The aim of this work is to present and explain the spatial distribution of dissolved arsenic in the subsurface water from 10 ^{0}C to 98 ^{0}C, and to identify the factors which are responsible for the distribution of arsenic in particular environments.

The study region covers about 22,000 km^2. It represents the central part of the Pannonian Basin, which is filled with Neogene sediments. In the studied depth interval environment of sedimentation is represented by the fine grained delta-slope, upper delta-slope, delta-plain facies, followed by lacustrine, fluvial and terrestrial sequences. Tectonic events resulted in sub-basins with highly variable sediment thicknesses and areas above elevated basement. The depth of the studied wells ranged from 9 to 2500 m comprising Late Miocene (Pannonian and Pontian), Pliocene and Quaternary layers.

Ca-$Mg(HCO_3)_2$, $NaHCO_3$, and NaCl are the main water types. In the groundwater up to 30 ^{o}C, the major cations are either Ca^{2+} and Mg^{2+}, or Na^+, and the major anion is HCO_3^-, along the flow path transition is continuous from Ca^{2+} and Mg^{2+} to Na^+. Above 30 ^{o}C the major cation is Na^+ and the major anion is HCO_3^-. The alkalinitiy is increasing with the depth, the minimum and maximum values are 3 and 60 meq/l, respectively. Also the variation of the alkalinity is increasing with depth: in the shallowest samples the range is from 3 to 22 meq/l, in the deepest samples from15 to 60 meq/l. In several samples the dominant anion is Cl^- . The concentrations of Cl^- range from 1 to 7715 mg/l suggesting the diversity of the chemical water quality. Humic substances were predominant in the fluviatile aquifers, in deeper and warmer waters other organic compounds were determined, as well. Concentrations of minor, trace and organic components show high variability.

The arsenic concentration ranges from 0 to180 μg/l. To establish the spatial distribution geographical location and depth dependence were studied. The group with the highest arsenic concentrations is located in the upper 500 m of the fluviatile Quaternary sediments in the southern part of the Duna-Tisza interfluves and South Tisza basin, in the River Maros alluvial fan, and in the Körös basin. The largest proportion of the samples with elevated arsenic level is taken from the eastern part of the study area; in the River Maros alluvial fan and in the Körös basin. In the deeper samples, in the fluvio-lacustrine and lacustrine sediments the maximum concentrations of arsenic is below 80 μg/l.

Origin of water, and effect of temperature, pH, redox potential, inorganic and organic compounds are discussed to identify the factors controlling the spatial pattern of the dissolved arsenic.

Origin of subsurface water

In the $\delta^{18}O$ - $\delta^{2}H$ diagram the samples on the local meteoric water line (LMWL) are of meteoric or paleometeoric origin, whereas those which are below the LMWL are water of non-meteoric origin or mixed water with non-meteoric contribution. In this study each cold sample below 30 ^{0}C, and most thermal water samples above 30 ^{0}C are of meteoric origin. Below the LMWL three lines are distinguished, the samples located on each line represent discharging water, originated from the deepest studied layers of three distinct geological settings: the Duna-Tisza interfluves and South Tisza basin, the Körös basin, and the area above basement high at the north-eastern part of the study area. Besides, there are sparse samples from the sediments above elevated basement throughout the study area. The samples below the LMWL are paleometeoric water with significant contribution of ascending brackish component from the Pannonian layers. The latter is the remnant of the Lake Pannon trapped during the sedimentation in the Miocene. The sea origin is shown by the Br^- to Cl^- ratio similar to that of the present seawater. Correlation between δ^2H and Cl^- displays the progress of mixing. Increasing ^2H δ values and Cl^- concentrations reflect the increasing proportion of the brackish water in the mixed waters. The difference in the Cl^- concentrations between the deep sub-basins and the basement high areas is attributed to different hydrogeological circumstances. In the deep sub-basins the ascending water squeezed through a regional aquitard (named Algyő formation) which operates as a semipermeable membrane, so the squeezed water is depleted in Cl^-. In the basement high areas fractures and faults result in locally higher hydraulic conductivity of the regional aquitard, and in the ascending water the concentration of Cl^- remains high.

