HYDROGEOLOGICAL BACKGROUND AND HEAVY METAL CONTAMINATION OF GROUNDWATER IN INDUSTRIAL ZONE: PLOVDIV-ASSENOVGRAD (BULGARIA)

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Abstract:

The industrial zone "Plovdiv-Assenovgrad" (about 200 km^2) is situated in the southern part of the Upper Thracian Plain (the largest plain in Southern Bulgaria). During 1961 a metallurgical factory, called KCM, was built between the towns of Plovdiv (the second largest town in Bulgaria) and Assenovgrad (Picture 1). Recently, the production of the KCM is about 55,000 t/y Pb, 65,000 t/y Zn, 80,000 t/y H_2SO_4. The slag is up to 30,000 t/y and part of it - 20,000 t/y is used in cement factories and about 10,000 t/y are stored in two slag-dumps – an older one (period 1961-1970) and a new one (period 1971-up to now)(Picture 2). The KCM itself, and two slag-dumps are the main sources of heavy metal pollution in the studied area including ground water.

Pic.1. Metallurgical factory KCM

Pic.2. The new slag-dump

The main goal of this investigation is to define the contamination of ground water and the main sources of pollution. It was started with a precise review of the major Technical Reports and Documentation from previous hydro-geological surveys in this region. Then a special Database for the region was elaborated. Hydro-geological, hydro-chemical, soil and other types of information have been included in the Database. Data from more than 200 boreholes and all new information are being continuously introduced.

More than 100 of existing points (boreholes, springs, wells etc.) were revised. Later on, 30 of them (the most contaminated) were chosen as monitoring points for seasonal observation. Several thematic maps are prepared on the ground of the Database.

Hydrogeological background

The studied area is situated in the southern part of the Upper Thracian Plain, Southern Bulgaria. This intermountain depression (a graben) is filled up with relatively young sediments and two major aquifers are formed in these unconsolidated sandy and gravelly layers – Quaternary and Neogene. They are differentiated only by lithological indications and by filtration properties.

The data of numerous boreholes and wells, drilled for different purposes, in the investigation area, show that Quaternary sediments are widespread in studied area. Neogene sediments are widely developed too, but they are not outcroping on the surface. They are reached or passed through by some boreholes situated in or near to the studied area. It was established that the thickness of the Quaternary sediments and the Neogene sediments is different. It varies from 17 m up to 98 m for the first one and from 17 m to 370 m for the second one.

Sediments genetically consist of different types: prolluvial, delluvial, alluvial and mix delluvial-prolluvial-alluvial depositions. The quaternary sediments consist of boulder, gravel and sand materials that had formed talus fans. Alluvial sediments of rivers Maritza and Chepelarska mainly consist of pebbles and sands (Picture 3). The Neogene sediments consist of clay sands, sands, sandy clay or clay.

There are two main aquifers: (a) in Quaternary sediments, and (b) in Neogene layers. There is hydraulic connection in some places, so that Neogene and Quaternary aquifers often form a common aquifer system with similar lithological components. Additional hydraulic connections are performed in some boreholes and wells, where the casing and drilling were not properly done. The effective thickness (mainly sand layers) of Quaternary aquifer is up to 30 m. The ground waters are unconfined or semiconfined with variable heads.

The filtration properties of the Quaternary alluvial deposits are relatively high, due to the big effective porosity and purity of the sandy-gravely layers. The hydraulic conductivity is ranging from 50 to 300 m/day. Corresponding transmissivity of the Quaternary layers varies between 1000 and 5000 m^2/day. Very productive zones in the Quaternary aquifer are encountered (specific capacity of some wells is up to 20 – 25 l/s/m).

The bedrock was reached by several boreholes drilled in the center of the town Asenovgrad , as well as in the southern part of the studied area. The bedrock consists of metamorphic rocks (Asenovgrad Formation). Geothermal water was discovered, with temperature up to 36°C (borehole No. 6) and TDS higher than 1 g/l, which is accumulated in Precambrian marbles. The recharge of groundwater is by precipitation at the places where Precambrian marbles occur at the surface (on the Rodope Mountain). No connection is observed in the studied area between the ground water of Precambrian marbles and upper Neogene and Quaternary aquifers, so this thermal water is not of importance for this study because it is naturally protected against contamination.

Climatic data from 3 national meteorological stations in the region are available. Hydrological measurements are carried out at two river gauges stations – on Chaya River (south of the region) and on Maritza River in the town of Plovdiv.

The most recent data about precipitations, river discharge and groundwater fluctuations are illustrated on Fig. 1.

Methodology

Thirty monitoring points for seasonal sampling and water level measuring have been chosen. The chemical composition of water and the hydrogeological information are taken under consideration.

