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SUSPENDED PARTICULATE MATTER AS AN INDICATOR OF METALS POLLUTION IN RIVERIN SYSTEM

CHARAKTERYSTYKA ZAWIESINY JAKO WSKAŹNIKA ZANIECZYSZCZENIA ANTROPOGENNEGO METALAMI SYSTEMÓW RZECZNYCH

Abstract: Content of heavy metals is strongly dependent on the composition of suspendend particulate matter (SPM). Metals contamination of the aquatic environment can be natural origin as well as is a result of human activities. SPM is an important indicator of processes occurring in the basin. Mineralogical and geochemical identification and determination of the origin of the suspension components is necessary to evaluate the role of SPM in the accumulation and transport of trace metals in Odra river. Research were carried in the Upper and the Middle Odra River and its tributaries. SPM samples were analyzed with SEM-EDS application and metals in water and SPM were determined by ICP-MS. Result of SEM-EDS shows the presence of carbonates – mainly calcite, silicates – especially quartz and feldspars as well as illit. Obtained results allowed to recognize a variety of plankton species. It should be noted that very common in SPM feldspar and quartz contain relatively low amount of metal, as opposed to clay minerals that are responsible for the pollution. In SPM samples the presence of significant quantities of anthropogenic dust were recognized. Observed metal pollution of the Odra river basin is dangerous because of their toxic nature and the threat to living organisms. Suspended matter seems to be one of the best indicator of antropogenic pollution in riverin system.

Keywords: suspended particulate matter (SPM), heavy metals in Odra river

Trace metals are present in aqueous systems in the form of soluble, colloidal and associated with the solid phase – *suspended particulate matter* (SPM) and river sediment. Clear identification of the SPM transport in the river system is very complex and requires accurate diagnosis of lithological and geochemical basins and a detailed assessment of its impact on the course of chemical reactions in the rivers [1–4]. Quality and quantity of SPM depending on the shape and geology of the river bed (riverbed erosion), of the catchment area (surface denudation) as well as the climate and seasons [5]. In order to determine the degree of contamination by heavy metals of anthropogenic

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origin it should be taken into account geochemical background and suggested the adoption of geochemical background values for clay rocks (similar to SPM mineralogical and chemical composition and physical properties) determined by Turekian and Wedephola [6]. In the SPM similar to sediment – metals accumulate in the finest fraction mainly constructed of clay mineral, iron oxides and manganese and organic matter. Detailed research of heavy metals sources of in river suspended matter are presented by Jedwab [7–8] and Van Maledern et al [9]. Jambers et al [10] determined the high content of organic matter in a particle-rich in Mn, Cr, Zn, Ni. The strong correlation between organic matter and particles rich in heavy metals proves its sorption capacity. These studies have shown the presence of high content of kaolinite in the spring and increased the content of chlorite and biotite during the rainy season. In the spring time the amount of organic matter increasing few times. It is important to mentioned that aluminosilicates can be coated with organic and then be recognized as organic matter. Organic matter can play an important role in the formation and aggregation of minerals [10]. It also confirms that the amount of organic matter in the spring is much higher and variable and the total amount of the SPM during the year is relatively constant. The objectives of this preliminary study were to identify mineralogical and geochemical composition of the suspended matter in the Odra River. Furthermore, discus mobility and potential bioavailability of metals in comparison with the total amount. The Odra River catchment area is 136 528 km^2. In total, there are about 1700 sources of pollutions at the Odra River catchment area, out of which 700 significantly influence the conditions of river system. In the past, in the catchment area of the upper and middle Odra exploited large amounts of iron ore, copper, uranium, arsenic and minor amounts of gold and pyrite. Currently in operation are turoszowskie lignite, copper ore and clays, carbonates and natural aggregates and rock materials, fluorite, barite, gypsum and anhydrite deposits, and having only metallogenic importance of chromium, copper, arsenic, gold, tin, cobalt, nickel and other metals ore. The geological structure, industrial and agricultural activity and localisation of main industrial centers, which are: mining (coal, copper), metallurgy (non-ferrous), electroplating plants, production of dyes, pigments production, pesticides, anticorrosive materials and power industry caused many environmental problems in the Odra Catchment Area. There are many publications about the effect of mining and processing industry on environment in Poland [11–14]. Information on total concentration of metals in SPM is not sufficient to assess their potential toxicity, which depend on their chemical forms [15–16]. Metal speciation are widely used to determined different forms of metals in river system [17–18]. Nevertheless, chemical extraction procedures have been applied mostly on sediments but rarely on SPM. All presented results are supposed to confirm that metals and their forms in suspended particulate matter seems to be be one of the best indicator of antropogenical pollution in riverin system.

