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Review

The speciation and physico-chemical forms of metals in surface waters and sediments

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ABSTRACT

Surface waters can be contaminated in many ways, e.g., by solutions and suspended matter. Moreover, insoluble substances in colloidal form, in suspension or adsorbed on solid bodies can dissolve in response to changing physical and chemical conditions and become a secondary source of surface water pollution, thereby endangering wildlife. In addition, if we take into account varying rates of flow, contaminants can be transported over considerable distances. Hydrological processes, which determine factors, such as the rate of sedimentation, also influence the quality of surface waters; bottom sediments can contain large quantities of accumulated organic and inorganic compounds, including heavy metals. The physical and chemical properties of aquatic ecosystems are characterized by a number of interdependent parameters. Hence, factors such as temperature, oxygen content and pH of a water body can alter the solubility of the salts present in it, the forms of occurrence of particular species, as well as their bioavailability and toxicity. Thus it is necessary to determine the various species of metals present in the different compartments of the aquatic ecosystem.

Keywords: surface waters, bottom sediments, speciation, heavy metals

INTRODUCTION

Aquatic ecosystems are triple-phase systems in which the principal phase is the liquid phase, *i.e.*, water. At one interface it borders the gaseous phase, *i.e.*, the atmospheric air, while at the other it is in contact with the solid phase, the geological substrate (bedrock), which is usually covered with a layer of bottom sediments. The water itself may carry suspended matter, some of which consists of living animals and plants. Thus there are very many sources and migration pathways of the multifarious substances contributing to the quality of surface waters.

Natural waters provide a living environment for a myriad of plant and animal organisms, and their

chemical composition is characterized by the presence and mutual quantitative relations of macro- and microcomponents. The mineral and organic substances in such waters can occur in dissolved, colloidal or suspended form; which form they take is determined by the physical and chemical properties of the water.

The quality of natural waters is assessed on the basis of the relevant physical, chemical and biological parameters. However, the relations between them are extremely complex, and interpreting the dynamics and trends in water quality is no easy task. The quantities and types of contaminants are governed *inter alia* by the types and extents of land use in the watershed, whereas the magnitude of

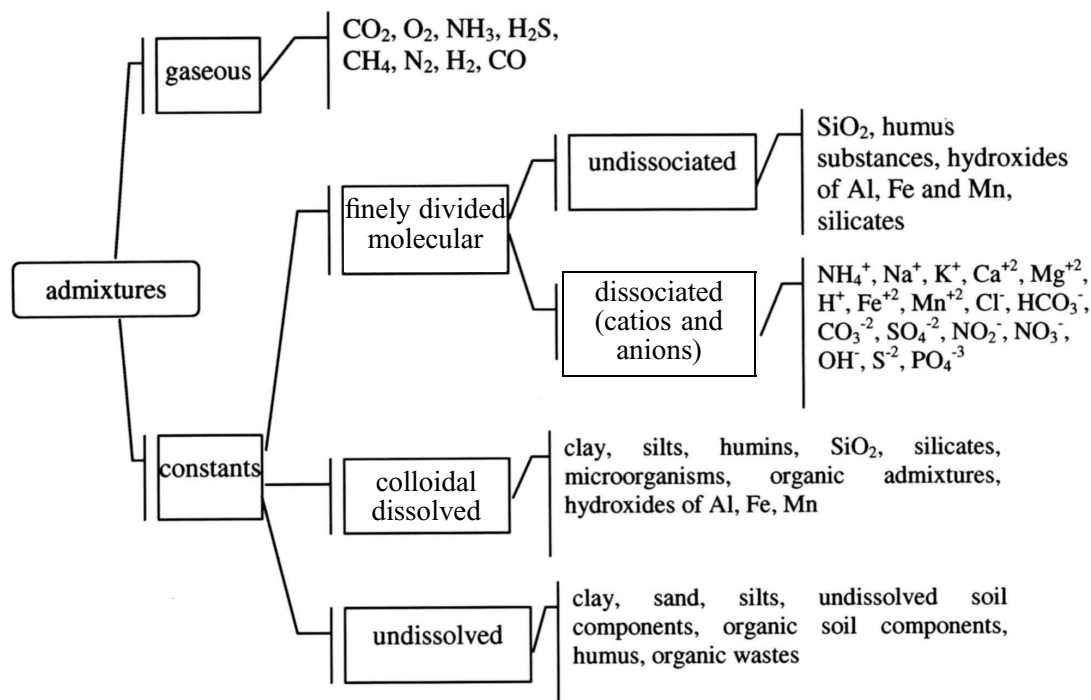


Figure 1 Substances from natural sources (admixtures) usually present in surface waters (Rabajczyk, 2007b).

exchange between the substances present in the water and those deposited at the bottom of rivers and basins is determined chiefly by the rate and intensity of the water flow (Florinsky, 2000; Rabajczyk, 2007a). Therefore, the major factors shaping the composition of surface waters must include:

- the geological structure of the watershed and the magnitude of the soil sorption complex;
- the topography of the watershed;
- the weathering and dissolution of the minerals of which the watershed is built;
- physical processes, such as sedimentation and sorption;
- chemical processes taking place in the aquatic environment, such as hydrolysis, redox, precipitation and complexing reactions;
- the rate and intensity of water flow;
- the size of the area of contact between water and atmospheric air;
- the mixing of waters of different compositions;
- the types of aquatic organisms and the dynamism of biological transformations;
- weather conditions, including temperature and precipitation as rain or snowfall;
- the means and extent of land use in the watershed and the utilization of waters there;
- the types of hydroengineering structures and the extent of river regulation;
- the depth of water basins and their location with respect to sources of contamination (Florinsky, 2000; Walker *et al.*, 2005).

The seasons of the year also affect the physico-chemical properties of waters to a large extent. The concentrations of mineral salts and other substances are highest in very cold winters and very dry summers, whereas those of organic substances and ammonia are highest during algal blooms. Salinities are lowest in spring melt waters and high flood waters (Shmueli and Shamir, 2001).

The concentrations of substances present in waters on average range from a few ng m^{-3} to a few hundred g m^{-3} . Substances enter the waters as a result of natural processes, the so-called admixtures (Figure 1), and also compounds from anthropogenic activities, which contaminate waters (Stögbauer *et al.*, 2008).

The surface water environment is under constant human pressure. Pollutants of surface waters, which reach aquatic ecosystems directly or indirectly, are present in various forms, for instance, in solution or in suspension. The suspended matter can be in the form of droplets or particles, and a multitude of substances can be dissolved in these droplets or be adsorbed by the solid particles. Water can transport all these forms over considerable distances. Matter in the form of dust tends to fall to the bottom in

surface waters, whereas liquid pollutions may float up to the surface or be deposited on the bottom along with the solid particles (Walker *et al.*, 2005; Ladd *et al.*, 1998). The most persistent pollutants are the heavy metals: their levels in the different compartments of water bodies vary: the greatest amounts being found in suspended matter and the least in the water column (Adamiec and Helios-Rybicka, 2002; Aleksander-Kwaterczak and Helios-Rybicka, 2004; Helios-Rybicka *et al.*, 2005; Luck *et al.*, 2008).

The toxicity of metals in aqueous solutions, which depends on the form of occurrence of the individual species, is also a significant aspect. Which species of a metal occurs in waters depends, not only on the pH, but also on the presence of ligands such as hydroxides, carbonates, chlorides and humic substances (HS) (Janes and Playle, 1995; Sprague, 1995; Van Ginneken *et al.*, 1999; Wood *et al.*, 1999). In the presence of these ligands in aqueous solutions, the sorption of metals competes with their complexation with HS. HS form stable chelate complexes with free metal ions and hydroxides. However, the stability of the humus-metal complex depends on the pH of the solution and the type of metal ion, whereas the nature of the organic-mineral bond and the form of the complex depends on the concentrations of both metal and HS, to mention but two factors (Meinelt *et al.*, 2001).

Integral to the aquatic environment, bottom sediments play an important part in the biochemical cycle of elements as they are the site of deposition and chemical transformation of many compounds entering water bodies. They also provide a living environment for aquatic organisms. This is manifested by the biochemical transformations of compounds deposited in the sediments. Evaluating an influence of pollutants on the quality of surface water requires research on concentrations and sources of anthropogenic compounds. This aspect of bottom deposits makes them especially useful material for research enabling us to determine major sources of pollution because they work as an absorption column and provide a clear picture of the phenomena occurring in water. Because the metals quite easily migrate to water phase it can be assumed that the concentration level of metals in bottom deposits is a sensitive indicator of the environmental cleanliness.

Defining the physical and chemical forms of the substances present in the various compartments of the ecosystem can lead to an understanding of how

metals are transported in an aquatic environment, and the conditions under which substances deposited in the bottom sediments can be remobilized into the water. Prediction of real chemical threats, delayed in time, is therefore only possible if the particular species of metals in solution and in the bottom sediments can be identified. In addition, the speciation of heavy metals enables their toxicity and biological assimilation to be estimated, which is crucial for the survival and development of aquatic organisms.

The determination of the chemical species of compounds present in aquatic ecosystems, both in solution and in the bottom sediments, carried out in the context of the bioavailability of the various species and their forms of occurrence, can supply data that are essential for the assessment of threats to the environment. The toxicity of elements, as well as the presence or absence of synergism and antagonism with respect to other elements, and hence their positive or negative effects on the functioning of living organisms, depends on the species in which they occur. In discussions on the problems of contamination it is therefore important to differentiate between particular oxidation states and the forms of occurrence of metals, not only at the instant they enter the environment, but also during their migrations and transformations in its different compartments.

METAL IN SURFACE WATERS

Metals are usually perceived as pollutants. But it should be stressed that they are substances that occur naturally in the environment. Heavy metals enter surface waters from many sources, for example from the atmosphere as a result of heavy rain or snowfall; they are often leached out of the bedrock or soil. However, is their discharge from industrial plants that give that levels exceed permitted concentrations. Therefore, wherever humans have caused metals to be released from the rocks in which they were once deposited as a result of volcanic activity or subsequent erosion, they become contaminants (Stögbauer *et al.*, 2008).

The extent to which humans contribute to the global cycling of metals can be described by a parameter known as the anthropogenic enrichment factor (AEF) (Table 1) (Walker *et al.*, 2005).

Human activities are responsible for the general transport of most substances, which include Al, Cd, Cr, Cu, Fe, Pb and Zn. Lead has a high AEF due

Table 1 Enrichment factors for the total annual global emissions of cadmium, lead and zinc in the 1980s

Metal	Source (10 ⁶ kg year ⁻¹)		Total quantity (T) (10 ⁶ kg year ⁻¹)	AEF (A/T) 100 (%)
	Anthropogenic (A)	Natural		
Cadmium (Cd)	8	1	9	89
Lead (Pb)	300	10	310	97
Zinc (Zn)	130	50	180	72

Reference: Walker *et al.*, 2005.

largely to its common use as a fuel additive and its release during the combustion of fuel. Crucially, metals are not biodegradable, and do not therefore break down into less harmful substances. Their detoxification by organisms depends entirely on the active metal ions being “concealed” within protein structures or deposited in an insoluble form in intercellular granules for long-term storage or for excretion with feces (Walker *et al.*, 2005). This, in turn, given the right conditions, can lead to secondary contamination of aquatic ecosystems.

