

## QUALITY STATUS OF THE WATER IN THE UPPER THRACIAN PLIO-QUATERNARY AQUIFER (SOUTH BULGARIA)

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**Abstract:** The present paper presents some results of research works in the frame of the EC 5<sup>th</sup>FP "BaSeLiNe" project (contract No EVK1-CT1999-00006). According to the BaSeLiNe concept the groundwater bodies' status is considered as their present hydrochemical conditions and the tendency for their long-term variations "...being derived from natural geological, biological, or atmospheric sources". The paper considers the methodology and some concrete results for evaluating the "BaSeLiNe status" of aquifers, where significant anthropogenic influence exists, but waters are still in a good sustainable quality. For that purpose the Upper Thracian Plio-Quaternary aquifer in South Bulgaria is chosen.

**Keywords:** Groundwater quality, BaSeLiNe concept, Aquifer, Bulgaria

### WASSERQUALITÄT IM GRUNDWASSERLEITER DES QUATERNÄR-PLIOZÄNS IN DER TRAKIA EBENE (SÜDBULGARIEN)

**Zusammenfassung:** Die Qualität des Grundwassers im Grundwasserleiter des Quaterner-Pliozaens in der Trakia Ebene wurde im 5. Rahmenprogramm der Europäischen Union unter wasserchemischen Gesichtspunkten untersucht. Das Ziel war die so genannten BaSeLiNe Konzentrationen, sowie die wichtigsten, die Wasserzusammensetzung bestimmenden Faktoren zu ermitteln. In der Region ist eine detaillierte Grundwasserprobenahme durchgeführt worden und es ist ein breites Datennetz von Makro- und Mikrokomponenten, sowie auch von anderen hydrochemischen Beschaffenheiten aufgestellt worden, um die gegenwärtigen Grundwasserleiterbedingungen zu klären. Die Analyse der vorhandenen Informationen ist mittels moderner statistischer Methoden und Software durchgeführt worden. Unabhängig davon, dass die Region dicht besiedelt mit entwickelter Industrie und Landwirtschaft ist, sind die erforschten Gewässer noch im guten und stabilen Qualitätszustand.

**Schlüsselworte:** Grundwasserqualität, Konzept BaSeLiNe, Grundwasserleiter, Bulgarien

#### Introduction

The Plio-Quaternary aquifer belongs to the Upper-Thracian lowland in south Bulgaria (Fig. 1). The Lowland is a part of the Maritza River basin with the elevation ranging from 400 m to less than 100 m, gradually decreasing to the east and southeast direction. Its predominate part is situated between 50-300 m more than 70%. The Maritza River basin is the biggest on the Balkan peninsula, having area of 53000 km<sup>2</sup> till the river mouth and 21084 km<sup>2</sup> (and length 321 km.) till the Bulgarian state border. The highest Bulgarian mountains surround the basin, while the river spring is below the highest peak at the Balkans, Musala – 2925m asl. The Plio-Quaternary aquifer is the most important groundwater bearing formation with a surface of about 2000 km<sup>2</sup>. The groundwater accumulated in the common aquifer is major water source for the domestic water supply and industries – about 95%, while 5%

depends on surface water. Major water source for the irrigation system are reservoirs, river intakes and groundwater. The area is relatively densely populated with well-developed industry and agriculture.



Figure 1. Location of the Plio-Quaternary aquifer

### 1. Geology and Hydrogeology

The region is part of the northern edge of the Alpine orogenic belt, which is the latest major tectonic event throughout Tertiary, being shallow complicated graben, filled by the materials pertaining to Tertiary and Quaternary (see Figure 2).

