

Environmental Factors Affecting Speciation of Mercury in the Bottom Sediments; an Overview

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Abstract

This paper presents a discussion of selected factors affecting distribution and behaviour of mercury species in bottom sediments. This paper demonstrates that microorganisms, inorganic sulphides, organic matter, iron and manganese hydroxides, red-ox potential, chlorides and temperature are the main factors controlling the behaviour of this element in bottom sediments.

Keywords: mercury, speciation, bottom sediments, organic matter, sulphides, hydroxides, pH, temperature, redox-potential, salinity, microorganisms

Introduction

The concentration of mercury in bottom sediments, where it can undergo many transformations, is a very good indicator of water pollution with this element. On the one hand, bottom sediments are where mercury accumulates as a result of simple sedimentation, and on the other, mercury is released from the sediments becoming available for further biogeochemical transformations. The rates of these two processes depend significantly on the specific environmental conditions in a given water system. As a result of complex chemical, physical and biological transformations some mercury species can convert into more toxic ones. Tragic examples of intoxication with methylmercury and dimethylmercury have been noted in Japan. These mercury species were responsible for the

lethal poisoning of people who had eaten contaminated fish [1]. This fact aroused great interest in the problems of mercury speciation in the natural environment, including bottom sediments.

Methylmercury is the most common among the species determined in different kinds of natural samples. It is known to be considerably toxic to living organisms, although its typical contribution to total concentration of mercury in bottom sediments does not exceed 1–1.5% [2]. In order to perform full ecotoxicological characterisation of bottom sediments it is necessary not only to determine mercury species occurring there but also to identify the factors affecting mercury transformations in the sediment. The study reported has been undertaken to identify the factors influencing the speciation of mercury in bottom sediments.

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Concentrations of Mercury Species in Bottom Sediments

There are considerable differences in the concentration of mercury between different types of deposits. The natural total concentration of mercury in the bottom sediments can vary from 10 to 200 ng/g of dry mass, which is of the same order of magnitude as noted in non-polluted soils [3]. Very high concentrations of mercury are found in the sediments from highly polluted areas and often from estuaries of some rivers. For example, the bottom sediments of the Elba River (Germany) were highly polluted with mercury, whose total content reached 12 µg/g dry mass [4]. Moreover, the mercury concentrations reported for extremely polluted Minamata Bay (Japan) were up to 908 µg/g dry mass [5]. Higher concentrations of mercury in the coastal zones and river estuaries are a result of the transportation of this element with river waters polluted with mercury bound to the suspension phase. For instance, in the water of the rivers falling into Chesapeake Bay (USA), the contribution of mercury bound to the suspension phase was estimated at 55% [6]. However, a much higher proportion, even up to 99%, was noted in the river estuaries [7]. In general, a contribution of mercury bound to the suspension phase is minor in the open waters and much more significant in rivers and coastal zones [8, 9].

Usually, the concentration of methylmercury in the bottom sediments varies between 1-1.5% of total mercury, while it makes less than 0.5% in the estuaries and seas [10, 11]. Kannan & Falandysz [11] suggest that the product of total mercury concentration and the methylmercury concentration could be a useful index describing the degree of pollution in a given water reservoir. According to these authors, in the non-polluted areas this index takes values lower than 1. In the bottom sediments of the Gdańsk Bay (Poland) the contribution of methylmercury was less than 0.5% of total mercury concentration with this index values from 0.02 to 2.27 (average 0.65) ng/g dry mass. From among the samples studied, the highest index was found for the bottom sediments of the harbour in Hamburg and the rivers Elba and Mulde, where its value varied from 2.5 to 9.7 [12, 13]. Ullrich *et al.* [2] point out, that some additional amounts of methylmercury can be formed during the preparation process of samples for the speciation analysis. Some authors point out that some additional amounts of methylmercury can be formed during the sample preparation for speciation analysis and suggest that the contribution of methylmercury in the total mercury concentration above 1% is rather improbable. Besides, the bottom sediments are the sites of both methylation and demethylation processes, so the concentrations of methylmercury reflect rather a kind of 'net' methylation being a result of an equilibrium between these two processes [14].

