

# Research on the Degree of Contamination of Surface and Groundwater used as Sources for Drinking Water Production

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*The paper presents detailed results of the analysis of surface water (Mureș river) and groundwater (Criș basin) on the content of ammonium, nitrites, nitrates, arsenic, iron, zinc, cadmium and copper, compared to the maximum values admitted by the current legislation. These waters are sources of drinking water for human consumption, after complex processes of treatment. We have found that tolerance limits are exceeded in the case of ammonium content, arsenic and iron for groundwater and iron content for the surface water. Generally, the groundwater has lower concentrations than surface water, for all elements analyzed.*

*Keywords: drinking water, pollutants, hydrogeology, contamination, UV-VIS and Atomic Absorption Spectrometry*

Drinkable water is used for domestic needs (drinking, cooking, washing), public needs (trade, institutions, maintenance of streets and green spaces, ornamental fountains), the needs of livestock, industrial needs and firefighting.

In the recent specialized literature, there are similar studies dealing with the geochemical and microbiological evolution of water quality indicators, carried on different water bodies [1, 2]. Also, recent studies regarding the water quality from lakes or river systems in South-Eastern Europe have been carried out [3-6].

In order to become drinking water, the water extracted from rivers or from underground wells needs to be subject to a rigorous treatment, whose scheme is dependent on water quantity and quality required by the consumer on one hand, and on the other hand on the available water sources and the percentage of water pollutants from these sources [7-10].

Drinking water quality is regulated by law; water intended for human consumption must comply with maximum permissible values of parameters, these values being presented in table 1 [9, 11].

Based on these considerations, this paper aims to present the results of detailed analyzes of water from the Mureș river (surface water) and Criș basin (water from underground wells) which are used as a source of drinking water for human consumption.

In the same time, knowing the concentration of toxic chemical compounds existing in these waters will be the starting point in determining the proper treatment technology for preparing it to be drinking water.

## Hydrogeological Considerations

In the western part of Romania, Neogene deposits include medium-deep and deep aquifers. The total thickness is higher than 2500 m [12], but only the levels located up to 400 m are of hydrogeological importance for drinking water.

The shallow aquifer (groundwater aquifer) is fed mainly from atmospheric precipitation and surface waters. This presents large variations in terms of flow. The groundwater

**Table 1**  
MAXIMUM PERMISSIBLE VALUES OF CHEMICAL PARAMETERS FOR WATER INTENDED FOR HUMAN CONSUMPTION

Parameters /UM	Maximum permissible values
Arsenic µg/L	10.0
Cadmium µg/L	5.0
Chromium µg/L	50.0
Copper µg/L	100.0
Mercury µg/L	1.0
Nickel µg/L	20.0
Nitrate mg/L	50.0
Nitrite mg/L	0.5
Lead µg/L	10.0
Selene µg/L	10.0
Antimony µg/L	50.0
Aluminum µg/L	200.0
Ammonium mg/L	0.5
Iron µg/L	200.0
Manganese µg/L	50.0
Zinc µg/L	5000.0
pH	6.5 – 9.5
Conductivity, S cm <sup>-1</sup> , at 20°C	2500.0
Turbidity (UNT)	< 5.0

aquifer system consists of one or more layers, with hydrodynamic links between them, usually placed up to a depth of 25-30 m.

The most important groundwater aquifers are located in the Holocene deposits (represented by sandy clay, silts, sand, gravel), which form the river Mureș meadow, and in the upper Pleistocene-Holocene deposits of river Mureș alluvial cone.

In general, the water is drinkable but, due to an insufficient development of the covering layer, the groundwater aquifer is highly vulnerable to pollution. Within the interfluvies, groundwater aquifers located below the reddish clay layers or at the bottom of loess deposits generally have a uniform development and the water is freely available or is slightly ascensional.

