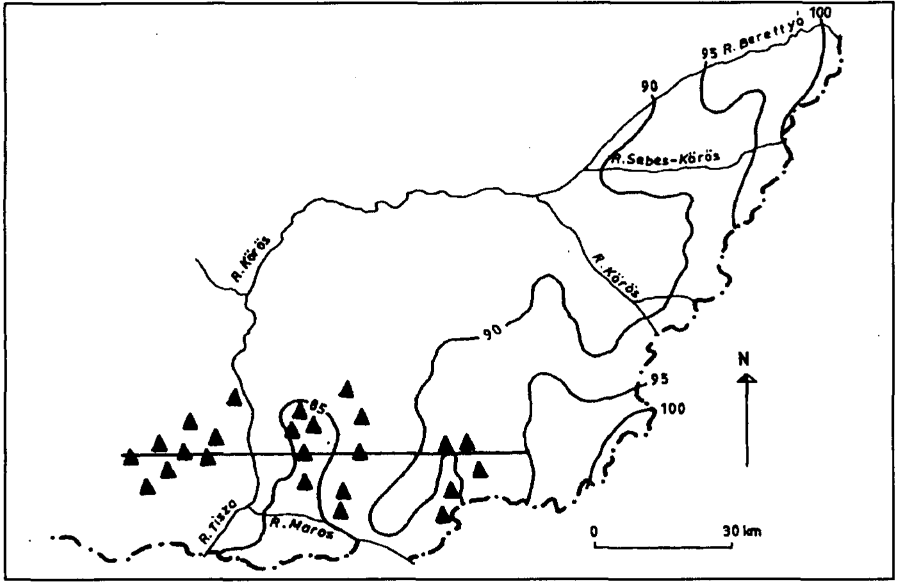

Fig. 6A. Location of the water samples used up for the geochemical simulation.

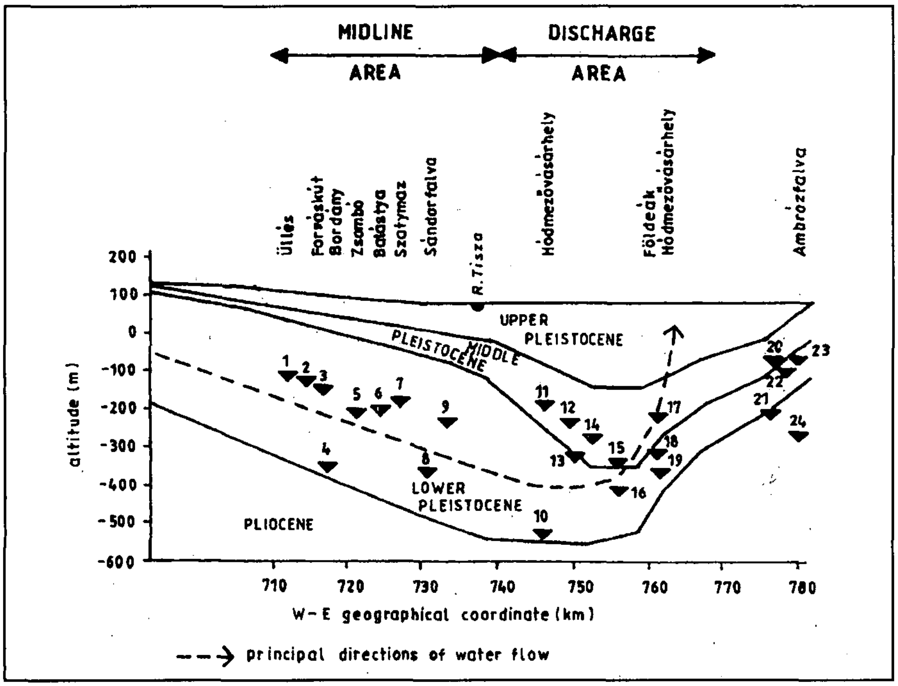

Fig. 6B. W-E cross-section and sampled sites along the cross section.

The second stage was the simulation of cation exchange along the flow path in the discharge area. PHREEQM a combined geochemical and mixing model was used to simulate ion exchange. To develop the chromatographic pattern, displacement of initial water by flushing water is required (Appelo, Willemsen, 1987). The initial water forms an exchange complex on clay minerals, then the displacing water with different chemical composition flushes the initial pore water content and develops a new equilibrium between the flushing water and the exchanger resulting characteristic distribution of dissolved ions. In the discharge area, the large increase in Na^+ and the loss of Ba^{2+},Sr^{2+}, Ca^{2+} and Mg^{2+} display the typical pattern of cation exchange along the flow path (Fig. 5A-D). To model the cation exchange between Na^+ and Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, 24 wells were chosen. The location of these wells can be seen in Fig. 6A-B.

