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SOME ASPECTS OF ANTHROPOGENIC ACTIVITIES OVER GROUNDWATER QUALITY

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ABSTRACT

As rule groundwater quantity and quality forming is determined by interaction of basic natural and anthropogenic factors. The anthropogenic influence appears multilateral: urbanization, industry, agriculture and others. In the Sofia kettle it is already reflected in the general organic groundwater pollution. It is expressed in the sharp raising values of the permanganate oxidation, appearance of nitrite, phosphates and ammonium, which trace the alteration into oxidizability - deoxidization parameters of the system soil-water. This alteration causes the groundwater loading with the harmful for the human being heavy metals: such as: Fe, Mn and Zn.

Urbanization poses a risk to groundwater quality in several ways, many of witch can be characterized with the next categories: Disposal of domestic and industrial waste; Disposal of sewage effluents and sewage sludge, spillages and atmospheric dust produced from some industrial enterprises.

The domestic wastes are largely biodegradable. Leachate may be produced if there is a source of water equal to or greater than about 120mm per meter of fill. If water is eliminated, domestic refuse will decompose slowly and little leachate may be produced, but if water is allowed to enter the fill a hilly polluting leachate be produced, with a strength some ten times greater than domestic sewage. The polluting potential of such leachate is greatly increased if industrial wastes are included in the refuse. Industrial wastes may include metal sludge, acids, oils, tarry wastes, phenols, pharmaceutical wastes and many other materials, of which some may be inimical to underground water quality.

The discharge of untreated and partially treated sewage into the ground can occasionally give rise to microbial and ammonia contamination in nearby abstraction wells. Usually the cause is found to be a broken pipe or leakage from sewers and cesspools. Generally, bacterial removal is remarkably effective.

The disposal of sludge from sewage treatment works is a continuing problem. Some of the sewage sludge is incinerated, disposed at landfills and the remainder spread onto farmland as useful organic fertilizer. Normally this does not constitute a serious hazard because of the bacterial removal and biodegradation of organic matter, which occurs in the top few meters of soil and unsaturated bedrock.

Run-off from housing developments may contain dirt - wash from roads, oils from spillages and leakages from domestic heating systems. Urban run - off may contain, in addition, wastes from shop and industrial yards and sewage from over-loaded or broken sewers, while run-off from industrial developments may include a wide variety of organic and toxic substances. . Stockpiles of rock salt for de-icing highways constitute another potential source of pollution. Methods of disposal may be by means of soakaways, porous pipes, or sometime boreholes.

Aquifers are also vulnerable to spillages from industrial plants, fuel storage tanks and pipelines and from the wide variety of chemicals transported by road

Although the excavation themselves do not cause pollution of underground waters the storage of fuel and other materials, spillages from fixed and mobile plant, and on-site disposal of sewage, can present a hazard to aquifers, particularly as ingress of pollutants directly to the water table can occur. However, the provision of satisfactory safeguards can minimize the risk of pollution.

In the Sofia district the anthropological influences appear multilaterally: urbanization, industry, agriculture and other. The water groundwater utilization is appointed mainly into two directions: agriculture and industry.

List of groundwater monthly observed stations:
1-s- German village
2-s - Vrajdebna district
3-s - Novi Iskar town
4-s - Levski district
5-s - Orlandovtzi district
6-s - Svetovrachane village
7-s - Chelopechane village

From all active anthropological factors on the examined the Sofia field districts brightly exhibits the influence of agricultural activities, causing general organic pollution (in particular - nitrate) of the Quaternary aquifer. As a whole, the hydrodynamic regime in the observation points during the spring months (predominately May) records general increase

of the permanganate oxidizing values ($_2O_{Mn}$), appearance of nitrites, phosphates, ammonium and raised metal saturation - mainly with Fe and Mg ions and in more rare cases Zn.