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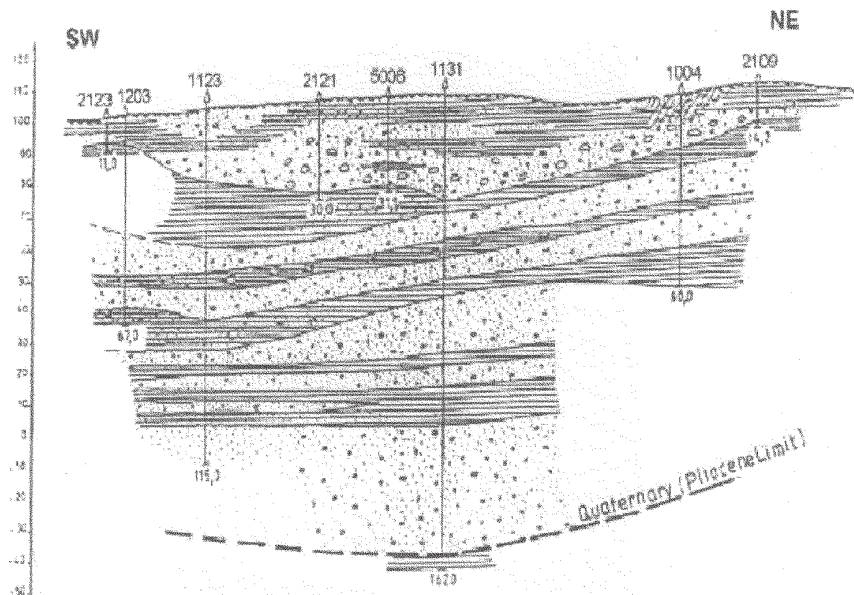


Fig. 1. Geological section through the top of the alluvial cone of the river Mureș [13]

The medium-depth aquifer is situated in porous-permeable deposits of the river Mureș alluvial cone, one of the most important aquifer structures in Romania. It represents the lower part (Pleistocene deposits 50-120 m) of a package consisting of Quaternary layers made of gravels, sands and clays deposited in a torrential regime with specific cross structure.

The geological section in figure 1, shows the space distribution and relationships between different lithological and granulometric compositions on a SW-NE line in the third area of the cone, near its border line.

The deposits within the alluvial cone are covered by loess formations represented by yellow macroporous silts which show limestone concretions.

The hydrogeological particularity of this type of structure consists in permeable horizons separated by clays with lenticular development, and as such the aquifer located near the land surface communicates directly with the medium-depth aquifers of the cone. For this particular characteristic there could not be found different piezometric surfaces for the two bodies, they is an aquifer system with a unitary hydraulic function [14].

### Experimental part

For this study we took samples of water from the Mureș river (surface water) and Criș basin (underground water) that were subject to detailed analysis, determining a number of parameters presented in table 1, absolutely necessary to achieve legal prescriptions for drinking water, such as:

- concentration of ammonium,  $\text{NH}_4^+$ ;
- concentration of nitrites,  $\text{NO}_2^-$ ;
- concentration of nitrates,  $\text{NO}_3^-$ ;
- content of iron, arsenic, zinc, cadmium and copper.

Samples water collection was made from the Mureș River at the entrance in Arad and for those from the Criș basin have been made from several collecting points that are listed in the map as in figure 2.

### Determining the concentration of ammonium ions ( $\text{NH}_4^+$ )

For the determination the concentration of ammonium ions ( $\text{NH}_4^+$ ) of the water samples, as standardized method of analysis was used Romanian Standard STAS - 6328-85.

The principle of determining method for the concentration of this component used in this paper consists in spectrophotometric measuring of the frequency at  $\lambda = 655 \text{ nm}$ , of the blue compound formed by reaction of the ammonium ion with salicylate and hypochlorite ions in the presence of nitroso-pentacianophenate (III) sodium (sodium nitroprusside). Measuring the intensity of blue color formed as a result of the mentioned reactions was performed with a Specord UV-VIS spectrometer, after having first drawing a standard curve.

Establishing the standard curve required the preparation of a solution of ammonia of known concentration, in fact  $2 \text{ mg/L}$ , out of which accurately measured volumes were extracted and diluted with double distilled water. In each of these solutions were added  $4 \text{ cm}^3$  reactive, mixed and then were subject to photocolormetering. The data for



Fig. 2. Location of water sources from Arad County, over which were analyzed the level of impurities

Volume of ammonium standard solution, cm <sup>3</sup> concentration NH <sub>4</sub> <sup>+</sup> = 2 mg/L	Volume of water, cm <sup>3</sup>	C, NH <sub>4</sub> <sup>+</sup> mg/L
0.00	40	0.000
1.00	39	0.050
2.00	38	0.100
3.00	37	0.150
4.00	36	0.200
5.00	35	0.250
6.00	34	0.300

