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RESEARCHES ON THE POLLUTION OF UNDERGROUND WATERS IN A CERTAIN PART OF GALATI DISTRICT

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ABSTRACT

The paper underlines the importance of monitoring the quality of the underground waters and presents the experimental results as regards the pollution of underground waters in a certain part of Galati district. The final target of underground waters quality monitoring is to design quality and quantitative prediction models and provide monitoring and optimization programs for environment investigations. Much interest is currently attached to the rehabilitation of, aquifer.

KEYWORDS: contaminants, underground waters, monitorisation, quality

1. Introduction

Since water quality is a world wide priority and the only pollution -free water source is the underground reservoir, avoiding its contamination is crucial for mankind. The underground water contamination is associated with a multitude of unpleasant aspects such as taste, smell, colour, hardness, existence of microroganisms and toxic, flammable or explosive matter. Underground water contamination may render impossible the use of, aquifer for longer periods of time, such as decades or even centuries. This is mainly due to the very low velocity of the underground waters. Due to the underground and surface waters inter-influence there is a strong interdependence between their qualities as well. The surface waters represent boundary conditions for the underground range, both from the hydraulic and contaminant concentration viewpoints.

Hydrologic cycle

Water features higher mobility than lithosphere but lower than the atmosphere. Such mobility implies physical and even chemical transformations and is easy to take place according to certain physical laws. At planet scale, the hydrosphere is a functional system where sun and/or earth energy penetrates into. Said energy generates a continuous movement of waters, thus forming certain regular or periodic circuits. It is common knowledge the saying „water natural circuits”. In more general terms, this means that water on ocean and continent surfaces evaporates, gets higher and precipitates as rain and snow thus coming back to the ocean either directly or through running waters and iceberg.

Subprocesses specific to the hydrologic cycle

Precipitations
Dams
Surface drainage
Infiltrations
Flowing into unsaturated soils
Flowing of underground waters through saturated soils
River flowing
Evaporation

The basic pollution sources for the underground waters [1, 2] are:

1. Excessive extraction from deep wells (more than the underground water supply)

2. Contaminants penetration into underground water through surface waters:

a) from house basements or disposal of waters;

b) from industry effluents (waste water, insufficiently filtered);

c) from solid garbage mixed with water;

d) from excessive use of pesticide and fodders in agriculture ;

e) from accidental leakages.

3. excessive salinity. This is caused by low precipitations unable to feed the underground water supply.