In the investigated districts water material composition during the spring (strengthened agricultural activity) is predetermined by the intensive vertical seepage through soils cultivated with different sorts of fertilisers. In this respect the nitrate pollution (village German 1-point, residential district Vrajdebna 2-point and village Chelopechane 7-p), it is essential the fact that it goes into three stages:

- nitrogen migration through soil layer;
- it's movement across unsaturated zone;
- circulation into saturated zone.

During every stage specific processes perform (biological, physical, physical-chemical), which are influenced by different factors - heterogeneity of the surroundings, the layer's active porosity, the water level alterations, indexes of the conventional transfer, parameters of diffraction and others. Also over the nitrate migration very strong influence exerts the temperature. It is directly connected with the active activities of the plants and microorganisms in the soil layer, creating so called soil barrier. It could be relied on it only during the plantations` vegetation period. The increased nitrate content during the spring period leads to decrease of the oxygen concentration (increase of the permanganate oxidisation $_2O_{Mn}$) and respectively change the Eh -pH of the soil-rock system.

Analogous pattern, but more slightly expressed, is manifested during September. At the end of the summer, because of the slowed down water exchange and the duration of the processes of dissolving, exolution and ionic exchange, the general mineralization of the water increases. As a result of the autumn rainfalls, causing water level raising, groundwater again are enriched with organic substances (indigestible by the plants nitrogen), and heavy metals. Taking into account increasing mineralization and their salt composition it is recommended the use of low irrigation norms with big frequency.

In respect of their industry utilization we should take into account that the water are: mainly middle - hard and hard; with thin hard incrustation forming; semi and foam -free; corrosive, i.e. required preliminary softening.

The problems connected with usage of groundwater for irrigation and domestic water supply are due to the excessive nitrogen application by fertilizers in Sofia district. On one hand, this is due to inappropriate managed fertilization, followed by N leaching which leads to the groundwater contamination/ average at and above 50mg/l NO_3. On the other hand we should emphasize that several factors affect the accumulation in plants. The level of fertilized N applied is important, though in many cases there is no simple relationship. Other important factors include moisture conditions, amount of sunlight and even the use of herbicides. Many cases of nitrate accumulation by plants occur during drought conditions – the decline in moisture depresses the activity of the nitrate redustase enzyme. In such conditions (August – September) we usually use our NO_3 –contaminated water for irrigation. In this way we just support a high content of NO_3 in our agricultural crops. The situation is complicated because we have not established limits on the amounts of nitrate in a plant matter for some vegetables, e.g. 3g NO_3 kg^{-1} fresh weight, for lettuce and there also simple tools available for measuring the nitrate content generally indicator papers or there also simple tools available for measuring the nitrate content generally indicator papers or similar devices, and the precision's is not great.

Recently, we have no data reporting the link between the NO_3 content in our food and water and some cases of methaemoglobonemia or suggestive link between nitrate uptake and the incidence of certain cancers. But we should emphasize that in some villages around Sofia city farmers, simultaneously consuming vegetables and contaminated groundwater, are really exposed to the adverse circumstances by high NO_3 ingesting.

Methaemoglobonemia

In particular, it is now well established that nitrite is cause Methaemoglobonemia, often referred to as the blue-baby-syndrome (2). In this disease the capacity of the blood to carry oxygen is lessened, and affected people – normally infants- exhibit a slate-blue discoloration (cyanosis) of the skin, usually beginning around the lips, finger and toes, and spreading to the face and body.
In addition should be point, that the medical examinations prove the appearance of the disease connected with the combined presence of iron and nitrates in water. In the human constitution, in conditions of alkaline medium, runs the deoxidization reaction, i.e. the transition NO_3 - NO2. The released oxygen oxidizes the divalent iron - Fe_2 to Fe_3, which leads to appearance of methahemoglobin, causing muscular exhaustion and widening of the vascular system .

