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THE COMPLEX ENVIRONMENTAL EVALUATION OF THE SOIL-GROUNDWATER SYSTEM IN URBAN AREAS: THE EXAMPLE OF SZEGED

Theses of Ph.D. dissertation

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INTRODUCTION AND OBJECTIVES

More ore than half the world's population lives in cities today, and this ratio steadily increases, which means that more and more people are affected by the negative effects of the urban environment. Due to intense anthropogenic activities characterising cities, the environment has been damaged irreversibly in many cities by now, including subsurface water resources and soils. Soil contamination may involve not only human health risk, but it can also be a potential source of groundwater pollution. Groundwater contamination, then, may get into surface watercourses and confined aquifers, as a result, it may have rather negative effects on many elements of the environmental system. In order to study the spread of these pollutants, it is essential to reveal the conditions of groundwater flow, and the migration processes of the contaminants in the unsaturated zone. In the light of the possible threats mentioned above, the quality of groundwater must not be studied and evaluated in itself, but only as complex pedological, hydrological, hydrogeological and hydrogeochemical system.

In addition to the already outlined processes occurring in cities, the reason I chose this topic as the main theme of my doctoral research is that although national researches into the urban environment have come to the fore, analyses which include more spheres are rather wanting in complexity. Therefore, I wanted to broaden the knowledge relating to the soils and groundwater system of big cities, especially the modifying effects of anthropogenic activities. I chose Szeged, the third most populous city of Hungary, as the sample area of my research, as the city being a mixture of urban and rural areas is most suitable for studying the processes and pollutions caused by anthropogenic activities.

The main objective of the doctoral research work was to produce a comprehensive geochemical, hydrodynamical, and hydrogeochemical analysis and evaluation of the urban soil-groundwater system. The present doctoral dissertation combines three research topics: the analyses of groundwater quality, groundwater flow properties, and the protective ability of soil against groundwater pollution. The objectives of my research also include the investigation of the status and changes of the groundwater quality system in Szeged with respect to inorganic contaminants as well as the identification of the potential sources of contamination. Furthermore, I aimed at exploring the geochemical relationships between the measured components, I also set out to separate the artificial urban effects influencing groundwater fluctuation, to analyze the relationship between groundwater flow and changes in the amount of precipitation, and to study the fractal behaviour of groundwater level time-series. Another goal of mine was to assess the quality state of soils in the vicinity of the most contaminated groundwater wells with soil profile analyses, and to reveal the heavy metal (Ni and Cu) adsorption properties of soils. In addition, I intended to model the vertical migration of the potential infiltration of heavy metals from the unsaturated zone into the groundwater, and, finally, to explore the complexity of the relationships within the soil-groundwater system.

RESEARCH METHODS

The sample area of my research was Szeged, where there is an extensive groundwater observation well network. I included 28 wells of the city's monitoring network in the groundwater quality analyses in the course of which I took groundwater samples per month, then every two month for two years (from October 2010 to September 2012). 17 of these wells were chosen for groundwater level monitoring which provided one-and-a-half-year long time series data (from January 2012 to July 2013), and these data were further extended to include the 14.5-year-old (from January 2000 to July 2013) time series data of 14 ATIVIZIG groundwater wells. Soil sampling took place in November 2011, in the immediate vicinity of the six most polluted groundwater wells. In May 2012, precipitation samples were taken from fresh-fallen rain in several parts of the city, each part representing diverse functions.