Sampling and methods

Research were carried in the Upper and the Middle Odra River. In order to identify the composition of SPM in Chalupki, Scinawa nad Bytom Odrzanski samples of SPM were taken in June 2000 and were analyzed with SEM-EDS application. For the sampling of SPM-samples water from a depth of about 1m was taken to PE-bottles and PE-barrels. After sedimentation a part of the cleared water were decanted. Concentrated suspended matter were filtrater (membrane filter d = 0.45 μm) and freeze dried. Furthermore this material were used for mineralogical and geochemical analyses. The SEM-EDS (HITACHI S-4200 VOYAGER acceleration voltage: 15 keV) was used for preliminary analysis. Samples were dusted with carbon before observation. SEM-EDS analysis were used for identification of individual mineral grains, plankton species and for qualitative information about SPM samples. Detection is possible at certain points.

Results and discussion

SEM results show the presence of carbonates, mainly calcite, silicates – especially quartz and feldspar, illit (Fig. 1).

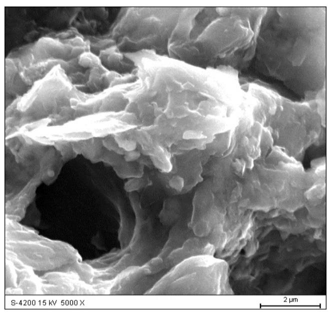

Fig. 1. SEM photo – Illit Chalupki

It should be noted that very common in SPM feldspar (Fig. 2) and quartz (Fig. 3) contain relatively low amount of metal, as opposed to clay minerals that are responsible for the pollution. Fine fraction is composed mainly of silicates, including ilit, smectite and other clay minerals.

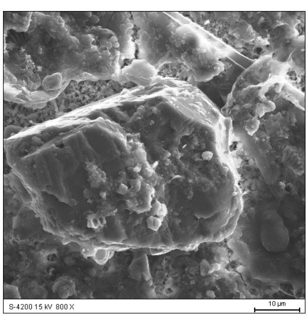

Fig. 2. SEM photo – Feldspar Bytom Odrzanski

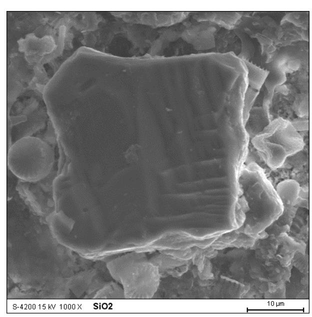

Fig. 3. SEM photo – Quartz – Bytom Odrzanski [19]

Obtained microscopic analyses results allowed to recognize a variety of plankton species, the most common are *Navicula lancelot* (Fig. 4), *Cyclotella meneghiniana* and *Nitzschia acicularis* (Fig. 5). Among others are *Asterionella formosa*, *Aulacoseira granulata*, *Cyclotella radiosa*, *Cymbella silesiaca*, *Diatoma vulgaris*, *Melosira varians*, *Meridion circulare*, *Navicula cryptocephala*, *Nitzschia dubia.*