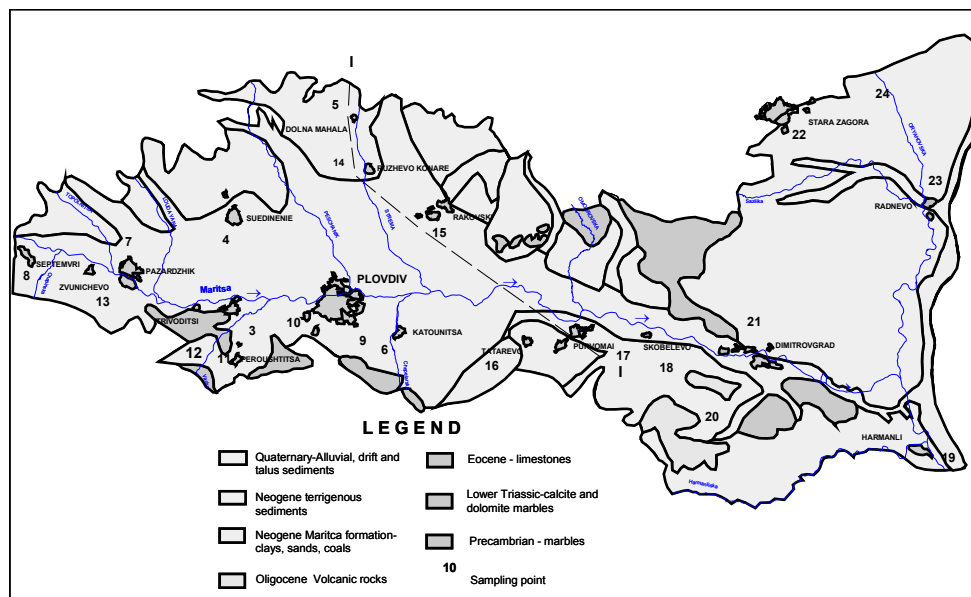


Figure 2. Geological map of the studied area

Precambrian and Paleozoic plutonic and metamorphic rocks outcrop mainly in the mountain areas. Mesozoic formations presented by carbonate rocks are exposed typically at small areas in the southeast parts. Tertiary sedimentary rocks cover the most of that topographically flat area. Paleogene-Oligocene volcanic rocks are outcropping in fewer southern zones. The Upper Eocene is presented by continental molasses-coal-bearing and marine sediments. Pliocene terrigenous sediments are composed of conglomerates, sand, clayey sand and clay ranging from 10-50 to 500 m depending on the depth of the strongly dislocated block basement. Its average thickness is about 150 m. Quaternary unconsolidated deposits are distributed in the mountain foot and along the Maritza River and

its tributaries. Results of previous exploration boreholes show that the depth of the basement rocks ranges from 5-10 meters at small tributaries to more than 100 m downstream the Maritza River.

Quaternary deposits distributed in the plain and hilly part of the region are considered as unconfined aquifer. The Pliocene unconfined aquifer is partially merged to the Upper one mostly in the west and southeast parts, forming common Plio-Quaternary aquifer with an average thickness locally reaching to 200 m. The alluvial sediments in some places are partially isolated due to the existing clay strips forming locally confined conditions. The Plio-Quaternary aquifer has high productivity as its permeability coefficient ranges from 50 to 400 m/d, while the transmissivity values vary between 200-500 to 2000 m<sup>2</sup>/d reaching locally 4000 m<sup>2</sup>/d (Antonov Hr., D.Danchev, 1980). Lower transmissivity values ranging from 100 to 400 m<sup>2</sup>/d are obtained in the Pliocene. Values less than 100 m<sup>2</sup>/d are taken in the Pliocene outcropping north and northeast areas. Groundwater flow hydraulic gradient is 0.003 for the northern part of the aquifer, while it is 0.005 for the southern one. The average multi-annual amount of groundwater discharging to the rivers is about 13 m<sup>3</sup>/s. Groundwater is recharged by several sources as follow: precipitation, the Maritza river and its tributaries' waters during the high flow period, and finally by irrigated water. Groundwater tables range from 0.0 up to 15.0 m depth, being most frequently – 2.0 to 4.0 m below the surface (Machkova M. and D. Dimitrov, 1999).

## **2. Sampling program**

In accordance with the investigation program a total of 22 samples were collected from boreholes in the period 4 - 10 November 2002. All boreholes are constructed in pumping stations providing relatively good spatial coverage over the Plio-Quaternary aquifer in the studied region (Fig. 2). The pumping stations are exploited continuously while water is used for different purposes mainly for drinking and industrial water supply. At the same time the pumping stations are observation points of the National Groundwater Monitoring Network (NGWMN). With the exception of few cases, the samples present a mixture of waters, since they derive from different stratigraphic horizons (Machkova et al, 1994). As a consequence, the variations of the hydrochemical composition might not be necessarily related to the hydro-geochemical reactions along the groundwater flow.

Based on chemical data obtained by the field study as well as historical information available, reliable conclusions about the regional variations of water quality may be drawn. Various physical and chemical characteristics were measured on-site during the field work. Major and trace elements (more than 80) as well as total organic carbon (TOC) was analyzed in the chemical laboratory of the University of Mining and Geology in Sofia. The British Geological Survey analyzed representative set of 18 samples and this way data about a significant number of trace elements were obtained. The chemical determinations coming from those two sources were combined and further used and evaluated for the purposes of this study.

## **3. Historical chemical data**

The set of historical chemical data includes information about 22 observation points (boreholes), all of them belonging to the NGWMN. Chemical data coming from NGWMN cover the period from 1980 to present. Sampling frequency is quite different, mostly seasonal. The selected boreholes are the same, used for the sampling programme in

November 2002, mentioned above. There is limited historical data available about the chemical ingredients. Information about major components exists, whereas that for trace components is scarce.

