

The Relationship Between Metal Forms Found in River Bottom Sediments and Land Development (Review)

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1. Introduction

Components of the environment comprise three-phase aquatic ecosystems, whose basic phase is the liquid, i.e. water. On the one hand, it borders the gas phase, which is the atmospheric air, on the other – the solid phase, i.e. the ground which is most frequently covered with bottom sediment. In addition, water contains suspensions which may be formed by inorganic matter and living organisms, representing both flora and fauna. Consequently, the sources of origin and migration routes of various substances which affect surface water quality are numerous.

An integral part of the aquatic environment is bottom sediments. They play a significant role in the biochemical cycle of elements as the place of deposition and chemical transitions of many compounds which find their way into water. Moreover, they constitute a habitat of water organisms, which results in biochemical transitions of the compounds deposited in the sediments. An assessment of pollution impact on surface water quality requires a study of anthropogenic concentration levels and sources. In this respect, bottom sediments which function as sorption column offer particularly useful material for research aimed at determination of major sources of pollution as well as providing a clear picture of what happens in the pelagic zone. Given the relatively easy metal migration from the environment to the water phase, it may be assumed that the metal concentration level in bottom sediments is a sensitive indicator of environmental cleanliness.

Together with water, soluble and insoluble substances in various states of matter migrate and may encounter resistance from a large variety of factors. The latter are usually taken to include internal and external friction, changes in shapes and cross-section dimensions, river load separation and transport, local obstacles to water flow in the river channel, vegetation overgrowing the river channel, as well as irregularities and curvatures of the horizontal system. The total resistance of the river channel is the sum of partial resistances due to individual factors, but the proportion of a factor in total resistances varies depending on flow volume as well as season, which need to be considered in hydrological analyses.

For research into the processes which occur in surface waters, particularly those which shape bottom sediments, significant is the issue of direct measurement of river load movement intensity. Accurate understanding of the processes which occur in the river load,

including erosion, and transport - together with the accumulation of its material - is especially important, chiefly for determination of the speed and route of the pollution accumulated in the sediment [1].

Metals bonded through physical adsorption and chemisorption are in the state of equilibrium with the intermolecular water of bottom sediment and can very easily penetrate into the solution which occurs mainly at increasing water salinification (in particular, an increase in chloride ion content, the ions complexing some of the metals). Metals, in turn, which are bonded through co-precipitation with hydrated iron and manganese oxides and carbonates penetrate into the solution with greater difficulty. This can occur under strongly reductive conditions in the case of metal oxides, and in the case of carbonates - under considerable environmental acidification [2].

Primary and secondary (i.e. of pollution origin) metals are found in environmental material in various chemical forms. In view of that, an assessment of their mobility ought to include several aspects. The content of mobile metal forms which can take direct part in the biocycle, including soluble, ion-exchangeable and unstable complex metal associations, should be determined. An equally important issue is the content of solid metal forms as a potential reserve in the biocycle (e.g. chemisorption ions, poorly soluble salts or metal forms which are part of complex associations with organic matter) and isomorphous contaminants of various metal forms, the siliceous in particular [3].

Considering the relatively easy migration of metals from the environment to the water phase, it may be assumed that the metal concentration level in bottom sediments is a sensitive indicator of environmental cleanliness. Yet in order to obtain information on potential metal mobility in the investigated environment as well as assessing environmental impact of pollutants contained in the sediment which may be removed therefrom as a result of changing physical, chemical or biological conditions [4], it is necessary to perform an operational speciation analysis (fractionation).

A speciation analysis of compounds in aquatic ecosystems, performed with a focus on bioavailability of individual entities and forms in which they occur, provides an opportunity to obtain the data necessary to define environmental hazards. The forms in which elements occur condition their toxicity, synergism and antagonism, or lack of these in relation to other elements, and hence - positive or negative impact on the functioning of living organisms. In a discussion of pollution-related problems, it is important to differentiate between various oxidation states and forms in which metals occur, both at the stage of their penetration into the environment, their migration and changes to particular elements of the biosphere.

Studies of bottom sediments, both in watercourses and in reservoirs, which have been conducted for several years, point to various forms of metals cumulated at the bottoms of aquatic ecosystems. Depending on biological, chemical and physical properties of the environment, elements such as Cd, Cr, Cu, Fe, Pb, Ni and Zn can occur in a variety of forms and be related to, for example, organic or oxide matter. Some studies show, that oxic sediments tend to accumulate transition metals and a few other elements, e.g. Mn, Cu, Ni, Co, V and Mo, while anoxic sediments overlain by bottom waters with very low or no oxygen accumulate these metals, with exception of Mn, plus many of the otherwise relatively unreactive oxyanions [5-7].