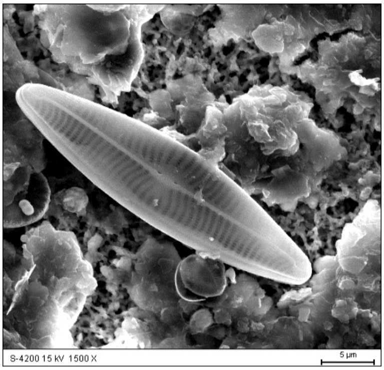

Fig. 4. SEM photo – *Navicula lanceolata* – Chalupki

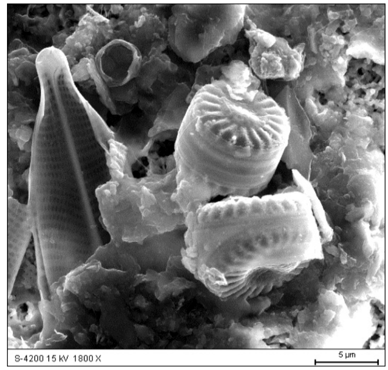

Fig. 5. SEM photo – *Cyclotella meneghiniana*, *Nitzschia acicularis* – Scinawa

In SPM samples the presence of large quantities of anthropogenic dust and grain were recognized (Fig. 6, 7).

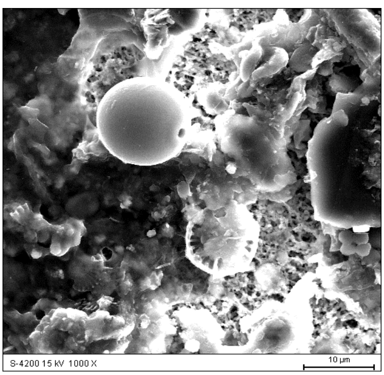

Fig. 6. SEM photo – Antropogenical fly ash – Chalupki [19]

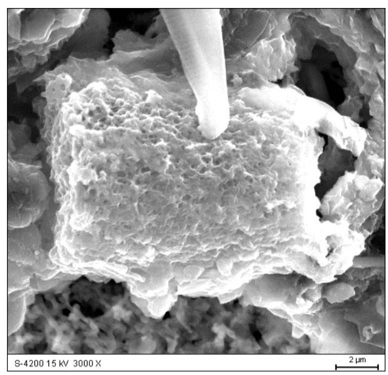

Fig. 7. SEM photo – Aluminosilicate Mn-Ca Anthropogenical origin [19]

Additionally Ca, K and Mg studies were carried out. Obtained concentrations were respectively (average amount mg/dm^3) 71.5, 8.77, 18, 37. In meantime author carried out the detailed study of the amount of SPM and metal content in water and SPM. Over 150 samples of water and SPM were taken from Chalupki to Krosno Odrzanskie during 5 sampling Campaigns from November 1997 to June 2000. Concentration of suspended matter varied significantly from 0.88 to 115.8 mg/kg. Studies showed that Odra River was significantly polluted with Cd and Zn and moderately with other heavy metals (Pb, Ni, Cr, Fe, Cu, Mn) and As, both in the case of water and SPM. Highest Cd, Cu and Zn concentration in water were observed in the middle Odra River. Average concentrations for Cd, Pb, Cu, Zn and As in riverin water were respectively (µg/dm^3) 0.14, 1.77, 8.24, 55.4 and 2.33. Metal contents in SPM varied in wide ranges (mg/kg): 8.0–302 As, 1.75–39.8 Cd, 24.4–401 Pb, 22.1–1287 Ni, 42.4–351 Cr, 6.2–399 Cu, 351–31369 Zn, 1152–11010 Mn and 23881–121316 Fe. Above results and discussion are presented in [19–20]. In case of Cd, Zn, Cu the detected levels of metals in both water and SPM exceeded LAWA targets value [21]. The enrichment factor calculated according to the background values proposed by Turekian and Wedephol [6] and by Martin and Maybeck [3] for As, are as follow: 28.4 (Cd) > 22.8 (Zn) > 11.2 (As) > 8.4 (Pb) > 2.2 (Cu) > 1.5 (Ni) > 1.3 (Cr), [21].