The contribution of methylmercury in the concentration of total mercury varies also in the vertical profile of sediments. In the upper layers it was 0.65±0.34%, while in deeper ones it was only 0.01 - 0.05%, which was explained

as related to greater activity of micro-organisms in the upper levels of bottom deposits [15]. In the porous water, the contribution of methylmercury in the concentration of total mercury is higher, reaching 10-20% [16]. The contribution of methylmercury contained in the porous water in the concentration of total methylmercury in the bottom sediment (pore water and solid phase of the sediment) is estimated as ~1%, while that present only in the solid phase in the concentration of total mercury is estimated as 0.4% [17]. In the suspension, likewise in the bottom sediment, the concentration of methylmercury varies from 20% to 80% of the total concentration of methylmercury in the water [18, 19]. For example, the concentration of methylmercury in the suspension from the North Sea was below the detection limit, so it was lower than 48 pg/L (1–81 ng/g), while the contribution of methylmercury in the concentration of total mercury in the suspension was on average 3% [8].

Determinations of dimethylmercury in the solid phase of the bottom sediments have never been performed. First of all, due to the analytical problems, but also because dimethylmercury is very volatile and hardly water-soluble. Thus, it easily evaporates and becomes unavailable for water organisms. Moreover, dimethylmercury is unstable and undergoes fast degradation to the methylmercury [20]. For instance, in the bottom sediments from Sepetiba Bay (Brazil) dimethylmercury occurred in concentrations from 211 to 233 ng/g [21].

The concentration of divalent mercury Hg(II) in the bottom sediments ranges between 0.54±0.17 and 9.0±5.5 ng/g [11]. Usually, the highest concentrations of Hg(II) are noted in the deep-sea sediments, lower in the river estuaries and even lower in the fresh water reservoirs. The contribution of methylmercury and Hg(II) in the concentration of total mercury is on average lower than 10% in the bottom sediments [11]. This relatively small contribution of methylmercury and Hg(II) means that mercury occurs mainly in the low-bioavailable sulphide species and/or organic matter.

Inorganic Sulphur and Mercury Species

A characteristic feature of mercury is its strong affinity to sulphur, which is of great importance for biogeochemistry of this element. It also controls the chemistry of mercury in anaerobic sites. The dominant mercury species in the anaerobic conditions are mono- and bi-sulphide complexes such as HgS, HgS₂H₂, HgS₂H⁻ and HgS₂²⁻ [22]. From among the organic sulphur-mercury compounds, the most important is CH₃HgS⁻. In anaerobic conditions at low concentrations of sulphides methylmercury is mostly bound with organic matter [23]. Mercury sulphide (HgS) is poorly water soluble, precipitates in sediments and determines the solubility of Hg(II) compounds in the anaerobic conditions in the sediments. It is supposed that HgS is deposited while accompanying particles of organic matter or iron oxides [17]. The solubility of HgS in the environment considerably

increases with increasing content of sulphide ions S^{2-} and becomes sufficient to form soluble sulphide and disulphide complexes [24]. This property is responsible for great concentrations of the soluble mercury species in anaerobic zones of the bottom sediment [3]. For example, in the bottom sediments of highly polluted Tokuyama Bay (Japan) no organic mercury species were detected, while the concentration of the total mercury varied from 10900 to 22200 ng/g dry mass. The most abundant mercury species were complexes of sulphides, making between 50 and 90% and the remaining mercury free ions and elementary mercury [25]. This situation can be explained by the fact that a very high concentration of mercury inhibits development of microorganisms responsible for mercury methylation. The absence of organic mercury species can be explained as well by high sulphide concentration in bottom sediments. Similarly, in bottom sediments of the polluted Almaden area (Spain) the methylmercury was not found, but the most abundant mercury species were sulphides [26]. Organic matter is of great importance in controlling the concentration of mercury in water environments as it can prompt a release of mercury from poorly soluble HgS. It has been found that hydrophobic components of dissolved organic matter (a mixture of humic and fulvic acids) are more effective in releasing mercury from the cinnabar than the hydrophilic ones. Furthermore, it has been proved that the presence of Ca^{2+} strongly inhibits the release of mercury from HgS by organic matter [27]. According to recent data, metal sulphides seem to play an important role in aerobic conditions. Their concentration in river waters reached up to 120 $\mu\text{g/L}$, with 90% of them copper, iron and zinc sulphides. The metal sulphide complexes do not form the simple protonated compounds (e.g. $M(HS)^+$), but non-protonated clusters (e.g. M_3S_3 , M_4S_6 , M_2S_4), characterised by high stability constants. The occurrence of metal sulphides in aerobic conditions is useful in controlling the toxicity of many toxic metals, including mercury [28].