The interest in the sequential extraction technique for studies of metals in water sediments has been consistently growing, and more than ten methods are in use presently, enabling the separation of individual element fractions. The methods include those of Gatehouse et al. [8], Tessier et al. [9], Sposito et al. [10], Ure et al. [11] and Hall et al. [12]. To characterise

functional speciation of metals in bottom sediment, Tessier's five-stage method [9] which enables the separation of five fractions is most commonly applied. Consequently, most frequently analysed are the fractions in which metals occur in the following forms:

- exchangeable (F1): these are metals adsorbed on the surface of solids which can pass to the solution due to changes to ionic composition of water or shift of balance in the sorption-desorption system; this fraction is available and relatively mobile;
- bonded to carbonates (F2): these are metals which occur in the form of carbonates or are co-precipitated with carbonates; as a result of decreasing pH values, the carbonate balance is disturbed which causes passage of metals to the solution;
- bonded to hydrated iron and manganese oxides (F3): these are metals adsorbed on the extended surface of the precipitating hydrated iron and manganese oxides under anaerobic (reductive) conditions; due to iron and manganese reduction, the sediment can be dissolved and metals can pass into the solution;
- bonded to organic matter (F4): these are metals adsorbed on the surface of organic matter or metals bonded to that matter; they are temporarily immobilised, but due to naturally progressing sediment mineralisation, they can – with time – pass to one of the other fractions;
- permanently bonded with minerals (F5): these are metals built into the crystal network of both secondary and primary minerals; they are permanently immobilised and, under natural conditions, do not pose a threat to the ecosystem [9].

The physical and chemical properties of aquatic ecosystems are characterised by several mutually dependent parameters. Depending on factors such as geological structure, land development, the form in which individual pollutants migrate to the aquatic ecosystem, climate factors (including temperature and humidity), the amount of oxygen or the environment's acidity, change may occur in solubility of salts present in the waters, forms in which individual entities occur, their bioavailability and toxicity. Consequently, familiarity with the mechanisms of heavy metal mobility in the aquatic environment, the specification of conditions which may cause re-mobilisation of substances deposited in bottom sediments into the environment and the ensuing assessment of real time-delayed chemical hazards is a very significant issue for aquatic ecosystem quality maintenance as well as elimination of aquatic ecosystem pollution sources.

It should be noted that few of heavy metals, like manganese and iron, are of particular importance to river system, moreover manganese can be the most important oxidant in environmental. Fe and Mn cycling is a key thermodynamic regulator and kinetic catalyst in natural waters and their presence is connected with the oxygen, nitrogen, carbon, sulfur, and phosphorous geochemical cycles [13-15].

The transport and fate of heavy metal in natural waters is strongly affected by Fe and Mn oxide precipitation and dissolution. Heavy metals adsorb on Fe and Mn oxide, create and determine a form of physical and chemical properties of the sediments. The heavy metals are also incorporated in the Fe and Mn oxide matrix as impurities when precipitation occurs or when new mixed metal/Fe and metal/Mn coprecipitates are possible [15, 16]. Aqueous Fe(II) and Mn(II) are significant in natural waters only in the absence of O₂. Insoluble Fe(III) and Mn(III/IV) oxides form under oxic conditions. But manganese-oxide reductive dissolution is generally thought to occur concurrently with the reductive dissolution of Fe oxides [17]. Their solubilities limit the aqueous concentrations of Fe and Mn species. The metamorphosis among redox states and physical states are frequently slow in the absence of catalysis, e.g. aqueous solutions of Mn(II) in the presence of O₂ at

pH=8.4 are exoergic toward oxidation, yet the uncatalyzed reaction proceeds slowly across years [15].

Long-term deposition of compounds such as iron and manganese oxides and carbonates in the sediment may lead to these substances being turned into permanent crystal structures, which can cause total exclusion of the co-precipitated heavy metals from the cycle. Another situation occurs when metals are bonded to an organic substance. Its decomposition may cause passage of metals into the solution or their transition into other insoluble forms. Considerable amounts of metals may be trapped in the silicate crystal network, or form poorly soluble compounds. In practice, these metals cannot pose a hazard to the environment under natural conditions [18].

2. Forms of metals in sediments of selected rivers

From the chemical viewpoint, metals in sediments can occur in the forms of carbonates, hydroxides, silicates, sulphides, phosphates, or compounds with organic ligands at various crystallisation stages of various stoichiometry and water content [19]. Moreover, some of these associations may be adsorbed on larger molecules. However, a change in salinity or increasing concentration of the metal-complexing Cl^- is sufficient for the adsorbed substances to pass into the pelagic zone. The metals bonded to organic matter, upon its decomposition, are also released while those found in silicate crystal networks do not actually pass to the pelagic zone [18].

Climate, development of the catchment area, the geological substratum, and the river type are but some of the factors which have affected river quality. Research into metal speciation in bottom sediments conducted in various parts of the globe suggests that each aquatic ecosystem ought to receive individual treatment. Even various bottom sediment sampling sites within a single river are affected by different factors (Table 1).

A case in point may be the studies into bottom sediments of the Bobrza River, a right tributary of the Czarna Nida River, conducted by the present author [28, 29]. The river flows across terrain built of middle-Devonian limestone and dolomite, and across a depression filled with Pleistocene sediments of fluvial and glacial accumulation. This terrain is characterised by a large density of industrial plants and mines (cement and lime industry); closeness to a railway line and communications routes which are a source of dust pollution emissions, containing both metallic and non-metallic elements; as well as numerous tributaries which receive municipal and industrial wastewater. Sampling sites were located in front of and past the area where cement and lime industrial plants are situated.