***Table** 7.* Chemical composition of the samples along the cross-section.

location	area	W-E coord	altitude	depth	alkalinity	COD	pH	T	Cl	Na$^+$	Ca^{2+}	Mg^{2+}
		km	m	m	meqv./l	mg/l		^{0}C	mmol/l	mmol/l	mmol/l	mmol/l
1. Üllés	midline	711,70	101	200,0	4,9	1,0	7,3	17	0,06	1,09	1,19	0,87
2. Zákány	midline	714,80	98	218,0	5,5	2,3	7,8	19	0,06	0,90	1,31	0,89
3. Forráskút	midline	716,30	94	245,0	5,3	1,9	7,7	19	0,06	0,84	1,43	0,97
4. Bordány	midline	717,20	82	437,0	5,3	0,8	7,6	24	0,08	1,25	1,31	0,98
5. Zsombó	midline	721,10	91	301,0	5,7	0,9	7,6	23	0,08	0,85	1,45	0,91
6. Balástya	midline	724,20	88	295,0	4,5	2,8	7,7	20	0,11	0,71	1,41	0,82
7. Szatymaz	midline	726,80	86	272,0	5,5	1,8	7,5	21	0,14	1,00	1,66	0,98
8. Sándorfalva	midline	730,70	84	460,0	5,0	3,5	7,7	26	0,08	0,90	1,41	0,89
9. Dóc	midline	733,00	83	300,0	5,0	1,8	7,4	20	0,08	1,38	1,30	0,89
10 .Hódmezővásárhely	discharge	746,00	78	605,0	5,4	2,1	7,9	30	0,08	3,07	0,73	0,54
11. Hódmezővásárhely	discharge	746,00	82	278,0	5,4	2,3	7,8	23	0,08	1,99	1,00	0,71
12. Hódmezővásárhely	discharge	749,20	82	324,0	5,2	2,0	7,8	21	0,08	2,15	1,06	0,74
13. Hódmezővásárhely	discharge	750,00	80	410,0	5,0	1,8	7,7	24	0,08	1,61	1,05	0,81
14. Ferencszállás	discharge	751,00	85	305,0	6,0	1,9	7,8	24	0,08	2,91	0,88	0,61
15. Kiszombor	discharge	756,50	85	420,0	6,2	1,6	7,6	25	0,11	4,13	0,49	0,31
16. Kiszombor	discharge	756,50	85	442,0	6,2	1,7	8,1	28	0,11	4,07	0,51	0,31
17. Hódmezővásárhely	discharge	757,60	82	300,0	5,9	2,6	8,0	22	0,11	5,14	0,22	0,19
18. Földeák	discharge	761,00	90	410,0	6,7	4,1	7,9	26	0,14	6,58	0,12	0,09
19. Hódmezővásárhely	discharge	761,60	84	450,0	7,7	3,3	8,3	27	0,08	7,75	0,11	0,09
20. Csanádalberti		778,00	86	156,0	16,4	10,0	8,1	23	0,39	14,80	0,33	0,34
21. Nagylak		778,60	84	292,0	15,2	8,5	7,9	23	0,37	14,64	0,50	0,52
22. Ambrózfalva		779,50	93	173,0	14,7	9,6	7,8	18	0,42	11,80	0,83	0,72
23. Csanádpalota		779,50	85	156,0	15,4	8,4	7,8	16	0,28	12,67	0,76	0,85
24. Pitvaros		780,30	87	341,0	14,5	10,7	8,0	24	0,90	13,90	0,38	0,30

Table 7 (continued)