For example the concentration of NO_3 determined into groundwater derived from wells disposed in Sofia district (German, Svetovratchane, Vragdebna etc.) are unacceptable (above 22.6 mg/l NO_3- N). These high contents of NO_3 are mainly due to the excessive fertilizer input – NH_4NO_3, ammonium salts and organic forms such as urea $(NH_2)CO$, which are very soluble. There are also very favorable conditions for N leaching and the highest contents of NO_3 are appeared in spring and late summer. Predominantly, water from wells is used for the irrigation of vegetables, which are the part of chain water- plant- animal – human, and rarely is used as drinking water. Thus in this case (Sofia district) we have should take this fact into account because nitrate clearly harmful to human beings in an least one respect:

Another problem is appeared to be connected with the atmospheric pollution due to the different kind of industrial enterprise activities. For example the Kremicovzi steel factory, the biggest Bulgarian steel producer discharges about 44000 tons dust in the atmosphere. Heavy metals in the air emissions enter into the soil mainly by precipitation. In general soils are saturated with arsenic, manganese and lead. The maximum contents of heavy metals are closely linked to the upper soil layers and two main subsequences follow this fact.

On one hand heavy metals are toxic for soil microorganisms and reduce the plant growth and productivity.

This depends on their specific chemical forms at the time of impaction and the extent of their solubility:

- simple or complex in soil solution;
- exchangeable ions;
- link to organic substances;
- occluded or co-precipitated with oxides, carbonates and phosphates or other secondary minerals;
- ions in the crystalline lattices of the primary minerals.

The different type of chemical forms depends on temperature and pH of the soil. As pH of the soil medium is lower as heavy metals are more mobile and more available for plant activity.

Soluble forms will be free to move by diffusion and react with other soil constituents; biotic forms will be released as decomposition form. Insoluble forms will move down the soil profile and contaminate groundwater directly.

On the other hand heavy metals are potential threat for groundwater contamination. Usually groundwater pollution is noticed after the pollutants have already entered the aquifer, which is too late. Groundwater monitoring without monitoring the unsaturated zone is illogical. We should bring all relevant information about water, solutes and even gas transfer, obtained in-sito and in the laboratory. In addition it enable the determination of groundwater recharge, contaminant travel rates in the unsaturated zone and the field distribution coefficient for contaminants. Natural variability of all porous media characteristics at different depths may also be studied.

Up to now groundwater level in this concrete region varies between 7.50 - 8.25 m under surface land and concentrations of Mn in groundwater have already been higher than potable water requirements standard. The studied heavy metals in the soils are: manganese (Mn), zinc (Zn), lead (Pb), cadmium (Cd) and arsenium (As). Some of them exceed the maximum permissible levels (MPL).

The estimated soils' heavy metals contents has been provided in three villages (Gorny Bogrov, Yana and Rudnika, subsequently situated away of Kremikovzi and tracking the prevailing wind directions (East and South East). For the first two villages we have data concerning three different soil layers: depth 0-40, 40-80 and 80-120 cm and for the Rudnika depths are: 0-40 and 40-80 cm.

In general, soils are saturated with arsenic, manganese and lead. The contents of arsenic in the Gorny Bogrov and Yana villages are four - five times more than the maximum permissible levels (MPL). Only in the Rudnika the concentrations of arsenic and manganese are lower than the (MPL). Two-three times higher than MPL concentrations of manganese around Gorny Bogrov and Yana villages have been observed. The highest contents of manganese have been estimated in the Yana area in the surface layer and it decreases the depth. The contents of lead in the studied area have been measured also, noting obvious declining values with the distance from the Kremikovzi plant. In the studied regions the evaluated concentrations of Cu and Cd are less than maximum permissible levels.

In the future investigations a regular check of: groundwater recharge; the field of distribution of contaminated zone; the concentrations of heavy metals into the unsaturated zone; creation of lithological profile; establishment of pore fluid composition and of capillary pressure in constant points of a profile; laboratory study of water-solute transfer parameters will be desirable especially in spring and late autumn months when an intensive vertical flow exists. That will be a reasonable act on the basis of the complexity of the problem and all ecological difficulties in our country.

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