**Table 2**  
VOLUME OF SOLUTIONS USED IN CALIBRATION

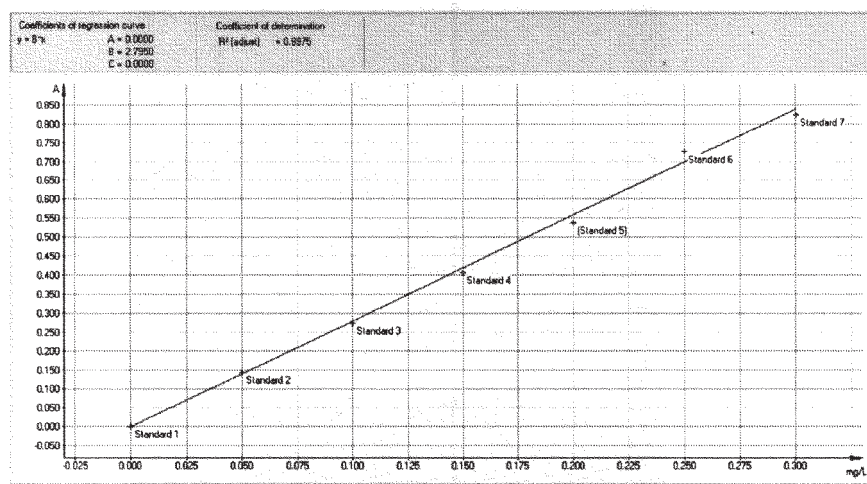


Fig.3. The standard curve for determining the content of ammonium ions

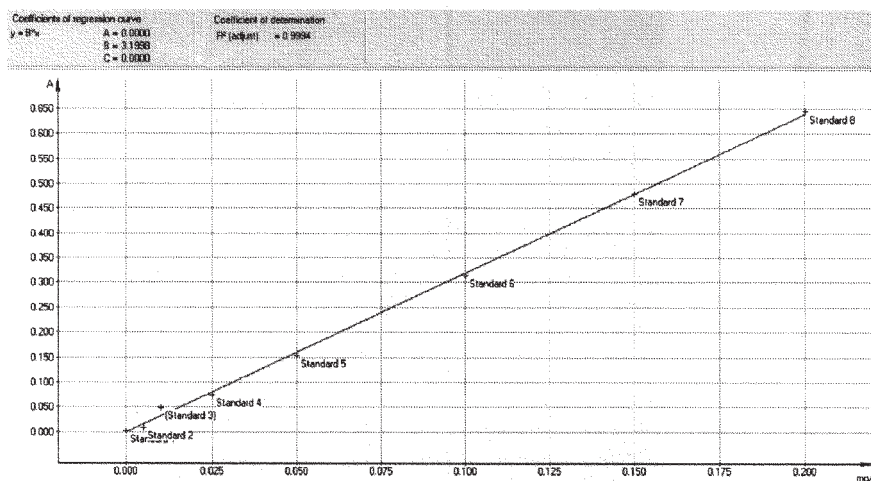


Fig.4. The calibration curve for establishing the nitrites content

obtaining the solutions for the standard curve is listed in table 2.

The data from table 2 were used, following the photocolormetering of the solutions to drawing the standard curve, presented in figure 3, made with WinASPECT PC software (Calibration of the Standard Curve).

Analyzed water samples taken from the Mureş river and Criş basin were subject to the same operations on dilution and treatment with that reagent, after which the color intensity was measured with the same spectrophotometer. Using the standard curve we have determined the concentration of NH<sub>4</sub><sup>+</sup> ions, recorded in table 3.

#### Determining the nitrites content (NO<sub>2</sub><sup>-</sup>)

For the determination of the concentration of the nitrites (NO<sub>2</sub><sup>-</sup>) of the water samples, as standardized method of analysis was used SR EN/ISO 26777/2002 or SR ISO 6777:1996/A99:2002.

The method principle consists in the spectrophotometric measuring of the red colored water, formed in the reaction between the azotizes ions and reagent 4-amino-benzene-sulfonamide in the presence of ortho-

phosphoric acid. The wavelength of the measurement was 540 nm and the calibration was performed using solutions of sodium nitrite known concentrations, the calibration chart being presented in figure 4. Using this method, the nitrite concentrations were determined for the Mureş river water and the water from the Criş basin, the values being listed in table 3.