	As	Fe	Zn^{2+}	Mn	Ba^{2+}	Li$^+$	Sr^{2+}	Si
	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l
1.	0,0003	0,0056	0,0001	0,0006	0,0011	0,0005	0,0036	0,4010
2.	0,0004	0,0073	0,0000	0,0005	0,0010	0,0004	0,0034	0,4030
3.	0,0001	0,0058	0,0001	0,0006	0,0011	0,0006	0,0033	0,4610
4.	0,0002	0,0045	0,0002	0,0006	0,0013	0,0013	0,0041	0,4610
5.	0,0001	0,0032	0,0001	0,0007	0,0012	0,0006	0,0031	0,4690
6.	0,0001	0,0032	0,0004	0,0009	0,0008	0,0003	0,0027	0,4700
7.	0,0001	0,0081	0,0004	0,0009	0,0012	0,0006	0,0034	0,4630
8.	0,0001	0,0041	0,0002	0,0007	0,0012	0,0004	0,0034	0,4650
9.	0,0002	0,0042	0,0001	0,0007	0,0011	0,0005	0,0045	0,4120
10.	0,0001	0,0019	0,0001	0,0007	0,0011	0,0008	0,0050	0,3680
11.	0,0005	0,0018	0,0001	0,0009	0,0009	0,0006	0,0046	0,3500
12.	0,0004	0,0004	0,0001	0,0008	0,0009	0,0011	0,0052	0,3690
13.	0,0001	0,0025	0,0002	0,0008	0,0011	0,0006	0,0055	0,3920
14.	0,0004	0,0022	0,0001	0,0007	0,0010	0,0007	0,0043	0,3470
15.	0,0003	0,0031	0,0002	0,0005	0,0008	0,0007	0,0024	0,3260
16.	0,0002	0,0029	0,0002	0,0007	0,0010	0,0007	0,0024	0,3240
17.	0,0006	0,0021	0,0001	0,0005	0,0004	0,0006	0,0010	0,2820
18.	0,0004	0,0012	0,0000	0,0004	0,0002	0,0007	0,0005	0,2640
19.	0,0007	0,0037	0,0000	0,0003	0,0003	0,0006	0,0006	0,2720
20.	0,0001	0,0027	0,0002	0,0005	0,0008	0,0018	0,0027	0,3320
21.	0,0000	0,0033	0,0000	0,0004	0,0009	0,0017	0,0035	0,3650
22.	0,0005	0,0050	0,0010	0,0037	0,0010	0,0013	0,0049	0,3600
23.	0,0001	0,0060	0,0002	0,0007	0,0012	0,0015	0,0059	0,3280
24.	0,0001	0,0019	0,0006	0,0007	0,0007	0,0016	0,0015	0,3470

Table 7. contains the composition of the water samples. The distance from the begining (745 km coordinate) to the end of the flow line (765 km coordinate) is 20 km. The whole distance was divided into two layers and 10 cells for the calculation. Cell length is 2.0 km. The first layer consisting of 6 cells corresponds to the coarser grained sediment, the second layer consisting of 4 cells represents the finer grained sediment. Two layers have different cation exchange capacity (CEC). CEC value in the coarser sample (Bácsalmás, 132 m) 1.20 mequiv./100g, in the finer sample (Mindszent 476 m) 1.7 mequiv./100g (Varsányi, Ó. Kovács, 1996). Considering the bulk density of 2.6 g/cm^3 and the porosity of 30%, recalculation of CEC to mequiv./l gives 75 mequiv/l for the coarser grained sediment and 105 mequiv./l for the finer grained sediment. Since the original pore water of the River Danube deposits exchanged at the end of Pleistocene (Varsányi, 1994), the present water quality differs from the original water quality. To execute the

Table 8. Simulated concentrations along the cross-section:

cells	W-E	Ca^{2+}	Mg^{2+}	Na^+	Ba^{2+}	Sr^{2+}
	km	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l
0.	727,5	1,20	1,00	1,00	0,0010	0,0040
1.	747,0	1,08	1,04	1,41	0,0014	0,0056
2.	749,0	0,97	0,97	1,80	0,0014	0,0056
3.	751,0	0,77	0,81	2,50	0,0012	0,0049
4.	753,0	0,52	0,54	3,60	0,0008	0,0034
5.	755,0	0,24	0,25	4,80	0,0004	0,0016
6.	757,0	0,12	0,12	5,40	0,0002	0,0008
7.	759,0	0,09	0,09	5,60	0,0002	0,0006
8.	761,0	0,09	0,09	5,90	0,0001	0,0006
9.	763,0	0,09	0,09	6,04	0,0002	0,0006
10.	765,0	0,09	0,09	6,20	0,0002	0,0006
11.	780,0	0,56	0,55	13,55	0,0009	0,0037