#### 4. Interpretation of the new sampled data

All plots and tables are based on the new chemical data obtained. That was implemented applying the “Basic Statistics” procedures (STATISTICA, StatSoft, Inc., 2000). Two Trilinear plots were made based on the new set and on the historical chemical information. Concentration equal to the corresponding detection limit has been used for statistical procedures when concentrations were below the detection limit of the analysis.

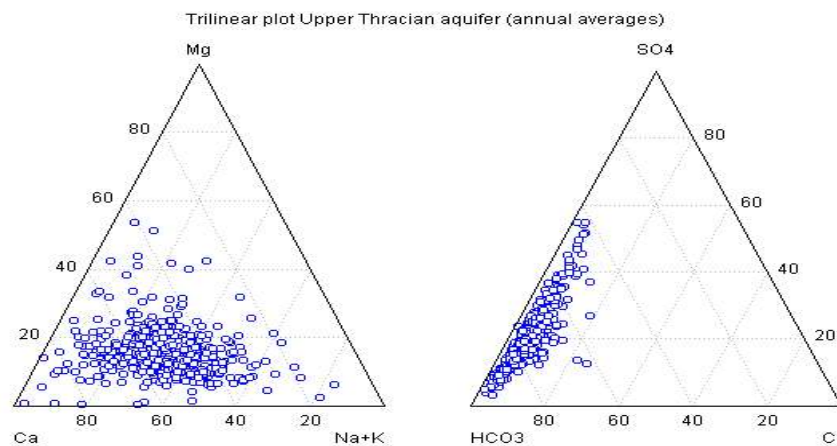


Figure 3. Trilinear plots

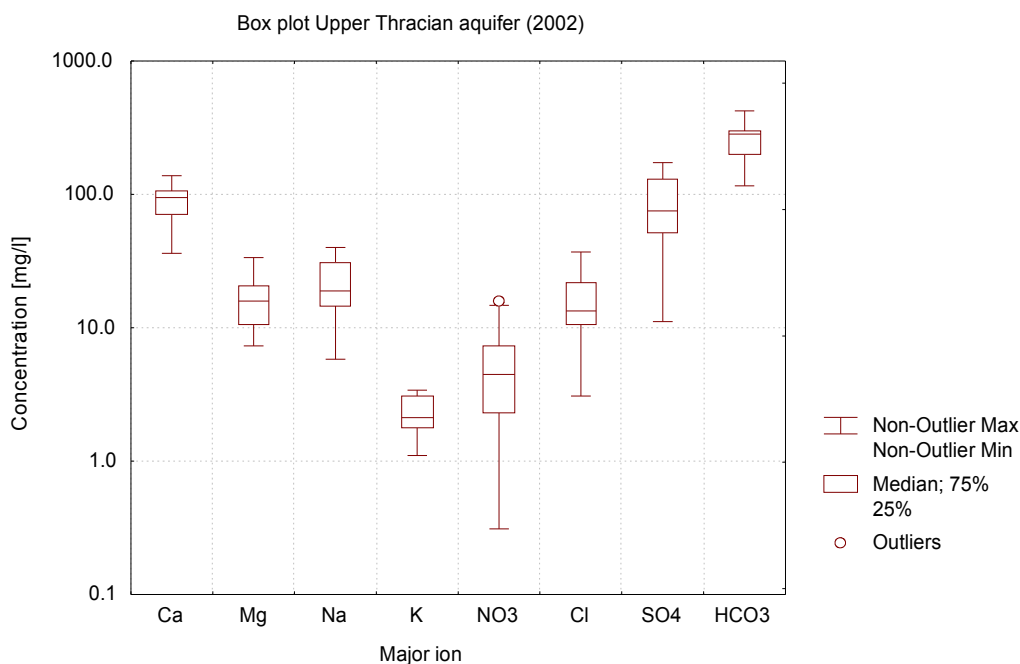
#### 5. Hydrochemical characteristics

The hydrochemical characteristics are summarized by descriptive statistics. The annual averages for the long period are shown graphically in the Trilinear plot (Fig. 3), while the box plots (Fig. 4<sup>a,b</sup>) and cumulative frequency plots (Fig. 5<sup>a,b</sup>) are based on the new data sets. The left graph of Fig. 3 shows quite a big dispersion of the points, without specific grouping at Ca, Na+K and especially Mg axes. That is why, concerning the type of waters we may conclude that the samples are a mixture of waters, since they derive from different stratigraphic horizons.

