Pollution by Heavy Metals of the Near-Surface Soil Layers and the Groundwater (Ground and Interclay Horizons) in the City of Poznań

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Abstract

The paper reports on the results of the contents of selected heavy metals (copper, lead, cadmium, chromium, zinc, nickel) in near-surface ground layers and in water from the ground and interclay horizons in the area of the city of Poznań. The authors used data collected from routine analyses performed during preparation of hydrogeological documentation prior to planned or already constructed structures. In the investigated ground, the contents of heavy metals were analysed versus the type of ground (clay, sand, anthropogenic soils, humus layer) and the depth of sample collection. In the groundwater the contents of the heavy metals were analysed versus the depth of the water table and its isolation from ground surface – in the free groundwater and in the interclay water horizons.

Keywords: groundwater, heavy metals, soil, embankments, sand, cohesive soil

Introduction

Copper, lead, cadmium, chromium, nickel and zinc occur naturally in the environment in very small, hence trace, amounts. Their natural cycle in the nature is equilibrated, so their released and bound amounts are the same. Development of industry, transportation, mining, agriculture and the process of urbanisation has disturbed the natural cycle. Increased use of metals has changed the equilibrium between the amount of metals introduced into the natural environment and that deposited in geological formations. Having analysed this phenomenon Bowen classified Cd, Cr, Pb, Zn, Cu to the group of elements of very high accumulation coefficient. Moreover, because of their harmful effect on living organisms these elements belong to the group of microcomponents posing high potential threat to the natural environment [1, 2].

The Area and Material of Study

The city of Poznań was founded on the Ostrów Tumski island situated on the Warta River, in close vicinity of the its tributaries Cybina and Bogdanka. The city has developed on the left and right banks of the river and presently it occupies an area of over 260 km². Geomorphologically Poznań lies along the gorge section of the
Warta river separating two parts of the bottom moraine highland [3]. The external geological structure of the area developed in the late Pleistocene, during the last glaciation and in Holocene. Geologically the highlands are built mainly of direct accumulation deposits brought by the northpolish (północnopolskie) glaciation in the leszczyńska phase. According to the lithological classification these are mainly loamy sands or sandy loams. The loams are covered with post-water-glaciation deposits (sands of various grain size), making sands developed in the Poznań phase of the last glaciation. The river valleys are filled with alluvial sediments (river sand), comprising of organic origin sediments (humus layers) and rarely with flood water sediments (muds and silts).

The paper presents analysis of data taken from 180 tests of the soil samples and 160 tests of the groundwater samples. The samples were collected either at the stage of preliminary geological study needed for hydrogeological documentation for the planned or already erected structures that could negatively affect the natural groundwater balance, or as part of monitoring of the local groundwater status or as part of the natural environment study conducted by GT Projekt in Poznań.

The samples of the soil were usually collected at the depths of: 0.3 m, 1.0 m and 2.0 m. At some sites due to local terrain conditions and type of study the samples were collected at other depths. Analysis of these samples provided information on changes in the heavy metal concentration in the ground/soil versus the depth of the samples collection. Another aim of our study was to check a possible correlation between the content of the heavy metals and the type of geological formation of the samples. According to PN-86/B-02480 the following four geological formation types were distinguished: top soil, man made soil/embankments, sands and cohesive deposits.

The classification is based on the following definitions:

a) topsoil – the near-surface layer of the lithosphere formed as a result of plant vegetation and the presence of microflora and microfauna. The layer is a natural formation with no interference of man.

b) man made soil/embankments – are made by man from a mixture of natural substances (sand, clay) and waste products (pieces of wood, rubble, glass and others). The presence of waste products indicates their not natural origin.

c) sand – incohesive deposits (less than 2% silty fraction). In the analysed area their presence is related to glaciation (fluvio-glacial sands), presence of rivers (alluvial sands) and others;

b) cohesive soil – deposits containing over 2% of silt fraction. In the analysed area they come directly from the northpolish (północnopolski) or rarely middlepolish (środkowopolski) glaciation.

The groundwater was collected from the first and/or second water horizon. The first water horizon is that of free water table or locally under pressure water table in incohesive deposits or that of percolations/seepage in the cohesive deposits. The depth of the first water horizon depends on the geomorphology of the area (highland, river valley or boundary area), the amount of precipitations (the lowest at the end of summer and beginning of autumn, the highest in spring) and the mode of use of the area. In the analysed area the first water horizon occurred at the depth from 0.80 to 10.20 m (median) and 3.70 m p. p. t. (below ground surface). The second water horizon in the analysed area is the upper interclay layer [4]. In this horizon water occurs in interclay sand deposits surrounded by hardly permeable layers of moraine clay from middlepolish (środkowopolskie) glaciation – at the bottom, and with a layer of moraine clay from the latest glaciation – at the top. This layer of moraine clay makes a natural barrier protecting against the influence of surface pollutants. The thickness of the clay layer is different and varies from 2 to over 13 m, it is locally reduced for anthropogenic reasons. The groundwater at this horizon is under pressure (this is confined groundwater). The mean (median) depth of the water table is over 9 m p. p. t. (below ground surface).

