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MICROANALYSIS OF GROUNDWATER ELEMENTS WITH RESPECT TO TIME AND DEPTH IN THE HORTOBÁGY REGION IN HUNGARY

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Abstract. Out of the several groundwater samples taken from the project area in the Hortobágy region in east of Hungary between years 2001 to 2006, 10 samples (5 each from summer and winter) were chosen and studied for microelements, especially heavy metals. The samples were analysed for chromium, zinc, cobalt, nickel, barium, aluminium, copper, molybdenum, boron, lead, cadmium, strontium and lithium at the MÁFI Lab using ICP–OES. The data was refined and the plots hence were studied for variation over the given time period and seasonal variation between the 10 wells, and along the depth. The observations are useful to determine whether there has been any noticeable variation in the concentration on the elements beyond safe limits. The WHO–EU safe water standards are used to determine the quality of the water.

Keywords: Hortobágy, heavy metals, time and depth analysis, seasonal variation, WHO–EU water quality standards, European Union Groundwater Directive

1. INTRODUCTION

This project area, “Nyirőlapos” is situated to the east of Hungary in the Hortobágy, NE part of the Great Hungarian Plain. It is the first national park in Hungary and is elected among the World Heritage sites since 1999 (Tardy, ed., 2002). The Hortobágy is Hungary's largest protected area, and the biggest grassland that remained in Central Europe. Its area is over 800 sq.km. The topography of the area is nearly flat and the project area is around 0.4 sq.km. The geology of the region is formed by fluvial deposition of the River Tisza from the Holocene and Pleistocene (Rónai, 1985). The Hortobágy plain is largely uninhabited and has very few anthropogenic interventions and activities. This means that the pollution levels in this region are very low. The surface is very flat with a gradient less then 0,001%. The aquifer is build of alluvial sediments from the Pleistocene and Holocene (Tóth & Kuti, 1998). The conditions changes very fast in a small area. Meteorologically, the area is arid. Being a protected bio reserve, there are not many anthropogenic activities on this land, and the major activity is sheep grazing.

2. BACKGROUND AND PURPOSE OF THE STUDY

The Groundwater Directive was proposed by the EU for the purpose of having a uniform and safe groundwater quality. All the member states have to comply with the directive. This new directive establishes a regime, which sets groundwater quality standards and introduces measures to prevent or limit inputs of pollutants into groundwater. The purpose of the study is to examine the variation in the concentration of the heavy metals and a few other elements and their interaction with the subsurface environment over a period of time. Along with this, the variation of the concentrations at different depths is also a significant indicator of the reactivity of the groundwater elements.

The main concern is to examine the coherence between the changes of chemical type from the groundwater in dependency of the groundwater-depth and the time in this area. This investigation is based on analysis of data between 2001 and 2006.

The groundwater depth in the area (Vadose Zone) is almost 1 to 2 meters below the GL (groundwater level), and the zone of saturation (Phreatic) follows below this (Kuti et al., 2002.). The elements analysed are chromium, zinc, cobalt, nickel, barium, aluminium, copper, strontium, molybdenum, boron, lead, cadmium and lithium.

3. HEAVY METALS AND GROUNDWATER CONTAMINATION

Groundwater contamination is one of the most severe problems faced by the modern society. The incredible reliance on groundwater as a source of fresh water makes the situation even more susceptible. Of all the other sources of contamination, heavy metals contamination is one of the most severe one. The occurrence of this phenomenon is correlated with the degree of industrialization and intensity of chemical usage. Heavy metals are elements with high atomic number and hence are less reactive and have a longer residence time. Heavy metals like lead, mercury, cadmium, copper and others are the most common heavy metals that have a severe long term and short term effect on the groundwater quality.

3.1. Heavy metal sources in groundwater

Concentrations of cadmium, lead and mercury in rocks are approximately 1.0, 5.0 and 0.5 mg/kg (parts per million). These chemicals are not very soluble and natural concentrations in groundwater are less than 0.5 µg/L (parts per billion).

Cadmium, lead and mercury have many anthropogenic sources. Cadmium is widely used in industrial applications, including the manufacture of batteries. It is also found in industrial wastes, sewage sludge, mining wastes, and fossil fuel combustion products. Lead was once commonly used in automobile fuels, paint and plumbing. Although these uses have decreased, lead is still used in batteries and alloys, and it is found in sewage wastes and in fossil fuel combustion products. High lead concentrations can be hypothesised in an area of 10 to 15 meters on the either sides of highways as localised effects. Due to advancements in automobile fuel technologies and catalytic converters, lead emissions have been reduced to a great extend, and cadmium traces are more significant than lead.