The waters are fresh with SEC (electric conductivity) varying from 325.0 till 1116.0  $\mu\text{S}/\text{cm}$ , the median value being 644.0  $\mu\text{S}/\text{cm}$ . The temperatures are relatively high (median value 14.7°C) and pH (7.29) and the Eh (320.0 mV) are quite normal, although the dissolved oxygen concentration is relatively low (median value of about 6.30 mg/l). The groundwater in the Plio-Quaternary aquifer is mainly from Ca-HCO<sub>3</sub> and Ca-HCO<sub>3</sub>-SO<sub>4</sub> types and in some places of Ca-Na-HCO<sub>3</sub> type.

#### 6. Major components

From summarized characteristics and box plots on Figure 4<sup>a</sup> the major component concentrations can be seen. The median values of Ca<sup>2+</sup> (91.2 mg/l), Mg<sup>2+</sup> (15.2 mg/l) and HCO<sub>3</sub><sup>-</sup> (277.6 mg/l) all for 2002 are relatively high and together with the cumulative frequency plot showing a normal distribution (Fig. 5<sup>a</sup>) indicate the predominant role of the water-rock interactions.



*Figure 4<sup>a</sup>. Range of major ions*

At the same time the cumulative frequency plots for Na<sup>+</sup>, SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> show more complex distribution, which could signify additional sources of these ingredients, i.e. pollution. Relatively high is also the median value of the base neutralizing capacity to pH 8.3 related to the CO<sub>2</sub> concentration - about 0.30 mmol/l.

## 7. Minor and trace components

The concentration values of the minor and trace components are given in box plots Figure 4<sup>b</sup> as well Figure 5<sup>b</sup>. From the cations Sr<sup>2+</sup> (169.4-1821.4 µg/l; median 415.5 µg/l) and Ba<sup>2+</sup> (12.9-267.7 µg/l; median 57.9 µg/l), released from rocks like carbonate minerals, gypsum and celestite have relatively high and varying concentrations with a complex distribution deviating from the normal one. Similar behaviors have Fe, Zn and Mn reaching median concentration of 8.55 µg/l, 8.3 µg/l and 1.55 µg/l respectively. The variation is very high for the Mn<sup>2+</sup> with values up to 1.09 mg/l in “Septemvri” (Fig.2 - point №8) and even 2.51 mg/l in “Dimitrovgrad” (Fig2. - point №21) vicinities (both in the alluvial terrace of the Maritza river).

From the other minor and trace components As (up to 2.5 µg/l, but with a low median value of 1 µg/l), B (median value of 20.0 µg/l), Cr (7.65 µg/l), Cu (1.45 µg/l), Li (4.0 µg/l), Mo (0.8 µg/l), Pb (0.25 µg/l), Rb (0.22 µg/l), Re (0.05 µg/l), Sb (0.06 µg/l), Sc (2.49 µg/l), Se (1.05 µg/l), V (1.0 µg/l) and especially uranium with a median concentration value of 5.68 µg/l, but rarely 56.33 µg/l in the borehole of “Parvoma” (Fig.2 - point №17) should be mentioned.