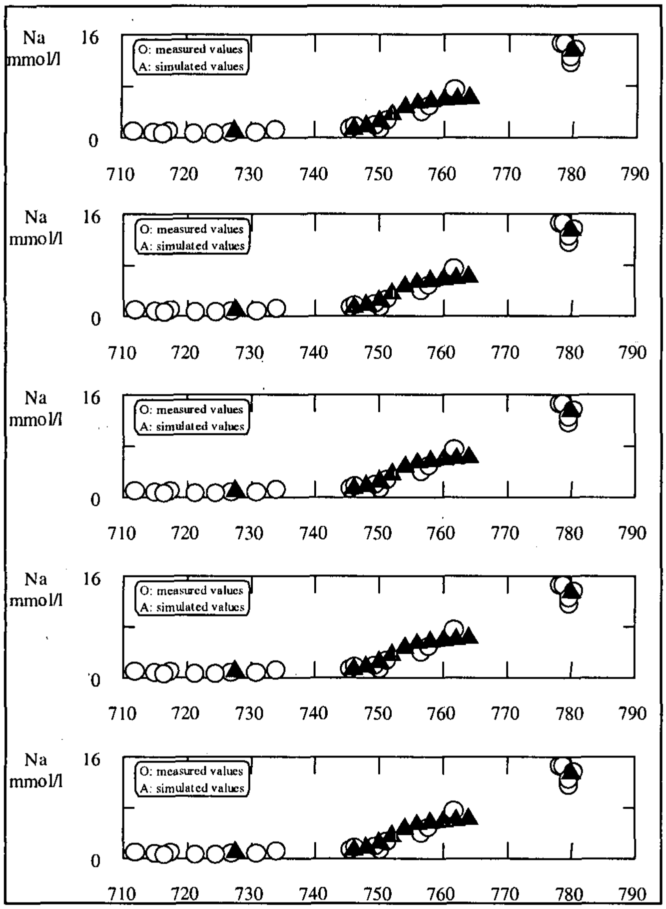

Fig. 7: Measured and simulated concentrations along the cross-section.

calculation it was necessary to know the composition of the original water. To obtain information about the original water chemistry, the water quality from an aquifer, where restricted water circulation is supposed, was chosen as initial water. This aquifer is located next to the River Danube deposits in the east part of the study area. Five water samples from this area were used to calculate the average composition of the initial water. The original pore water composition is characterized by high Na^+ and COD concentration and low As, Fe, Mn content (Table 7, sample 20-24.). The chemical composition of the flushing water is that calculated with the help of PHREEQE at the first stage of the simulation. The whole pore volumes of cells was flushed out in 15 steps, dispersivity is 1300 m, and porosity 0.3. The ion exchange calculation was carried out by PHREEQM and the result of the calculation is summarized in Table 8. The flushing water quality corresponds to sample 0, and the initial water quality corresponds to sample 11. Along the cross section the measured and simulated concentration of Sr^{2+}, Ba^{2+}, Ca^{2+}, Mg^{2+} can be seen in Fig. 7. According to Fig. 7, in the midline area – between 710 and 745 km coordinate – there is no evidence for ion exchange. In the discharge area – between 745 and 765 km - the simulation follows quite well the pattern of concentration along the flow path, which gives an evidence for ion exchange of Sr^{2+} and Ba^{2+} for Na^+.

CONCLUSIONS

The groundwater chemistry does not show remarkable correlation with depth in the study area. The concentration of some studied chemical components (Sr^{2+}, Ba^{2+}, As, Si) changes in the direction of water flow.

The study area can be divided into two parts on the basis of trace components dissolved in water. Location of these groups corresponds to the midline and discharge area of the same water flow.

Geochemical processes controlling the trace element distribution are different in the midline and in the discharge area. In the midline area, the content of Sr^{2+}, Ba^{2+}, Li^+ and Si is controlled by silicate weathering. Fe and Mn concentration in groundwater is determined by dissolution of Fe- and Mn-oxides. Weathering of the sediment depends on pH of the groundwater which is influenced by the partial pressure of CO_2 originated from organic matter transformation. Arsenic adsorption plays an important role in As distribution in water of this area. The factors controlling the extent of As adsorption are: pH, oxidative transformation of organic matters and dissolution of Mn-oxides besides the composition of the sediments (rate of the clay fraction, Fe-oxides content).

In the discharge area As content is controlled by two gechemical processes. One is As desorption from the surface of the sediments, which occurs because of increase in pH. The other is the transformation of organic matters, which influences indirectly As concentration throuhg the dissolution of Fe- and Mn-oxides.

Geochemical modelling gave an evidence for cation exchange. This process controls Sr^{2+}, and Ba^{2+} concentration in the discharge area.

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