#### Determining the content of nitrates (NO<sub>3</sub><sup>-</sup>)

For the determination the concentration of the nitrates (NO<sub>3</sub><sup>-</sup>) of the water samples, standardized method of analysis was SR/ISO 7890 – 1/1998.

Also in this case we have used a method that uses the same work principle, meaning a photo colorimetric measuring of a compound formed by the reaction of nitrate ions and the reagent 2,6-dimetilfeno, in the presence of sulfuric acid and phosphoric acid, the wavelength for reading being 324 nm. The calibration was accomplished using solution of nitrate of known concentrations and the calibration curve is presented in figure 5.

Based on the same method we have performed the determination of nitrates content from the water samples

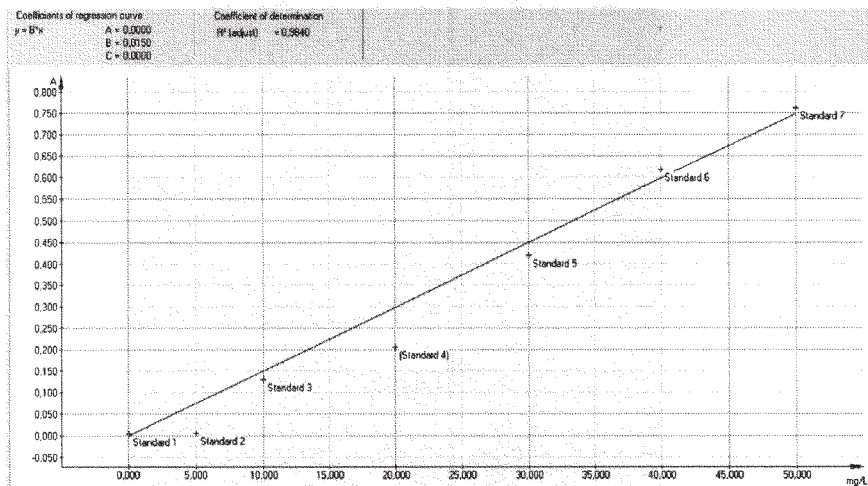


Fig 5. The calibration curve for determining the nitrate content

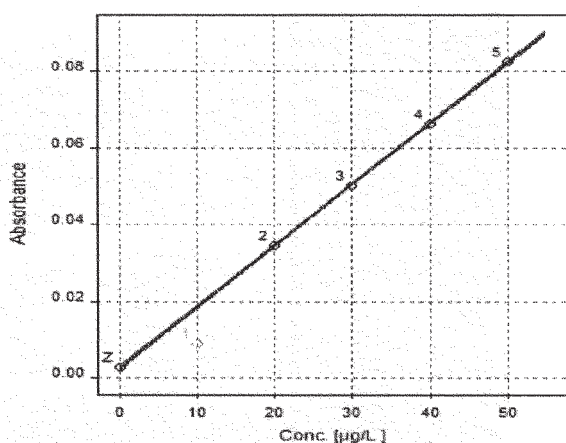


Fig. 6. The calibration curve for determining the arsenic content

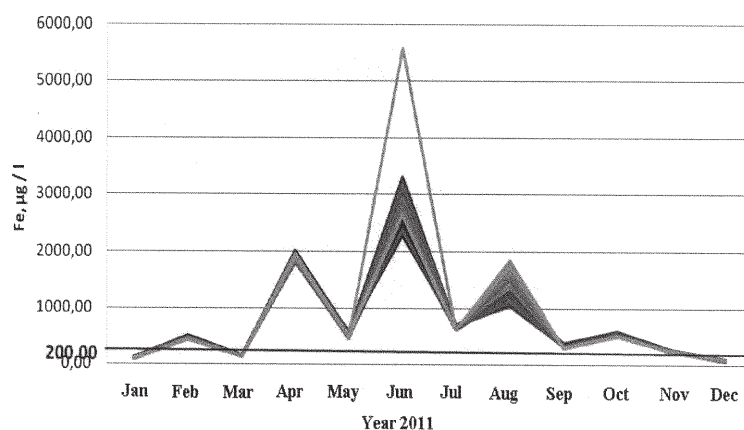


Fig.7. Variation of iron content (Fe), into the Mures river, 2011

of Mureş River and Criş basin, the data being recorded in table 3.

