Assessment of the hazard posed by metal forms in water and sediments

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HIGHLIGHTS

- Heavy metals mobile forms and bioavailability determination, in Utrata river
- PHREEQC2 mathematical model was used.
- High percentage of mobile and eco-toxic forms of zinc, copper and lead was found.

GRAPHICAL ABSTRACT
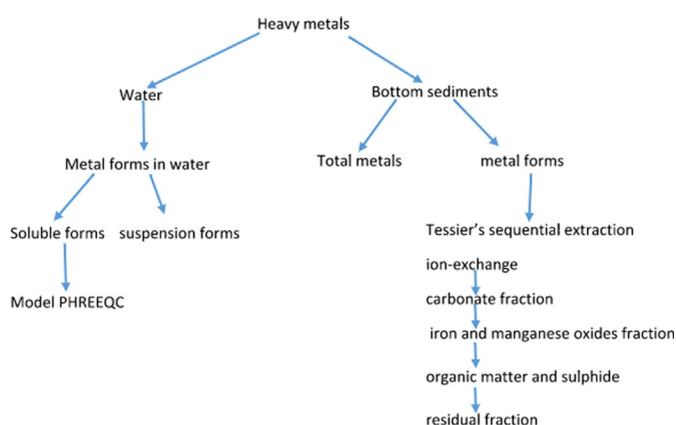
ABSTRACT

This study aimed to describe the prevalence heavy metals (Zn, Cu, Pb, and Cd) forms in the ecosystem of the Utrata river in order to determine the mobile forms and bioavailability of metals. To extract the dissolved forms of metals in the water of the Utrata PHREEQC2 geochemical speciation model was used. The river waters show a high percentage of mobile and eco-toxic forms of Zn, Cu and Pb. The percentage of carbonate forms for all the studied metals was low (<1%). The content of carbonates in the water and the prevailing physical and chemical conditions (pH, hardness, alkalinity) reduce the share of toxic metal forms, which precipitate as hardly soluble carbonate salts of Zn, Cu, Cd and Pb. Cu in the water in 90% of cases appeared in the form of hydroxyl compounds. To identify the forms of metal occurrence in the sediments Tessier's sequential extraction was used, allowing to assay bound metals in five fractions (ion exchange, carbonate, adsorption, organic, residual), whose nature and bioavailability varies in aquatic environments. The study has shown a large share of metals in labile and bioavailable forms. The speciation analysis revealed an absolute dominance of the organic fraction in the binding of Cu and Pb. Potent affinity for this fraction was also exhibited by Cd. The rations of exchangeable Zn and Cu forms in the sediments were similar. Both these metals had the lowest share in the most mobile ion exchange fraction.

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1. Introduction

It is known nowadays, that in order to establish the impact of heavy metals on aquatic communities, it is not sufficient to evaluate their total content, which does not provide information on metal bioavailability

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and the subsequent threat posed to living organisms. Metal bioavailability is dependent upon the forms that they adopt in a given element of the environment, and in order to establish those forms speciation testing is used (Gao and Chen, 2012; Pejmana et al., 2015).

The data most frequently presented in the literature refers to the general metal content in water, being a sum of dissolved forms and forms bound with the suspended solids. An important mode of interaction between metals and aquatic ecosystems is the form of the pollutants. Dissolved substances continuously undergo a chemical exchange with the suspended fraction and bottom sediments, which disturbs the balance of pollutants in the water - sediments system. The recognition of metal forms present in the aquatic environment allows for the assessment of their migration from bottom sediments to waterbody and to analyze the processes of their transformation and binding.

Chemical composition of surface water sediments, including the amount of ingredients hazardous to living organisms, that are present there is affected by numerous natural and anthropogenic factors (Alonso Castillo et al., 2013; Brils, 2008; Helios-Rybicka and Aleksander-Kwaterczak, 2009; Huo et al., 2015; Liu et al., 2015; Wang et al., 2015; Zhang and Gao, 2015). The composition depends primarily on geological structure of the catchment area, geomorphology and climate conditions that determine the rock weathering process and activating, migration and accumulation of elements in the environment (Bojakowska et al., 2003; Gu et al., 2015; Ma et al., 2016; Pejmana et al., 2015). Sedimentation of the material floating in the fluvial channel depends on the power of the stream of flowing water and the channel structure (Martin et al., 1989).

The type of mineral ingredients affects granulometric composition and the compactness of bottom sediments, whereas granulation affects the accumulation of substances from the water phase and the degree of their binding on the surface of the solid phase (Förstner and Salomons, 1981; Paramasivam et al., 2015; Xu et al., 2014). In the majority of studies, it has been established that over 90% of fluvial sediments are composed by a fraction of over 0.06 mm, composed of quartzes, and to a lesser extent by feldspars and carbonates (Wojtkowska and Bogacki, 2012; Adiyiah et al., 2014).

In many cases the chemical composition of bottom sediments is a better index of environmental pollution than the water composition. The element content changes significantly between sediment layers, reflecting chronologic changes in the pollution of the waterbody (Ciszewski, 2003; Sikora et al., 2001; Wojtkowska, 2011; Liu et al., 2015; Xu et al., 2014). Higher metal content allows the differentiation between sediments deposited after and before the activation of the source of pollution (Campbell and Stokes, 1985; Huo et al., 2015; Kabata-Pendias, 1996).