Special Database called *WATMETAPOL DATABASE* is elaborated. Hydro-geological, hydro-chemical, soil and other types of information are included in the Database.

The hydrogeological database contains all existing information for the "ground water points". All obtained information for this period is also included in the database. The relationships between separated tables in this database are established by means of the unique identification key of the given water point, also called "ID_Point" (Fig. 2). The main table in this database is called "BASIC_POINT_INFORMATION", which contains information concerning the location, type of represented entity,

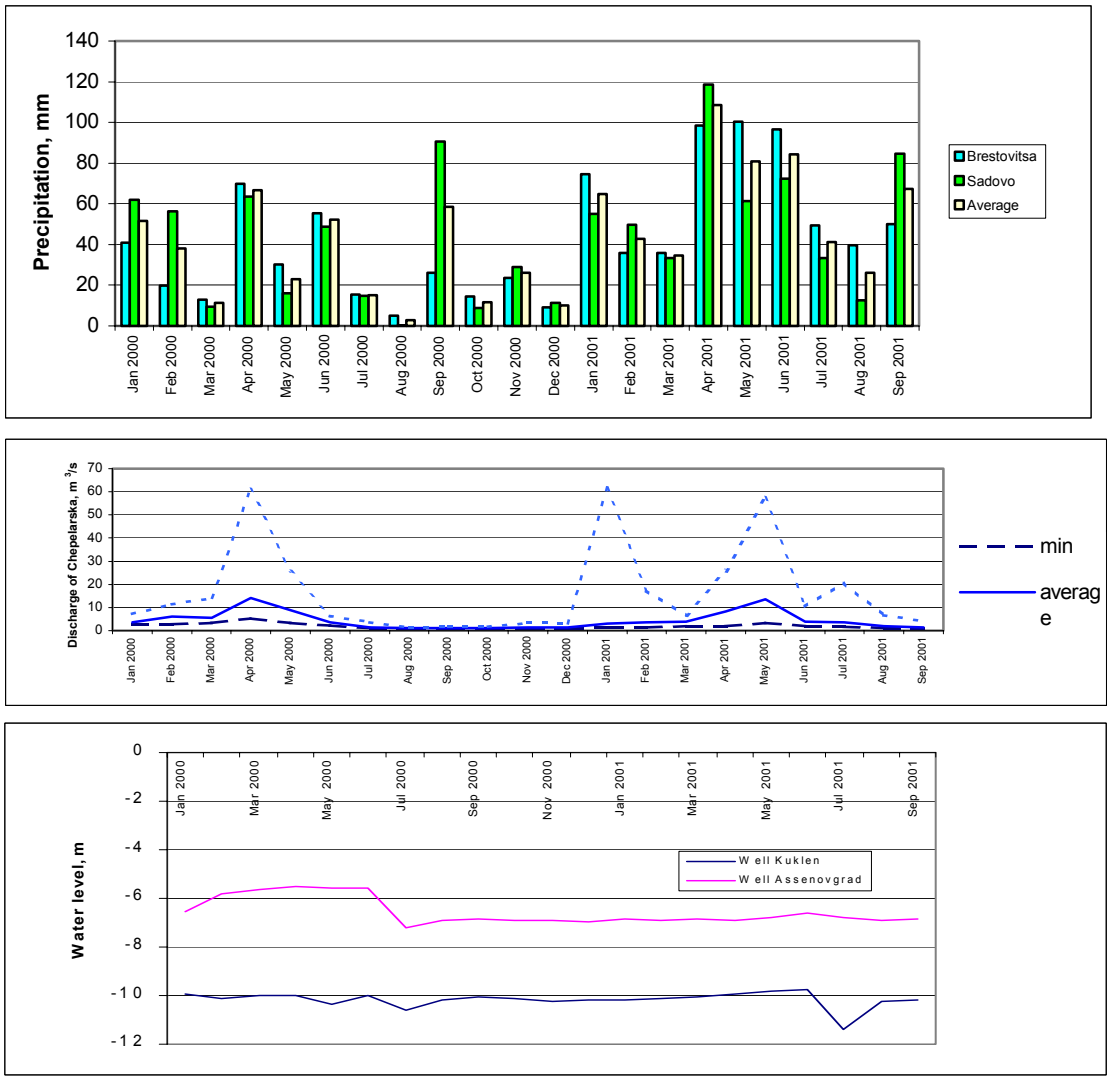

Figure 1

number of point, and some technical characteristic related to the represented entity (Borehole treatment, Borehole execution and Reference).

Information about the hydrogeological tests and field measurements is stored in two tables: "Quantitative data" and "Hydro". The first one represents values of hydraulic conductivity (m/d), transmissivity (m^2/d), porosity (%), capacity (l/s) and date of measurement. The second one represents measured values for hydraulic head (m), measurement date, measurement (m), pH, Eh, water and air temperature, dissolved oxygen.