Chromium is an important industrial metal used in diverse products and processes (Nriagu, 1988a, b). At many locations, Cr has been released to the environment via leakage, poor storage, or improper disposal practices (Palmer & Wittbrodt, 1991). Within the environment, Cr is found primarily in two oxidation states: Cr(VI) and Cr(III). Cr(VI) is of a specific toxic nature and special concern, while Cr(III), being less toxic is relatively harmless.

Copper, nickel and zinc are metals that occur in significant quantities in rocks. Concentrations in rocks range from about 10.0 to 100.0 mg/kg (parts per million). Concentrations in soil are similar. These metals are somewhat mobile in soil, with the exception of trivalent chromium, which is immobile. There are many anthropogenic sources of these chemicals. Industrial uses include alloys, paints, pigments, electroplating, batteries, automotive parts, coatings and electrical wiring. Copper and zinc are important nutrients for plants, and are also used as insecticides or fungicides. These metals have limited mobility in soil, and anthropogenic impacts to groundwater are small. In Hungary, almost one third of the country’s groundwater suffers from a shortage or deficit of Cu and Zn. The minimum requirement of Cu and Zn for plants is 8 ppm and 40 ppm respectively.

Boron is another chemical element, often found in rock and soil. It is slowly released into both groundwater and surface water. Owing to its lightweight, it may be liberated relatively easily as a gas in the form of boric acid. Boron forms an extensive series of chemical complexes, but water analyses normally report boron concentrations in terms of elemental boron (B).

4. PRINCIPLES AND PROCESSES IN SUBSURFACE ENVIRONMENT

Groundwater geochemistry is an interdisciplinary approach concerning the chemistry of water in the subsurface environment. The chemical composition of the groundwater is the combined result of the composition of water that enters the groundwater reservoir and the reactions with minerals present in the rock that may modify the water composition. Apart from the natural processes, in recent years, anthropogenic mechanisms also influence the groundwater geochemistry. Due to the long residence time of groundwater in the invisible subsurface environment, the effects of pollution are seen only tens of years later. It is however important to properly understand the processes occurring in aquifers and other subsurface components in order to predict the effects of present day human activities on a certain time scale (Appelo & Postma, 1999).

Several chemicals from water can be adsorbed in soil and in aquifers. Sorption is the change in concentration of a chemical in a solid matter as a result of mass transfer amongst solution and solute. Sorption processes can be subdivided into adsorption, absorption and ion exchange. Adsorption is a surface phenomenon while absorption and ion exchange are chemical and electro chemical phenomenon respectively. The relevance of the process is subject to solvent and solute property, apart from other factors such as temperature and pH.

Apart from these mechanisms, factors like the atmosphere, soil type, vadose and phreatic zones, numerous biological and chemical processes like biodegradation, redox reaction and decay taking place in soil and groundwater influence the groundwater chemistry.

Reduction and oxidation processes exert an important control on the distribution of species such as O_2, Fe^{2+}, H_2S, CH_4, etc. Redox reactions are also significant in other aquifer problems such as fertilizer nitrate pollution, landfill leaching infiltration, acid mine drainage and morbidity of heavy metals. Redox reactions involve transfer of electron from one atom to the other. Bacteria present in the subsurface environment might catalyse these reactions. Nitrification and denitrification is a common and significant redox reaction taking place in the sub surface environment

Groundwater contaminant transport is an important and interesting phenomenon. Mass transport in groundwater is much more complicated phenomenon than surface water and there are several factors and mechanisms that influence this phenomenon. It depends on factors like groundwater flow, geological background, the processes of material transport and the degradation. Besides the hydraulic properties, certain aquifer properties need to be considered.

5. SAMPLING

Sampling is a procedure of procuring the sample from the groundwater, transporting it to the laboratory in a way that the natural quality of the sample is retained to as much as possible avoiding any sort of contamination. Groundwater sampling is not a simple procedure and utter care has to be taken to get precise and reliable results. MÁFI has sufficient sampling equipment and expertise for sampling up to 10 meters below ground level.