In the laboratory, the groundwater samples were analysed to determine the concentration of twelve inorganic contaminants (Cu, Co, Cr, Cd, Pb, Ni, Zn, As, NO_3^-, NO_2^-, NH_4^+ and PO_4^{3-}) with flow injection analysis (FIA) and inductively coupled plasma optical emission spectrometry (ICP-OES). The rainwater and the soil samples were analysed to determine the concentration of seven heavy metals (Cu, Co, Cr, Cd, Pb, Ni, Zn), rainwater was analysed with inductively coupled plasma optical emission spectrometry, soils samples (after having been exposed to aqua regia digestion) were analysed with atomic absorption spectroscopy (AAS). The pH-values of the soil samples were determined with a potentiometer, the Arany yarn number was determined with the Arany yarn test, the organic matter content (H%) was determined with colorimetric analysis, the carbonate content ($CaCO_3$%) was determined with Scheibler's calcimetric method, and the total water-soluble salt content of the soil samples (total salt%) with a conductivity meter. The particle size distribution was analysed with laser diffraction spectroscopy, and the results of this test allowed me to sort the samples on the basis of their texture. Undisturbed samples were analysed with permeameter to determine soil saturation hydraulic conductivity (K), and mass analysis was applied to determine bulk density, total porosity, and moisture content.

I analysed the adsorption properties of twenty soil samples relating to copper (Cu) and nickel (Ni) in static equilibrium experiments. I added $NiSO_4$ and $CuSO_4$ solutions of different initial solution concentration (C_0) to the soil samples in the course of the model experiments, then, after shaking the samples, I measured the equilibrium solution concentrations (C_e) of each suspension with an atomic adsorption spectrometer. I calculated the metal concentration bound by the soil (q) with respect to the dilution ratio (2.5) knowledge, using the C_0 and C_e values. In order to draw the adsorption isotherms, I plotted the Ni and Cu concentrations of the equilibrium solution (C_e) against the equilibrium adsorbed Ni and Cu concentrations (q). The Langmuir function was fitted to the points resulting from the previously drawn adsorption curves, which helped me to determine the values of adsorption capacity (a) and the values of the adsorption equilibrium constant (K_d). I used the Microcal Origin 6.0 software to draw the adsorption isotherms and to fit the Langmuir function.

Classification of the soil and groundwater was based on the "B" contamination limit values of the 6/2009. (04.14) joint regulation of the KvVM-EüM-FVM. Data processing and evaluation were done by using Microsoft Office Excel 2010, and IBM SPSS Statistics 20 software. The maps were created with the ESRI ArcGIS 10 software.

Prior to the evaluation of the measurement results and the calculated data with statistical analyses, I carried out normality analysis and logarithmic transformation. Nonparametric Spearman rank correlation was used to do correlation calculations. On the basis of the Kaiser criterion, principal component analysis was used to classify the studied components, and to explore the geochemical background processes. The spatial separation of the sampling wells (based on groundwater chemistry) was performed by applying Fisher's linear discriminant analysis. The relationships between groundwater fluctuation and changes in precipitation (impact time) were analysed with cross-correlation calculations. In order to analyze both the potential long-term memory of the fluctuation of the groundwater and the Tisza, and their fractal behaviour, R/S (Rescaled Range) analysis was used. I carried out the R/S statistics with Benoit 1.3 fractal geometry software, which is suitable for determining the fractal properties of water level time series, and estimating the Hurst exponents.

Modelling infiltration hydraulics and transport processes of the soil-colloid-groundwater system was carried out by applying the VS2DT 2.2 module of the WHI UnSat software. Measured and calculated laboratory data were used to create the two-dimensional vertical migration models, and the models were run to study the 1, 5, 10, 50 and 100 year-long periods pertaining to the studied heavy metals (Ni and Cu), which were also analysed in the adsorption tests.

SUMMARY OF RESULTS, THESES

1. **Based on the data of the groundwater temperature time series, the temperature of the groundwater on the outskirts of the study area is several °C cooler than that of the city centre's, which proves the existence of the "urban subsurface heat island" phenomenon.**

   a) The temperature of the 28 monitoring wells located in Szeged and its surroundings was continuously measured in the course of the two-year-long water quality monitoring (from October

2010 to September 2012). Based on these results, the temperature of the groundwater wells located on the outskirts is 5–6 °C cooler than the temperature of those wells which are located in the downtown. Consequently, the existence of a “subsurface heat island” is as real as that of the urban heat island relating to air temperature.

b) The intensity of this "subsurface heat island" (the difference between groundwater temperatures measured in the city centre and the outskirts) exceeded even 10 °C as well in extreme cases. The intensity of the heat island is usually the highest in spring (March), the smallest differences (3–4 ° C) appear in October and November (similarly to the intensity of the air temperature urban heat island).