In the aquatic environment a heavy metal can occur in several forms:

- as a free ion – the form most toxic to living organisms;
- as an ion bound to different ligands – complex compounds are formed;
- as the precipitated molecule of a compound, suspended in the liquid phase or adsorbed on the surface of suspended or colloidal matter (Manahan, 2003).

This division is the result of many complex factors, among which are the chemical properties of the metal, the ability of its compounds to be adsorbed on solid particles, the formation of hydrated ions, ion pairs, hydrolyzed forms and complex compounds. In addition, the form of occurrence of an element is strictly dependent on the physico-chemical conditions in the water, changes in which affect the speciation of the compounds present in it. The species of metals therefore depend on such factors as the water temperature, the amount of dissolved oxygen, the biological activity of organisms (Hornig *et al.*, 2009; Vicente-Martorell *et al.*, 2009) and the bedrock. One of the most important of these factors, however, is the pH of the water. In slightly alkaline water with a high oxygen content, metal ions convert to poorly soluble forms that tend to adsorb on the suspended matter in the water (Gaur *et al.*, 2005; Vicente-Martorell *et al.*, 2009).

Metals at the air–water interface

At the air–water interface there is a thin layer up to several hundred micrometers thick; this surface microlayer is a chemically and physically unique environment, with properties differing from those of the sub-surface water (Norkrans, 1980; Lion and Leckie, 1981; Hardy *et al.*, 1985; Zhengbin *et al.*, 1998; Falkowska, 2001; Trojanowski *et al.*, 2001). Spatially and temporally variable exchanges take place across this surface membrane as a result of simultaneous biological, chemical and radiational transformations in the water and air, as well as transport processes in both environments. The stability of the surface membrane is governed *inter alia* by adhesion forces, due to intermolecular attraction at the boundary between the two media–water and air (Maki and Remsen, 1989; Trojanowski *et al.*, 2001).

The surface microlayer therefore affects the exchange of gases as well as the mechanisms underlying transport from the water to the air and *vice versa*. Dissolved substances, particles and microorganisms are carried to this zone by simple diffusion, rising gas bubbles, and convection from bottom sediments and subsurface waters. At the same time, the surface microlayer is replenished by atmospheric fallout, *i.e.*, dusts and aerosols. All these processes lead to the accumulation of chemical substances and microorganisms (Norkrans, 1980). Thus the concentration of chemical and microbiological components in surface microlayers varies very considerably variability during a 24 h period (Sieburth, 1983; Maki and Remsen, 1989; Falkowska, 2001).

The concentrations of heavy metals in both the surface microlayers and the subsurface water vary considerably in 24 h, due, for example, to vertical transport processes in the water column within the surface microlayer and beyond it (Antonowicz, 2007). Studies carried out in a mountain stream in Montana (USA) in two consecutive years yielded very similar 24 h concentration profiles of these metals in water, indicating that the fluctuations in

Table 2 Mean content of Cr, Pb and Al in suspended particular matter in some rivers

River	Cr ($\mu\text{g g}^{-1}$)	Pb ($\mu\text{g g}^{-1}$)	Al ($\mu\text{g g}^{-1}$)
Mekong (delta - Vietnam)	49	42	113 000
Chang Jiang (China)		50	108 000
Huanghe (China)		17	84 000
Pearl (USA)	121.3	95.1	107 000
Mackenzie (Canada)	8.5	24	78 000
Garonne (France)	255	47.6	118 000
Scheldt (Belgium/the Netherlands)	110–285	63–207	
Amazon (South America)	193	21–105	
Mississippi (USA)	72	39	88 000
Danube (Central and SE Europe)	100	84	60 100
Orinoco (South America)	70	23	113 000

Reference: Cenci and Martin, 2004.

heavy metal concentrations during 24 h are a cyclic phenomenon. Gammons *et al.* (2005) demonstrated the recurrence of the 24 h transport of metals such as Cu and Zn in the subsurface water layer.

Analysis of water samples from Lake Gardno (Poland) also revealed substantial changes in the concentrations of metals, including Cd, Pb, Zn and Cu, in the subsurface layers (from which samples were drawn using the glass plate and Garrett grid techniques) and in the surface microlayer. It was in this latter layer that the highest concentrations of all these heavy metals except Cu were detected; the highest Cu levels were in the subsurface layer (Antonowicz, 2007).

The accumulation and migration of substances in the surface microlayer and beyond are brought about not only physicochemical processes, but microorganisms also exert a considerable influence on the transport of numerous chemical compounds, for instance, by incorporation into their cellular structures (Sieburth, 1983; Maki and Remsen, 1989; Falkowska, 2001; Antonowicz, 2007). The diversity and complicated nature of the physical, chemical and biological processes taking place at the air–water phase boundary determine the content and rate of change of substances, including Al, Cd, Cr, Cu, Fe, Pb, Zn, in the surface layers of water.

Metals at the solid–solution interface

Heavy metals have strongly adsorbent properties. They are retained at phase boundaries for example on the surfaces of surficial sediments, river banks, aquatic vegetation, hydroengineering structures, suspended particles and other solid bodies in the water. Chemical processes taking place in natural waters, *e.g.*, oxidation, may cause them to precipitate

out of solution. Thus metal concentrations in the various compartments of surface waters decrease in the order: suspended matter > sediment > water (Saeedi *et al.*, 2004; Luck *et al.*, 2008).

Most reactions taking place in the aquatic environment do so at the solid phase–solution interface. Suspended particulate matter (SPM), a significant component of surface waters, therefore plays a major role in the transport of metal contaminants (EPA, 1999; Blo *et al.*, 2003; Cenci and Martin, 2004). The solid phase of SPM consists mainly of inorganic colloids such as clays, oxides, hydroxides and metal carbonates. Two fractions are distinguishable in the SPM phase in aquatic systems: particles of diameter > 1 μm , which fall quite quickly to the bottom, and those of diameter < 1 μm , which remain in suspension and favor the transport of adsorbed substances over large distances. Nevertheless, the quantities of metals within, and adsorbed on the surface of, suspended particles vary, depending on the local land use, geological substrate (bedrock), climate and even season (Table 2).

Colloidal particles are not normally deposited in river systems. But when an agglomerate becomes the right size and the water flow is of an appropriate intensity, and certain compounds such as chlorides and sulfates are present (Cenci and Martin, 2004), such particles may form aggregations that are then deposited on the bottom sediments. Thus it is very important to distinguish chemical species in the dissolved state from contaminants associated with suspended and colloidal particles in SPM (Blo *et al.*, 2003).

Investigations into the effect of filtering water samples on the determined contents of certain metals, *e.g.*, Cd, Zn and Cu (Ladd *et al.*, 1998;

Table 3 Classes of purity according to the German LAWA classification based on the quantity of chromium in different compartments of the ecosystem

Class	Degree of contamination	Quantity of Cr (mg kg ⁻¹)	
		In sediment and suspended matter	In water
I	Not contaminated	≤ 80	≤ 1.3
I–II	Not contaminated to moderately contaminated	≤ 160	≤ 2.5
II	Moderately contaminated	≤ 320	≤ 5.0
II–III	Moderately to strongly contaminated	≤ 640	≤ 10
III	Strongly contaminated	≤ 180	≤ 20
III–IV	Strongly to very strongly contaminated	≤ 2,560	≤ 40
IV	Very strongly contaminated	> 2,560	> 40

Reference: Irmer, 2007.

Cidu and Frau, 2009) unequivocally demonstrated the wide differences between metal concentrations in filtered samples and those in raw (unfiltered) ones.

These differences are affected by the quantity of SPM in the water sample. A higher SPM content adsorbs a large part of the metals, and only small amounts of analytes remain in the water in the form of free ions (Saeedi *et al.*, 2004). It is a common observation that the SPM content increases and the concentration of dissolved substances decreases as water levels rise and flow rates intensify (Gaur *et al.*, 2005).

A uniform classification of the degree of contamination of the various compartments of the aquatic environment, taking account of the water, SPM and sediments, is applied in Germany (LAWA); it covers seven classes of purity (Table 3). Polish standards assess only the quality of the water and sediments; there are no guidelines for classifying SPM (Helios-Rybicka *et al.*, 2005).

Physico-chemical processes

The extremely rich diversity of physico-chemical and biological processes taking place in surface waters means that precipitation and sedimentation are usually the dominant processes, causing heavy metals to accumulate in the bottom sediments. Sorption diminishes the content of organic and inorganic compounds in the water. Similar changes may cause seasonal fluctuations in the pH (Walker *et al.*, 2005) and redox potential of the water.

Acid rain can cause the pH of waters to fall abruptly, as a consequence of which the level of dissolved metals in them will rise more or less equally suddenly (Gaur *et al.*, 2005). Streams draining mining areas are highly acidic and contain large concentrations of dissolved metals but very few

aquatic organisms. As the stream in its lower course becomes diluted with unpolluted water, the pH rises and the metals precipitate to the bottom (Walker *et al.*, 2005).

An important aspect determining the form that heavy metals take in surface waters is the occurrence, especially in lakes and reservoirs, of a strongly oxygenated layer and a near-bottom layer; this is particularly the case when the hypolimnion, with its characteristically low level of dissolved oxygen, is present. In the oxygenated zone dissolved salts of Mn and Fe are oxidized, after which they are precipitated as insoluble hydrated oxides. At the same time heavy metals are co-precipitated (Walker *et al.*, 2005; Li *et al.*, 2007). These processes supply the bottom sediments with substances of diverse structures and properties. The agglomerates that form, because of their extensive surface area, accelerate the pH-dependent physical adsorption and chemisorption of heavy metals (Turner, 1995).

However, this is a process that may only temporarily reduce the concentrations of metals, since there is always the possibility of secondary contamination resulting from desorption and the transport of substances accumulated on the surface of solid bodies into the bulk water (under the right conditions). The soluble complexes with organic and inorganic ligands that then form may cause the secondary release of various heavy metal species into the water. For example, the reduction of iron and manganese in combination with their remobilization into the water and the release of heavy metals may take place when conditions in the near-bottom layer are anoxic and strongly reducing (Salomons and Baccini, 1986).

Adsorbed and chemisorbed metals are in equilibrium with the interstitial water in the bottom sediment, but they can very easily transfer into the bulk

water; as happens when the salinity rises, *i.e.*, when there is an increase in the chloride content, which can complex with some of their metals. Metals bound to the hydrated oxides of iron and manganese and to carbonates (as a result of co-precipitation) transfer to the water with more difficulty. Such a situation can occur under strongly reducing conditions in the case of metal oxides, and in a strongly acidic environment in the case of carbonates (Turner, 1995).