The impact of the origin of water on the arsenic concentration is examined by comparing the arsenic concentrations in the thermal water of meteoric origin to those which contain brackish contribution. In each group of thermal waters, independently of their origin, the maximum arsenic concentrations are similar and don’t exceed 70 μg/l. In the mixed water in both deep sub-basins, and in the sparse samples from the areas above elevated basement throughout the study area, the arsenic concentrations are independent of the proportion of the non-meteoric contribution. It seems probable that the effect of seawater on the concentration of arsenic in these waters is overwritten by factors or processes other than straightforward mixing of the meteoric and non-meteoric water. In the sub-basins the membrane filtration through the compacted clay may be the process which masks the effect of the brackish water on the concentration of arsenic. The sparsely located samples originate from distinct water bodies, so the local water-rock interactions may modify the effect of mixing on the concentration of the arsenic. In the mixed water from the basement high area of the north-eastern region, however, the concentration of arsenic is decreasing with the increasing proportion of the brackish water, suggesting very low concentration of the arsenic in the freshening water of the Lake Pannon.

pH and redox potential

The mobilizable fraction of arsenic is generally associated with iron oxide minerals and natural organic matter, and the release of arsenic is controlled by redox potential and pH. Interpretation of the measured electrode potentials needs careful considerations, because measured values are meaningful only for those components whose behaviour is electrochemically reversible at the electrode surface. In the natural systems many redox couples don't comply with this condition, because they don't accept or donate electron at the electrode. Mainly those couples behave reversibly, which contain soluble iron or sulphur species at activity exceeding 10^{-5} and achieve redox equilibrium. Instead of the measured redox potential based on the Nernst equation, another approach of redox reactions is applied; the low of mass action for redox half reaction, which includes the electron activity. Similarly to the pH concept $pe = -\log [e^{-}]$, where high positive pe values indicate oxidizing and low negative values reducing conditions, so the pe term is interpreted as a tendency to release or accept electrons.

In the pH and pe diagram two types of patterns can be distinguished. There is a scattered pattern of the samples, in which the pH and pe are independent, but in the predominant part of the samples there is an inverse relationship between the pH and pe. The samples with pH the dependent pe are from fluviatile aquifers located in the upper 500 m of the sediment. Each sample in which the concentration of arsenic exceeds 70 μg/l is found in this group of groundwater however, there are samples of lower arsenic concentrations, as well. The equation of the regression line is:

$$pe = -2\ pH + 16 \qquad (1)$$

This pattern of the studied water samples originates in equilibrium redox reactions of redox active couples, when one electron and two H^+ are involved in the reaction. Relevant redox couples may be arsenic, iron and organic species. The natural pH-pe conditions were compared to the stability diagram of the As-O-H, Fe-CO_2-H_2O and semiquinone-hydroquinon systems.

Standard Gibbs energy (ΔG_f^0) and enthalpy (ΔH_f^0) of formation at 25 °C published are used for the calculations.

As-O-H system

In the As-O-H system the

$$H_3AsO_3{}^o + H_2O \leftrightarrow H_2AsO_4^- + 3H^+ + 2e^- \qquad (2)$$

$$H_3AsO_3{}^o + H_2O \leftrightarrow HAsO_4^{2-} + 4H^+ + 2e^- \qquad (3)$$

$$H_2AsO_4^- \leftrightarrow HAsO_4^{2-} + H^+ \qquad (4)$$

half reactions are considered.