Data containing the lithology and stratigraphy are in Geology table. Each stratum penetrated by a borehole is described here by "one to many" relationship.

Also, data related to technical characteristics of wells in the table "BASIC_POINT_INFORMATION".

Information that identifies the analysed ground water quality and describes the results is stored in two tables "Results_of_chemical_analysis" and "ICP_ results". Because for each analysed sample several parameters are identified, a "one to many" relationship is established. The link is made using unique point item called ID_Point. Both tables contains the name of each measured parameter, its respective value, the date of analysis was done and operator.

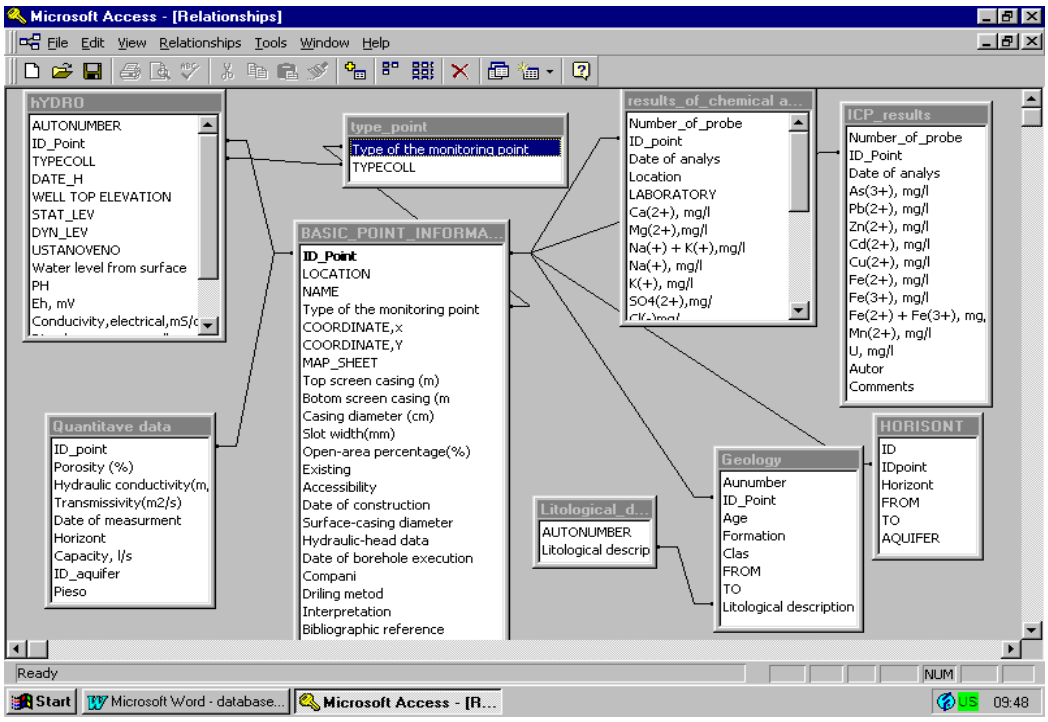

Fig. 2 Relationships between separated tables in the database.

Results

Chemical and physico-chemical analyses of all seasonal water samples for the identification of 24 physico-chemical parameters, including Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, NO_3^{-}, NO_2^{-}, F^{-}, NH_4^{+} were carried out according to Standard Methods for the Examination of Water and Waste-water (APHA/AWWA/WEF 1992) and BDS Standards for Drinking and Industrial Waters (BDS 2825-83). The waters are $Ca(Mg)HCO_3$ (SO_4) type, mainly HCO_3-Ca type and HCO_3-SO_4-Ca. Abundance of Cl^{-}, NO_3^{-} and SO_4^{2-} varies considerably between wells. The presence of considerably high values for ammonium and nitrate ions as well increased concentrations of nitrites and sulphates suggest groundwater contamination by infiltrating surface water polluted by leakage from waste heaps and sewage discharges. The most integratly macro-contaminated waters are established in high endangered area around KCM and AGRIA plants, also in the zones of the villages of Yagodovo, Krumovo, Brestnik and the town of Plovdiv (Fig. 3).

Ground, surface and waste water samples were investigated for the following 34 elements: Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Zn, Hg, Be, B, V, Sn, Mo, Se, Ag, Te, Tl, Ti, U, Ca, Li, Mg, Sr, Bi, Ga, In, K, and Na. The analysis were carried out with HR-ICP-AES Jobin Yvon ULTIMA 2000, (at UIA-MiTAC and GEOLAB), in conformity with ISO 11885. The obtained results are eloquent enough: the higher polluted groundwaters with Pb (Fig. 3), Cd and Cu are situated in the most endangered area around the plants, analogous are the results for the Zn (Fig. 3), Fe and Mn contamination, with a supplement pollution data for more distant points. The metal- and As-pollution is indisputable in the waste waters and in Chaya river after the influx of the KCM channel. Arsenic is registered in groundwaters close to KCM. Some Tl, Hg, Se, Sb, Al are established. Concentrations higher than MPL for Cr, Co, B, Mo, Sn, Ti, V, Be, Te, U, Ag are not registered. (For Bi, Ga, In, Li, Sr there are not data for MPL).