4. Pollution caused by insufficient drainage systems.

5. Pollution caused by filtering plants, unsuitably operated.

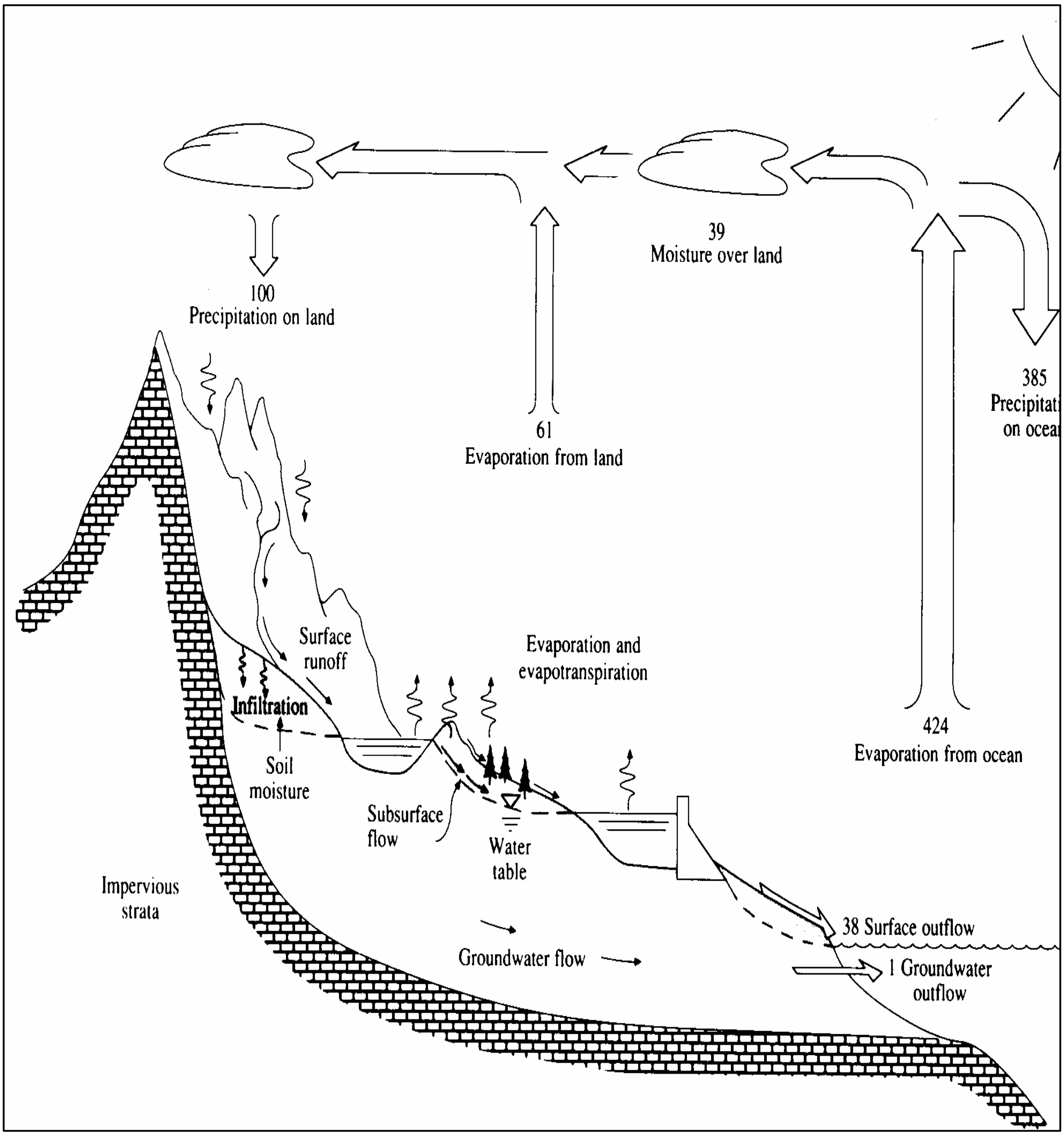

Fig.1. *Hydrodynamic cycle acc. to Chow et al., 1988, Water circuit on Terra.*

Pollution sources

They can be localized: on the terrain surface or underground; above the underground water level; under the underground water level.

2. Evaluation methods

An adequate approach to a pollution problem implies:

1) data acquisition and processing;
2) conceive and use the prediction models
3) check how prediction functions.

The Romania’s total water resources are about 40 billions m^3/year, out of which, under the present hydrographic arrangement, approx 13 milliards m^3/year. The water resources from inland rivers amount to only 5 billions m^3 / year under natural environment and almost double under various arrangements; it should also be added 3 billions m^3/year of underground water and about 10 billions m^3/year supplied by the Danube. In general, the pollution sources and main contaminants are the same for both surface and underground waters; also similar are the impact and measures taken to improve water quality.

2.1. Characteristics of water monitoring systems

The water monitoring systems aims at controlling the quality of the hydrographic basin waters (including rivers, lakes, gulfs), in seas and oceans along with underground, thermal and mineral waters [4].

Water monitoring involves various types of measurements:

-chemical measurements to determine the dissolved oxygen, suspension matters, nutrients, oils , metals, pesticides , etc.;

- physical measurements to determine temperature, flow rates, colour, turbidity;
- biological measurements to estimate the variety and abundance of aquatic plants and animals , and also the testing organisms capacity of surviving in certain water samples .

As regards the time taken to monitor water quality , there is:

- permanent intensive monitoring performed in plants (waste water filtering, drinking water treatment);
- temporary or seasonal monitoring – beach survey in summer, for example;
- emergency monitoring– accidental contaminants leaks.

The most important objectives of a water monitoring system are:

• Determining water general features and identification of its modifications and tendencies in time;

• Identification of specific problems or emergency cases likely to affect water quality;

• Collect information (providing data bases) in order to further develop contamination prevention and fighting programs;

• evaluate whether the target of some programs (eg implementation of pollution control systems) has been reached;

• to promptly cope (by warning systems) with accidents/natural calamities, leakage, heavy rains, floods.