In the As-O-H system three fields appear; $HAsO_4^{2-}$, $H_2AsO_4^-$ and $H_3AsO_3^o$. Under oxidising conditions above 6.9 pH the dominant dissolved species is $HAsO_4^{2-}$, and below $H_2AsO_4^-$. Under reducing conditions, in the whole measured pH range the uncharged dissolved arsenite ($H_3AsO_3^o$) is the stable species. The samples are located in the stability field of $HAsO_4^{2-}$ and $H_3AsO_3^o$. The samples with the pH dependent redox potential are in the field of $HAsO_4^{2-}$. The regression line is parallel with the redox boundary between $HAsO_4^{2-}$ and $H_3AsO_3^o$ in the standard state As-O-H system. The equation of the redox boundary is:

$$pe = -2.0\ pH + 14.3 \qquad (5)$$

The distance between them originates in the difference between the equilibrium As-O-H system of standard state and the natural conditions in the sedimentary aquifers. This difference is due to two factors; deviation of the temperature from the 25 ^{0}C and deviation of the activity of dissolved ions ($HAsO_4^{2-}$ and $H_3AsO_3{}^o$) from unit in the groundwater.

The temperature of the samples varies from 10 to 30 ^{0}C. The effect of temperature on the equilibrium constant of the redox transition between $HAsO_4^{2-}$ and $H_3AsO_3^o$ was calculated at the above temperatures. The logK of the equation (3) is -28.6 at 25 ^{0}C , while at 10 ^{0}C it is -29.7 and at 30 ^{0}C -28.2, which results in 0.5 pe rise and 0.2 pe drop of the redox boundary comparing to the 25 ^{0}C. All these indicate that the effect of temperature in this narrow range of the temperature is negligible.

The log[$HAsO_4^{2-}$] / [$H_3AsO_3^o$] was calculated on the basis of the Nernst equation. The mean of the log[$HAsO_4^{2-}$] / [$H_3AsO_3^o$] values is 3.4, which means that in the stability field of $HAsO_4^{2-}$ the activity of the $HAsO_4^{2-}$ is three orders of magnitude higher than that of the $H_3AsO_3{}^o$. The near constant activity ratios require similar and equilibrium redox circumstances in the dominant part of the groundwater originating from fluviatile aquifers.

In the other samples the pH and pe are independent, indicating various pH and redox circumstances. The cold groundwater samples (<30 ^{0}C) are located in the $HAsO_4^{2-}$ field, but above those samples in which the pH and pe correlate. Between the redox boundary and the correlating samples both cold and geothermal samples are found, but the deepest geothermal samples appear in the $H_3AsO_3^o$ field. All these samples the concentration of dissolved arsenic is below 70 μg/l.

Fe-CO_2-H_2O system

In the Fe-CO_2-H_2O system the solid phases were carefully selected to reflect the field conditions in the study area. In a previous investigation after extraction with hydroxylamine hydrochloride 1.8 - 25.8 g/kg secondary poorly crystalised FeOOH were determined in core samples, and precipitation of siderite was supposed based on the ratio of the dissolved arsenic and iron. For this reason amorphous FeOOH and $FeCO_3$ as solid phases and dissolved Fe^{2+} were chosen to delineate the stability conditions in the Fe-CO_2-H_2O system.

$$Fe^{2+} + 2H_2O \leftrightarrow FeOOH + 3H^+ + e^- \qquad (6)$$

$$FeCO_3 + 2H_2O \leftrightarrow FeOOH + HCO_3^- + 2H^+ + e^- \qquad (7)$$

$$Fe^{2+} + HCO_3^- \leftrightarrow FeCO_3 + H^+ \qquad (8)$$

half reactions were used to construct the pH-pe stability diagram.

To calculate the boundaries between the solid phases and dissolved Fe^{2+}, the activities of Fe^{2+} and HCO_3^- must be fixed, because they are involved in the equations (6), (7) and (8). The fixed activities are estimated from the mean values and ionic strength of the geothermal samples, which are located in the negative pe range.