Three samples were taken from each well at each level (in natural, in NO_3 and ICP). The samples were tested for pH, temperature and electrical conductivity on the site itself and the samples were transferred to the lab in proper decontaminated plastic bottles for further analysis. Figure 1 shows the wells sampled. Note the three wells for the three different levels.

6. DATA INTERPRETATION AND ANALYSIS

6.1. General

The available data over the years is was not homogeneous and several readings are missing. The large data is not spread over the years uniformly the sheer volume of data would make the plots complicating and confusing. For this reason, annual hot and cold weather data set was chosen for the analysis so that the results can be computed conclusively with the seasonal variation.

Nine boreholes were chosen and the data from three different groundwater levels (GL) was analysed, (fig. 1). The borehole depths were 1. GL to 3 m, 2. GL 3 m to 7 m and 3. GL 7 m to 10 m. The samples were analysed in the lab for heavy metals and other elements and the results tabulated periodically. These concentrations were used to study the variation in concentration of the various elements.

Fig. 1: The wells at different levels

6.2. Interpretation

Several data points were missing and the data available was insufficient. For elements like Cr, Co, Al, Mo Pb and Cd, only wide data ranges are available which change over a wide range especially after the first two years. For instance, Cr concentrations are found to be in a range of <10 μg over the first two years. After this, there is a drastic fall in the range to <1 μg. This gives a sudden fall in the plot and this might appear as a sudden decrease in the Cr levels in the groundwater, which is highly unlikely unless certain remediation methods have been applied. Similar trend is observed for the other elements mentioned above. The most plausible explanation for this pattern is that there might have been a change in the analytical method of analysis or change of equipment. The Laboratory of MÁFI reverted and confirmed that the optics for the ICP–OES Mass Spectrometer were changed in this period and hence better results could be documented. This justifies the sudden drop in the levels of certain elements winter of 2002 onwards.

Medium and low-depth data for wells 5, 6 and 7 (A and B) is missing for the entire periods of the analysis. This makes the analysis more complicated and less conclusive. Only the top-level data is uses for this purpose.

The analysis is kept simple and phenomenon such as cross contamination of aquifers is not considered. The wells are considered as totally separate and the variation at different depths is also considered irrespective of the vertical stratigraphical changes.

Bores used for sampling are made of materials, which contain elements like

Mo and Cd. In certain cases, it is possible that the elements are leached out into the soil and the levels of certain elements might be elevated. However, this phenomenon is predominant in soil sampling and probability of occurring in groundwater sampling is rare. It might or might not have affected the sampling.

SPSS 11.0 was used to process the available data and make it more smooth, uniform and reliable. SPSS 11.0 is widely used software for Statistical analysis. The intermediate missing values were also interpolated using the software and the output is a much more reliable dataset than the actual data.

6.3. Groundwater level

Groundwater data was procured from MÁFI for the years 2001 to 2006 and the general trend was observed. The main variation in the groundwater levels is seasonal. The increase and decrease in the levels in the cold and warm seasons was similar over the entire period of the analysis.

The rainy season in the great Hungarian plain is from May to August, with a clear rise at June. The driest months are January to March. The hottest months are June, July and August, while the coldest are December to February. Evaporation and evapo-transpiration is a more dominant process lasting over 8 month of a year.

7. ANALYSIS AND RESULTS

The data is analysed on a multi level basis. It was processed for the variation at three levels.

- Variation between the wells (1 to 9)
- Variation between different depths (1, 1A and 1B, fig. 2)
- Annual seasonal variation.

Table 1- Quality Standards for groundwater, USEPA and EU

Element	***Max Concentration (μg/L)***	
	USEPA	**EU**
Cr	20,000 and 700 (for Tri and Hexavalent)	50
Zn	2000 – 5000	3000*
Co	–	–
Ni	100	20
Ba	2000	300*
Al	50–200	200
Cu	1000	2000
Sr	–	–
Mo	30	70*
B	600	1000
Pb	15	10
Cd	4	5
Li	–	–

** : WHO standards, EU limits not specified.*
–: Unspecified

7.1. Results

The time– and depth–based variations in groundwater depend on the geological and meteorological circumstances. The results of the concentrations are compared with the USEPA standards for Groundwater Quality. The water quality standards are as follows (Table 1).