The presence of a given metal form is strictly related to water pH and Eh levels that affect metal solubility and concentration (Campbell and Stokes, 1985; Farag et al., 1993; Gu et al., 2015; Huo et al., 2015; Pejmana et al., 2015; Wybieralski and Maciejewska, 2003). Iron and aluminum form very strong complexes with dissolved organic matter (DOM), which Pbs to leaving e.g. Cu^{2+} in a bioavailable form (Schubauer et al., 1993). Presenting the interaction of metals with organic matter still remains a significant challenge due to diversified properties and structure of the Natural Organic Matter (NOM) (Fu et al., 2014; De Schamphelaere and Janssen, 2004; Wu et al., 2015).

NOM can alter the mobility of metal ions in aquatic systems in two ways. First, interactions of NOM with the metals to form NOM-metal complexes decrease the amount of sorption of the metals to solid soil material. Second, NOM can also change the transport behavior of mineral colloids by suppressing aggregation and consequently altering settling or filtration behavior of the aggregates (Schmitt et al., 2002).

Therefore, the assessment of heavy metals contamination in sediments is urgently needed to interpret the bioavailability, mobility and toxicity of heavy metals and provide basic information for utilization and supervision.

The main objectives of this study were: (Ackay et al., 2003) to determine the concentrations of heavy metals including Cd, Cu, Pb and Zn in the surface sediments Utrata river; (Adiyiah et al., 2014) to assess their potential ecological risks.

2. Materials and methods

The study was conducted upon the Utrata river flowing in the central part of Poland. Utrata's catchment area equals 792 km^2 and it is 78.2 km long. The Utrata catchment area is industrialized, and sewage is discharged from several dozen plants. For the purposes of the study a 15 km segment in the Pruszków district was selected. Surface water and the Utrata catchment aquifer are polluted through sewage discharge and pollutant infiltration in the form of leachate and run-off from the above-mentioned sources as well as through air pollution and bottom sediments (internal recirculation). The Raszynka river, a right tributary of the Utrata river, belongs to degraded rivers. Its left tributary carries contaminated waters from the built environment.

Quality assessment of water and bottom sediments from the Utrata river was conducted in the period from September 2005 to March 2009. Samples were taken in spring and autumn seasons. Water and bottom sediment sampling were performed in 11 sites; 8 of which were in the Utrata stream, and 3 other in the Raszynka and Żbikówka tributaries, and the Potulicki pond (Fig. 1).

Samples for chemical tests were taken from the defined sites from a surface layer, 0–0.5 m. Sampler Ruttner (KC Denmark Research Equipment, Denmark), was used to collect water samples. Part of sampled water was filtered with the use of a Fison filtering system, applying nitrocellulose membrane filters with a pore diameter of 0.45 μm.

Heavy metals, Zn, Cu, Pb and Cd, were determined in the water and solid phase residue left on the filters. A membrane filter with retained solids was dried to constant weight at 105 °C, and subsequently underwent mineralization. Wet mineralization was conducted by placing an aliquot in a concentrated acid mixture (5 ml HNO$_3$ 65% and 2 ml HClO$_4$ 60%). Sediment samples from the surface layer with the thickness of approx. 10 cm were collected with a Kajak sampler (KC Denmark Research Equipment, Denmark). Sampled bottom sediments were air-dried at room temperature. Total metal content was established for the dried sediment fraction with the particle diameter < 0.090 mm. A 1 g sample was weighed from the separated fraction. Wet mineralization was used with the mixture of concentrated acids (9 ml HNO$_3$, 65% and 3 ml HClO$_4$ 60%). Mineralization was conducted in the digestion block, with a bottom sediment and acid mixture placed in the Teflon container.

The content of heavy metals selected for testing in the aqueous sample was determined using Graphite Furnace Atomic Absorption Spectrometry (GF-AAS) and in the suspension and bottom sediments, after wet mineralization and extraction, it was determined using Flame Atomic Adsorption Spectroscopy (FAAS), based on reference curves determined for a series of already prepared MERCK reference solutions.

In this study, the concentration of forms of Zn, Cu, Cd and Pb in water were modeled using a geochemical speciation model PHREEQC2. Metal forms in water were determined using AQUACHEM program, software built into the interface of software for geochemical modeling, PHREEQC2 (Paquin et al., 2002).

This is speciation-solubility model, used to simulate the chemical reactions and transport processes in natural water or polluted water. It allows the modeling of reaction, both reversible and irreversible, which take place eg. in the water–gas–solid system. Geochemical reactions can be simulated with the assumption they progress through the system of immediate balance or taking into account the kinetics. The program allows one-dimensional, multi-advection-dispersion modeling of mass transport in the rock, in the hypothetical column or the flow of water. The calculations are based on the Debye–Hückel theory. Input data for modeling programs is the following: pH, temperature and total concentration of Zn^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+} (μmol/L), as well as Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, NO_3^-, NH_4^+, SO_4^{2-} and PO_4^{3-} (mmol/L).