The investigated river contains no natural, related to substratum structure, sources of pollution with zinc, cadmium or iron. Consequently, the presence of metals in the aquatic ecosystem is a result of human activity. The total metal content in the bottom sediment is evidence of the bottom sediments being burdened with Zn, Cd and Pb from anthropogenic sources. The Bobrza River bottom sediments are characterised by large amounts of Zn, Cd and Pb in the forms of carbonates or precipitating hydrated iron and manganese oxides, co-precipitated with carbonates and adsorbed on the extended surface. Considerably lower analyte amounts are found in Fractions F1 (exchangeable) and F4 (adsorbed on the surface of organic matter or bonded to that matter). The lowest amounts of Zn and Pb are found in the fraction permanently bonded to minerals (F5), and of Cd – in the exchangeable fraction (F1).

River/ Country	Description	Metal	Forms	Ref
Daugava River/ Latvia	The key characteristics of the hydrological regime are high and permanent flood in spring, a summer-autumn high-water caused by rains, lowered levels in midsummer, and low-water periods in winter; composed of Devonian sediments: dolomite, clay, dolomite marlstone, marl, and limestone; land use: about 45% covered with forests, 48% is agricultural land, inland waters- 3%, wetlands -3%, urban areas up 1%	Pb	F5>F4>F2>F3>F1 (FP) F4>F3>F5>F2>F1 (LP)	[20]
		Cd	F5>F4>F3>F2>F1 (FP) F3>F4>F2>F1>F5 (LP)	
Anyang River/ Korea	Limestone and limesilicates also occur along the western side of the river; The pollution of the river water is probably due to the rapid urbanization and industrialization from the early 1970s, giving rise to a large increase in population. Among the industries, the electronic sector comprises the largest part (44%), followed by machinery (24.5%) and chemicals/ textiles (14%)	Pb	F3>F4,F5>F2>F1 (FP) F5>F1>F2>F4>F3 (LP)	[21]
		Fe	F3>F5>F4>F2>F1 (FP) F3>F5>F4>F1>F2 (LP)	
		Cu	F1>F3>F4>F2>F5 (FP) F4>F3>F5>F1>F2 (LP)	
		Cd	F5>F4>F3>F2>F1 (FP) F3>F4>F5>F1,F2 (LP)	
		Zn	F3>F5>F2>F4>F1 (FP) F1>F3>F2>F5>F4 (LP)	
Yamuna River / India	On the basis of the different geological and ecological characteristics, the river has been divided into five segments - Himalayan, Upper, Delhi, Eutrophicated and Diluted - of which Delhi is the most polluted stretch of the river; The river receives treated and untreated effluents from various towns and cities located on its banks. The major industrial towns at its banks before their confluence at Allahabad are Yamunanagar, Delhi, Mathura and Agra	Cu	F1>F3>F2>F4>F5 (FP) F4>F3>F1>F2>F5 (LP)	[22]
		Pb	F1>F5>F3>F2,F4 (FP) F5>F1>F3,F4>F2 (LP)	
		Cd	F4>F5>F3,F1>F2 (FP) F1>F4,F5>F2>F3 (LP)	
		Zn	F1>F3>F2>F4>F5 (FP) F1>F3,F4>F5>F2 (LP)	
Nile River / Egypt	the majority of heavy industry (sugar factories in Komombo, Ques, Armant, Dëshna and El-Hawamdia and the oil and Coca-Cola factories in Souha) is concentrated in Greater Cairo and Alexandria; changes in river water quality are primarily due to a combination of land and water use as well as water management interventions such as: (a) different hydrodynamic regimes regulated by the Nile barrages, (b) agricultural return flows, and (c) domestic and industrial waste discharges including oil and wastes from passenger and river boats. These changes are more pronounced as the river flows through the densely populated urban and industrial	Cd	F5>F4>F2>F3>F1 (FP) F5>F2>F4>F3>F1 (LP)	[23-24]
		Cu	F5>F4>F2>F3>F1 (FP) F5>F4>F2>F1,F3 (LP)	
		Cr	F5>F4>F1,F2,F3 (FP) F5>F4>F1,F2,F3 (LP)	
		Fe	F5>F3,F4>F1,F2 (FP) F5>F3,F4>F1,F2 (LP)	
		Pb	F4>F3>F1,F2,F5 (FP) F4>F1>F3>F5>F2 (LP)	
		Mn	F5>F3>F2>F4,F1 (FP) F5>F1,F3>F2>F4 (LP)	
		Ni	F5>F4>F3>F1>F2 (FP) F5>F4>F1>F3>F2 (LP)	
Zn	F5>F4>F2,F3>F1 (FP) F5>F4>F3>F1,F2 (LP)			