#### Determining the content of As, Fe, Zn, Cd and Cu

For the determination the concentration of the As, Fe, Zn, Cd and Cu of the water samples, standardized method of analysis was SR EN ISO/15586/2004.

The method used to accomplish this task is based on the ability of the metal free atoms to selectively absorb light, the measurement being performed by spectrometry of electro-thermal atomization in graphite oven. Thus, a light source is sent to the heated graphite furnace and since the light is being selectively absorbed by the atoms of a particular metal, its intensity can be measured. The method is applicable for determining the concentration up to 50 micrograms/L for these elements and for Cd can be up to 5 micrograms/L.

The work method consists in injecting into the graphite furnace of the atomic absorption spectrometer a part of the solution analyzed. The furnace is electrically heated, by gradually increasing the temperature, the sample is dried, pyrolyzed and atomized.

The concentration of an element from the sample is also determined with the help of a calibration curve. The calibration was performed for each individual element with a standard calibration solution (double distilled water) and 5 equidistant calibration solutions obtained by diluting the control solution of known concentration (50 g/L).

The control samples were inserted into the measuring equipment along with a range of appropriate modifiers solutions for each item as follows:

- solution 0.1 g/L Pd(NO<sub>3</sub>)<sub>2</sub> and HNO<sub>3</sub> 15% for determining As and Zn;

- solution 0.05 g/L Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and HNO<sub>3</sub> 17% for determining Fe and Cd.

The calibration curve for establishing the arsenic content, for example, that was the basis of performing the analyses of the water samples from Mureş River and Criş basin are presented in figure 6.

For the determination of the other components, meaning iron, zinc, cadmium and copper, there were used similar calibration curves, whose aspect is similar to the one from the arsenic analysis. Using this work method we have obtained the concentration of heavy metals from the analyzed samples, the results being also recorded in table 3.

#### Results and discussions

The data on concentrations of the elements listed above, determined on water samples taken from the Mureş river (surface water) and Criş basin (underground water) are listed in table 3 and represent an average for those 12 determinations carried out throughout 2011. In this sense, both for surface water and deep water, beforehand was made a total of 16 variation graphs of concentrations of toxic elements over a year, one for each analyzed element.

The data listed in table 3 represents the average annual values of these concentrations calculated based on data from these graphs.

We selected from carried graphical representations only those relevant graphs where pollutants exceeding legal concentrations and are presented in figures 7-10.

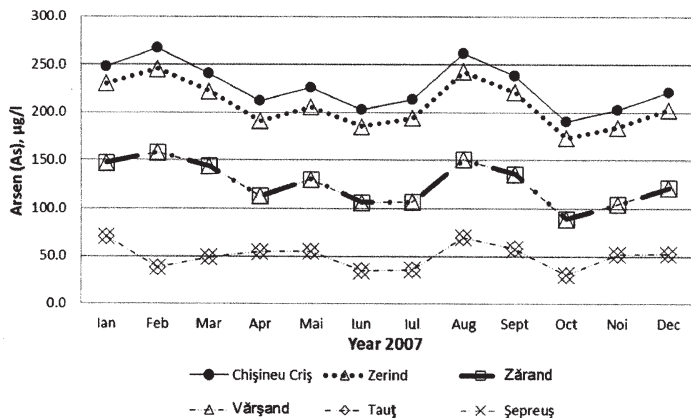


Fig 8. Variation of ammonium (NH<sub>4</sub>) content in aquifer structure of the Cris hydrographic basin, 2011

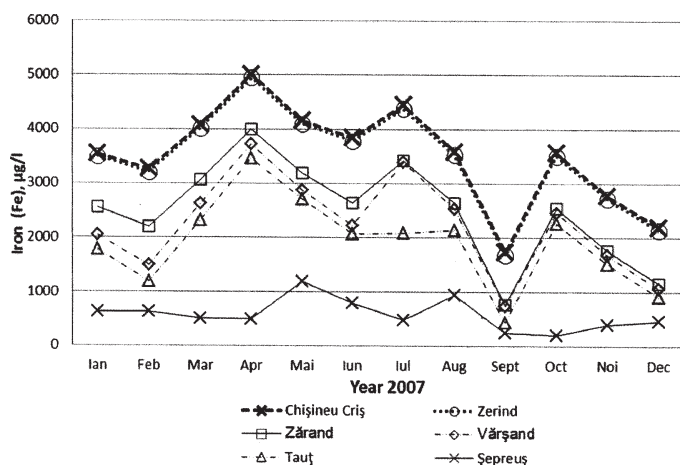


Fig. 9. Variation of arsenic (As) content in aquifer structure of the Cris hydrographic basin, 2011