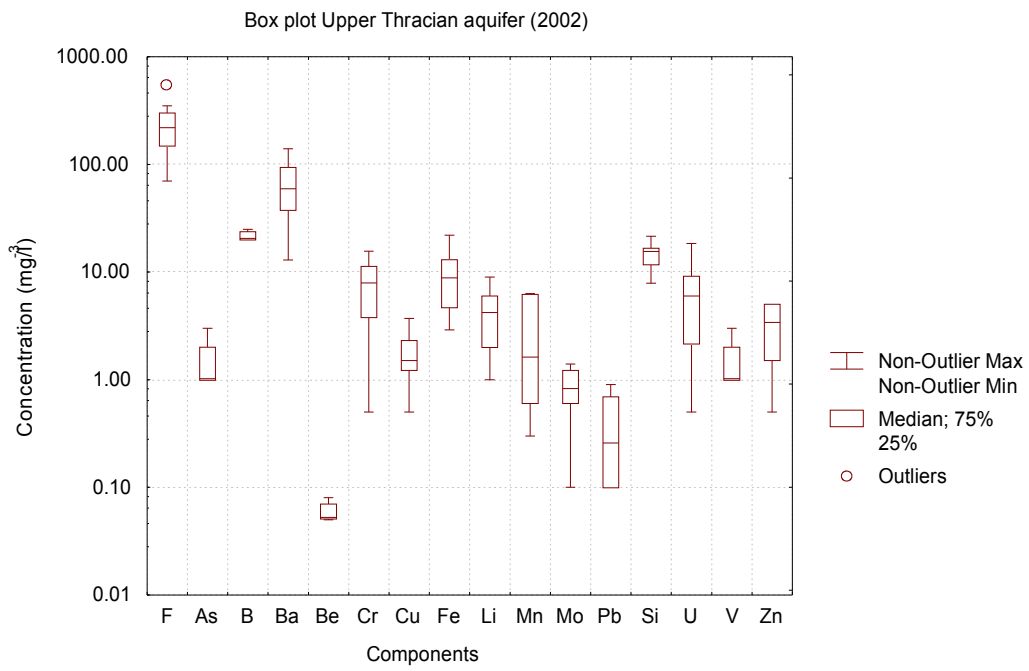


Figure 4<sup>b</sup>. Range of minor ions and trace elements

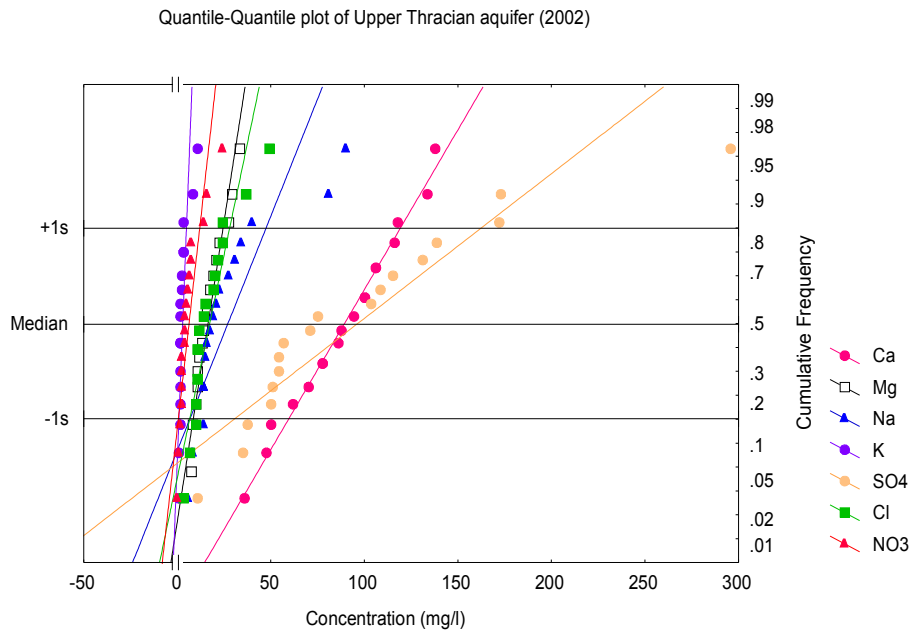


Figure 5<sup>a</sup> Cumulative probability plots of major ions

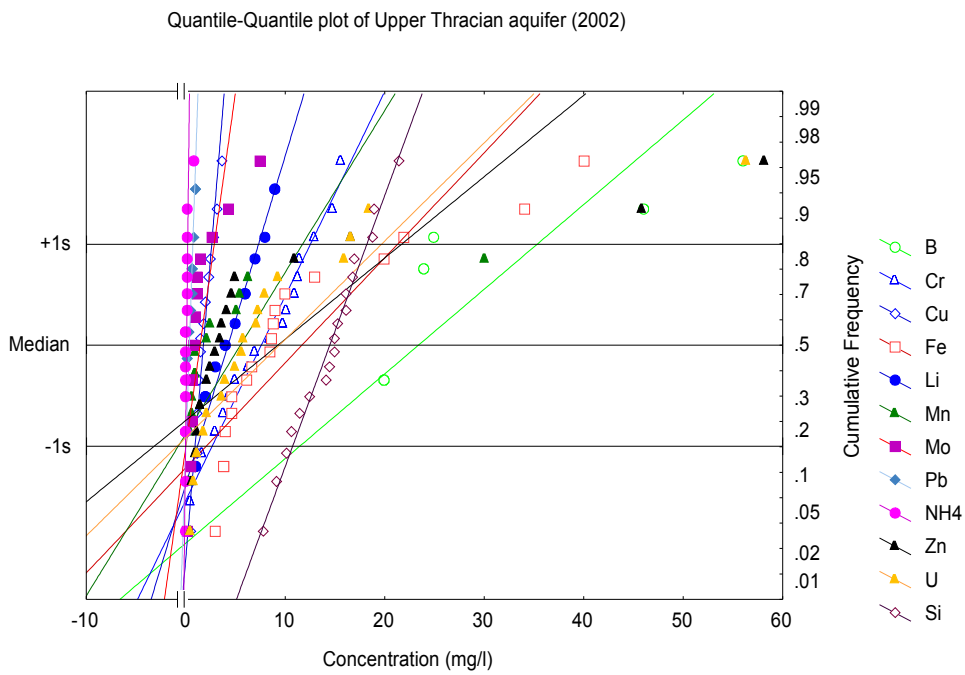


Figure 5<sup>b</sup>. Cumulative probability plots of minor ions and trace elements