Some monitoring systems can achieve simultaneously part of these objectives, others are designed for a particular task/target. As a principle, national entities for environment protection and pollution prevention submit the pollution management and control programs to the local agencies and support them in developing said programs and reporting the results.

2.2. Methodology of water quality control

Water quality research involves several aspects [5}:

a) establishing the research objectives.

The objective of the research may be monitoring the drinking water quality, the factors influencing the water quality and removal of those elements likely to harm people’s health.

b) establishing the main indicators or parameters being monitored;

Two elements are taken into account: types of indicators and their level. The former is usually established depending on the nature of the water being investigated (drinking, surface waste waters). The number of indicators should not be too large so as to make results interpretations easier.

c) establishing the analysis methods

All qualitative and quantitative methods of the analytical chemistry can be applied taking into account the following criteria:

■ an as small as possible detection limit (this is the min. concentration detectable by 95% probability);

■ high sensitivity to allow for the deceleration of the smallest variation, inside the sample, of the substance concentration (sensitivity is estimated by the measurable distance from the parameter being measured);

■ high selectivity, which means to avoid interference of other substances;

■ accuracy (the values obtained should be as close as possible to the actual concentrations in the sample);

■ fastness (to allow for the determination of the substance in the shortest period of time).

One element that should be taken into account is the degree of difficulty of the method especially when analysis is very frequently performed. Both manual and instrumental methods can be used. The composition of the water sample should reflect the composition of the water being sampled. The sampling place may differ according to the use and objective pursued: water distribution network- in the case of drinking water; inlet and outlet of the water filtering plant to monitor its efficiency etc. Moment and frequency of sampling depend on various parameters such as: water quality, distribution regime, source flow rate, etc.

There are:

■ instantaneous samplings (single samples), when parameter variations are low and measurement is performed manually;

■ permanent samplings (average samples), when parameters variations are high and instruments are used for the purpose of measurement.

Establishing unitary systems of terms to express results. This should be unitary so that the results may be correlated for a further relevant conclusion. In short, the general characterisation of waters and water quality control enable an overview estimation and determination of certain physical, chemical, bacterial and biological features.

2. 3. Water sampling

Sampling is an extremely important stage in the water physical-chemical analysis process because sampling can affect the analysis results. Therefore the samples should be relevant and sampling should not cause alterations of water compositions and quality because of improper techniques or inaccurate conditions for material preparation.

Sampling vessels must be cleaned to remove organic matter or other impurities likely to alter the sample composition.

Upon sampling, the bottle is rinsed 2-3 times in the water to be sampled, then is completely filled with this water and sealed off so that no bubbles should remain inside the bottle.

Sampling procedures depends on the water source, namely:

- water is collected from the water supply network after the tap has been cleaned inside and outside with a clean buffer and the stagnant water flows freely through the pipeline for about 5 min.;
- in the case of intermittent supply, one sample is collected from the first jet so as to have the first water passing through the tap and another sample is taken after two hours’ continuous flowing;
- in case of storage reservoirs, sampling is performed at the reservoir outlets;
- in pumped-water fountains, water sampling is performed after 10 minutes’ pumping;
- in bucket fountains, water sampling is carried out by immersing the bucket 10-30 cm deep under the water surface and then water is poured into the sampling bottle;
- in case of surface waters , sampling is performed by fastening the bottle into a special holder which provides the necessary weight to the bottle to easily go down under the water level. These sampling devices allows bottle opening only when it has reached the required depth. Sampling is carried out along the water stream where depth is maximum, upstream from any affecting effluent and downstream where there is a total blending of the receiver and the effluent ;
- in case of waste waters, single/unique, average and proportional average samples are taken.

As regards the unique samples, they are sampled once, either from the general effluent, from the distinct sectorial effluents (eg. industrial waters), or from the partial effluents of a certain sector or a certain institution (in case of sewage and households wastes). The average samples are taken at 30-60 minutes intervals in preset amounts and stirred together in a common bottle.

For average proportional samples, water is also sampled at 30-60 minutes intervals but in various amounts proportional to the effluent flow rate and subsequently stirred together into a common bottle.

Each sample should be accompanied by a sheet containing the most important data: date and place of sampling, water depth and temperature, the analysis objective, etc.