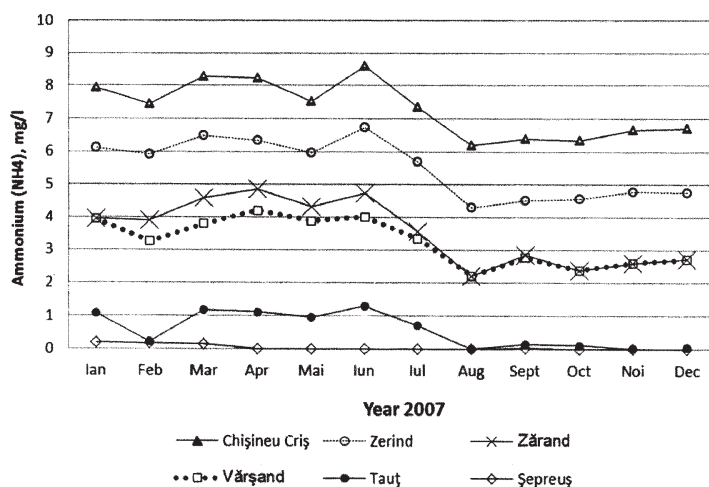


Fig.10. Variation of iron (Fe) content in aquifer structure of the Cris hydrographic basin, 2011

Element/ion	U/M	Value obtained for surface water	Value obtained for underground water	Maximum value permitted by law
NH <sub>4</sub> <sup>+</sup>	mg/L	0.207	0.626	0.500
NO <sub>2</sub> <sup>-</sup>	mg/L	0.128	0.016	0.500
NO <sub>3</sub> <sup>-</sup>	mg/L	23.700	4.300	50.000
As	µg/L	5.800	23.600	10.000
Cd	µg/L	0.100	0.100	5.000
Cu	µg/L	16.500	3.000	100.000
Fe	µg/L	773.200	472.500	200.000
Zn	µg/L	51.800	36.600	5,000.000

**Table 3**  
THE VALUES OF THE ELEMENTS  
FROM THE SURFACE AND  
UNDERGROUND WATER

From the chart present in this figure results that the highest values of iron concentration was recorded during the period of year with high precipitations (April-September). The mountain course of Mureş river collects iron impurities entailed from the mountainsides during the summer rains.

The analysis of graphs from figures 8-10 shows that changes in concentrations of pollutants depend especially on geographical area of analysis points and the most

significant deviations are recorded in the plain areas while in the mountain areas variations are insignificant.

The discussion of these results shows that there are differences between concentrations of elements for the two water sources. Thus, groundwater, in most cases, have lower concentrations of the elements studied compared to the same elements from surface water. Differences were observed only for ammonium ion concentration and for arsenic concentration.

At the same time it may be observed that, with few exceptions, the concentrations determined for most elements, both for surface water and groundwater, falls within the limits set by law. Exceptions were noted referring to ammonium and arsenic content from groundwater water and the iron concentration in both cases.

The data obtained by performing the current analyzes have shown that for critical cases, i.e. concentrations exceeding limits established by law, there are required special technologies leading to a reduction of the target elements, i.e. decreasing the concentrations of ammonium, arsenic and iron for ground waters, respectively the iron content for surface water.

The specific technologies for these cases are the subject of other paper from this domain.

## Conclusions

The data obtained lead to the following conclusions:

- the surface waters present concentrations that exceed the limits permitted by law for the iron content;
- for the groundwater, the pollutants that exceed the limits permitted by law are the ions of ammonium, arsenic and iron;
- in general, the in depth waters present lower concentrations of the analyzed pollutants than the surface waters;
- annual variations in concentration of analyzed elements for surface water depend on the collecting period of samples (weather conditions, droughts or rain);
- for underground waters these variations depend especially on the area of analysis points. The most significant deviations from the average is recorded in the plain areas while in the mountain areas variations are insignificant;
- for the cases where the content of the analyzed substances exceeds the legal limits there will be foreseen special technologies in order to reduce their concentration, within the limits allowed by the law.

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