## 8. Pollution indicators

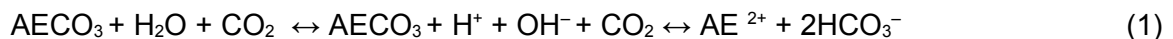
This aquifer is strongly affected by the human activities and in many places the ingredient concentrations are far above the baseline ones. In general, the aquifer is free from organic pollutants, but the presence of  $\text{NH}_4^+$  (median concentration value 0.044 mg/l as N; maximum in point 6 - "Katunitza" – 0.73 mg/l) and  $\text{NO}_2^-$  (0.005 mg/l as N), as well as the high local concentration values of  $\text{Mn}^{2+}$  and partly of Fe indicate the reducing underground conditions in some points near the rivers. In the most cases the redox potential is high enough so that aerobic atmosphere is prevailing.

The nitrates as pollution indicators mainly of environment unfriendly land fertilization in some regions (i.e. point 3 – 107.35 mg/l; point 15 – 69.96 mg/l; point 16 – 64.68; point 20 – 62.00 mg/l) are over the maximum permissible levels.

It should be mentioned that for all samples and respectively statistical estimates TOC is quite low, below the detection limit. At the same time, the median value of COD, as another indicator of organic pollution, is 0.5 mg/l with increasing tendency, as given below.

## 9. Main correlations and hydrogeochemical process

Only positive correlation coefficients are significant: for instance between  $\text{HCO}_3^-$  and pH, DO (dissolved oxygen), SEC,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$ . In this case the predominant hydrogeochemical processes are not only from the type water-carbonate minerals:



(here AE – alkaline earth element), but also with the participation of sodium aluminosilicates i.e. hydrolysis with incongruent dissolution and with a stable secondary formed low soluble mineral-kaolinite takes place.

The values about the thermodynamic calculated characteristics (according to Paces, 1983; Velikov, 1985; Velikov and Panayotova, 2001) are under 1 for the saturation coefficients with respect to calcite and dolomite. Only in point 9, Plovdiv the calcite saturation value is slightly over 1 (1.09) showing minor over-saturation. The role of the aluminosilicate rocks – water interactions can be illustrated by the transformation index anortite-kaolinite, which has values – 7.22 till –5.05.

The relatively high Na/Cl ratio (being mostly 2-5 but for some points even more, i.e. 7.42 for point 12) proves not only the role of this leaching process, but to a certain extent the influence of ion exchange of clay minerals in the aquifer.

For  $\text{Rb}^+$  the ion exchange in the clay zones could be also of importance taking into account also the correlations of the  $\text{Rb}^+$  concentrations with these of  $\text{Na}^+$  and  $\text{K}^+$ , but also of Mo and  $\text{Mn}^{2+}$ . The good correlations of  $\text{Sr}^{2+}$  with  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{Ba}^{2+}$ ,  $\text{Sc}^+$  and Se show that the source of  $\text{Sr}^{2+}$  is not only from carbonate minerals, but also from gypsum and even celestite ( $\text{SrSO}_4$ ).

As mentioned above, the reducing conditions in some places of the aquifer near the Maritza river are due to degradation of organic materials in the insufficient presence of dissolved oxygen. Approximate illustrations of the decreasing DO (dissolved oxygen) and Eh and increasing SEC levels, when approaching the river, could be seen on Figure 6. It could be seen



that getting closer to the main river channel and down to the lower part of the basin waters become more mineralized, while redox potential is getting higher. A sharp redox boundary cannot be located.