$Fe^{2+} = 2*10^{-6}$ mol/l, $\gamma_2 = 0.62$ γ_2 activity coefficient for the divalent ions

$HCO_3^- = 14*10^{-3}$ mol/l, $\gamma_1 = 0.88$ γ_1 activity coefficient for the monovalent ions

Under oxidizing conditions the stability fields of the amorphous FeOOH covers the whole measured pH range. In this stability field, the concentrations of iron measured in the groundwater samples exceed the solubility of FeOOH. The elevated concentration of the dissolved iron can be attributed to the natural organic matter in the groundwater. It was reported that humic substances at the concentration as low as 5 μg/l can substantially enhance the solubility of FeOOH. Since in the studied groundwater samples the average concentration of humic substances is 5.2 mg/l (with a minimum of 0.1 mg/l), it is probable that complexation with humic substances results in the elevated concentrations of the dissolved iron.

Under reducing circumstances $FeCO_3$ is a stable mineral above pH 7.7. Below this pH the field of the dissolved Fe^{2+} is found. The location of the pH boundary depends on the fixed activity of Fe^{2+} and HCO_3^-, with decreasing activities the pH boundary shifts towards higher pH. In the stability field of $FeCO_3$ the concentrations of iron measured in the geothermal samples are below the fixed iron concentration, and in the half of those samples which are in the field of Fe^{2+} exceed it. In the samples originate from the aquifers deeper than 1000 m, where the measured redox potentials show reducing circumstances the reductive dissolution of FeOOH and the adsorbed or co-precipitated arsenic is supposed as the main mobilizing process of the arsenic.

Combination of the As-O-H and $Fe\text{-}CO_2\text{-}H_2O$ diagrams demonstrates that the redox boundaries between $HAsO_4^{2-}$ and $H_3AsO_3^{o}$ and between amorphous FeOOH and $FeCO_3$ are very close to each other and the slopes of the lines are identical. The stability fields of $HAsO_4^{2-}$ and FeOOH are overlapped in the range of the measured pH and redox potential. Within the intersection of the two fields most samples originate from the fluvial sediment, in the predominant part of the samples the pH and pe correlate. In the latter group the highest mean and maximum arsenic concentrations are 49 μg/l and 180 μg/l, respectively. The other samples from the fluviatile sediment are more oxidized, the average is 32 μg/l, and the maximum is 84 μg/l. In this intersection there are less oxidized samples between the correlating samples and the redox boundary: the mean and the maximum values are 19 μg/l and 24 μg/l, respectively. Two distinct ways of the mobilization are probable in the oxidized samples. One is desorption of As(V) from FeOOH. Under oxidising, acidic conditions arsenate is strongly adsorbed by oxide minerals, but above pH 6 desorption raises the concentration of dissolved arsenic. The other process is in connection with the complexation with humic substances. Considering that in the presence of iron, the dissolved organic matter (DOM) may bind considerable amounts of arsenic through formation of Fe-bridged As - Fe-DOM complexes it is probable that complexation with humic substances raises the concentrations of both iron and arsenic in groundwater.

Reduced samples are below the arsenic and iron redox boundaries. In reduced circumstances, where depending on pH, $H_3AsO_3^o$ is in equilibrium with either Fe^{2+} or $FeCO_3$, the reductive dissolution of FeOOH may results in the mobilization of the adsorbed or coprecipitated arsenic. Here only geothermal samples are found, the mean and maximum of arsenic are 13 μg/l and 49 μg/l, respectively, i.e. the reduced circumstances is associated with the lowest arsenic concentration.

Dissolved organic matter

The redox boundary implies equilibrium between $HAsO_4^{2-}$ and $H_3AsO_3{}^o$, the activity ratio of the species are unit along the boundary. Along the regression line parallel with the redox boundary although the mean value of the activity ratios is 2500 times higher than unit, the activity ratio is obviously constant, and similarly to the redox boundary reflects redox equilibrium. The equation (3) is a half reaction. There must of course also exist another half reaction in an equilibrium redox reaction. DOM is a strong candidate for the other half of the redox reaction.