	centres of Cairo and the Delta region			
Ganges River/ India	The river flows in the great alluvial plain, which is of Pleistocene-Holocene origin, and redistributes the weathered sediments of the Gangetic alluvial plain derived from the Himalayas; the river flowing through the districts of Pilibhit, Sajahanpur, Jaunpur and Ghazipur in Uttar Pradesh; there are a few small tributaries; The Gomti river drains over 10 districts. The sediments of the Gomti river are characterized by fine sand with slight changes along the river courses	Cr	F2>F5>F4 (F1,F3-non) (FP) F5>F2 (F1,F3,F4-non) (LP)	[25]
		Cd	F2>F3>F4 (F1,F5-non) (FP) F5>F1 (F2,F3,F4-non) (LP)	
		Fe	F5>F4>F2>F3 (F1-non) (FP) F5>F4>F3 (F1,F2-non) (LP)	
		Cu	F4>F2>F5>F3 (F1-non) (FP) F4>F5 (F1,F2,F3-non) (LP)	
Gediz (G) and Buyuk Menderes (BM)/ Turkey	Rivers are known to be under contamination menace by wastes derived from industrial sources (industrial operations represent approximately 1/5 of the total industrial activity in Turkey), sewage (there are four big cities discharges) and agricultural activities which correspond in these regions to 35% of the total in Turkey	Co	F3>F4,F5>F1,F2 (BM) F3>F4>F5>F1,F2 (G)	[26]
		Cr	F3>F5>F4>F1,F2(BM) F5>F3>F2>F1>F4 F2 (G)	
		Cu	F5>F4>F3>F2>F1(BM) F5>F4>F3>F2>F1 F2 (G)	
		Fe	F5>F3>F4>F1,F2(BM) F5>F3>F4>F2>F1 F2 (G)	
		Mn	F3>F5>F2>F4>F1(BM) F3>F5>F1>F2>F4 F2 (G)	
		Ni	F5>F3>F4>F2>F1(BM) F5>F4>F3>F2>F1 F2 (G)	
		Zn	F5>F3>F4>F2>F1(BM) F4>F3>F2>F5>F1 F2 (G)	
Asa River/ Nigeria	The Asa River is used for various purposes; domestic, industrial, farming, swimming and so on, both within and outside Ilorin town; there are some industries and establishments located along the course of the river in Ilorin that empty their waste discharges into this river either treated or otherwise. There is conspicuously a soap and detergent Industry, two beverage industries, a major hospital, a major market and a lot of farm practices are carried out along the bank of the river, to mention a few.	Mn	F5>F4>F3>F1,F2 (FP) F4,F5>F3>F1,F2 (LP)	[27]
		Fe	F5>F4>F3>F1,F2 (FP) F5>F4>F3>F2>F1 (LP)	
		Pb	F5>F3>F2>F4>F1 (FP) F5>F3>F4>F2>F1 (LP)	
		Cr	F5>F4>F3>F1>F2 (FP) F5>F4>F3>F1>F2 (LP)	
		Zn	F4>F5>F3>F1,F2 (FP) F4>F5>F3>F2>F1 (LP)	
		Cu	F5>F4>F2>F1>F3 (FP) F4>F5>F1>F2>F3 (LP)	

FP - first point, LP - last point.

Table 1. The metal forms in bottom sediments in selected rivers of the world.

Another distribution of metals in particular fractions has been noted in the studies into the Gorzyczanka River's sediments [29]. The channel of this river is built mostly of mudstone, siltstone, sandstone, shale, quartz and greywacke. Hence in the case of this river again there occur no natural, related to substratum structure, sources of pollution with zinc, cadmium, lead or other metals, with the exception of iron. The channel of the

Gorzyczanka is situated among farming fields, arable land and grassland, with the preponderance of orchards. Due to the crop type, appropriate pesticides and fertilisers are used, the latter containing pesticides, aromatic hydrocarbons, heavy metal salts (including zinc), acids, alkali and phenols. This land development causes metal distribution in individual fractions of bottom sediments to differ from that of the Bobrza River. The highest amount of metals in the Gorzyczanka River sediments has been noted in the organic (Zn) and oxide fractions (Cd and Pb).

Yet another fractionation result has been obtained in studies of the material collected from the Nida River, which belongs to the left basin of the upper Vistula, and its left and right tributaries, the Maskalis and the Brzeźnica. These river channels are built of marl, limestone and gypsum deposits, postglacial sands, boulder clays of varying sandification as well as loess deposits of various depths, overlying limestone deposits. As is the case with the Bobrza and Gorzyczanka rivers, there are no natural sources of metal pollution. Farmland takes 69.3% of the catchment area, in which arable land accounts for 55.6%, orchards – for 1.3%, and meadows and pastures – for 12.4%. Forests, mostly coniferous and mixed, cover ca. 21.8% of the catchment area. The southern part of the catchment contains minor industrial centres (Jędrzejów, Pińczów, Sędziszów) and spa towns (Busko-Zdrój); gypsum and limestone are mined there as well, in the vicinity of Pińczów and Gacki [29, 30].

The Nida River and its tributaries receive municipal wastewater from three towns and industrial waste from plants representing industries such as mining, cement and lime, plaster goods, building materials, metallurgy and agro-food production, which to a large extent affects the waste quality. The agro-industrial nature of the catchment area causes farmland surface flows to affect surface water cleanliness. Particularly favourable conditions for fertiliser outwash are found in the central and southern parts of the catchment, given their intensive farming, impervious substratum, a dense river network and hilly terrain.