Studies of the bottom sediments of both flowing waters and bodies of standing water, the metals accumulating at the bottom of these aquatic ecosystems are present in a wide diversity of species. Depending on the physical, chemical and biological properties of the water in question, such elements as Al, Cd, Cr, Cu, Fe, Pb and Zn can occur as different species and be bound to organic matter or oxides.

The long-term presence in the sediment of such compounds as the oxides of iron and manganese, and also carbonates, can cause them to transform into stable crystalline structures, which, in turn, can cause the total removal of co-precipitated heavy metals from circulation. The situation is different, however, when metals are bound to an organic substance, where its decomposition can cause the metal to pass into solution or be converted into other, insoluble forms. Considerable quantities of metals can be incorporated in the crystal lattice of silicates or form insoluble compounds. Under natural conditions, metals in these states are practically harmless to the environment (Li *et al.*, 2007).

From the chemical point of view, metals can be present in sediments in the form of carbonates, hydroxides, silicates, sulfides, phosphates, and also complexes with organic ligands in various stages of crystallization with differing stoichiometry and water contents (Sager *et al.*, 1990). Moreover, some of these compounds can be adsorbed on larger particles. But a change in salinity or a rise in the concentration of metal-complexing chloride ion is sufficient to cause the adsorbed substances to dissolve in the water. Also, metals bound to organic matter are released following its decomposition, whereas those that are in silicate crystal lattices do not enter the water (Li *et al.*, 2007).

The difference between the composition of river sediments and the content of substances dissolved in the water becomes particularly pronounced when the reactions of the individual metals with water are taken into account. In polar solvents such as water, ionic compounds are readily soluble. But in the

solution, the different ions can react in different ways. Ions carrying small charges ($1+$, $2+$, $1-$, $2-$) usually dissolve as simple cations and anions; surrounded by molecules of water, *i.e.*, hydrated, they react with the water itself to only a slight degree. But smaller ions carrying a much larger charge do react with water. Stable ions, fairly large in size, are formed – these are the so-called oxyanions, like sulfate, nitrate and carbonate. The result of these processes is that an anion is formed, which readily dissolves, because the charge is spread over the large surface area of the ion (Andrews *et al.*, 1996; Walker *et al.*, 2005).

SPECIATION

Speciation analysis focuses on determining the contents of the several chemical species of an element and its physical manifestations. The diversity of species and their physico-chemical nature, and various research objectives, have meant that speciation analysis has had to be split into a number of types (Figure 2).

The speciation of metals, determining their bioavailability and toxicity, and assessing the extent of contamination of bottom sediments are all possible if sequential extraction is applied (Sahuquillo *et al.*, 2003).

Interest in this technique for studying metals in aquatic sediments is growing and, at present, more than a dozen methods for allocating the fractions of particular elements are known (Table 4).

To characterize the functional and operationally determined speciation of metals in bottom sediments, either Tessier's five-stage method, which allows five fractions to be separated, or the three-stage method recommended by the European Community Bureau of Reference (BCR) is applied. In consequence, the fractions in which metals occur in the following forms are usually analyzed:

- exchangeable – this fraction consists of metals adsorbed on the surface of solid bodies which, as a result of changes in the ionic composition of the water, *i.e.*, a shift in the sorption–desorption equilibrium, can pass into solution; this fraction is available and relatively mobile;
- associated with carbonates – metals in the form of carbonates or co-precipitated with carbonates; lowering the pH upsets the carbonate equilibrium, and the metals pass into solution;
- associated with the hydrated oxides of iron and

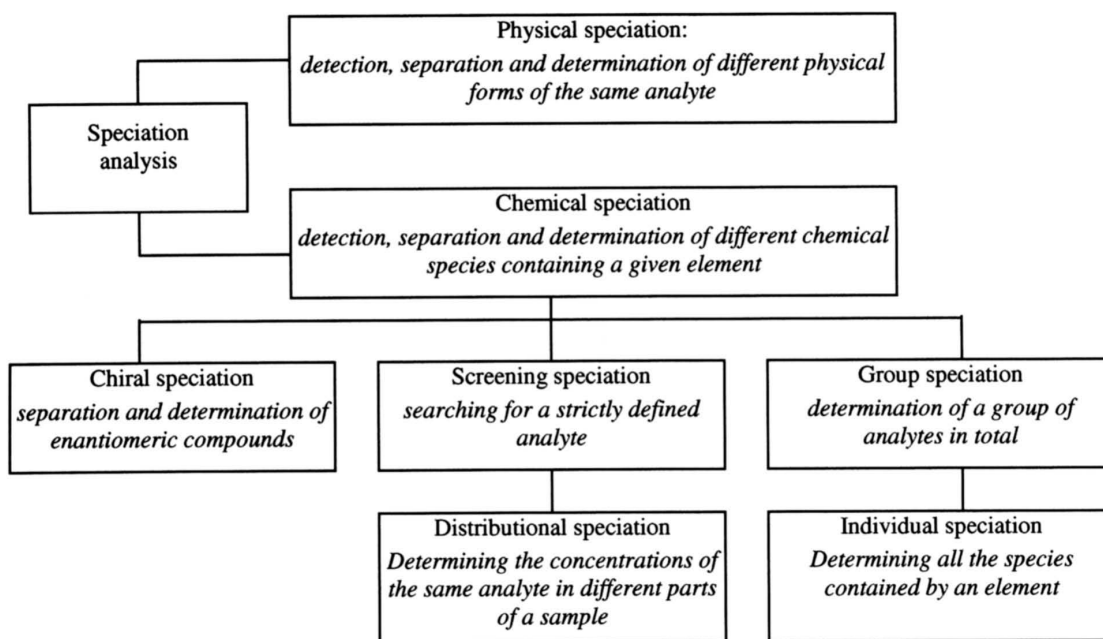


Figure 2 The basic types of speciation analysis (Kot and Namieśnik, 2000).

manganese – metals adsorbed on the extended surfaces of hydrated oxides of iron and manganese precipitating under anoxic (reducing) conditions; as a result of the reduction of iron and manganese the sediment may dissolve, and the metals pass into solution;

- associated with organic matter – metals adsorbed on the surface of organic matter or metals associated with such matter; though temporarily immobilized, they may later, as a consequence of the natural mineralization of the sediment, migrate to one of the other fractions;
- stably associated with minerals – metals incorporated in the crystal lattice of both primary and secondary minerals; they are permanently immobilized and under natural conditions do not constitute a threat to the ecosystem (Tessier *et al.*, 1979).

Leaching an incomplete amount of a given species of a metal in one extraction stage can increase its amount in the next stage. Reagents should therefore not form stable, poorly soluble complex compounds with ions extracted from environmental material to the eluate. In addition, the pH of the solution should be lower than that at which hydroxy-sediments precipitate. Care should therefore be taken to ensure that the conditions of sequential extraction in the mobile metal fractions of interest are approximately the same as those in the field (Ma and Rate, 2007).

EXTRACTION TECHNIQUES

Extraction techniques enable an analyte to be separated from its matrix; moreover, they eliminate or reduce interference on the part of other components, and increase the concentration of the analyte

Table 4 Fractions of heavy metals present in bottom sediments

Fraction	Reference
Exchangeable, carbonate, oxide, organic matter, remainder	Tessier <i>et al.</i> , 1979
Water-soluble, exchangeable, oxide, organic, sulfide, remainder	Gatehouse <i>et al.</i> , 1977
Exchangeable, adsorbed compounds, organic matter, remainder	Sposito <i>et al.</i> , 1982
Water-soluble, organic and humus, humus, carbonate, Fe hydroxide and sulfide, kaolinite	Pasenner <i>et al.</i> , 1984
Exchangeable, carbonate, oxide: Mn, oxide: Fe (amorphous), organic and sulfide, remainder	Kersten and Förstner, 1986
Water-soluble, exchangeable, organic (soluble), organic (fulvic and humic acids), readily soluble mineral, practically insoluble mineral, insoluble organic matter	Hirner <i>et al.</i> , 1990
Carbonate, oxide, organic and sulfide	Ure <i>et al.</i> , 1993
Exchangeable, carbonate, Fe and Mn oxide, sulfide, remainder	Bodog <i>et al.</i> , 1996
Exchangeable, EDTA-soluble, oxide, sulfide, remainder	Terashima and Taniguchi, 1996
Exchangeable, Fe hydroxide and Mn oxide, Fe oxide (crystalline), sulfide and organic, remainder	Hall <i>et al.</i> , 1996
Exchangeable, carbonate, oxide, organic, remainder	Kalembkiewicz and Sočo, 2002

Table 5 Techniques for extracting analytes from solid samples

Extraction of analytes from solid samples	Techniques
	Extraction to the gaseous phase
Equilibrium techniques	Solid phase microextraction (<i>SPME</i>), headspace (<i>HS</i> ; e.g. static headspace analysis <i>S-HS</i> ; headspace solid phase microextraction <i>HS-SPME</i>)
Non-equilibrium techniques	Purge-and-Trap trap (<i>PT</i>), Closed-loop-stripping analysis (<i>CLSA</i>)
	Extraction to the liquid phase
Classical solvent extraction	Shaking with solvent, Soxhlet extraction, extraction of analytes from a sample placed in a column using a stream of solvent, homogenization with the solvent, sequential extraction
Assisted extraction	Ultrasound assisted extraction (<i>UAE</i> ; sonification), Extraction using a solvent under high pressure (middle pressure liquid extraction <i>MPL</i>), Accelerated accelerated extraction at elevated temperature and pressure (accelerated solvent extraction <i>ASE</i>), microwave assisted extraction (<i>MAE</i>)
Supercritical Fluid Extraction (<i>SFE</i>)	Extraction with a liquid in the supercritical state (enhanced-fluidity liquid extraction <i>EFLE</i> ; supercritical accelerated liquid extraction <i>SALE</i>)

References: Namieśnik *et al.*, 2000; Kloskowski *et al.*, 2007.

in the extract to a level permitting quantitative analysis. Sequential analysis of bottom sediment samples is carried out with the aid of aqueous solutions of the appropriate composition using classical laboratory techniques. These cover several consecutive extraction procedures, during which the extraction solution of the right composition guarantees the isolation of only one of the species in which a given element is present in the sample. All the analytical techniques utilized in elemental trace analysis must be performed in accordance with the requirements obligatory in such analyses and must ensure the quantitative decomposition of certain components in the sample and the dissolution of inorganic components. It should be borne in mind, however, that the new matrix, which comes into existence after decomposition, must not hinder the determination using a particular analytical technique (Namieśnik *et al.*, 2000).

As not all analytical techniques require the same degree of sample decomposition, they can be classified as follows:

- not requiring prior sample decomposition, e.g., neutron activation analysis (NAA);
- requiring at least partial sample decomposition, e.g., graphite furnace atomic absorption spectrometry (GFAAS), flame atomic absorption spectrometry (FAAS), inductively coupled plasma atomic emission spectrometry (ICPAES);
- requiring complete decomposition, e.g., cathodic stripping voltamperometry (CSV), anodic stripping voltamperometry (ASV), ion-selective electrode potentiometry (ISEP).