Mercury dissolved in the pore water can be adsorbed by many components of the solid phase of the bottom sediment. For instance, excellent components to capture heavy metals (including mercury) are sulphide minerals [29]. Particularly important among these minerals are pyrite (FeS_2) and acid volatile sulphides ("AVS", e.g. FeS , MnS). Adsorption and co-precipitation of mercury on the AVS and pyrite can limit the amount of mercury dissolved in the porous water in anaerobic conditions. However, mercury bound with these minerals can be released to the porous water as a result of gradual oxidation of the sediment [17]. This behaviour was observed by Regnell *et al.* [30], who reported that the presence of iron and manganese hydroxides causes a decrease in mercury mobility, but simultaneously is responsible for an increase in the concentration of methylmercury. The same authors [30] also reported a positive correlation between the concentration of methylmercury and total concentration of iron and manganese in the bottom sediments. Moreover, a strong positive correlation between the concentration of

methylmercury and the concentration of AVS was found in the bottom sediments of the Elba River [4].

Microbiological Processes and Mercury Speciation

For the biological methylation of mercury in anaerobic conditions the most important are sulphate reducing bacteria (SRB) [31-33]. This group of bacteria includes the following species: *Clostridium butyricum*, *Desulfobulbus propionicus*, *Desulfovibrio desulfuricans*, *Desulfococcus multivorans*, *Desulfobacter* sp., *Desulfobacterium* sp. [33-35]. The process of mercury methylation takes place mainly in the upper layers of the bottom sediments as there the content of organic matter and the activity of microorganisms are the highest [36]. Moreover, methylation requires a sufficient level of sulphides. Formation of methylmercury is favoured in the acidic conditions at a relatively high concentration of mercury. It has been found that the amount of methylmercury increased in proportion to the concentration of free sulphide ions, reaching a maximum for 1.8 mg S^{2-} /g of sediment, then the concentration of $CH_3Hg(I)$ decreased, probably because of the formation of volatile dimethylmercury [37]. At too high a concentration of S^{2-} the dominant process is the formation of hardly soluble HgS - the concentration of Hg(II) is too low for methylation to occur [38]. Although the concentration of total mercury in the porous water increased with increasing content of sulphides, the concentration of methylmercury decreased. For the same sediments, no correlation was noted between the concentration of methylmercury in the sediments and the concentration of total mercury in the porous water. This observation confirms the hypothesis of the effect of sulphides on mercury speciation, and thus on the bioavailability of mercury for methylation. The negative correlation between the concentration of sulphides in the porous water and that of methylmercury in the sediment suggests that sulphides can limit production and accumulation of methylmercury in the bottom sediment [39]. According to recent reports, the rate of biotic methylation is not correlated with the concentration of mercury in the solid phase of the sediment, and only weakly depends on the mercury concentration in the dissolved phase, whereas it is strongly correlated with the concentration of sulphides favouring the formation of neutral water-soluble mercury sulphide species (HgS) [33, 40].

It is known that not only methylmercury but also dimethylmercury is formed as a result of micro-organism activity [14, 41]. The generation of volatile dimethylmercury by bacteria is believed to be their protection against intoxication with mercury compounds. The mechanisms controlling micro-organism resistance to mercury are still not well recognised. The rate of mono- and dimethylmercury formation depends on the concentration of mercury and pH of the environment. The formation of methylmercury is favoured in acidic conditions at relatively high concentrations of mercury, whereas the formation of dimethylmercury - in neutral or alkaline conditions, at

relatively low concentrations of mercury and in the presence of strong complex forming species such as H_2S . The experiment performed by Matilainen & Verta [42] proved that methylation took place in the sterilised samples of the bottom sediments, which pointed to the occurrence of abiotic processes of mercury methylation. In the same sterilised samples no demethylation of mercury was detected. According to the experimental data, approximately 1-2% of inorganic mercury $Hg(II)$ added to the samples was transformed into methylmercury. These results agree with the data from natural water reservoirs and indicate an equilibrium between the processes of methylation and the demethylation in bottom sediments [31].