Finally, GIS analysis was started with preparation of preliminary different maps: hydrogeological, hydrodynamic map and others.

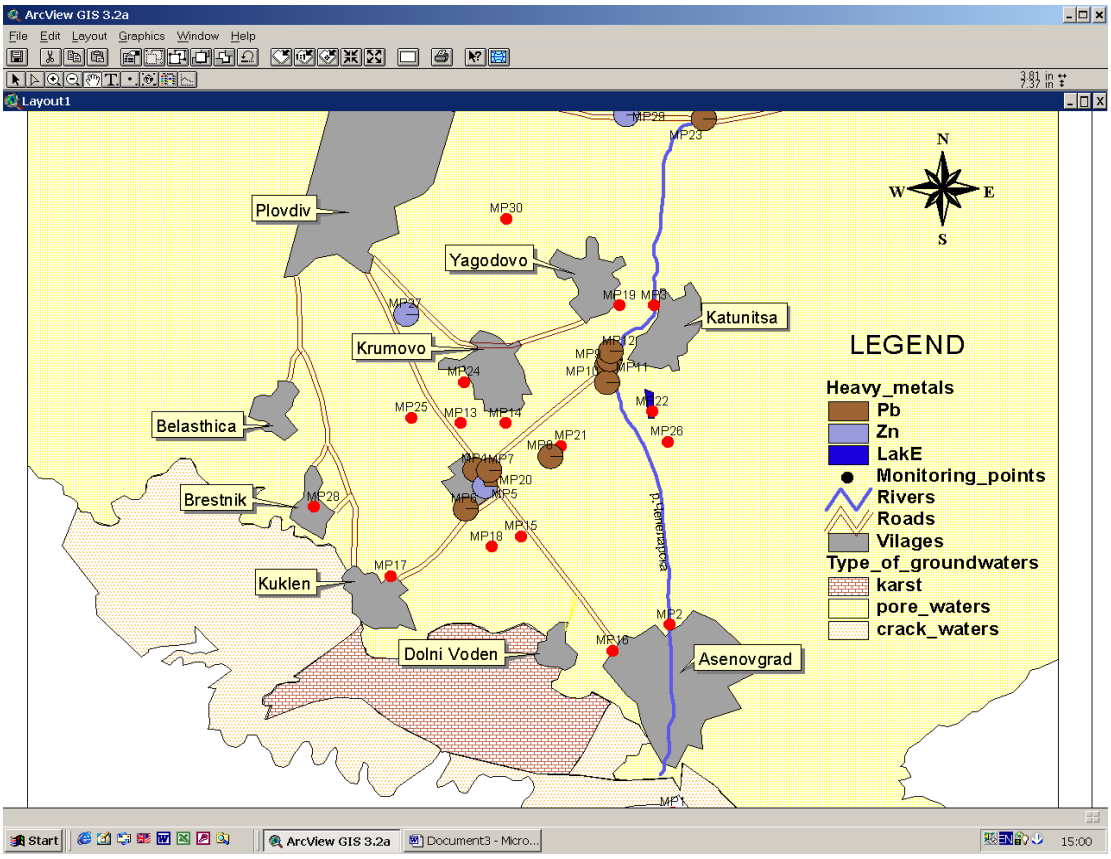

Figure 3

Conclusions and recommendations

The study of heavy metal contamination of groundwater in industrial zone: Plovdiv-Assenovgrad (Bulgaria) is going on. Some of the main conclusions and recommendations up to now are as follow:

1. The most integratly macro-contaminated ground and surface waters are established in the area around KCM and AGRIA, also in the zones of the villages of Yagodovo, Krumovo, Brestnik and the town of Plovdiv.

2. The high polluted ground waters with Pb, Zn, Cd and Cu are situated in the most endangered area around the plants as well Fe and Mn contamination.
3. The metal- and As-pollution is indisputable in the waste waters and in Chaya river after the influx of the KCM channel. Arsenic is registered in groundwaters close to KCM.
4. Some Tl, Hg, Se, Sb, Al are established. Concentrations higher than MPL for Cr, Co, B, Mo, Sn, Ti, V, Be, Te, U, Ag are not registered. (For Bi, Ga, In, Li, Sr there are not data for MPL).

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