Moreover, depending on the conditions of decomposition, the techniques for mineralizing samples can be divided into two main groups: “wet” and “dry”. Nevertheless, in the analysis of environmental contaminants, wet mineralization is of far greater importance. Mineralization of the sample matrix takes place in the presence of oxygen released from acids at elevated temperature – the main oxidizing agents used are HNO₃, H₂SO₄, HClO₄, HF and H₂O₂. Wet mineralization can be carried out in both open and closed systems; the latter is particularly indicated in trace analysis, as it helps to avoid analyte loss and secondary contamination of the sample. In addition, the decomposition can be carried out at elevated temperature and pressure, as a result of which the process takes less time (Namieśnik *et al.*, 2000; Hoenig, 2001).

Liquid extraction of solid samples is being applied on an ever-increasing scale. The relevant techniques include the classical ones, but also new approaches using additional factors like ultra-sound waves or microwave radiation, the aim of which is to improve the efficiency of the process, to shorten it, to lower its cost and to reduce the amounts of spent solvents (Table 5).

Microwave radiation of an appropriate energy enables the faster processing of the study material and its complete mineralization; moreover, element losses are fewer and sample contamination is less in comparison with other methods. This type of mineralization can be applied to nearly all kinds of samples, including those regarded as impossible to decompose using traditional techniques. For samples with a high organic content, e.g., a layer of forest

undergrowth, plant matter or organic sediment, digestion with HNO_3 can be replaced by microwave-assisted mineralization using HF. Since the Environmental Protection Agency recommended microwave-assisted digestion with HNO_3 this procedure has become standard for testing samples of soils, bottom sediments and muds (Sastre *et al.*, 2002).

The ultrasound-assisted extraction of an analyte from a sample is a clean method and, like the previous one, also shortens the procedure for preparing a sample for analysis. However, it is dependent on the strength of the ultrasound waves, the position at which the wave reaches a maximum, the time for which the wave is allowed to act on the sample, the kind and concentration of acid, the temperature of the process and the chemical properties of the matrix (Al-Merey *et al.*, 2002). Despite its many faults, ultrasound-assisted extraction is a standard procedure in laboratories (Rabajczyk, 2006). A good example is the analysis of bottom sediment samples from the Kizil River and the Hafik Pond in the city of Sivas in Turkey for the presence of Cu, Pb, Zn, Ni and Mn. The use of ultrasound to assist the extraction of metals from these sediments shortened the whole analytical process. This technique is a quick, inexpensive, simple and effective means of preparing samples for trace-metal determination using AAS (Elik, 2007).

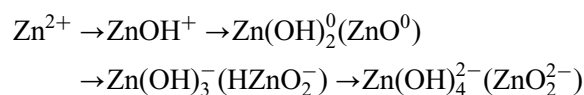
METALS IN AQUATIC SYSTEMS

Zinc

Zinc is widely distributed in nature and makes up $4 \times 10^{-3}\%$ of the Earth's crust. It occurs only in the form of sulfide, carbonate and silicate ores, mainly as calamine ($\text{Zn}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$), smithsonite (ZnCO_3), sphalerite (ZnS) and zincite (ZnO). Zinc and its compounds are used in the manufacture of alloys, paints, pigments, pharmaceuticals, cosmetics, crop protection products, wood preservatives, and also in the galvanization of metal surfaces (Mattielli *et al.*, 2009). The large number of applications of this metal may thus pose a significant threat to the environment. The principal source of its harmful quantities are wastewaters from zinc smelters, metal processing plants and chemical factories, *e.g.*, those producing viscose fiber (Simon-Hettich *et al.*, 2001). Zinc can also enter the environment *via* the combustion of coal and into natural waters from soils near deposits of zinc or other ores containing fairly large amounts of this element. It may be present in drinking water

where this is conveyed in galvanized pipes, especially if the water contains dissolved oxygen, free carbon dioxide and large amounts of chlorides (Simon-Hettich *et al.*, 2001; Mattielli *et al.*, 2009).

In surface waters zinc is generally of secondary origin. It readily dissolves in waters containing aggressive carbon dioxide and dissolved oxygen where this leads to the formation of the hydrogen carbonate $\text{Zn}(\text{HCO}_3)_2$. It occurs in the divalent form, and in hypergenic environments and soils it forms complex ions such as $[\text{ZnOH}]^+$, $[\text{ZnHCO}_3]^+$, $[\text{Zn}(\text{OH})_3]^-$, $[\text{Zn}(\text{OH})_4]^{2-}$, $[\text{ZnO}_2]^-$ (Masliy *et al.*, 2000). It should be noted that, depending on the environmental conditions, the hydrolysis products can pass from the cationic to the anionic form in accordance with the scheme:



(Bruce, 2009).

Weathering processes render all zinc compounds readily soluble, especially in acidic environments, and the ions released form highly mobile mineral or organo-mineral compounds. Mainly in the presence of sulfide ions, zinc is precipitated rapidly, but on organic substances it is sorbed (Simon-Hettich *et al.*, 2001). The latter process, however, is governed by the pH of the water: at $\text{pH} < 5.8$ sorption practically ceases, but at $\text{pH} = 5.8$ 60% of its cationic concentration is bound by humic acids. The assimilability of zinc and the associated risk of its entering the food chain is considerable, given the excellent solubility of the compounds in which it occurs. The migration of zinc in the environment and its uptake by plants and other soil organisms is favored by an acidic pH (Simon-Hettich *et al.*, 2001).

The species in which zinc occurs depend to a large extent on pH. When $\text{pH} = 7-7.5$ zinc salts hydrolyze but at $\text{pH} > 8$ the hydroxide $\text{Zn}(\text{OH})_2$ precipitates out. This is amphoteric and further increase in the pH may cause it to dissolve: the tetrahydroxyzincate(II) $[\text{Zn}(\text{OH})_4]^{2-}$ is then formed (Masliy *et al.*, 2000). At $\text{pH} < 7$, zinc is generally present as a divalent ion, which readily forms complexes with organic and inorganic compounds. It is rapidly adsorbed on the surface of SPM and bottom sediments (Bertling *et al.*, 2006; Directive 76/464/EEC).

In seawaters, zinc is sorbed on the silty and organic sediment fractions and on manganese oxides, hence its lower concentration in the water. Despite zinc's considerably tendency to migrate, relatively small

quantities of zinc permeate into subterranean waters. The toxicity of zinc is not great, but its level depends on the ionic species it occurs in, and varies with, the hardness and pH of the water. It is easily bioaccumulated in phyto- and zooplankton, as a result of which its concentration in these organisms can be up to 30 times higher than in the surrounding water (Directive 76/464/EEC).

Speciation studies have shown that sulfides and carbonates are the dominant forms in which zinc occurs in bottom sediments. In these sediments, zinc is also bound to Mn oxides and amphoteric Fe oxides. The content of organozinc compounds is somewhat lower, while the proportion of exchangeable and adsorbed forms considered to be bioavailable is the smallest (Bourg and Darmendrail, 1992). The mobility of zinc, and thus its bioavailability, depends on the pH of the water (Bertling *et al.*, 2006).

Cadmium

Although the geochemical properties of cadmium very much resemble those of zinc, Cd displays a greater tendency to form compounds with sulfur, is more mobile in most natural environments and is present in greater concentrations in basic igneous rocks and slates. It rarely occurs as a mineral, the most important ones being greenockite CdS and monteponite CdO. It is present in zinc ores in quantities of about 1% and in zinc blende up to 5% (US EPA, 2000). Cadmium is applied mainly in galvanized anti-corrosion coatings on steel products, in pigment form to obtain cadmium yellow in the manufacture of accumulators, and as a scintillator in nuclear reactors. Additional sources of Cd in water include wastewaters from the chemical, photographic and printing industries, as well as the corrosion of galvanized pipes (US EPA, 2000).

Cadmium is readily mobilized by weathering, and then bound by silty minerals containing iron hydroxide and organic substances (Kabata-Pendias and Pendias, 2000; Lai *et al.*, 2002). In waters it occurs in both dissolved and insoluble form, in organic and inorganic complexes, or as free ions (Meinelt *et al.*, 2001). It forms complex ions such as $[\text{CdOH}]^+$, $[\text{CdHCO}_3]^-$, $[\text{CdCl}]^-$, $[\text{Cd}(\text{OH})_4]^{2-}$, and organic chelates. In alkaline environments, poorly soluble cadmium carbonates and phosphates are precipitated (Chen *et al.*, 1997; Thakur *et al.*, 2006). In strongly polluted river waters about 70% of the total Cd

content is present in cationic form (Kabata-Pendias, 2000).

Cadmium is easily adsorbed on SPM forming complexes with organic and inorganic compounds and also with humic substances (Gjessing, 1981). Cd adsorbed on SPM is desorbed in the presence of chloride and sulfate at high ionic strengths (Cenci and Martin, 2004). The same applies to soluble hydrophobic forms of Cd, the quantity of which is a function of the salinity, the total dissolved organic carbon (DOC) and the availability of suitable organic ligands. Highly characteristic of cadmium is the lowering of the partition coefficient K_D (EPA, 402-r-99-004b ch5a) between the bottom sediment and the water with increasing salinity: this is due to the competitive adsorption of divalent cations, *e.g.*, Ca^{2+} and Mg^{2+} , and complexation by Cl^- (Turner, 1996; Cenci and Martin, 2004).

The dissolved forms of cadmium in water are Cd^{2+} , $[\text{Cd}(\text{OH})]^+$, $[\text{CdCO}_3(\text{aq})]^0$, $[\text{CdSO}_4(\text{aq})]^0$, $[\text{CdCl}]^+$. At $\text{pH} < 8$ cadmium exists as Cd^{2+} , while at higher pH $[\text{Cd}(\text{OH})]^+$ is formed. In a strongly basic environment the complexes $[\text{Cd}(\text{OH})_3]^-$ and $[\text{Cd}(\text{OH})_4]^{2-}$ can form (EPA, 402-r-99-004b ch5a). But in the presence of cyanide ions more stable compounds are formed, for example, chelates like $[\text{CdCN}^+]$, in which cyanide is the ligand. Cadmium can also form organometallic compounds. The monomethylcadmium ion $[\text{H}_3\text{CCd}^+]$ has been found in the surface layer of the North Atlantic and also in Arctic snowmelt, in which more than half of the Cd content was in the form of the monomethylcadmium ion (Manahan, 2003).

Bacteria play a large part in binding cadmium in sediments, often causing the metal to precipitate as a sulfide (Kabata-Pendias, 2000). When the pH of the water is neutral or basic, Cd in sediments neither dissolves nor passes into the water; nevertheless, dissolution also depends on the Cd species in question and its solubility.