2. **The quality of the groundwater in study area is determined by five geochemical background processes first of all, of which the most significant processes are those which represent the enrichment of the heavy metals (chalcophile elements, transitional metals).**

a) On the basis of the two-year long monitoring analysing the chemical status of groundwater, it has been proven that the groundwater of Szeged is heavily contaminated with inorganic components, often having extremely high concentrations. The concentrations of the individual components represented great temporal variety, so I employed Spearman’s correlation calculations to see whether there is a correlation between the changes of the components' concentrations. The results indicate a strong positive correlation between the transitional metals (Ni, Cr) ($r = 0.81$) and the chalcophile elements (Cu, Zn, Pb) ($r = 0.62–0.84$). The correlations found among the different water quality parameters are due to similar geochemical characteristics in all cases.

b) The principal component analysis (PCA) allowed the separation of five principal components (PC), which confirmed the findings revealed by the correlation analyses. The most significant background process determining the distribution of the studied components is the first principal component (PC1), which represents the enrichment of chalcophile elements. The second most significant background process (PC2) represents the enrichment of transitional metals, which indicates that the enrichment of heavy metals is the first to determine the quality of groundwater with respect to the analysed contaminants. The other processes include: a change in the total ion content (PC3); the nitrogen cycle (PC4); and the enrichment of arsenic and orthophosphate (PC5).

c) On the basis of the spatial distribution of the principal component values, the first background process dominates downtown and in the densely populated areas, the second background process dominates downtown as well, and in the northern parts of the city. The third background process represents the great variety of total ion content, however, no explicit centres can be found concerning this process except the fact that it is also a very important process downtown.

3. **Fisher's two-group discriminant analysis is well applicable to classifying urban groundwater wells on the basis of their water chemistry. By employing this method, the areas where anthropogenic activities affect the quality of groundwater can be separated well.**

a) I had an a priori assumption about grouping the wells on the basis of their water chemistry, i.e. the wells can be divided into two groups: downtown and suburban wells. In order to test my theory, I applied Fisher's (two-group) linear discriminant analysis, which was carried out using multiple variables of the principal components. The analysis resulted in the separation of the distinct groups on the basis of their water chemistry. As the result of the analysis, the samples were easy to be classified into one of the a priori groups ("belváros" and "külváros") with 100% accuracy, moreover, a transitional group was also identified.

b) On the basis of the resulting discriminant function (D = 0.48*PC1 + 0.25*PC2 + 0.98*PC3 + 0.96*PC4 + 1.02*PC5), the determining factor in discriminating the groups is the change of the inorganic compounds (PC3, PC4 and PC5), while the enrichment of transitional metals (PC2) have a less significant role in the process. This function also provides a safe classification of other samples of the sampling wells in the future.

c) The "end result map" shows a stable downtown core with 8 wells belonging to this category, 17 wells in the suburbs, and 3 wells in the transitional category. Based on the water quality parameters of each group, the wells of the downtown category are the most contaminated ones, which indicates anthropogenic influence. It also proves that the pollution in the "belváros" section are mainly of anthropogenic origin as these areas are characterised by the largest traffic, the largest proportion of the built-in areas and the highest population density. Based on the results mentioned above, this method can be used efficiently to the spatial separation of the groundwater wells of any city on the basis of their water chemical characteristics.