**Laboratory Methods**

The air-dry samples of the ground were sieved through nylon sieves of the mesh size of 2 mm. The weighted portions were mineralised with concentrated nitric acid and hydrogen peroxide for 2 hours at 100°C. The concentration of metals was determined by F-ASA on a spectrometer Analyst 300 produced by Perkin Elmer. Water samples were analysed by ETAAS on a spectrometer Spectra Plus produced by Varian.

**Results and Discussion**

The data on the content of heavy metals in the soil were analysed versus the depth of the soil profile and versus the type of ground formation. The statistical analysis was performed with Excel Statistics program. The contents of particular metals versus the depth of the soil profile are presented in Fig. 1. No data for chromium are included as this metal was determined almost exclusively in the man-made soil/embankments. The contents of copper, zinc and lead decrease with greater depth of sample collection, which means that these metals enter the soil from the surface layers and migrate inside. No significant changes with the profile depth are noted for cadmium, however, as the concentrations of this metal are very low this fact may follow from analytical limitations. Also no significant tendency of concentration changes with the profile depth was observed for nickel. This metal occurred in very low concentrations and the results were characterised by significant scatter, hence were influenced with considerable random error and their interpretation was difficult.
Pollution by Heavy Metals...

Fig. 1. The content of selected heavy metals in ground versus the depth of the soil profile.

Changes in the contents of the heavy metals studied versus the type of ground formation (topsoil, man made soil/embankments, sandy and cohesive deposits) are illustrated by the plots in Fig. 2 and 3. In a vast majority of the samples the concentrations of heavy metals were very low and only in few samples they were high, which means that the arithmetic mean is influenced with a relatively large error and brings unreliable information. In view of the above we assumed medians as the characteristic values. The highest concentrations of heavy metals were found in soil samples, containing large amounts of organic matter, mainly humus compounds capable of binding metals, which means that their natural concentrations in the soil are higher. The results of the heavy metal determinations in the soil were characterised by the greatest scatter, which indicates partial pollution of this layer. The topsoil is directly exposed to the atmospheric pollution and hence its main receiver. In the samples collected from man-made embankments the concentration of metals and the scatter of results were lower. The lowest concentrations of the heavy metals studied were found in sands and slightly higher in cohesive ground, which is fully understood, because they occur at greater depths and have no direct contact with sources of pollution. The lowest concentration of heavy metals in sands is a consequence of their structure. While the cohesive soils contain fine silty and clay fractions being a natural barrier for heavy metals. Moreover, the cohesive soils are characterised by a low coefficient of water permeability so the infiltration of the precipitation takes much longer, which together with developed surface area favours adsorption of dissolved metals.

A comparison of the results obtained with the admissible levels specified in the “Directive of the Minister of the Natural Environment of Sept. 9th, 2002, on the standards of soil and ground quality” indicates that the degree of the soil and ground pollution with heavy metals in the area studied is not high. As much as 75.9% of the results obtained for the samples in which the heavy metal contents were determined satisfied the requirements of group A land, i.e. the land under legal protection such as national parks, nature reservations, etc. The samples collected in urbanised environment such as Poznań were expected to represent the values typical of group B land. As much as 97.5% of the results meet the standards for group B. Only 3 of all samples studied showed strong contamination with heavy metals, exceeding the levels of the standards. One of the samples (soil) was strongly contaminated with copper, nickel and cadmium. The other two were the samples collected from an embankment and one of them was strongly polluted with lead, while the other with zinc, cadmium and lead. Analysis of the contents of metals in the four distinguished types of grounds revealed the highest level of the metals in cohesive soils and man made soil/embankments, manifested mainly as an elevated level of cadmium. However, in general the metal concentrations determined were not high.

Literature reported the contents of heavy metals determined in samples of 5 soil profiles in the Warta river, and the mean values of the metal concentrations were: Cu - 498.8 mg/kg, Zn - 137.0 mg/kg, Pb - 69.7 mg/kg, Cr - 24.8 mg/kg, Cd - 1.2 mg/kg and Ni - 8.4 mg/kg [5], however, the results of our study did not confirm these findings. The concentrations of copper, zinc and lead were much lower (Cu - 32.4 mg/kg, Zn - 32.8 mg/kg, Pb - 29.1 mg/kg), the concentration of cadmium was similar (Cd - 1.3 mg/kg), while the concentration of nickel in our samples was higher (Ni - 55.2 mg/kg). As indicated earlier, the arithmetic means of the concentrations can be influenced with a significant error following from inhomogeneous distribution of results in separate determinations. "The Geochemical Atlas of Poznań and its vicinity" issued by the Polish Geological Institute in 2005, reports the concentrations of heavy metals in the soil in the area studied [6]. The data presented in the Atlas are usually lower than those we obtained, which can reflect the fact that the samples analysed by the authors of the Atlas were collected from sites evenly distributed over the city area. The samples used in our study were collected at sites of planned or already constructed structures, so from the areas more exposed to pollution and contamination. In spite of that our results do not indicate a higher pollution of the grounds/soils in Poznań.