Lead

The most important lead mineral is galena PbS. Less common are cerussite PbCO_3 , anglesite PbSO_4 , crocoite PbCrO_4 , wulfenite PbMoO_4 and pyromorphite $\text{Pb}(\text{PO}_4)_3\text{Cl}$ (Kabata-Pendias and Pendias, 2000; Karukstis and Van Hecke, 2003). The poor solubility of these minerals means that lead migrates into the environment far less intensively than cadmium or zinc. Even so, contamination by this

element is unfortunately quite common. Lead can enter natural waters from industrial wastewaters, corrosion of tanks and piping, as well as materials made from lead or containing admixtures of the metal. Certain, usually small amounts of lead can come from the soil. Larger amounts are present when the water comes from areas containing veins of galena or from other layers containing admixed lead, and can reach levels of $1,000 \mu\text{g dm}^{-3}$ (Castellino *et al.*, 1995; Kabata-Pendias and Pendias, 2000).

Lead also enters water from the air. It is generally believed that the introduction in the mid-1990s of so-called lead-free petrol considerably reduced or even eliminated the threat from the presence of lead and other heavy metals in the natural environment. Emissions from road transport are mainly caused by lead additives in petrol. Lead additives in petrol are still the largest source of emissions to the air (60%) (Tukker *et al.*, 2001). The term "lead-free petrol" is purely conventional: it can, in fact, legally contain lead compounds in concentrations of up to 0.005 g dm^{-3} (Directive 2003/17/EC). The composition of the dusts emitted by internal combustion engines when starting up contain particles with widely varying concentrations of lead: PbBrCl , $(\text{PbO})_2\text{PbBrCl}$, PbCl_2 , Pb(OH)Cl , PbBr_2 and $(\text{PbO})_2\text{PbCl}_2$ (Castellino *et al.*, 1995).

The presence of free carbon dioxide in water is the factor determining the solubility of lead. If its content is negligible in comparison with that of bound CO_2 , the water does not dissolve lead compounds. But when the content of free CO_2 is equal to that of bound CO_2 , the water dissolves them, and in an excess of free CO_2 it reacts aggressively with Pb to form the hydrogen carbonate $\text{Pb(HCO}_3)_2$. The presence of sulfates and nitrates also favours lead corrosion (WHO, 1992; Marani *et al.*, 1995).

The natural level of lead in waters is low, since its salts – carbonates, sulfates and phosphates – are poorly soluble in water. Depending on the pH, Pb^{2+} ions, anionic, cationic or molecular complexes can occur. Stable complexes of lead with organic compounds, *e.g.*, humic substances during the infiltration of ground waters, are retained in the substrate. In soluble form, the metal occurs mainly as Pb^{2+} and $[\text{PbCO}_3(\text{aq})]^0$, and in an alkaline medium also as $[\text{Pb(CO}_3)_2]^{2-}$, $[\text{Pb(OH)}_2(\text{aq})]^0$ and $[\text{Pb(OH)}]^+$ (Marani *et al.*, 1995; Badawy *et al.*, 2002). Because of its poor solubility, the least lead is found in waters of pH 9.0–10.0 and with a sufficient level of hydrogen carbonates. The greater the basicity of the

water, the lower the solubility of lead. Other soluble forms of lead, besides Pb^{2+} and $[\text{Pb(OH)}]^+$, include $[\text{Pb}_4(\text{OH})_4]^{4+}$, $[\text{Pb}_6(\text{OH})_8]^{4+}$ and $[\text{Pb(OH)}_3]^-$ (Yusupov *et al.*, 2000; Badawy *et al.*, 2002).

In waters with high pH and salinity hydroxy-complexes like $[\text{Pb}_2(\text{H}_2\text{O})_5\text{OH}(\text{NO}_3)_2]^+ [\text{NO}_3]^-$, $[\text{Pb(H}_2\text{O)}_2(\text{OH})_2]$, $[\text{Pb(OH)}_3\text{H}_2\text{O}]^-$, $[\text{Pb}_2(\text{H}_2\text{O})_5\text{OH}(\text{NO}_3)_2]^+$, $[\text{Pb(H}_2\text{O)}_4]\text{NO}_3^+$ and $[\text{Pb(H}_2\text{O)}_3\text{OH}]^+$ may occur (Yusupov *et al.*, 2000).

If lead occurs in finely dispersed suspension or bound to the low-molecular-weight organic fraction, it can be retained for a long time in the water and be transported for considerable distances (Directive 76/464/EEC). Lead is readily accumulated by both living organisms and in bottom sediments (Rickard and Nriagu, 1978; Kabata-Pendias and Pendias, 2000). A direct link exists between the Pb content in bottom sediments with their mineralogical and granulometric composition, and also with the origin of the bedrock, emissions from road vehicles and industry. Under extremely polluted conditions or when contaminants are acidic, lead can enter the food chain with ease (EPA 402-r-99-004b ch5a).

Among organic forms, the alkyl derivatives are of major importance, mainly lead tetramethyl $(\text{CH}_3)_4\text{Pb}$ and lead tetraethyl $(\text{C}_2\text{H}_5)_4\text{Pb}$. Practically insoluble in water, these compounds are very soluble in fats and organic solvents. They easily convert to the trialkyl derivatives of lead, which are toxic. For example, lead tetraethyl is metabolized in the liver of living organisms to the highly toxic and stable triethyl lead ion – $\text{Pb(C}_2\text{H}_5)_3^+$ (Gallert and Winter, 2002).

As far as the sorption of lead on bottom sediment particles is concerned, the organic content and the sediment granulometry are of crucial importance. At $\text{pH} > 6$ and when no dissolved complex compounds are present, lead is completely adsorbed on the sediments. But in an acidic environment, lead is strongly adsorbed on humic substances (Sauvé *et al.*, 1998).

Aluminium

Aluminium is one of the most widespread elements in the Earth's crust, making up 7.8% of its mass. Occurring mainly in the form of numerous aluminosilicates, it is present in most primary rocks as well as in primary and secondary minerals. Instead, it is found combined in over 270 different minerals. The most important of these aluminosilicates are orthoclase $\text{K(AlSi}_3\text{O}_8)$, albite $\text{Na(AlSi}_3\text{O}_8)$, anorthite $\text{Ca(Al}_2\text{Si}_2\text{O}_8)$, sillimanite Al_2SiO_5 and kaolinite

$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, while biotite is a common mica mineral (the aluminosilicate of magnesium, potassium and iron). Marls and clays are weathering products of aluminosilicates (Kabata-Pendias and Pendias, 2000). Aluminium salts are widely applied in the dyeing, paper and tanning industries, as well as in the purification of water and sewage, where aluminium sulfate $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ is used as a coagulant.

The natural content of aluminium in the Earth's crust, as well as its susceptibility to the activity of external factors and the numerous reactions it undergoes in the environment, are reflected in the forms of its occurrence. All of these elements govern the degree of bioavailability and mobility of aluminium in aquatic systems (Matúš and Kubová, 2006). Aluminium levels in surface waters are usually from 60 to $300 \mu\text{g dm}^{-3}$; river waters have an average Al content of $64 \mu\text{g dm}^{-3}$ (Kabata-Pendias and Pendias, 2000). Al levels are low in those aquatic ecosystems where temperature, pH and redox potential and the amounts of inorganic and organic contaminants in the water are all constant. Variable environmental conditions can cause a shift in the sorption–desorption and/or water–sediment equilibria, thereby increasing the likelihood that dissolved, and hence bioavailable, forms of Al, will occur (Habs *et al.*, 1997).

Weathering practically does not cause Al to dissolve; it is soluble only at high or low pH. At pH 5.0–9.0, *i.e.*, the values typical of most natural waters, aluminium is insoluble. In the simplest case, three kinds of aluminium can be identified: soluble Al^{3+} , which is dominant under acidic conditions; insoluble aluminium hydroxide $\text{Al}(\text{OH})_3$, which occurs in a neutral environment; and $\text{Al}(\text{OH})_4^-$, prevalent in an alkaline medium. But if we include the partial dissociation products of $\text{Al}(\text{OH})_3$ and the formation of aluminium complexes with organic substances, the list of species occurring in surface waters becomes very much longer (Habs *et al.*, 1997).

Aluminium therefore occurs as hydroxide, sulfate, fluoride and fluoroaluminate complexes as well as in hydrated form, which hydrolyzes to yield a variety of polymolecular complexes including $[\text{Al}_2(\text{OH})_2]^{4+}$, $[\text{Al}_3(\text{OH})_4]^{5+}$, $[\text{Al}_6(\text{OH})_{15}]^{3+}$, $[\text{Al}_8(\text{OH})_{20}]^{4+}$, $[\text{Al}(\text{OH})_2(\text{H}_2\text{O})_4]^+$, $[\text{Al}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$, $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}]^{7+}$, which are in equilibrium with each other (Burgess, 1992; Milić *et al.*, 1991). Aluminium has amphoteric properties and so, depending on the pH, can occur in different species. In acidic waters, where $\text{pH} \leq 4$,

hydrated cations $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ are predominant. In the pH range 4.5–5.5 the $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ ion can form mixed complexes with organic and inorganic ligands present in the water, *e.g.*, humic substances and fluorides. At $\text{pH} \sim 6.0$ $\text{Al}(\text{OH})_3$ becomes slightly soluble and from $\text{pH} = 6.2$ Al produces a series of intermediate forms like $[\text{Al}(\text{OH})_2(\text{H}_2\text{O})_4]^+$ and $[\text{Al}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$; in alkaline waters the ions $[\text{Al}(\text{OH})_4(\text{H}_2\text{O})_2]^-$ and $[\text{Al}(\text{OH})_5(\text{H}_2\text{O})]^{2-}$ are present (Milić *et al.*, 1991; Nordin *et al.*, 1998).

The change in solubility accompanying the change in chemical forms is due to the broad differentiation in Al concentrations (Martin, 1994). Conditions for Al adsorption are best at $\text{pH} \sim 4.0$, when $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ ions and the toxic hydrolysis products $[\text{Al}(\text{OH})]^{2+}$ and $[\text{Al}(\text{OH})_2]^+$ are present in the water (Burgess, 1992). Aluminium is most soluble in strongly acidic environments, *e.g.*, in volcanic regions, in zones of sulfide ore oxidation, in strongly alkaline areas such as alkaline lakes, and in areas where low-pressure products are dissolved and carbonate rocks undergo thermal metamorphism (Martin, 1994).

As a result, aluminium can occur at concentrations exceeding permitted levels that are toxic to living organisms. In aqueous solution, Al has amphoteric properties and can form both cationic and anionic, organic and inorganic complexes, with a tendency towards polymerization (Zioła and Sobczyński, 2005; Habs *et al.*, 1997).