4. **The groundwater fluctuation is influenced by artificial effects in urban areas. In order to analyse the natural processes, the data indicating artificial influence need to be separated from the water level time series. Applying histograms of frequency proved to be an optimal method for solving this problem.**

a) After a detailed analysis (normality test, a comparison with the water level of the Tisza) of the groundwater level time series (13.5-year-long and 1.5-year-long), a significant modification of groundwater fluctuation was revealed in the case of the majority of the groundwater wells which was caused by artificial effects (urban water management). Due to the above mentioned artificial effects, the groundwater level does not rise above a certain near-surface level (which is different from well to well), independently of the amount of precipitation or the water level fluctuations of the Tisza. Thus, it can be stated that groundwater fluctuation is influenced by artificial effects, and in order to analyse the natural processes, the data indicating artificial influence need to be separated from the water level time series.

b) In order to separate the data indicating artificial impacts, I employed frequency histograms for each groundwater level time series. The histograms show very well that groundwater level above which the artificial effects dominate, as the "main" mode is separated from the "sub-"mode(s) here. By separating the "sub-"mode, the data indicating artificial impacts can be removed. According to this, histogram analysis can be used effectively to reveal the natural trends of urban groundwater fluctuation as well as to prepare the necessary tests.

5. **Applying the R/S (Rescaled Range) analysis is an effective method for analysing the fractal behaviour of groundwater level time series, and, according to my research, it can be integrated in urban environments well. The method allows the analysis of the flow properties of different urban groundwater bodies as well as the exploration of the potential long-term memory of the river and groundwater level time series. The method is also suitable for determining where a hydrological connection between the groundwater and the surface river exist.**

a) The time series of the water level of the Tisza and that of the groundwater were analysed with R/S analysis in order to determine their potential long-term memory. The Hurst exponents (H) resulting from the use of R/S analysis proved the persistent nature ($H > 0.5$) of both the Tisza and the groundwater. Concerning water fluctuation, persistence means that high water levels are more likely to be followed by high levels, and lower water levels are more likely to be followed by lower levels. I also proved the existence of long-term memory of the water fluctuation.

b) The results show that the R/S analysis, due to its scale invariant feature, is suitable for comparing time series of different length and measurement intervals. On the base of the results, the R/S analysis can be perfectly integrated into the heterogeneous urban environment, and it is also suitable for studying the fractal behavior of urban groundwater systems.
c) Based on the Hurst exponent of the individual groundwater wells, the groundwater fluctuation of some wells exhibit similar behaviour to the Tisza, hence the hydrological connection to the river. Hence, the Hurst exponents can be employed to separate those wells, in the vicinity of surface rivers, of which groundwater is hydrologically connected to the river.
d) By studying the spatial distribution of the Hurst exponents, I was able to prove that the geological structure and the hydraulic conductivity of the formations strongly influence the long-term memory of groundwater fluctuation.

6. Urban soils have been modified by urbanization and anthropogenic activities, which is indicated by construction debris and other artificial objects occurring in the soils, having a heterogeneous textural structure, the randomly changing organic matter content and particle size composition, the variable carbonate content and pH, and the contamination with heavy metals. The comparison of the heavy metal content of the soil with the groundwater lead to the same conclusions which indicate similar contamination sources and geochemical background processes.

a) The anthropogenic induced modification of the analysed soil profiles was already explicit at the time of the sampling, and it was indicated by the presence of debris and other artificial objects, the layer of the highly compacted topsoil, and the lack of genetic soil horizons in many samples.

b) The laboratory results confirmed the findings of the field analyses. The variety of physical properties, pH-value, carbonate content, and organic matter content all reflect the impact of anthropogenic activities. It is only the total dissolved salt content that does not show the impact of anthropogenic activities (e.g. de-icing with road salt), as each soil profile is characterized by low salinity.

c) Analysing the heavy metal concentration of the soil samples revealed similar contamination condition to that of the groundwater: the concentrations of the same heavy metals (Ni, Cu, Zn, Pb) were found to have exceeded the contamination limit values. Based on the results of my measurement, it can be stated that the soil surrounding contaminated groundwater wells is also contaminated with heavy metals.

d) The correlation analysis of the heavy metal content of the soil and groundwater lead to the same conclusions which state that the two groups of components are essential in determining the quality of both agents. One of these groups includes chalcophile elements (Cu-Zn-Pb), while the other includes transition metals (Ni-Cr-(Co)), of which total amount changes simultaneously in the soil and the groundwater as well.