Three systems can be used:

- water sampling device for volatile substances, associated with a closed-loop stripping device ;
- adsorption system based on macroporous resins;
- liquid-liquid extractor.

The last two devices can operate at various pH values. An extraction cell is less sensitive to the presence of solid suspensions than resins; on the other hand, resins allow for the recovery of a large number of compounds (eg. Humic acids).

2.4. Water samples preservation

Since water can change its chemical composition due to oxidation-reduction processes, microorganism operation and ion exchange between water and vessel walls, it is recommended to have an as short as possible interval between sampling and analysis (max. 4 hrs).

Temperature and pressure changes may result in loss of gaseous substances (O_2, CO_2, H_2S , CI_2, CH_4), this is the reason why it is recommended that gas measurements be performed at the sampling site or the water samples be treated with various reactants for preservation purpose.

Thus, to prevent metal ion deposition (Al^{3+}, Fe^{3+} , Cd^{2+}, $Mn^{2}+$) by hydrolysis, mineral acids are added.

The pH or hydrogen exponent (Sorensen) is understood as decimal logarithm of the hydrogen ion activity with changed signed:

$$pH = -\lg a_H$$

The water pH plays an important role in the vital processes of vegetal and animal organisms, human body and industrial processes.

2.5. Toxicity of substances

The toxic substances are „ exogenous or endogenous substances which act chemically upon organisms, in small quantities, causing vital malfunctions”. The ammonia reaches the rivers through waste waters containing ammonia and ammonia salts discharged from coke factories, chemistry and food industries. The aqueous ammonia solution features basic reaction, while ammonia salts dissociate according to the equality :

$$NH_4^+ + OH^- \longrightarrow NH_3 + H_2O .$$

With higher values of the pH the amount of free ammonia increases and with low pH values, there is an increase in the amount of ammonia ions. Wuhrmann and Woker’s researches have shown that the ammonia ions are not toxic for fish and ammonia salt toxicity is given by the ammonia molecules (Liebmann, 1960) Toxicity also depends on the amount of free CO_2 in water due to its influence on pH ; an increase in CO_2 leads to lower ammonia toxicity.

B) Cyanides have a very harmful influence on aquatic organisms. When discharged into water, soluble cyanides are hydrolized forming the cyanhydric acid, which penetrates the breathing apparatus of underwater organism, having a harmful to lethal effect on the breathing enzymes.

The toxicity of the cyanhidric acid solutions and soluble cyanides is accounted for by the action of nondissociated cyanhydric acid molecules which have a higher capacity of penetrating the tissues than ions.

The soluble cyanides hydrolyzes in water according to the scheme:

$KON + H_2O \longrightarrow K^+ + OH^- + HON$

The intensity of dissociation, implicitly the toxicity, are influenced by the pH of the solution. As the pH increases, the dissociation is higher and consequently the toxicity decreases.

Cyanides of heavy metals, together with alkaline cyanides form cyanidic complexes which also have a toxic action on hydro-organisms.

The cyanhydric acid and its salts have a harmful effect on the biological processes in the surface waters, causing inhibition of their self-filtering capacity; also, they cause inhibition of the biochemical processes in the biological systems in the wastes waters (Liebmann).

C) the phenols, hydrolixic derivatives of the aromatic hydrocarbons, fall into two categories : monophenols and polyphenols.

Phenols have a harmful effect on aquatic basins, implicitly on aquatic organisms, by:

-Consuming the oxygen dissolved into water;

-Giving water specific unpleasant taste and odour;

Affecting aquatic flora and fauna even down to decay. The degree of phenol toxicity vary much a major role being played by hydroquinone and least harmful being fluoroglucine. An increase in temperature makes phenols even more toxic.

Phenols combined with one another or with other chemical substances have higher cumulative toxic action.

D) Oil products are the most widely spread dirty agents of both surface and underground waters, giving water an unpleasant taste and odour. Water contaminated with such substances cannot be used as drinking water or food industry, irrigations, nautical sports. Directly, oil products act either mechanically preventing breathing and other physiological processes, or attacking cell membrane due to their toxicity of lipoids nature. Naphtenic acids are also toxic and affect the nervous systems and the skin irrigation net.