The factors determining the type of complex are the pH of the water, the temperature, concentration of ligands and the ionic strength of the solution (Matúš and Kubová, 2006). Depending on the type of complexing bond, aluminium compounds are more or less toxic towards living organisms (Bi *et al.* 2001; Berthon, 2002; Guibaud and Gautier, 2003). Inorganic, monomeric aluminium bound to fluoride or sulfate ions, is regarded as toxic (Driscoll and Schecher, 1990; Lydersen *et al.*, 1992; Guibaud and Gauthier, 2005).

In a highly acidic environment, sulfate is the main anion co-existing with soluble inorganic species of aluminium, forming complex compounds with them (Matúš and Kubová, 2006). The dominance of aluminosulfate complexes is dependent on the ambient sulfate concentration. When this is low, the aluminosulfate complexes take the AlSO_4^+ form; when it is higher, then $\text{Al}(\text{SO}_4)_2^-$ ions are dominant (Matúš and Kubová, 2006; Zioła and Sobczyński, 2005). AlSO_4^+ complexes are the principal ones only when the sulfate ion concentration is high and

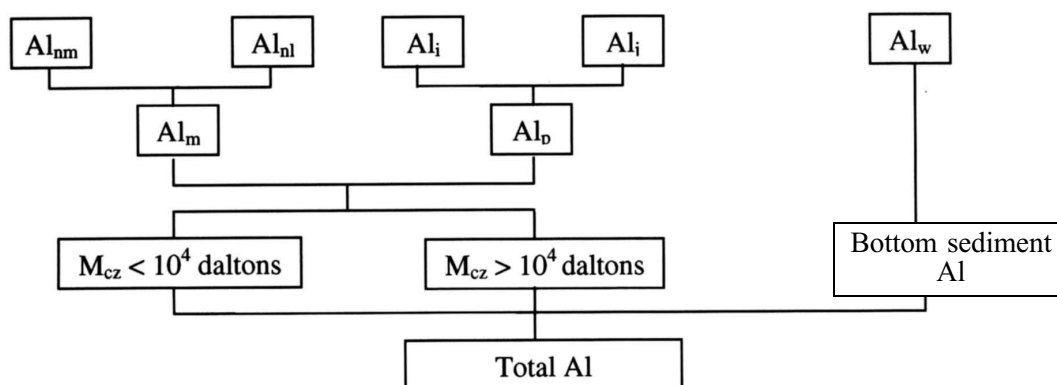


Figure 3 Classification of the forms in which aluminium occurs in the aquatic environment (Lydersen *et al.*, 1990), where: Al_m = total monomeric aluminium; Al_{nm} = inorganic monomeric aluminium (represented mainly by the ions Al^{3+} , $Al(OH)^{2+}$, $Al(OH)_2^{2+}$); Al_{nl} = non-labile monomeric aluminium; Al_p = total non-monomeric aluminium (represented mainly by polymeric colloidal forms); Al_i = strongly positively charged colloidal particles, colloid with strongly positive regions (in corner and areas with a disturbed structure), strongly polarized complexes; Al_j = weakly positively or negatively charged colloids and neutral or slightly polarized complexes; Al_w = complexes of aluminium(III) precipitated from solution (bottom sediment).

the pH low (<4.5); they are not as stable as Al-F complexes (Driscoll and Postek, 1995), *e.g.*, AlF_2^+ , $(AlF)^{2+}$ and AlF_6^{3-} (Mitrović *et al.*, 1996).

The criterion for classifying the forms in which aluminium occurs in the aquatic environment is based on the molecular weight and the polymeric or monomeric nature of the molecules (Lydersen *et al.*, 1990; Lydersen *et al.*, 2002) (Figure 3).

At pH 5–8 the insoluble aluminium(III) hydroxide $Al(OH)_3(H_2O)_3$ precipitates to the bottom sediment. The numerous organic and inorganic ligands present in environmental samples compete with aluminium; as a result of these reactions, the proportions of Al complexes and generally monomeric Al may change. Organic forms of monomeric aluminium can also exist in the aquatic environment (Lydersen *et al.*, 1990).

A change in pH from neutral to very acidic can more than double the amount of soluble aluminium in water, and raises the concentration of its exchangeable species four-fold. Increasing the acidity of the bottom sediment may cause the accumulation of mobile aluminium (water-soluble and exchangeable), and Al species bound to organic matter in the eluvial horizon. Larger amounts of aluminium strongly bound to an organic substance, amorphous aluminium and free aluminium are favored by the granulometric composition (lithology) and humus content rather than the pH (Bezák and Rabajczyk, 2002; Lükewille and Van Breemen, 2004). From the hydrochemical point of view the percentage of dissolved species in the overall transport is given by the transport index. The transport index and migration coefficient of aluminium are both small.

It needs to be emphasized that in spite of the relatively low levels of total overall aluminium in waters that have been analyzed, it is not until the quantitative and qualitative species of the metal are defined, especially its monomeric inorganic species containing a toxic form of Al, that we can assess the actual threat to a riverine ecosystem. The composition of monomeric inorganic aluminium includes its complexes with fluorides, phosphates and sulfates (Boudot *et al.*, 1994; Wauer *et al.*, 2004).

Copper

The Earth's crust contains 0.02% copper. This element occurs naturally in the native state and in many ores, the most common of which are bornite Cu_5FeS_4 , tetrahedrite $3Cu_2S Sb_2S_3$, enargite Cu_3AsS_4 , chalcocite Cu_2S , chalcopyrite $CuFeS_2$, cuprite Cu_2O , malachite $CuCO_3 Cu(OH)_2$ and azurite $2CuCO_3 Cu(OH)_2$ (Kabata-Pendias and Pendias, 2000; Yang and Ni, 2007).

Copper occurs in all types of waters, and its content in them is widely differentiated. The natural content of copper is $0.9\text{--}20\ \mu\text{g dm}^{-3}$ in river water and $0.02\text{--}0.3\ \mu\text{g dm}^{-3}$ in saline waters (Kabata-Pendias and Pendias, 2000). Cu is present in natural waters from wetlands of all kinds in only trace quantities, up to $0.01\ \mu\text{g dm}^{-3}$. On the other hand, there are considerable amounts of Cu, up to $80\ \mu\text{g dm}^{-3}$, in acidic waters associated with deposits of copper ores (Lagos and Cifuentes, 1996; Moore *et al.*, 1996). Higher levels of this element in waters are due to human activities. Copper is discharged into waters with the effluents from smelters, the Cu/Cu-

compound processing industries, and the electroplating industry. It also gets into waters in the form of fungicides, insecticides and algicides, in pigments and catalysts, and from piping and other corrodable equipment made from copper, brass or bronze, which come into contact with water, especially at high temperatures. A significant source of copper in seawater is atmospheric fallout (Kabata-Pendias and Pendias, 2000).

The dissolution of copper is favored by the presence of dissolved oxygen and nitrates in the water. Both soluble and insoluble species of Cu occur in aquatic ecosystems. In waters with a high concentration of hydrogen carbonates we find Cu^{2+} ions and the complexes $\text{CuCO}_3(\text{aq})$, $[\text{Cu}(\text{HCO}_3)_2]$, $[\text{Cu}(\text{OH})_3]^-$ and $[\text{Cu}(\text{OH})_4]^{2-}$ (Drogowska *et al.*, 1994). The total concentration of dissolved copper is expressed by the sum $\text{Cu}_T = [\text{Cu}^{2+}] + [\text{Cu}(\text{OH})^+] + 2[\text{Cu}_2(\text{OH})_2^{2+}]$, but the amount of $[\text{Cu}_2(\text{OH})_2^{2+}]$ depends on the total amount of Cu in the ecosystem (Bruce, 2009).

Copper forms complexes with silicates, sulfates, nitrates and phosphates. The organic compounds of copper include those with amino acids, polypeptides and humic substances; some of them can exist in colloidal form. Insoluble species of copper include sulfides, hydroxides and carbonates. In surface waters insoluble compounds of Cu make up 40–90% of its total amount, and some 99% of copper is transported in a form adsorbed on the silty fraction and as hydroxides (Moore *et al.*, 1996).

Chromium

In nature, chromium occurs almost exclusively in the form of compounds with oxygen. The most important of the numerous minerals are chromite FeCr_2O_4 , crocoite PbCrO_4 and chrome ochre Cr_2O_3 . Anthropogenic sources of chromium are the production of metallic chromium and its compounds, refractory materials, also the chemical, tanning and printing industries, and factories producing mineral and synthetic dyes and anticorrosion paints. Chromium is present in chimney dusts, ashes, cement, spent lubricants, oils, welding gases and tanned leather, and in industrial wastewaters and municipal sewage (Kalembkiewicz and Sočo, 2002; EPA, 402-r-99-004b ch5a).

Depending on the source of its discharge, chromium enters the environment in various forms, though usually as Cr(III) and Cr(VI) compounds. In the aquatic environment, depending on pH, pE, the

kind and quantity of inorganic ions, organic substances or the presence of organisms, chromium compounds can undergo further transformation to yield a whole gamut of chemical and physical species. These are mostly dissolved ionic species, complexes with inorganic ligands like hydroxide, sulfate and chloride, and organic ones, including chelates with humic and fulvic acids (Morel and Hering, 1994). Insoluble compounds in the form of solid or colloidal particles may occur along with soluble species adsorbed on suspended particles or colloids (EPA, 1999).

From the thermodynamic point of view, a whole range of hydroxycomplexes of chromium(III) can exist in aqueous solution: Cr^{3+} , $\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_3$, $\text{Cr}(\text{OH})_4^-$, $\text{Cr}_2(\text{OH})_2^{4+}$, $\text{Cr}_3(\text{OH})_4^{5+}$. At higher chloride and sulfate concentrations mixed complexes such as $\text{Cr}(\text{OH})\text{Cl}^+$ and $\text{Cr}(\text{SO}_4)^+$ can also occur (Świetlik, 1998; Barakat and Giusti, 2003). The participation of polynuclear complexes as well as chloride and sulfate complexes in waters with typical parameters is frequently ignored, as they usually occur in highly concentrated acidic solutions. Depending on pH, inorganically bound chromium(III) species are therefore prevalent in the aquatic environment. At pH 4.5–5.5 the dominant species is $\text{Cr}(\text{OH})^{2+}$, at pH 5.5–7.0 it is $\text{Cr}(\text{OH})_2^+$, and at pH 7.5–9.0 it is $\text{Cr}(\text{OH})_3$ (Świetlik, 1998).

Chromium(VI) can be present in aqueous solutions in the form of chromates, dichromates and chromic acid, as well as hydrogen chromates and hydrogen dichromates, which occur only in strongly acidic solutions. In typical surface waters, where the concentration of dissolved chromium does not exceed $5 \mu\text{g dm}^{-3}$, HCrO_4^- and CrO_4^{2-} ions nonetheless occur: chromate ions prevail at $\text{pH} > 7.0$, and hydrogen chromate at $\text{pH} < 6.0$ (Sperling *et al.*, 1992). Compounds of chromium(VI) are dominant in well oxygenated waters, with a fairly low organic matter content and a pH close to 8. But in waters of pH 5.0–7.0, where levels of easily reducible organic substances are high, the dominant species are those of chromium(III) (Pettine *et al.*, 1990).