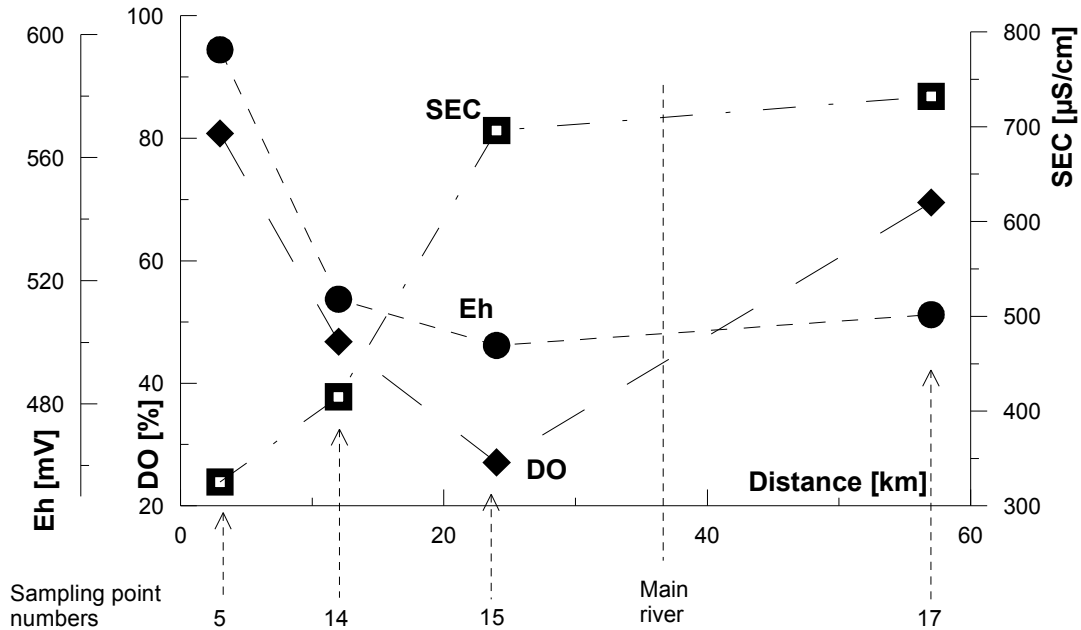
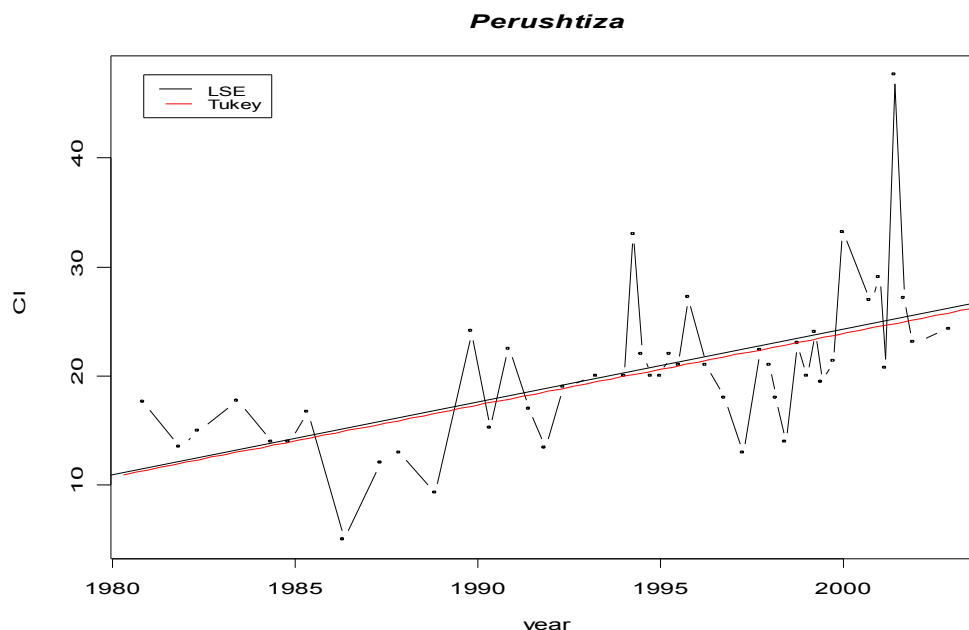


Figure 6. Development of DO, Eh and SEC along the profile I – I'.

## 10. Temporal and spatial variations

Some typical temporal variations in the last 20 years can be seen from Figure 7. The black straight line is the simple regression line estimated by the least squares method (Least squares estimates LSE) while the red dashed line presented in the plots is the Tukey's resistant regression line. Details can be found in Hoaglin et al. (1983).

As a general trend decreasing ground water levels can be reported. The hydrochemical characteristics have different trends in the different points of the aquifer more common being the decreasing of the pH,  $\text{Ca}^{2+}$  values as well weaker shown for the  $\text{SO}_4^{2-}$  values, the predominant increasing of the  $\text{Na}^+$  and  $\text{Cl}^-$  values, as well similar slight expressed trends of COD,  $\text{NO}_3^-$  and  $\text{HCO}_3^-$ . Trend lines evaluated through classical LSE and robust Tukey methods are given as an example in Fig. 7. Although in most cases remaining far below the maximum permissible concentrations the increasing trends are alarming and are to be calculated further in order better to prevent the unfavorable anthropogenic influence on the groundwater quality.