High metal amounts in the exchangeable form (20-40% of total sediment content) can indicate environmental acidification. In some authors' studies of bottom sediments [31-34], zinc content in the exchangeable form, for instance, was low and did not exceed 2-3% of this element's total content in the sediment. Its low mobility may have been caused by the pH of the analysed environments, which approximated 8.7, since at $\text{pH} > 8$ zinc is precipitated out of water [29].

The content of Fraction F2 of high bioavailability, or metals adsorbed on the extended surface of precipitated Fe and Mn oxides and hydroxides, amounted on average to 19% for Zn, 14% for Cd and 18% for Pb in studied sediments. However, the proportion of metal carbonate associations in bottom sediments was the lowest in the Nida River (8% Zn, 12% Cd and 11% Pb), and the highest in the Brzeźnica (26% Zn and Cd) and the Maskalis (17% Pb). Organic association content was the highest for lead (average of 40%), and the lowest for cadmium (16%), which may suggest for instance the occurrence of alkalisation processes in the environment, to which lead is subject as it turns into metalorganic compounds. Fraction F5, in turn, including analytes built into the crystal network of primary and secondary elements which are sediment components, indicates metals which are practically immobile, whose chemical compounds are passive, and biological ones – unavailable. The proportion of the residual fraction in the total zinc and lead content was small (2-11%), reaching 40% for cadmium in the sediment sampled in the Maskalis River [29].

Another example is the study of the Radomka River (a left tributary of the Vistula), and the Mleczna River (a tributary of the Radomka) [30]. The Radomka source substratum contains deposits of clayey resources and sandstone, iron ore (Jurassic siderites), and a phosphate belt. The predominant part of the Radomka valley holds shallow peat beds, and - occasionally - also brown coal. In its middle course, the river runs along a shallow marshy valley and then traverses the Kozienska Primeval Woodland Complex. The Radomka catchment area is predominantly agricultural, over 50% being occupied by arable land, 22% - by woodland, 11% - of meadows and 6% - by orchards. Loose and loamy sands preponderate (43% of farmland area). Podsol soils account for 38.5%, sandy soils - for 30.5%, organogenic soils - for 11.2%, while brown soils, black earths and degraded alluvial soils take up ca. 6% each. The Radomka basin waters are polluted mainly by municipal wastewater, with the proportion of industrial wastewater not exceeding 10-20% [30].

The differences in zinc content and origin in sediment samples from the Radomka and Nida river basins have been reflected in different distributions of zinc among the determined chemical fractions. The basic characteristic of the zinc found in the Radomka basin sediment samples is the obvious relationship between the content of anthropogenic zinc and the proportion of the carbonate fraction. In a sample with natural zinc content, the carbonate fraction bonds 23.2% zinc, while in a sediment sample with heavy zinc pollution ($267 \text{ mg} \cdot \text{kg}^{-1}$), this fraction's proportion amounts to 88.4%. In samples collected at other locations, with middling zinc contents ($24.8 \text{ mg} \cdot \text{kg}^{-1}$ and $158.7 \text{ mg} \cdot \text{kg}^{-1}$), 45.8% and 83.0% of zinc is bonded with the carbonate fraction. The proportion of the less mobile oxide zinc fraction remains at stable levels in all studied samples, ranging from 3.0 to 10.6%. Determination results for the oxidisable fraction indicate different conditions for the formation of this fraction in the Radomka and Mleczna river channels. In the Radomka-Domaniów and Radomka-Bartodzieje samples, concentrations of this form of zinc are comparable: $3.53 \text{ mg} \cdot \text{kg}^{-1}$ and $2.06 \text{ mg} \cdot \text{kg}^{-1}$, and it may be assumed that the zinc bonded to organic substance corresponds to this fraction. Higher contents of the oxidisable fraction, i.e. $6.7 \text{ mg} \cdot \text{kg}^{-1}$ and $9.2 \text{ mg} \cdot \text{kg}^{-1}$, determined in the sediments of the heavily polluted Mleczna River waters, are rather the sum of the organic and sulphide forms. The formation of the latter is fostered by the oxygen deficit which occurs in the Mleczna River waters. Inert in the environment, the residual fraction bonds from 20.0% to 35.6% of zinc in the Radomka River sediments, and but a few per cent (3-5%) in the Mleczna River sediments. It must be stressed that in all the other samples (except for the sample with the highest zinc content) from both studied catchments, regardless of total zinc content, zinc content in the residual fraction remains at the level of a few $\text{mg} \cdot \text{kg}^{-1}$ [30].