Observed metal pollution of the Odra river basin is dangerous because of their toxic nature and the threat to living organisms. Suspended matter accumulates metals mainly in the fine fraction – clay minerals, iron and manganese oxides and organic matter. In order to determine the metals mobility and the different forms of metal binding in the suspension sequential extraction procedure was applied. In June 2000 – 9 SPM samples from river and 6 from tributaries were taken in order to estimate the mobility and potential bioavailability of metals in SPM. Detailed results were published in [19]. After selective chemical extractions procedure according to Calmano [22] metals were analyzed by ICP-MS. In order to estimate accuracy of the analytical method, reagent blanks and certified reference materials (riverine water 1643d, Lake Sediment LSKD-4) were used to assure criteria related to quality of the analytical results. Unambiguously of ICP-MS technique was confirmed by TXRF.

Considering the mobility of metals in the suspended matter, the exchangeable and bound with carbonates, easily and moderately reducible, sulfidic and organic as well as metal in residuum were estimated using the sequential extraction procedure. Results show that about 25 % of As is bounded to carbonates. As is mainly associated with Mn oxides (60 %). Cadmium is easily exchangeable and associated with carbonates and Mn oxides. Most Pb associated with sulfides, organic substances and / or in residum. Zinc is bounded in the first two extraction steps respectively; 24 % and 18 % of Zn in the Odra River and its tributaries is exchangeable and carbonates associated up to 26 % and 14 % respectively in the tributaries of the Oder river. Other quantities mainly in the presence of organic substances and/or sulfides of amorphous (approximately 20 %) and related oxides of Mn, (about 26 % in the Odra tributaries 11 %). Copper is present mainly as associated with amorphous Fe oxides, both in the Odra River (34 %) and in its tributaries (53 %) and bounded with organic substances and/or amorphous sulfides or in residum (about 20 %). Chromium is present in SPM mainly in the form of amorphous Fe oxides (about 30 %). Detailed results were published in [19].

Conclusions

Metal pollution of the aquatic environment can be natural – caused by geology and geomorphology and/or is a result of human activities, therefore it is so important to analyze geology of the river bed and the catchment area as well as determine anthropogenic sources in the basin. Suspended matter seems to be the important indicator of the processes occurring in the basin and provide relevant information about anthropogenic metal pollution in riverin environment. The composition of river water is conditioned by a number of physical, chemical and biochemical processes. The most important mechanisms defining the migration of heavy metals between the solid and the solution are: sorption – desorption, precipitation – dissolution (treated as a special case of sorption), flocculation-agglomeration and the formation of complexes. Clay minerals, oxides and hydroxides of Fe and Mn, carbonates, organic matter and biological components are responsible for the accumulation of metals in the SPM. Result of SEM-EDS shows the presence of carbonates, mainly calcite, silicates – especially quartz and feldspars as well as illit and other clay minerals as well as antropogenical grains *eg* fly ash, Mn-Ca aluminosilicates in suspended matter of the Odra River. Obtained results allowed to recognize a variety of plankton species, most common are *Navicula lancelot, Stephanodiscus hantzschiin, Cyclotella meneghiniana and Nitzschia acicularis*. Widespread feldspar and quartz contain relatively low metal content, as opposed to clay minerals (fine fraction) and heavy minerals, which contain much higher concentration. Granulomeric SPM analysis shows that fine fraction (< 20 μm) dominates with average values of individual campaigns from 67 mass % in June 2000 to 84 mass % in November 1997 (after flood) [23]. TEM-EDX analyses identified following minerals in the SPM of the Odra River (fraction < 2 μm) – smectite/illite, beidellite, beidellite/montmorillonite, illite, kaolinite, chlorite, nontronite, montmorillonite and montmorillonite/vermiculite [23].