In natural aquatic environments, chromium does not persist for long in the dissolved state and is precipitated as a suspension (mostly hydroxides). The soluble species of chromium (CrO_4^{2-} and $\text{Cr}(\text{OH})_3$) are bioaccumulated, but phyto- and zooplankton readily absorb chromium in every form. Reducing the intensity of flow of a stream of water and reducing its carrying energy can cause

chromium adsorbed on suspended particles to be deposited in the sediment.

Iron

Iron is the most widespread heavy metal in nature, making up 5.08% of the Earth's crust (Greenwood and Earnshaw, 1998). All soils, rocks and natural waters contain compounds of iron(II) or iron(III). But in natural waters, this element is present in only low concentrations. In surface waters the usual level is a few mg dm^{-3} , but in some subterranean waters, where iron is mostly present as the divalent hydrogen carbonate and sulfate, the level can reach several tens of mg dm^{-3} . Iron enters waters as a result of the weathering of rocks and soils, and also through leaching and infiltration. Minerals containing iron in the form of oxides, hydroxides and sulfides, e.g., magnetite Fe_2O_3 , siderite FeCO_3 , limonite $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, goethite $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, pyrite FeS , and chalcopyrite CuFeS_2 , dissolve during hydrolysis and the action of aggressive CO_2 to form $\text{Fe}(\text{HCO}_3)_2$ (Cotton and Wilkinson, 1988; Greenwood and Earnshaw, 1998; Kabata-Pendias and Pendias, 2000). Some of these compounds can reach water bodies *via* ground waters, others may be derived from the breakdown of iron-bearing minerals in a water basin as a result of submarine erosion or the decomposition of basic magma during its underwater eruptions (Greenwood and Earnshaw, 1998).

Elevated levels of iron can also result from the discharge of industrial effluents, the corrosion of tanks, piping and other equipment and installations containing iron. Iron is present in effluents from the smelting, dyeing, electroplating and tanning industries. Iron compounds are used as coagulants in the desulfurization of gases and in sewage treatment. The presence in sewage of hexacyanoferrates(II) and hexacyanoferrates(III) is due to the manufacture of inorganic dyestuffs (Greenwood and Earnshaw, 1998; Kabata-Pendias and Pendias, 2000).

Iron can occur in dissolved or colloidal form or in suspension. The oxide of iron(III) is very insoluble, so that in rivers most iron is transported in suspension, and reactions of the solid body-solid body type are dominated. Colloids usually occur in the presence of organic substances, including humic substances, but they may also be present as inorganic species or as organic complexes. Waters from marshland or peatbogs, which contain substantial amounts of humic acids, contain iron(III) in the form of dissolved

complex salts, the so-called humusates (O'Neill, 1997). The precipitation of iron(III) hydroxide from such waters take place in the presence of bacteria, which decompose the salts releasing Fe^{2+} or Fe^{3+} ions. Iron(III) hydroxide is only very slightly soluble, so in waters poor in organics but rich in dissolved oxygen contain trace amounts of dissolved Fe^{3+} . Surface waters containing FeSO_4 besides iron complexes contain no $\text{Fe}(\text{HCO}_3)_2$, the content of which is governed by the amount of CO_2 and the lack of oxygen (Greenwood and Earnshaw, 1998; Fujii *et al.*, 2008).

Depending on the bacteriological and chemical composition of natural waters, and also the presence of oxygen, iron can occur in the form of di- or trivalent compounds. As a consequence of oxidation and reduction, processes that depend on the ambient oxygen conditions, the Eh potential and the pH of the water, zones of occurrence of iron compounds can be established in deep bodies of standing water. Near the bottom, where reduction processes occur, iron(II) is prevalent, but closer to the surface, where there are larger amounts of oxygen dissolved in the water, iron(III) is dominant. If the boundary between the oxidation and reduction zones lies high above the bottom, iron sulfides may form in the water (O'Neill, 1997).

The region of stability of iron(III) hydroxide covers a wide Eh – pH range. In the case of metal ions, the region of stability lies below that of the water, which indicates that metal ions are unstable and, in the case of iron, tend to convert to Fe^{2+} or $\text{Fe}(\text{OH})_3$ (Schwertmann, 1991; Greenwood and Earnshaw, 1998).

In the presence of a large quantity of organic substance, which may be a source of carbon dioxide, and also increasing pH and simultaneously decreasing oxidizing potential, FeCO_3 precipitates (O'Neill, 1997; Greenwood and Earnshaw, 1998; Pullin and Cabaniss, 2003). In surface waters of minimal basicity, the hydrolysis of FeSO_4 may be only partial, as the sulfuric acid produced by this reaction reduces the pH to <4.6 , which almost completely stops the hydrolysis of FeSO_4 (Hopkinson and Barbeau, 2007). Increasing amounts of sulfur compounds and organic matter cause the formation of sulfides in the sediments, which preferentially react with iron and indirectly cause the dissolution of vivianite (the hydrated phosphate(V) of iron(II) $\text{Fe}_3[\text{PO}_4]_2 \cdot 8\text{H}_2\text{O}$) (Murphy *et al.*, 2002). But when large amounts of FeS are formed and the concentration of iron exceeds that of

the sulfide, the formation of vivianite is the dominant process (Golterman, 2001; Hupfer *et al.*, 1998).

In surface waters containing a large amount of organic compounds, especially humic substances, the precipitation of $\text{Fe}(\text{OH})_3$ due to the decomposition of iron(II) sulfate is hampered, because the humic substances act as protective colloids preventing the precipitation of $\text{Fe}(\text{OH})_3$ (Hopkinson and Barbeau, 2007). Iron is transported mainly in the form of protective colloids. The $\text{Fe}(\text{OH})_3$ precipitates into the near-bottom layer, where for lack of dissolved oxygen anaerobic processes are the norm. Iron(III) compounds readily precipitate out of the water, gradually making it turbid and coloring it brown (Hopkinson and Barbeau, 2007; Fujii *et al.*, 2008; Pullin and Cabaniss, 2003).

In the presence of oxygen or oxidizing substances, Fe(II) rapidly oxidizes to Fe(III), which is then precipitated in the form of hydrated iron oxides. In subterranean waters, which are devoid of oxygen, oxidation may be driven by ferrobacteria (*Ferrobacillus*, *Gallionella*) (Coupland *et al.*, 2004). Depending on the ambient pH, the following iron(III) species may occur: Fe^{3+} , FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{OH})_{3(s)}$, $\text{Fe}(\text{OH})_4^-$. At pH 1–4.5 the total dissolved iron is expressed by the relationship $\text{Fe}_T = [\text{Fe}^{3+}] + [\text{FeOH}^{2+}] + [\text{Fe}(\text{OH})_2^+] + 2[\text{Fe}_2(\text{OH})_2^{4+}]$ (Bruce, 2009).

In natural systems, there are many different dissolved forms of compounds that affect the behavior of iron. As a result of reactions in aquatic system leading the formation of relatively insoluble compounds (*e.g.*, sulfides or phosphates) or stable complexes (*e.g.*, organic acids with iron(III)). Formed compounds prevent the precipitation of iron (Hopkinson and Barbeau, 2007). $[\text{FeCl}]^{2+}$ and $[\text{FeCl}_2]^+$ are formed in the presence of chlorides, and $[\text{FeHPO}_4]^+$ and $[\text{FeH}_2\text{PO}_4]^{2+}$ where large amounts of phosphates occur. But Fe^{3+} species depend on the pH (Cotton and Wilkinson, 1988).

The most widespread species of iron are Fe^{2+} ions, which occur under acidic reducing conditions; insoluble forms of these ions are hematite, goethite (FeOOH) and other hydrated oxides. The hydrated compounds of iron can undergo various transformations in the aquatic environment; but when they are the first to be precipitated from hematite, their transformation is very slow (Olila and Reddy, 1997; O'Neill, 1997; Alagarsamy, 2009).

The initial red-brown precipitate of iron(III) oxide is usually the gelatinous, hydrated oxide of iron(III) $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$, which gradually dehydrates to Fe_2O_3 ;

this process, however, may take years to complete (Manahan, 2000). The freshly-precipitated iron(III) species is more easily redissolved than when it is partially or wholly dehydrated. The fresh precipitate has a very large surface area, and the stoichiometric equilibrium of its electrical charge is upset. In consequence, many other ions, particularly metals, can be sorbed and co-precipitated, which favours their accumulation in the bottom sediments (Golterman, 2004; Alagarsamy, 2009).

In combination with phosphorus and mineral suspended matter, iron falls to the bottom in the form of organic detritus. If oxidizing conditions prevail at the sediment–water interface, Fe^{+3} ions bind phosphate ions and in this form are deposited in the sediments. This process is, however, retarded by the formation on the surface of the sediments of Fe^{+2} complexes with sulfides that are formed from the sulfates present in aquatic ecosystems under extremely reducing conditions (Olila and Reddy, 1997; O'Neill, 1997; Alagarsamy, 2009). The stability of the complex $\text{Fe}(\text{OOH}) \sim \text{P}$ protects it from reduction, which means that it is more stable than free $\text{Fe}(\text{OOH})$. When phosphates are adsorbed on $\text{Fe}(\text{OOH})$, a quantity of energy is released that depends on the Fe:P ratio. The lower this ratio, the less energy is required for reduction (Golterman, 1998).

CONCLUSIONS

The chemical composition of surface waters varies according to geological structure, type of substrate and land use. Metals such as Al, Cd, Cr, Cu, Fe, Pb and Zn enter waters as a result not only of natural processes, but also of the direct and indirect activities of humans. The multifarious sources of substances, the chemical properties of the various species, their ability to be adsorbed on solid particles and to form hydrated ions or ion pairs, and also the chemical, physical and biological conditions in the aquatic environment, all affect the diversity of species of metals present in surface waters.

In the aquatic environment, heavy metal cations can occur in many forms: ions, ions bound to different ligands, and precipitated molecules that can be adsorbed on suspended particles and colloids or themselves suspended in the water.