The results of chemical fractionation of zinc in river sediments do not differ from the recently published results for other European river sediments. The study by Mossop and Davidson [35] gives the results of chemical fractionation of zinc in the White Cart River sediments (Great Britain) which contain $81 \text{ mg} \cdot \text{kg}^{-1}$ Zn: F(1)-Zn 42%, F(2)-Zn 13%, F(3)-Zn 19%, and the residual fraction - 26%. In the Ceruj River sediments (Romania) which contain from $120 \text{ mg} \cdot \text{kg}^{-1}$ to $650 \text{ mg} \cdot \text{kg}^{-1}$ of zinc, the carbonate fraction bonds from 30% to 70% of zinc. In sediments with the highest zinc content, Fraction F(1) predominates [36]. Similar results have been obtained by Helios-Rybicka et al. [37] for the heavily polluted Odra River sediments, the ion-exchangeable and carbonate fractions in the sediment grain fraction $<0.63 \text{ } \mu\text{m}$ bonding up to 50% of zinc. In the Pisuerga River sediments (Spain), which receives industrial and municipal wastewater, depending on the sampling

site, the main zinc fractions are the mobile (34%), the reducible (40%) or the oxidisable (53%) [38].

Similarly, bottom sediment studies in Asian rivers suggest considerable impact of human use of rivers and catchment areas on physical and chemical properties of the sediments, including the occurrence of heavy metal forms. An example is the fractionation of bottom sediments from the Pearl River, the largest river system flowing into the South China Sea, and the analysis of the obtained extracts for Pb, Cu and Zn [39]. The Pearl River delta is a very large agglomeration located in the south of China, featuring large numbers of factories, inexpensive manufacturing plants, multi-million cities and environmental pollution. The sediment samples were taken at various depths, from seventeen sites, fractionated with Tessier's method and subsequently analysed for Pb, Cu and Zn content. The proportions of Pb associated with various fractions were as follows: residual > Fe-Mn oxide > organic > carbonate > exchangeable. Yet fraction F5 (residual) is of little significance in bottom sediments on the west of the river's delta, and the highest amounts of Pb have been recorded in fractions F3 and F4. The varied lead distribution in various samples is conditioned by human activity and is of anthropogenic character. Zinc distribution on the surface and in particular layers taken from various depths varies. The majority of Zn is found in Fraction V. Smaller amounts have been noted, respectively, in fractions F3 (Fe-Mn oxide) and F4 (organic), while the lowest comparable amounts have been found in exchangeable and carbonate fractions. A similar distribution has been found for Cu, whose content was as follows: residual > organic > Fe-Mn oxide > carbonate > exchangeable. High Cu content in fractions F4 and F5 causes this element to be less mobile than Pb and Zn [39].

Another fraction distribution in bottom sediments has been determined through fractionation of bottom sediment samples of the Narmada River in India [40]. The material has been collected at twelve sites along the entire river length and analysed for Fe, Mn, Ni, Zn, Cr, Cu, Pb and Cd content. The Narmada river channel is built primarily of basalt type rock with a red soil cover. The river is fed by several other rivers; it flows across urbanised areas, and is traversed by communications routes; additionally, it has several dams and dykes - accordingly, the areas located within its range are classified as degraded.

The copper fractionation profile indicates that a major portion is bonded to the residual fraction and the complexation with organic matter fraction. A substantial proportion of copper is also found in reducible (Fe-Mn oxide) and organic fractions, probably due to its more pronounced tendency for complexation with organic matter. The nickel fractionation profile indicates that in general nickel is associated in decreasing amounts in the following fraction order: residual > exchangeable > reducible > bonded to carbonate > oxidisable fraction. The chromium fractionation profile indicates that more than 50% of chromium is associated with first three fractions (exchangeable, carbonate bound and reducible) at most of the sites and can enter the food chain. The lead fractionation profile indicates that more than 90% of lead is associated with the residual fraction. A small portion (1-4%) is also associated with the exchangeable fraction, which indicates an anthropogenic source from municipal and industrial discharges. The cadmium fractionation profile indicates that a major portion of cadmium is associated with the residual fraction. About 25% of cadmium is also associated with the first three fractions (exchangeable, carbonate and reducible) and may be easily remobilised by changes in environmental conditions. The association of cadmium with the exchangeable fraction indicates the dominance of

anthropogenic sources through atmospheric deposition and municipal discharges. The toxic nature of cadmium and its association with these fractions may cause deleterious effects to aquatic life [40].

Heavy metal binding forms for Cu, Zn and Pb have been determined at four representative sediment sampling sites in the canals of Delft (The Netherlands), with the use of Tessier's chemical extraction method [41]. The different heavy metal binding fractions in the sediment indicate that Cu is mostly (51–83%) present in the F4 (organic/sulphidic) phase, followed by the residual phase (F5), which was relatively prominent in the "background station" (highly polluted). Contributions of the remaining, labile fractions F1 – F3 were low, i.e. max. 5% in total. The dominant binding form for Zn was found to be Fraction F3 ("bound to Fe/Mn oxides"; ca. 60%), with most of the remainder in fractions F4 and F5. Finally, for Pb, the overall picture was more varied, with dominant binding forms being either fraction F5 (unpolluted and highly polluted stations) or F3 (slightly and medium polluted stations), and relatively high proportions of other binding forms. Thus, the average proportion of Fraction F1 (exchangeable) amounted to 15%, compared with 2.4% for Cu and Zn [41].