There were no significant changes depending on the season in the suspended matter concentration and metals amounts in the Odra river and its tributaries. High levels of metals in SPM, in particular, As and Cd were found in the upper course of the river from Chalupki to Raciborz and in the middle – from Glogow to Krosno Odrzanskie. Above-mentioned metals can be a significant threat to aquatic ecosystems due to harmfulness, toxicity and high mobility. The study showed extremely high Cd contamination of the river in all compartment – water, suspended matter and in sediment of the Odra River [19]. The significant source of metal in water and suspended matter seems to be the agricultural and industrial activity that takes place in the Odra Catchment Area. Analyzing metals in water and SPM (constant parameters of river water Eh, pH, salinity) it is evident from earlier studies of the Odra River that Cu, As, Cr, Ni and Zn was mainly transported by river water, while Cd, Pb and Fe by river suspended matter [19, 21]. It should be noted that highest concentrations of metals in the riverin water were found in the same locations where there are high contents of these metals in SPM. Comparison of metal content in SPM and sediment of the Odra river revealed similar values for the content of average concentrations in these components. My earlier research based on 5 Sampling Campaigns and over 50 sampling points during each sampling campaigns allow to conclude that changes in the concentrations of metals in sediments are “insignificant” in comparison with the suspended matter [24]. Suspended matter is more “flexible”. Therefore, it is proposed to consider SPM as the indicator of metal pollution of anthropogenic origin in the river system. Another reason it is less complicated procedure for collecting a representative sample compare to sediment as well as better homogeneity and less time-consuming analytical procedure. Information on total concentration of metals is not sufficient to assess their potential bioavailability and mobility, which depend on their chemical forms and transport phases. Selective chemical extractions are widely used to determine the different forms of metals in aquatic systems despite some uncertainties *eg* re-adsorption onto other phases during extraction. It seems very reasonable to measure the amount of mobile forms of selected metals – in particular metals that can be easily released into water *eg* Cd, As, Zn.

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CHARAKTERYSTYKA ZAWIESINY JAKO WSKAŹNIKA ZANIECZYSZCZENIA ANTROPOGENNEGO METALAMI SYSTEMU RZECZNEGO

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Abstrakt: Zawiesina jest ważnym wskaźnikiem procesów zachodzących w dorzeczu. Zanieczyszczenie środowiska wodnego metalami może być pochodzenia naturalnego, głównie jednak ma charakter antropogenny. Naturalnym źródłem metali w systemie rzecznym są określone formacje skalne i minerały ulegające wietrzeniu i erozji. Jakość i ilość zawiesiny jest uzależniona od ukształtowania i budowy geologicznej koryta rzecznego, wielkości dorzecza, jak również klimatu oraz okresów wegetacji. Rozpoznanie mineralogiczne i geochemiczne zawiesiny oraz określenie jej składu i genezy składników ją budujących jest niezbędne do oceny roli zawiesiny w akumulacji i transporcie metali śladowych w rzece. W tym celu przeprowadzone zostały badania SEM-EDS składu zawiesiny. Stwierdzono występowanie węglanów – głównie kalcytu oraz krzemianów i glinokrzemianów, a w szczególności kwarcu i skaleni potasowych. Uzyskane wyniki pozwoliły rozpoznać różnorodne gatunki planktonu, a w szczególności, takie jak *Navicula lancelota, Stephanodiscus hantzschiin, Nitzschia acicularis* oraz *Cyclotella meneghiniana.* W próbkach stwierdzono obecność znacznej ilości pyłów antropogennych. Dodatkowo przeprowadzono badania Ca, K i Mg. Stężenia pierwiastków wynosiły odpowiednio 71,5 mg/dm^3, 8,77 mg/dm^3, 18,37 mg/dm^3. Równolegle autorka prowadziła szczegółowe badania ilość zawiesiny i zawartość w niej metali. Badania wykazały znaczne zanieczyszczenia Cd, Zn i umiarkowane pozostałymi metalami ciężkimi (Pb, Ni, Cr, Fe, Cu, Mn) i As. W celu określenia mobilności przeprowadzono badania form związania metali w zawiesinie. Badania wykazały, że Cd, Zn i As stwarzają największe zagrożenie dla systemu rzeki Odry. Badania SEM-EDS oraz metali i ich form związania z wykorzystaniem ICP-MS pozwoliły na kompleksową ocenę zawiesiny jako potencjonalnego wskaźnika zanieczyszczenia antropogennego metalami systemu rzecznego.

Słowa kluczowe: zawiesina, metale ciężkie, Odra