In a previous work calculations demonstrated that due to kinetically driven transformation, the sediment organic matter was the source of the dissolved inorganic and organic carbon. In the samples below 30 ^{0}C humic and fulvic acids represent the DOM. Their concentrations vary in wide range, but with increasing temperature the maximum values and variability of data are decreasing. Above 40^{0}C besides humic substances other organic compounds, like polycyclic aromatic hydrocarbons (PAHs), phenolic components and short chain aliphatic acid anions appear.

Beside the kinetically driven organic degradation, equilibrium redox reactions of the DOM, especially that of the humic and fulvic acids have been reported, as well. The humic substances are complex aromatic macromolecules containing phenolic OH and quinone structures. The redox reactivity of humic substances is caused by the oxidized and reduced quinones. Due to the presence of the dissolved humic substances in a particular part of the water samples the As(III) ↔ As(V) redox couple may be in equilibrium with redox active functional groups of quinoid nature in the polyphenolic-rich humic substances. To calculate the stability fields in a standard state quinone (Q^{2-}) – semiquinone ($HQ^{2-\cdot}$) – hydroquinone (H_2Q^{2-}) system, the thermodynamic data of a model quinone (9,10-anthraquinone-2,6-disulfonic acid) characteristic for humic substances were taken from the relevant literature. The reactions involved in the quinone-hydroquinone transformation:

$$\begin{tikzcd}
Q^{2-} \arrow[r, leftrightarrow] & HQ^{2-\cdot} \arrow[r, leftrightarrow] \arrow[d, leftrightarrow] & H_2Q^{2-} \arrow[d, leftrightarrow] \\
 & Q^{3-\cdot} & HQ^{3-} \arrow[d, leftrightarrow] \\
 & & Q^{4-}
\end{tikzcd}$$

The relevant equations in the pH range of the studied water:

$$HQ^{2-\cdot} \leftrightarrow Q^{3-\cdot} + H^+ \qquad \log K = -3.20 \quad (10)$$

$$H_2Q^{2-} \leftrightarrow HQ^{2-\cdot} + H^+ + e^- \qquad E_0 = -0.561\ V \qquad \log K = -9.47 \qquad (11)$$

$$HQ^{2-\cdot} \leftrightarrow Q^{2-} + H^+ + e^- \qquad E_0 = 0.055\ V \qquad \log K = -0.93 \qquad (12)$$

$$H_2Q^{2-} \leftrightarrow HQ^{3-} + H^+ \qquad \log K = -8.10 \qquad (13)$$

Similarly to the regression line of the samples on the pH-pe diagram and to the $HAsO_4^{2-} \leftrightarrow H_3AsO_3^{o}$ redox boundary the semiquinone ($HQ^{2-\cdot}$) – hydroquinone (H_2Q^{2-}) redox boundary can be described by the equation of the straight line: pe = 2pH + const. The three lines are parallel suggesting that the correlation between the measured pH and pe in the studied samples is resulted in by the As(III) ↔ As(V) and hydroquinone ↔ semiquinone ($Q^{2-\cdot}$) half reactions. It is obvious that the above thermodynamic data apply only to the model quinone, but the equation (10) is valid for any quinone type reaction; parallel shifts of the boundaries occur, but the slope of the lines remains unchanged.

Although in most groundwater samples correlation was found between the pH and pe, there are scattering samples, as well. The scattering samples originate from the whole studied depth interval. The COD and the concentration of humic substances correlate significantly, but the relationship indicates different oxidizability of humic substances in shallowest unconfined, fluviatile, fluviatile-lacustrine and lacustrine aquifers. The oxidizability is the lowest in the samples from the fluviatile sediments. The different oxidizability indicates differences in the functional groups, including quinones as redox active functional groups and suggests diverse redox circumstances. It is probable that in the different sedimentary environments and at different temperatures the redox behaviour of the humic substances is different, and the semiquinon-hydroquinon redox reactions controls the redox potential only in the fluviatile sediment.