E) Heavy metals. The salts of heavy metals represent a very serious contamination source for the surface waters, because of their toxicity and stability, causing disturbances of the biological balance with negative effects on the self- filtering process, fish stock and various usage of water.

In the heavy metal contaminated rivers it has been found a decrease in the number of species and individuals, along with a certain gradation in the different groups and species of organisms in terms of their resistance to a certain metal ion.

2.6. Analysis of the indicator „suspension”

Suspension matter represents substances which are insoluble in water, can be separated by filtering, centrifugation or settling (max 2 mm diameter) According to density, suspension matter can be settled and unsettled (including floating matter). The method basically consists in separating suspensions by filtering and centrifugation, followed by drying and weighting the residues down to their constant mass. The precipitable suspension matters can be determined by two methods: volumetrically; gravimetrically.

The principle of the volumetric method:

The precipitable suspended matters are determined by free precipitation within a given time interval in a graded cylinder or in Imhoff cone. Devices/instruments required : glass Imhoff cone, 1000 cm^3 , of 1 cm^3 divisions, graded glass cylinder , de 1000 cm^3, han-holder rod, and disk for stirring purpose. The principle of the gravimetric method: precipitable suspended matters are determined by the difference between the total suspended matters in the sample and the unsettled suspended matters , after free settling/precipitation, during a given time.

2.7. Analysis of indicator „CBO5”

The biochemical oxygen consumption after n days (CBO_n) is the massive concentration of dissolved oxygen under specific conditions by biochemical oxidation of the organic and/or inorganic substances in water. „n” is the incubation period, this being equal to 5 or 7. The working sequence is as follows: the sample being analyzed is brought to 20 grades Celsius and aerated if necessary. If aerated, the sample is left to rest for about 15 min. The air bubbles and possible supersaturation in oxygen are eliminated. Determination by measuring the dissolved oxygen – iodometric method:

After incubation the concentration of oxygen dissolved in each bottle of the first series is measured.

The bio-chemical oxygen consumption after n days, expressed in milligrams per litre, is calculated by the equation :

$CBO_n = (C1 – C2)$,

where: C1-concentration of dissolved oxygen in the sample being analyzed at the initial moment in milligrams per litre; C2-concentration of oxygen dissolved in the sample being analyzed after n days, in milligrams per litre.

2.8 .Analysis of indicator „CCOCr"

The chemical consumption of oxygen is the oxygen concentration equivalent to the amount of potassium dichromate consumed by the matter dissolved and in suspension, when a water sample is treated with this oxidant. The chemical consumption of oxygen in water, determined by the potassium dichromate, may be regarded as an approximate method of the theoretical oxygen consumption, which represents the amount of oxygen consumed by total chemical oxidation of the organic compounds to inorganic ones.

3. Experimental results

Considering the particulars of the water quality monitoring and the associated research methods, the experimental results as regards the underground waters contamination in Chiajna, Galati district, have been obtained and interpreted from three stations, figures 2 ÷ 10.

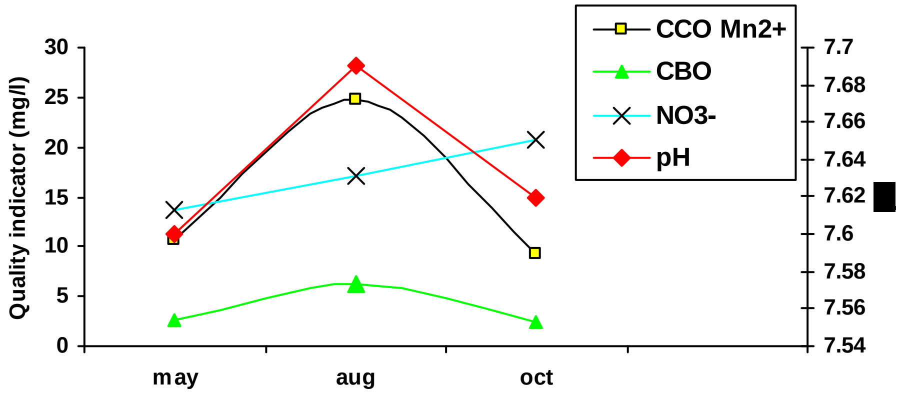

Fig.2. *Values of pH, $CCOMn^{2+}$, CBO_5, NO_3^- of underground waters, station 1.*