Elements migrating into an aquatic environment are deposited in the bottom sediments, where they are temporarily immobilized and may constitute a threat to the life of organisms in that body of water. Under

Table 6 Forms of occurrence of metals in different compartments of surface waters

Metal	Forms of occurrence	
	Water	Bottom sediment
1	2	3
Cd	<ul style="list-style-type: none"> -Easily mobilized during weathering processes -Occurs as the Cd^{2+} ion and bound to humic substance -at pH < 8 occurs as Cd^{2+}; with rising pH $[Cd(OH)]^+$ is formed -In a strongly basic environment the complexes $[Cd(OH)_3]^-$ and $[Cd(OH)_4]^{2-}$ can form -Forms organic chelates; readily adsorbed on SPM forming complexes with organic, inorganic and humic compounds -Acidic environment: Cd^{2+}, $CdSO_4^0$, $CdCl^+$; alkaline environment: Cd^{2+}, $CdCl^+$, $CdSO_4^0$, $CdHCO_3^+$ 	<ul style="list-style-type: none"> -Rapidly bound in river sediments – in the presence of bacteria precipitates as a sulfide -In an alkaline environment, precipitates as slightly soluble carbonates and phosphates -Bound by silty minerals, iron hydroxide and organic substances -Bacteria play a large part in binding Cd in sediments, often causing it to be precipitated in the form of sulfides -At pH ≥ 7 Cd in sediments does not dissolve and does not pass into the water (this process also depends on the species in which the element occurs and the solubility of the compound in question)
Fe	<ul style="list-style-type: none"> -In river waters iron species bound to other compounds are dominant; Fe(II) occurs as the soluble hydrogen carbonate, bound to humic substance -Forms compounds readily soluble in water of pH < 7 -Particles of colloidal iron < 0.5 μm in size are difficult to separate from the dissolved form -In the presence of Cl^-, forms $[FeCl]^{2+}$ and $[FeCl_2]^+$, and with high phosphate contents forms $[FeHPO_4]^+$ and $[FeH_2PO_4]^{2+}$ -Fe^{2+}: acidic medium; Fe^{2+}, $FeSO_4^+$, $FeHPO_4^+$; alkaline medium: $FeCO_3^0$, Fe^{2+}, $FeHCO_3^+$, $FeSO_4^0$ -Fe^{3+}: acidic medium: $FeOH^{2+}$, $Fe(OH)_3^0$, org; alkaline medium: $Fe(OH)_3^0$, org. 	<ul style="list-style-type: none"> -Fe(II) is rapidly oxidized in surface layers and various oxides precipitate -Colloidal oxides play an enormous role in the sorption and coagulation of other colloidal substances and ions (chiefly trace metals) -Fe(iii) occurs in the form of insoluble oxides and the hydroxide $Fe(OH)_3$ -The fine-grained and colloidal hydroxides of iron are sorbed to a large extent on the surfaces of mineral and organic particles -Fe_3O_4, Fe_2O_3, $FeOOH$, $Fe(OH)_2$, $Fe(OH)_3$
Ce	<ul style="list-style-type: none"> -Dissolution favoured by the presence of O_2 and NO_3^- -A large concentration of hydrogen carbonates favours the presence of Cu^{2+} ions and complexes - $[Cu(OH)_4]^{2-}$, $[Cu(HCO_3)_2]$, $[Cu(OH)_3]^-$ -Forms complexes with silicates, sulfates, nitrates and phosphates as well as with amino acids, polypeptides and humic substances (some may occur in colloidal form) -Acidic medium: org. Cu^{2+}; alkaline medium: $CuCO_3^0$, org. $CuB(OH)^{4+}$, $Cu[B(OH)_4]^{4-}$ 	<ul style="list-style-type: none"> -A large concentration of hydrogen carbonates favours precipitation of $CuCO_3(aq)$ -In undissolved form. Cu occurs in water as sulfides, hydroxides and carbonates -Insoluble compounds make up 40–90% of the total amount of Cu in aquatic ecosystems -Cu is transported in a form adsorbed by the silty fraction and hydroxides
Zn	<ul style="list-style-type: none"> -Zn(II) occurs as the ionic species Zn^{2+}; -in hypergenic environments forms simple inorganic complexes of the type: $[Zn(OH)]^+$, $[Zn(HCO_3)]^+$, $[Zn(OH)_3]^-$ -In weathering processes, all zinc compounds are readily soluble, especially in acidic environments -Ions released form highly mobile mineral or organomineral species 	<ul style="list-style-type: none"> -Zn is rapidly precipitated mainly in the presence of sulfide and carbonate, hence these ions are the dominant species in bottom sediments -Sorption of Zn by organic substances depends on the pH: at pH ~ 5.8 60% of the cationic concentration of Zn is bound by humic acids, but at lower pH sorption practically ceases

Table 6 Forms of occurrence of metals in different compartments of surface waters (*continued*)

Metal	Forms of occurrence	
	Water	Bottom sediment
1	2	3
	<p>–Acidic environment: Zn^{2+}, $ZnSO_4^0$, org, $Zn(H_2O)_6^{2+}$, $Zn(H_2O)_5(OH)^+$; alkaline environment: $ZnHCO_3^+$, $ZnCO_3^0$, org, Zn^{2+}, $ZnSO_4^0$, $ZnB(OH)_4^+$</p>	<p>–Zn occurs in a form bound by Mn oxides and the amphoteric oxides of Fe</p> <p>–The proportions of exchangeable and adsorbed species, both bioavailable, are the smallest</p>
Cr	<p>–Cr(VI) forms readily soluble compounds</p> <p>–At concentrations of $< 500 \text{ mg dm}^3$ occurs mainly as $HCrO_4^-$ and $HCrO_4^{2-}$</p> <p>–Reduction of Cr(VI) to Cr(III) takes place in the presence of Fe(II) or soluble organic substances</p> <p>–Cr(VI) is prevalent under oxidizing conditions, but Cr(III) under reducing conditions</p> <p>–Cr^{3+}: acidic environment: $CrOH^{2+}$; alkaline environment: $Cr(OH)_4^-$</p> <p>–Cr^{6+}: acidic environment: CrO_4^{2-}; alkaline environment: CrO_4^-</p>	<p>–Cr(III) forms poorly soluble compounds, under reducing conditions occurs mainly as $Cr(OH)_3$; precipitates at $pH > 7$;</p> <p>–Readily and stably adsorbed by Fe and Mn hydroxides, silty minerals, peat zeolites</p> <p>–Cr(VI) is weakly adsorbed mainly on the oxides, hydroxides and oxyhydroxides of Fe and Al</p> <p>–Under anoxic conditions Cr(III) is immobile and is not released</p> <p>–Cr(III) is strongly bound to sediment particles</p>
Al	<p>–Soluble Al^{3+} is dominant under acidic conditions, $Al(OH)_4^-$ is prevalent under alkaline conditions</p> <p>–Occurs as complexes with hydroxide and sulfate, fluoride and fluoraluminate, and in the hydrated form, which undergoes hydrolysis</p> <p>–Various polynuclear complexes, e.g., $[Al_3(OH)_4]^{3+}$, $[Al_5(OH)_{15}]^{3+}$, $[Al(OH)(H_2O)_5]^{2+}$, $[Al(OH)_2(H_2O)_4]^+$, $[Al_8(OH)_{20}]^{4+}$</p> <p>–At pH 4.5–5.5 mixed complexes of the $[Al(H_2O)_6]^{3+}$ ion with organic and inorganic ligands, e.g., with humic acids and fluorides</p> <p>–From pH = 6.2 forms a series of intermediate species like $[Al(OH)_2(H_2O)_4]^+$, $[Al(OH)(H_2O)_5]^{2+}$, whereas in an alkaline environment the following ions are present: $[Al(OH)_4(H_2O)_2]^-$, $[Al(OH)_5(H_2O)]^{2-}$, $Al(OH)_4^-$, org</p> <p>–$AlSO_4^+$ complexes are the principal ones at high sulfate levels and $pH < 4.5$; at high SO_4^{2-} levels $Al(SO_4)_2^-$ ions are prevalent</p>	<p>–Insoluble aluminium hydroxide $Al(OH)_3(H_2O)_3$ occurs in a neutral environment</p> <p>–Insoluble in the pH range 5.0–9.0</p> <p>–At $pH \leq 4$ optimal conditions for adsorption</p> <p>–Present in the form of carbonates, silicates, sulfides, phosphates and complex compounds with organic ligands</p> <p>–Increasing acidity causes the accumulation of mobile aluminium and species bound to organic matter in the eluvial horizon</p>
Pb	<p>–Depending on pH Pb^{2+} ions, anionic or cationic or molecular complexes can occur;</p> <p>–Occurs in dissolved form mainly as Pb^{2+} and $[PbCO_3(aq)]^0$, in an alkaline environment also as $[Pb(CO_3)_2]^{2-}$, $[Pb(OH)_2(aq)]^0$, $[Pb(OH)]^+$, $[Pb_4(OH)_4]^{4+}$, $[Pb_6(OH)_8]^{4+}$ and $[Pb(OH)_3]^-$</p> <p>–At high pH and high salinity hydroxycomplexes may be present, e.g., $[Pb(H_2O)_2(OH)_2]$, $[Pb(OH)_3(H_2O)]^-$, $[Pb_2(H_2O)_5OH(NO_3)_2]^+$, $[NO_3^-]$, $[Pb_2(H_2O)_5OH](NO_3)_2^+$, $[Pb(H_2O)_4NO_3]^+$, $[Pb(H_2O)_5OH]^+$</p> <p>–In finely-dispersed suspension or bound to the low-molecular-weight organic fraction Pb is retained for a considerable time in the water and can be transported over long distances</p>	<p>–The natural content in bottom sediments is linked directly with the origin of the bedrocks and with the mineralogical and granulometric composition</p> <p>–The presence of free CO_2 determines the stability of precipitated compounds</p> <p>–Carbonates, sulfates and phosphates are practically insoluble in water</p> <p>–Stable complexes of Pb with organic compounds, e.g., humic substances, during the infiltration of ground waters, are retained in the substrate</p> <p>–The higher the basicity of the water, the lower the solubility of lead</p> <p>–Pb is readily bioaccumulated, and accumulated in the bottom sediments;</p> <p>–At pH 9.0–10.0 and in the presence of sufficient amounts of hydrogen carbonates, most Pb is in adsorbed form</p>

favourable conditions, they may be released back into the water, where they enter the trophic chain and participate in further stages of their environmental cycle. Changing conditions in the aquatic environment cause the chemical species in which metals occur, and hence their bioavailability, to change. But the tendency for a metal to pass into the water, that is, its mobility, depends on its species in the sediment or adsorbed on organic matter.

Knowledge of the levels of metals in water and bottom sediments can be used in gaining a full chemical insight into an aquatic environment; these parameters can also be indicators of the geochemical situation in a watershed and of the spread of contaminants. It is in the bottom sediments, the principal link in the cycle of elements, where these are accumulated and transformed, and where toxic compounds entering the water are decomposed. They are a representative indicator of long-term changes in the contamination of water bodies and can be utilized as an index of biological and chemical changes in the aquatic environment. Exchange reactions, among them the important redox and sorption processes, are continually taking place between the bottom sediments and the water.

Since metals are present in sediments in such a wide variety of species, it is insufficient to analyze the total concentration of any one of them in the various compartments of an aquatic environment in order to assess their effect. Such an analysis supplies no information on the potential mobility of metals and the possibilities of their removal from the water or sediments following a change in, say, pH or salinity or in the presence of complexing ligands. Neither does it permit an assessment of the potential threat to an environment from a metal present in the water in dissolved or colloidal form or deposited in the bottom sediments. Therefore, analysis of metals in the various compartments of the environment should enable the species in which an element is present in these compartments to be distinguished and quantitatively determined.

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