7. **Based on laboratory adsorption studies, the heterogeneous physical and chemical characteristics of urban soils are also manifested in their heavy metal adsorption capacity. Cu adsorbs to soil components to a much greater degree than Ni, so the adsorption affinity sequence of soils is: Cu > Ni. Cu adsorption is determined by carbonate content and pH primarily, while the adsorption of Ni is connected to organic matter content and clay content.**

a) The heavy metal adsorption experiments indicated that the adsorption of both Ni and Cu can be characterised by the Langmuir equation very well as the Langmuirian approach describes the adsorption interactions very well based on the R-squares of the fitted lines of the linearized Langmuir isotherm ($r^2 > 0.95$). The curves of the isotherms display a certain rhapsody, which reflects the heterogeneity of the physical and chemical properties of urban soils. The diversity of adsorption properties result from the modification of soils originating in urban effects. These city-specific modifications are as follows: more alkaline pH than that of the natural soils, high carbonate content (a result of lime-bearing construction materials, debris, etc.), vertically heterogeneous texture and organic matter content (indicating disturbed soil layers).

b) Ni was adsorbed in samples either with high organic matter content or high clay content the most, especially when the low organic matter content was accompanied with high clay content. It is the high carbonate content and the pH that are responsible for the high adsorption capability observed in the case of Cu adsorption first of all.

c) On the basis of the adsorption capacity values of the two heavy metals, Cu has a much greater adsorption capability on soil particles than Ni, moreover, the partition coefficients also indicate that Cu has an extremely high affinity to the soil. Thus, in the case of the two heavy metals, the Cu > Ni adsorption sequence was typical of urban soils which corresponds to the findings of the literature review as well.

8. On the basis of modeling the vertical migration of the studied heavy metals, it is confirmed that the models (and transport processes in the unsaturated zone) are primarily influenced by adsorption properties, hydraulic conductivity, and the depth of groundwater in relation to the surface. The results of the simulations show that the risk of groundwater being

contaminated with Ni is bigger than its contamination with Cu.

a) By modelling the vertical transport of Ni and Cu of the three-phase zone, I concluded that the risk of groundwater contamination relating to Ni-load is greater, which is supported by the findings of the adsorption analyses.
b) Based on the Ni and Co migration models, it can be stated that the Ni and Co concentration of seeping water is mainly influenced by the adsorption capacity of the layers. In addition, other important factors are the relative depth of the water table below the surface, the hydraulic conductivity of the layers, and their clay content. The results also highlight the fact that the model is very sensitive to these data, which emphasises the importance of laboratory tests (especially the adsorption studies).
c) Despite the same boundary conditions, the simulations ran for a hundred of years show that the soil adsorption efficiency of the soils decreases with time resulting in the increasing Ni and Co concentrations of groundwater. As for Ni, groundwater is exposed to additional load originating from the three-phase zone, because the water seeping in from the surface is able to mobilise Ni to such a great extent that it leads to even more contamination. As for Co, the seeping water in each soil profile diluted groundwater even in the hundredth year, so the Co contamination of groundwater is not originating from the unsaturated zone according to the simulation.

My doctoral research proved that the characteristics of both the soils and the groundwater system in Szeged have been modified strongly due to city-specific effects and anthropogenic activities. The changes concerning the groundwater system show up in the modification of groundwater fluctuation, the increase in temperature, and the high total ion and pollutant content the most. The soils are loaded with heavy metals, which affect the quality of groundwater too, but, in return, certain characteristics of groundwater also affect the soils (e.g. the depth and contamination of groundwater).

My research also point out that in order to understand the environmental processes taking place in (and between) the soil and the groundwater, it is not enough to study these two agents in themselves, but as complex pedological, hydrological, hydrogeological, and hydrogeochemical systems as well.

LIST OF PUBLICATIONS RELATED TO THE THESES

Fejes, I., M. Tóth, T., Farsang, A., 2014. A Tisza és a talajvízjárás hosszútávú kapcsolatrendszere Szegeden. FÖLDTANI KÖZLÖNY 144 (3), 275–286.

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