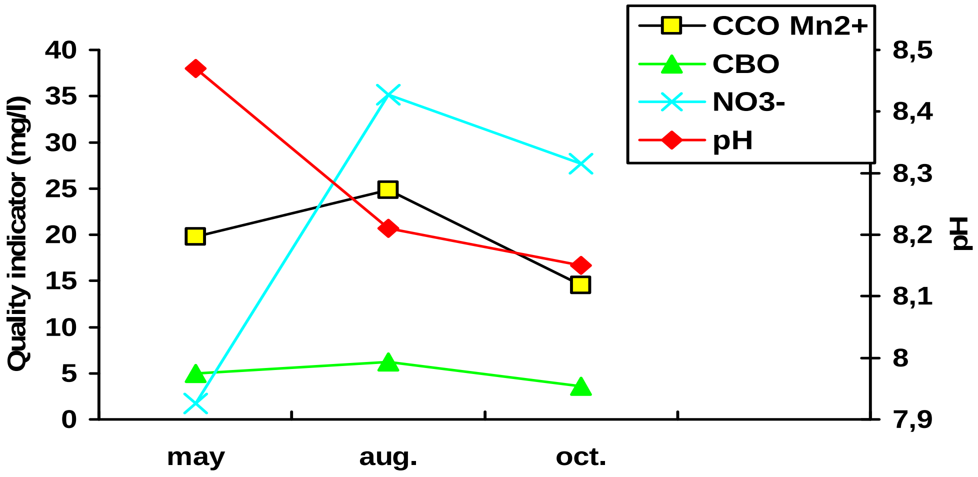

Fig.3. *Values of pH, $CCOMn^{2+}$, CBO_5, NO_3^- of underground waters, station 2.*

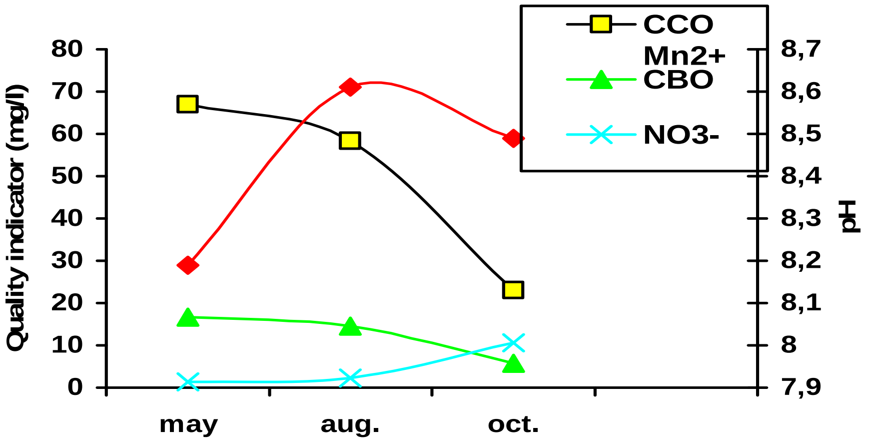

Fig.4. *Values of pH, CCOMn^{2+}, CBO$_5$, NO$_3^-$ of underground waters, station 8.*

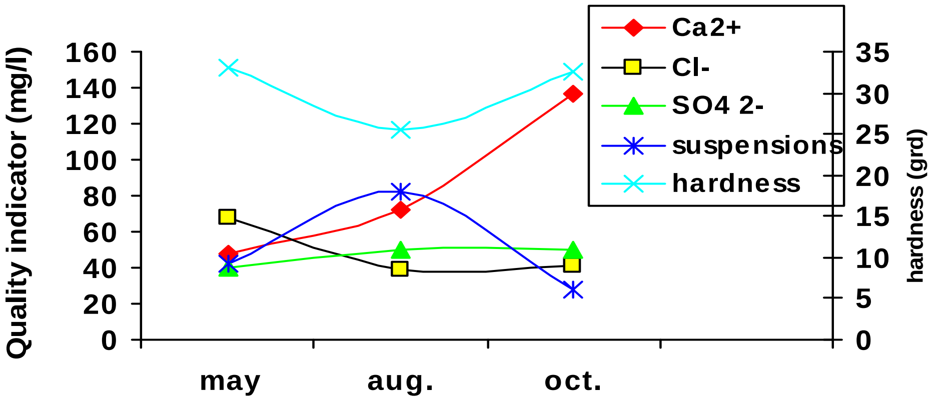

Fig.5. *Values of Ca^{2+}, Cl$^-$, SO$_4^{2-}$, water hardness, suspensions of underground waters, station 1.*