Hydrobiological Aspects of Mercury Speciation

Although HgS is strongly bound with the sediments it can be partly dissolved as a result of transformations with the involvement of bacteria or under the effect of oxidising conditions appearing as a consequence of bioturbation [17, 43-45]. For instance, in the bottom sediments of the Saguenay Fjord, high concentrations of soluble mercury were noted (>100 ng/L) at a depth of 15 or even 25 cm, which was explained by the influence of benthos organisms on the oxidation of mercury sulphide species [17]. Gobeil & Cossa [45] reported that the mercury flowing from deeper layers of the sediment to its near surface layers, only in the process of diffusion, made 3% of the amount of this element flowing from the water to the sediment. According to Gagnon *et al.* [17], this proportion is much higher and can reach up to 7%. On the other hand, Rutgers van der Loeff *et al.* [44] have shown that the size of mercury redeposition from the sediment to the water, resulting from benthos activity, was from 2 to 10 times greater than the redeposition caused by molecular diffusion. The flow of methylmercury from the bottom sediments to the bulk water, occurring through molecular diffusion, varied from 0.2 to 1500 ng/m²/day. Besides, seasonal changes were observed, being the greatest from late winter to early spring. Moreover, the flow of methylmercury revealed day fluctuations and in the dark it was about 6 times greater (830 ng/m²/day) than the estimated methylmercury flow as a result of diffusion, which suggests a strong influence of biological and /or chemical processes at the water/sediment interface on the methylmercury exchange [46]. The flow of methylmercury from the polluted deeper layers of the bottom sediments in the Saguenay Fjord to the near-surface layers was specified at 0.07 ng/cm²/year, which made only 0.01% of the mercury inflow to the sediment [17].

Organic Matter and Mercury Speciation

Organic matter is one of the most important components of bottom sediments and it is mostly responsible for binding metals. It has been estimated that organic matter can bind up to 95% of the divalent mercury species [47]. Also, methylmercury has a strong affinity to organic matter, where it is strongly bound by sulphur species [48, 49]. The

main sulphur species responsible for binding mercury are those reduced in functional groups such as thiol (R-SH), disulphide (R-SS-R) and disulphane (R-SSH) [48]. Apart from sulphur, oxygen and nitrogen atoms can also bind the mercury in organic matter, but to a significantly smaller degree because they form weaker bonds with mercury [49].

Organic matter plays a key role in the mobility of mercury in the environment, especially in the catchment areas. Important components of the organic matter are humus substances, whose contribution reaches up to 25% in the bottom sediments, 20% in marine water, 60% in river water and 70% in the wetlands [50]. Other components of organic matter include proteins, polysaccharides, lipids and dyes. The humus substances are difficult to ascribe to any class of organic compounds; therefore, they are arbitrarily divided into three classes according to their solubility: humic acids, fulvic acids and humines. The fulvic acids are soluble in a wide pH range, the humic acids only in alkaline conditions and the humines are insoluble. Moreover, fulvic acids are the most mobile having the smallest molar weight, humic acids are less mobile (intermediate molar weight) and humines are the least mobile (having the greatest molar weight). Taking into regard the relatively high concentration of humus matter in water and the fact that it accompanies $Hg(II)$ in its transportation from catchment areas, it seems to be a good potential agent methylating mercury [38]. This supposition is confirmed by the fact that in peat-bottom water reservoirs of great content of humus matter, the concentrations of methylmercury in water organisms are usually higher than average [51, 52]. It has been established that the abiotic methylation of mercury in the bottom sediments depends on temperature, pH, concentration of inorganic mercury and concentrations of humic and fulvic acids [53]. The activity of fulvic acids in the methylation of mercury was found to be greater than that of humic acids. Besides, the methylation of mercury by humus substances, at the pH and temperature close to those in the natural conditions, was lower than in higher temperatures and at higher concentrations of $Hg(II)$ [53]. Humic acids showed the methylmercury binding capacity 2 to 14 times higher than fulvic ones. Fractions of fulvic acids made of molecules of greater size proved to be more effective in methylmercury binding. No analogy was observed for humic acids, for which the molecular size did not correlate with the amount of bound methylmercury [54]. The formation of mercury $Hg(II)$ compounds with organic matter was found to be strongly dependent on pH, the concentrations of chlorides and the Ca^{2+} and Mg^{2+} ions. Moreover, complexes of $Hg(II)$ with organic matter can be precipitated from water by adsorption on $CaCO_3$ of biogenic origin [55].