As the conclusion the following have been established: The studied subsurface water samples represent different depositional environments from the Late Miocene delta-slope and delta-plain facies followed by the Pliocene and Quaternary lacustrine, fluviatil and terrestrial sequences in the upper 2500 m of the sediments. In certain regions and depth higher, in the other ones lower concentrations of dissolved arsenic were measured suggesting that geology and hydrogeology influence the distribution of dissolved arsenic. The highest concentrations of arsenic were measured in the confined fluviatile (Quaternary) aquifers in the upper 500 m of the sediment. The mean and the maximum concentrations are 49 μg/l and 180 μg/l, respectively.

The source material of the sediments indicated by Sr ratio influences the availability of the arsenic. Two main directions of the transport of source material are from NE and from NW filling in the eastern and the western regions, respectively. The concentration of dissolved arsenic is higher in the eastern region, probably due to the availability of the mobilizable arsenic.

In the delta plain and lacustrine sediment above the basement high faults and fractures increase the vertical hydraulic conductivity of the regional aquitard. In the deep ascending water deep brackish water (remnant of Lake Pannon) and paleometeoric water are mixed, the proportion of paleometeoric water is increasing upward, together with the concentration of arsenic. Direct proportion suggests low concentration of mobilizable arsenic in the sediment deposited in freshening and shoaling Lake Pannon. In deep sub-basins where the ascending mixed water squeezed through the compacted clay layer of the regional aquitard, the proportion of the brackish water and the concentration of arsenic are independent. At similar depth the arsenic concentrations are higher in the mixed water than in the formation water of paleometeoric origin.

Oxihydroxid minerals like FeOOH and organic matter take part in the mobilizing processes, which are controlled by pH and redox potential. In most cold (<30 ^{0}C) groundwater samples originating from fluviatile sediments the pH and pe correlate with each other, and both the average and the maximum arsenic concentrations are the highest. Equation of the regression line is pe= -2 pH +const. This line is parallel with the redox boundary between $HAsO_4^{2-}$ and $H_3AsO_3^{o}$ and between semiquinone ($Q^{3-\cdot}$) – hydroquinone (H_2Q^{2-}) redox species in the As-O-H and in the quinone-semiquinone-hydroquinone standard state pH-pe stability diagrams, respectively. This indicates that in particular groundwater samples redox equilibrium does exist, and the redox reaction controlling the measured redox potential consists of the As(III) – As(V) and hydroquinone – semiquinone half reactions. In the pH – pe stability diagrams these water samples are located in the stability fields of $HAsO_4^{2-}$, the semiquinone radical ($Q^{3-\cdot}$) and the amorphous FeOOH, i.e. under oxidizing conditions. Two distinct processes of the mobilization were established. One is desorption of $HAsO_4^{2-}$ from FeOOH minerals. Under oxidising conditions, above pH 6 desorption of arsenate occurs and the concentration of dissolved arsenic increases. The other process is the complexation of iron and arsenic with humic substances. The presence of iron, the DOM may bind considerable amounts of arsenic through formation of Fe-bridged As - Fe-DOM complexes. These processes account for the highest mean and maximum concentrations of dissolved arsenic.

In those oxidized samples where equilibrium redox processes were not recognized the average and maximum concentrations were lower. It was assumed that the difference originates in the different quality of the DOM, but this hypothesis needs further investigation.

In reducing conditions only geothermal samples are found. They are located in the stability fields of $H_3AsO_3^o$, hydroquinone species, and Fe(II). The concentration of arsenic is below 50 μg/l. Although reductive dissolution of FeOOH together with the adsorbed or co-precipitated arsenic is a plausible way of the mobilization of arsenic, this process does not explain the low concentration of arsenic. It seems probable that during geological time scale the circumstances were changes several times, and the mobilizable arsenic have been swept partially from the sediment.

The significance of factors controlling the concentration of dissolved arsenic are different in the aquifers of different depth and locations due to different circumstances like origin of water and sediment material, environments of sedimentation, pH and redox conditions, temperature and dissolved organic compounds.