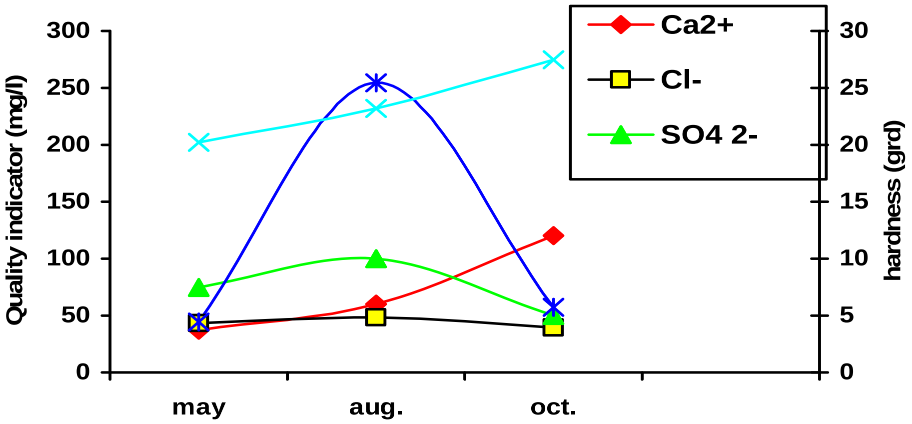

Fig.6. *Values of Ca^{2+}, Cl$^-$, SO$_4^{2-}$, water hardness, suspensions of underground waters, station 2.*

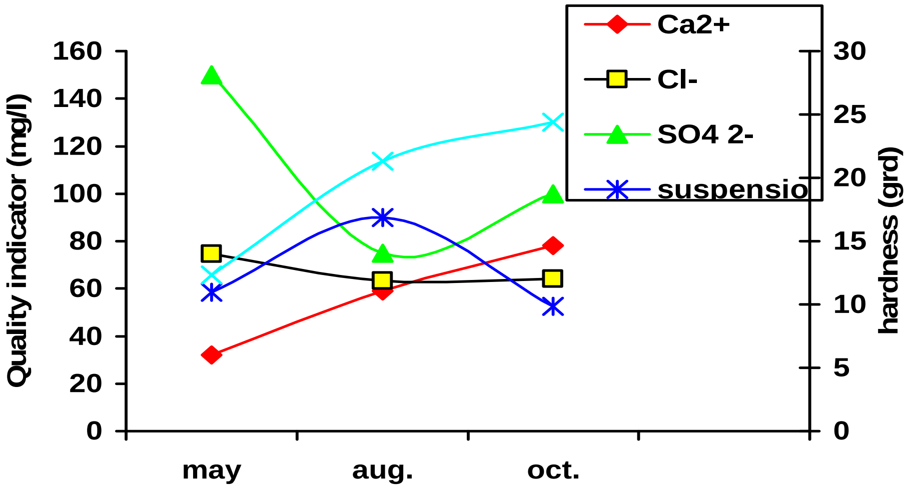

Fig.7. *Values of* Ca^{2+}, Cl^-, SO_4^{2-}, *water hardness, suspensions of underground waters, station 8.*