In contrast to others [38, 42], Kelderman and Osman [41] did not find significant ($p > 0.05$) correlations between loss on ignition (LOI) and cation exchange capacity (CEC) on the one hand, and heavy metal contents on the other. The same holds true for the relationship between CaCO_3 and heavy metal content, which is in agreement with other researchers' findings [38, 42, 43]. Mixed observations have been reported for correlations between Fe and Mn and heavy metal content [43, 44]. However, the relatively high R^2 values (i.e. between 0.65 and 0.9) are an indication of marked importance of Fe and Mn phases for heavy metal binding (mainly as (hydr)oxides) [41].

Interesting results were obtained by studying the sediments of Bobrza River. The samples were taken from two different places characterized by different degree of acidity and alkalinity. The 1st point located in the impact zone of the Kielce Pump Factory and Formaster Company. The soils in the area are acidic and count among podsol soils, formed primarily out of glacier accumulation formations or on non-carbonate Triassic sandstones [50, 51].

In the 2nd point a chemical composition of cement and lime dust is rather constant and mainly depends on the composition of raw materials used in technological process, production technology, way of clinker burning and type of additives enriching the cement. The dust emitted from calcareous institutions cement plant contains mainly CaO , SiO_2 , Al_2O_3 , K_2O and has high values of pH_{KCl} . The exhaust dust contains also heavy metals including Zn ($173.0 \text{ mg}\cdot\text{kg}^{-1}$), Pb ($140.0 \text{ mg}\cdot\text{kg}^{-1}$) and Cd ($3.0 \text{ mg}\cdot\text{kg}^{-1}$) which causes enrichment of the soil and water environment with compounds of these elements [50, 51]. The presence of high metal contents in bottom sediments in the form of carbonate and oxide fractions is the result of environmental alkalisation and deposition of dusts containing alkaline metal oxides together with non-ferrous metal oxides.

Different types of land development at the level of a single river (Fig. 1-3) make it impossible to develop one general scheme for metal migration in the water – bottom sediment system. The number of factors, particularly anthropogenic ones, which determine the ion composition of water, the amount and type of the suspension, oxygenation extent, presence of microorganisms, and – consequently – forms in which metals are found in the ecosystem is too high to enable a definite statement that under certain conditions remobilisation or precipitation of a poorly soluble compound of a given metal will occur.

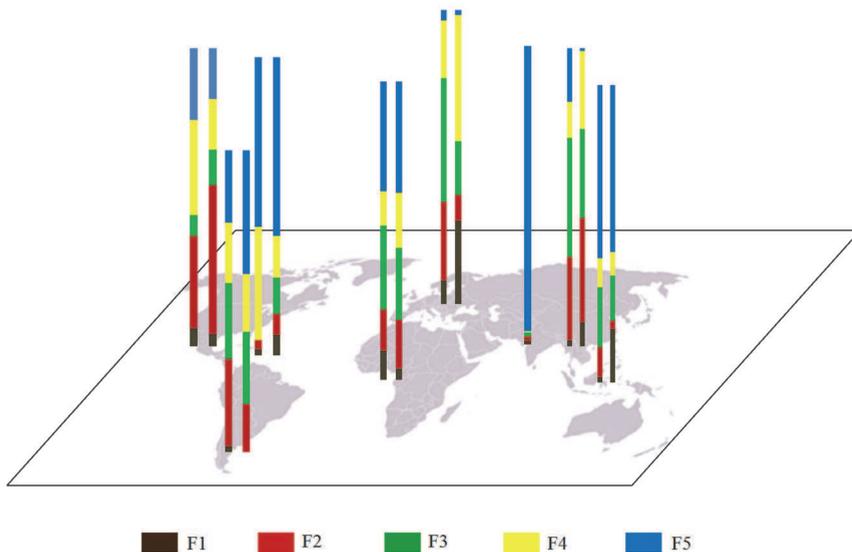


Fig. 1. The lead forms in bottom sediments in selected rivers of the world [on the basis of: 27, 29, 40, 45-49]

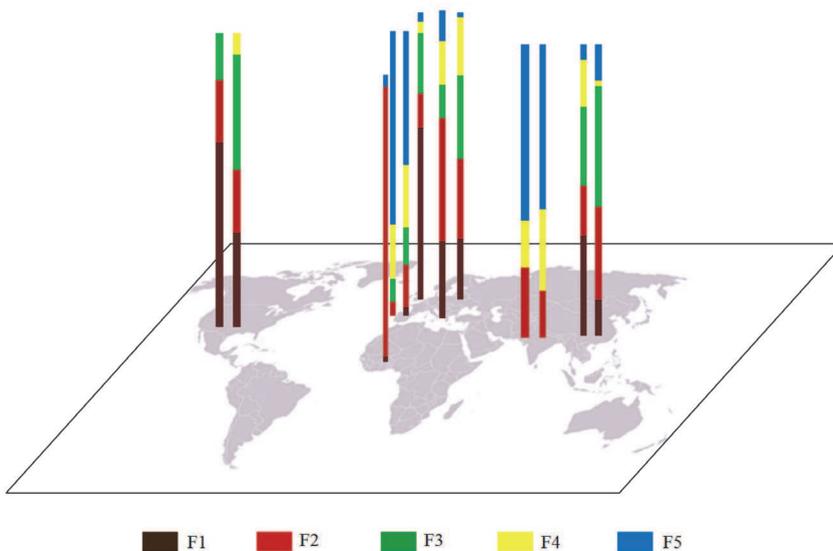


Fig. 2. The chromium forms in bottom sediments in selected rivers of the world [on the basis of: 51-55, 57-60].