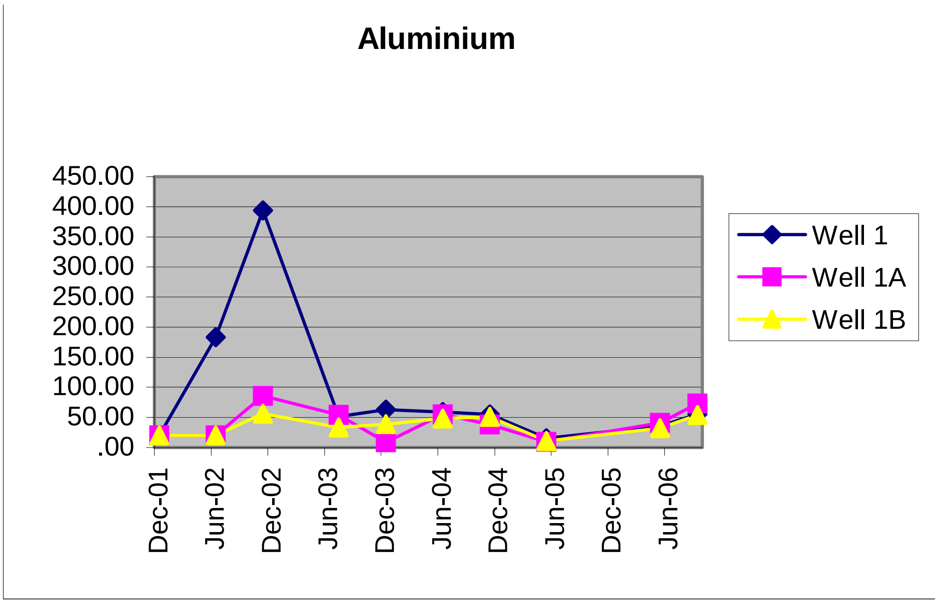

Fig. 2: Plot showing aluminium concentration (μg/L) in well 1. Note the sudden variation in winter 2002.

8. CONCLUSION

1. It was observed that the data homogeneity was not good through out the study, especially for certain elements like Cr, Co, Pb and Cd. Less actual values were available. However, since the overall concentrations of these elements are well below the safe limits, this non-homogeneity can be neglected.
2. The quality of data has improved over time. After winter 2002, the values are more precise and realistic. This is a result of the equipment upgrade in the MÁFI Laboratory.
3. The data for almost all the elements for the wells 5, 6 and 7 (A and B) is missing. There is no information of the variation in concentration in these wells during this time. It is hence assumed that the variation is proportional to that of the other wells and elements.
4. It can be seen that the concentrations in winter 2002 for elements nickel, cobalt and aluminium increase suddenly and then go down in the following summer. This is indicated by the sudden peak in the graphs (third point on the graph) in

most of the wells in this period. This increase is unnatural and the highly unlikely in a real scenario. Since there is no source of contamination of that degree in the area, this can be assumed to be a sampling or analytical error. As mentioned earlier, the lab equipment was upgraded and this is the first reading after the upgrade. Hence it can be assumed that this variation is due to the equipment set-up and not due to any contamination on the site.

5. The overall concentration of all the elements remains more or less constant and below the safe limits. The water is fit for consumption and will not have any health effects, as far as the elements in this study are concerned. The reason being that the area under consideration is not in the vicinity of any human activity such as industries, mining etc and there are no anthropogenic contamination sources that might alter the groundwater quality.
6. No unnatural variation in the concentrations was observed in any of the wells. The slight variation in certain wells for certain elements can be due to errors in sampling, analytical method and lab testing. No log of activities in the area over the period is available. This makes it hard to determine the reason for the variation observed in certain wells. Interaction amongst each other is highly unlikely due to the nature of the elements, low reactivity and the interaction with the other elements in soil and groundwater is ruled out due to the scope of the study.
7. Generally the concentration of dissolved substances decreased with the depth due to the various processes described in the chapter above. There are a few exceptions like well 4 (Al), well 3 (Ba) etc. However, since the soil profile is not known, the chemical processes behind this cannot be predicted.
8. Seasonal variation for the elements was mostly insignificant. The precipitation rates and variation of groundwater levels has no significant effect on the concentration of the elements.

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*** * *** EOD: *Environmental Outcomes Division,* Ground Water Monitoring & Assessment Program, Minnesota Pollution Control Agency

*** * *** WISE 2006. *Water Information System for Europe, Groundwater Directive* (2006/118/EC) of the European Commission

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