*Figure 7. Trend line of Cl concentrations at point No. 3.*

Another approach to receive more information on the spatial variations of the hydrochemical variables is direct mapping with subsequent drawing contour lines of the concentrations. East longitude, for X axis, and north latitude, for Y axis, are used to position the sampling points. The Kriging method (Golden Software, 2000) is used to produce the grid and establish the contours. Considering the maps drawn on the basis of the 2002 values one could distinguish (Fig. 8) the following particularities of the hydrochemical parameters spatial distribution:

- The role of the main river channel as dividing line in the aquifer is quite well expressed. The lack of exchange of waters between the north and south part of the aquifer is likely leading to two different spatial distributions of the hydrochemical parameters. Unfortunately the number of available sampling points and their distribution do not allow definite conclusion on the matter.
- Some ingredients show spotted higher concentrations on the background of low values. That case clearly shows the influence of the anthropogenic factor on groundwater status there.
- Considerable concentrations of non-ferrous metals and some trace elements are observed. They are relatively well observed over the studied region, which means that the factor causing those concentrations exists in many places of the aquifer. And really it is known that the south mountainous part of the region is rich of poly-metal ore deposits.
- Similar is the situation with some trace elements and especially uranium. Some Pliocene deposits reach of uranium exist in the aquifer. They were for some period of time exploited, leaching uranium by sulfur acid. Although related to the natural background these non-ferrous metals and trace elements are additionally mobilized by the industrial and agricultural activities.

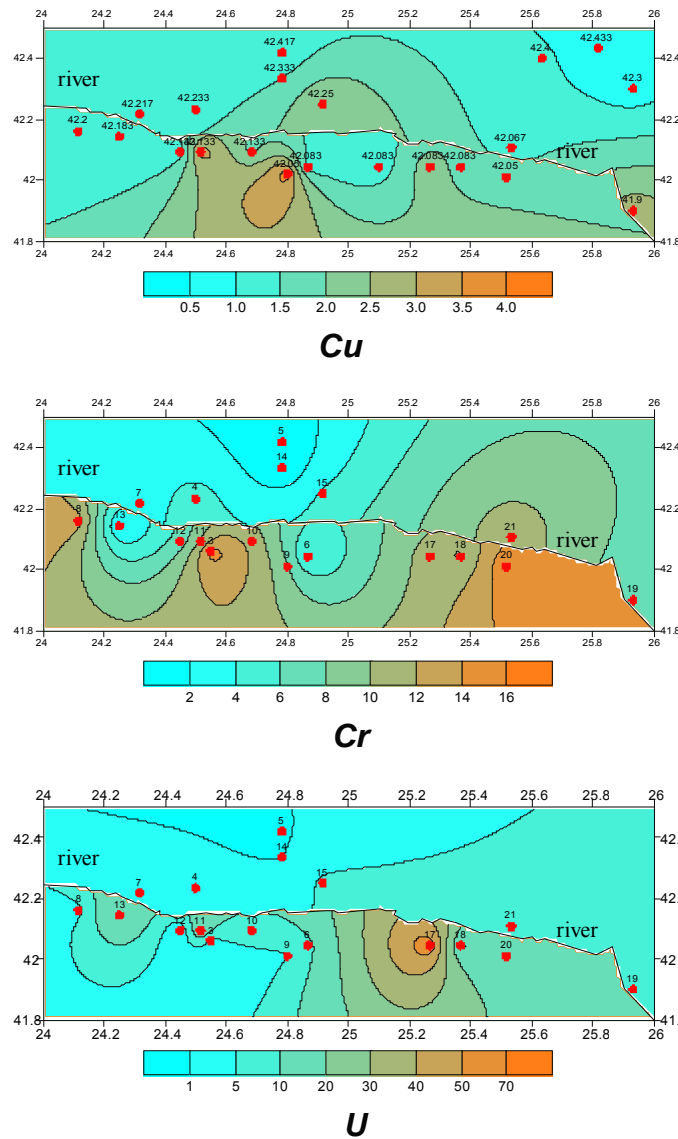


Figure 8. Spatial distribution of some trace elements concentrations [ $\mu\text{g/l}$ ]

## 11. Conclusions

The study of the groundwater quality generally shows that the waters are influenced by anthropogenic activities, but still are of good sustainable quality.

The observed tendencies in different hydrochemical parameters are due to mixed influence of natural and anthropogenic factors. Baseline trends could not be clearly distinguished, as they are in most cases masked with the influence of the anthropogenic factors. Concerning the type of waters we may conclude that the samples are mixture of waters, since they derive from different stratigraphic horizons. The latest can be proved also having in mind the main cations' distribution.

The formation of the hydrochemical composition of groundwaters naturally depends on the carbonate and silicate rocks – water interactions and on the infiltration of fresh river waters close to the main river channel and major tributaries.

The role of the main river channel, as a hydraulic boundary between groundwater bodies located along its both sides, is quite visible, especially with respect to these components, which

variations are caused by anthropogenic factors. Interesting in that respect is the distribution of pH and Uranium, the latter being leached underground by sulfuric acid in the near past.

## **12. Acknowledgements**

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