The contents of the selected heavy metals in ground water are shown in the plots in Fig. 4,5. Similarly as for the samples of the soils, the analysis was made for the medians. The arithmetic means were much higher, e.g. the median concentration of zinc in the ground water was 0.0748 mg Zn/L, while the arithmetic mean was 3.4097 mg Zn/L, which was a consequence of a single incident of a very high concentration of 175 mg Zn/L. The differences were higher for the samples of ground water, which were not isolated from the surface by a layer of hardly permeable clay. According to the standards given in the "Directive of the Minister of the Natural Environment on classification of surface and ground waters, monitoring procedures, interpretation of results
Fig. 2. The content of heavy metals (Cd, Cu, Ni) in the ground versus the type of topsoil.
Fig. 3. The content of heavy metals (Zn, Pb) in the ground versus the type of topsoil.
Fig. 4. The content of heavy metals (Cd, Cu, Ni) in groundwaters (ground horizon and interclay horizon).

and presentation of the status of ground and surface waters\(^6\), 40% of the water samples studied represented class 4 and 5, i.e. classes of poor and bad quality. The situation was the main responsibility of the high contents of cadmium (elevated level in 22.6% samples) and lead (elevated level in 18.0% samples). The smallest number of samples were contaminated with chromium (2.2%) and nickel (4.4%). The data obtained for the interclay water samples, isolated from the surface by a layer of hardly permeable clay, showed much less scatter of results. Taking into respect the contents of studied metals, 20.5% of the samples analysed were classified as representing water of poor or unacceptable quality. This classification follows mainly from high contents of lead (15.4% samples) and cadmium (12.8% samples). The contents of the other metals allowed for classification of these waters as of satisfactory, good and very good quality. To check for possible pattern of the presence of particular metals in the ground waters over the area studied, the correlation coefficients of the metals co-occurrence were calculated. In the ground water samples the correlation coefficients did not exceed 0.25, hence no statistically significant correlation between the concentrations of particular metals was found. In the interclay water samples the correlation coefficients, \( r \), characterising co-occurrence of four pairs of metals were much higher: \( \text{Ni} - \text{Cd} \) \( r = 0.58 \), \( \text{Pb} - \text{Ni} \) \( r = 0.57 \), \( \text{Pb} - \text{Cd} \) \( r = 0.68 \), \( \text{Pb} - \text{Cr} \) \( r = 0.67 \), indicating statistically significant relations. The relations can indicate preservation of the natural composition close to that of the geochemical background. No statistically significant correlations were found for the ground water, which indicates significant changes in their composition caused undoubtedly by anthropogenic factors.

In the years 1992-1994 a study was undertaken to establish the quality of the underground waters of the first waterbearing horizon (ground waters) among others in the area of Poznań [7]. The samples to be studied were collected from public wells in the area of the city. In the samples the contents of heavy metals were also determined and their concentrations did not differ much from results presented in this paper.
On the basis of analysis of the hydrogeological documentation Lesińska [8] presented the maximum amounts of heavy metals in the ground waters: Cu - 1.153 mg/L; Zn - 350 mg/L; Pb - 65 mg/L; Cr - 0.17 mg/L; Cd - 11 mg/L; Ni - 2.29 mg/L. However, these values were found in the samples coming from the sites subjected to strong anthropogenic pressure, including e.g. waste dumps. The samples we analysed came from sites that were not directly contaminated.

Analysis of the heavy metals contents in the samples of the ground water is clearly indicative of a state of pollution with heavy metals. The pollution occurs on the surface of the area from where it migrates into the ground water of the first horizon, which is not isolated from the surface by a layer of hardly water permeable clay. Such an interpretation is supported by the earlier results of ground profile investigation. The quality of the interclay waters, isolated from the surface by a hardly water permeable layer, is much better. Taking into respect the fact that the water from the first and second waterbearing horizons are an emergency source of drinking water for Poznań inhabitants, their poor quality is a serious problem.

**Conclusions**

The data analysed indicates the state of pollution/contamination of the ground surface layers in the area of Poznań. However, the pollution is very low and only incidentally high. In general, taking into regard the contents of cadmium, lead, copper, nickel and zinc, the soils are not polluted and they meet the standard requirements of urbanized areas. The state of pollution of the ground waters is much more serious. The contents of heavy metals, in particular cadmium and lead, indicate considerable effect of anthropogenic factors on the quality of the ground waters. This effect is much less pronounced on the interclay water in which the contents of the heavy metals studied are much lower and their composition is close to that of the natural background.
References