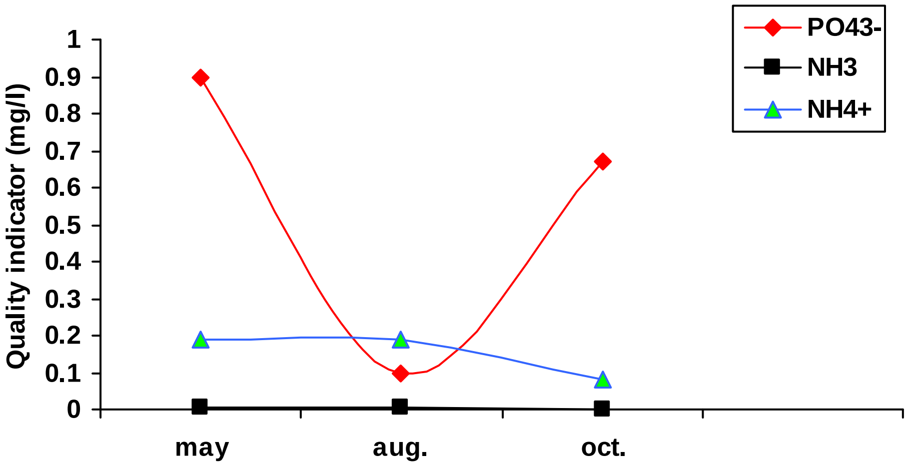

Fig.8. *Values of* PO_4^{3-}, NH_3, NH_4^+, *of underground waters, station 1.*

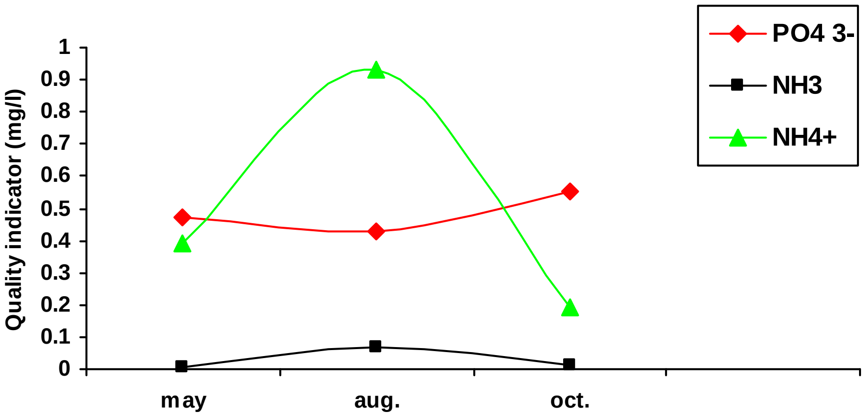

Fig.9. *Values of* PO_4^{3-}, NH_3, NH_4^+, *of underground waters, station 2.*

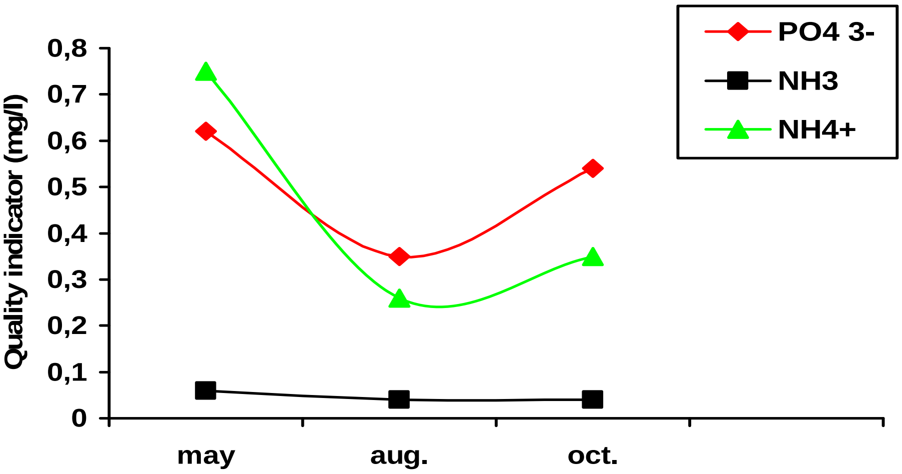

Fig.10. *Values of PO_4^{3-}, NH_3, NH_4^+, of underground waters, station 8.*

4. Conclusions

Underground water quality indicators vary depending on the moment when and the site where the related measurements are made;

The content of NO_3^- increases in time, the largest amounts being reported in the month of October;

The content of calcium ions in the underground water reaches a peak in October, increases in time and depends on the site of measurement;

The values of PO_4^{3-} are high at all measuring stations and they fail to meet a certain rule; therefore , one of the main sources of the underground water contamination in these areas is represented by the chemical fodders used in agriculture;

In all waters analyzed large amounts of chlorides and anions of SO_4^{2-} along with large amounts of suspension matters have been found.

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