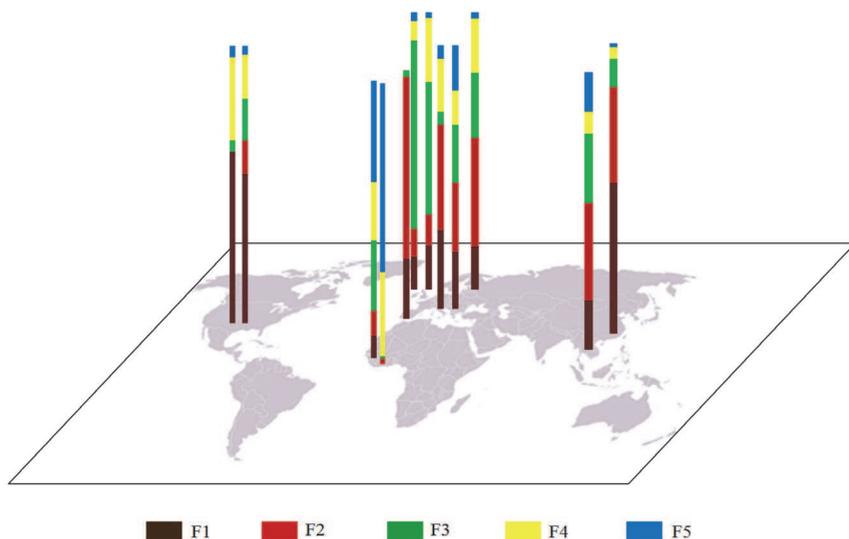


Fig. 3. The copper forms in bottom sediments in selected rivers of the world [on the basis of: 51-59].

3. Conclusions

Surface waters, depending on their geological structure, substratum type and land development, are characterised by varied chemical composition. Metals such as Cd, Cr, Cu, Fe, Pb, Ni or Zn pass into water as a result of natural processes, as well as direct and indirect human activity. The number of sources from which substances originate, chemical properties of individual entities, their capacity for adsorption on solid particles, and forming hydrated ions or ion pairs, together with biological, physical and chemical conditions of the aquatic environment, all affect the variety of metal forms found in surface waters. Elements, while migrating from the environment, are deposited in bottom sediments, where they are temporarily immobilised and may pose a hazard to biological life in a given ecosystem.

The knowledge of the quantity of metals in waters and bottom sediments may be used for ultimate chemical assessment of an aquatic environment and serve as an indicator of the geochemical status of a given catchment as well as the spread of pollution. Due to their properties, bottom sediments which are the main component of the elemental cycle, and the centre of accumulation, chemical transitions, and decomposition of toxic compounds which enter the aquatic environment, are a rather representative indicator of long-term changes in aquatic ecosystem pollution. They may be used as indicators of biological and chemical change in the aquatic environment.

However, they may also pose a hazard of secondary pollution to the ecosystem as a result of desorption and passage of substances accumulated on the surface of solids into water. The soluble complex compounds which are then formed with organic and inorganic ligands present in rivers may cause secondary release of heavy metals in various forms, more or less dangerous to living organisms.

Consequently, each aquatic ecosystem ought to receive individual treatment, allowances being made for both natural factors (including geochemical background, or climate) and

anthropogenic factors (land development in the catchment and the river itself). In order to develop schemes for metal migration or the probability of secondary pollution of the ecosystem which can enhance water resources management, it is necessary to conduct research in representative river segments, comparable in terms of natural factors but different in terms of anthropogenic ones.

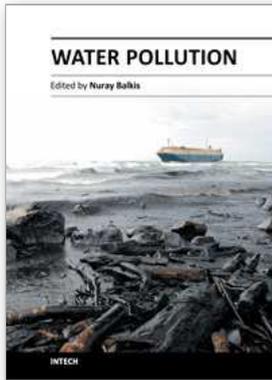
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Water Pollution

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Water pollution is a major global problem that requires ongoing evaluation and revision of water resource policy at all levels (from international down to individual aquifers and wells). It has been suggested that it is the leading worldwide cause of deaths and diseases, and that it accounts for the deaths of more than 14,000 people daily. In addition to the acute problems of water pollution in developing countries, industrialized countries continue to struggle with pollution problems as well. Water is typically referred to as polluted when it is impaired by anthropogenic contaminants and either does not support a human use, such as drinking water, and/or undergoes a marked shift in its ability to support its constituent biotic communities, such as fish. Natural phenomena such as volcanoes, algae blooms, storms, and earthquakes also cause major changes in water quality and the ecological status of water. Most water pollutants are eventually carried by rivers into the oceans.

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