Apart from affecting the abiotic methylation of mercury, humus matter can also influence the abiotic reduction of $Hg(II)$. The precise mechanism of abiotic reduction of $Hg(II)$ is still unidentified. However, it is supposed to depend on pH in the inverse ratio [56]: lower the pH, the greater the reduction. It is known that the presence of ions competing for bonding sites in the humus

matter such as Eu(II) and Cl⁻ can significantly lower the reduction rate [38, 57]. Also, the modification of humus matter by the esterification of carboxyl groups in it, significantly decreased the reduction of Hg(II) [56]. It is assumed that Hg(II) can be reduced by humus matter under the influence of sunlight but also without sunlight [38, 58]. Mechanisms of these transformations are not well known yet. According to experimental data [59, 60], much greater Hg⁰ was formed in the samples subjected to sunlight than in those kept in the dark. The efficiency of the reduction was related to the concentration and properties of the organic matter subjected to photodegradation [59, 60]. The process of Hg(II) reduction to elementary mercury can be realised on a biological or chemical pathway. On the basis of some experimental data certain authors suggest that the biological processes involving bacteria of the genus *Pseudomonas* and the other micro-organisms are the main reduction mechanism, while others pointed only to the photochemical reactions [60-62].

Iron and Manganese Hydroxides and Mercury Speciation

The inorganic mercury is strongly sorbed by particles suspended in water; therefore, in natural water reservoirs mercury is found mostly in a solid phase. Methylmercury is also sorbed on the surface of the suspended particles, but to a much lower degree than inorganic mercury [18]. Owing to this property, the suspension plays an important role for mercury transportation in the water environment [63]. Mercury binds with both organic and inorganic components of the suspension. The contribution of mercury bound with organic matter in the water environment is significant, because of the strong binding of mercury by humus matter. Adsorption on the clay minerals and bindings in their structure as well as by the iron and manganese hydroxides is less important for the speciation of mercury than for the other metals, since the most effective in mercury binding are organic matter and sulphides. This observation is based for example on the results of the sequential extraction study. Five fractions of mercury can be distinguished in the soil samples: water-soluble, ion-exchangeable, bound with iron and manganese hydroxides, bound with organic matter/sulphides and bound with the parent rock. From among these, the contribution of mercury in the fraction bound with iron and manganese hydroxides was max. 45%, while the greatest contribution of mercury (reaching up to 60%) was found in the fraction bound with organic matter/sulphides [64].

The inorganic compounds such as iron and manganese hydroxides can have a significant effect on mercury transportation. They provide an excellent surface for adsorption of organic matter and they alone are able to bind this toxic element [65]. From among iron and manganese hydroxides, goethite (FeO(OH)) is characterised by greater sorption capacity of methylmercury than hausmanite (Mn₃O₄) [66]. The importance of iron and manganese hydroxides derives from their high sorption capacity, the

ability to co-precipitate with mercury compounds, and the ability of mercury release from iron and manganese hydroxides [16].

Many authors have noted a correlation between the concentration of mercury and that of iron and/or manganese [65]. An interesting observation was that in the waters of the St. Lawrence river, in which the colloidal fraction mercury showed greater affinity to iron than to manganese, while in the suspension - to manganese [67]. Bloom *et al.* [15] reported that the mobility of methylmercury was related to the iron cycle, while the mobility of Hg(II) was controlled by the formation of soluble polysulphides or complexes with organic matter. The formation and dissolution of iron and manganese hydroxides strongly depend on the redox conditions and the content of oxygen in the water and in the sediment [32]. In anaerobic conditions, iron and manganese hydroxides undergo dissolution releasing mercury [16]. Mercury released to the porous water, including that released from organic matter, can be quickly bound by the freshly deposited organic matter or iron and manganese hydroxides. Therefore, part of the mercury from the down-core sediments can be redeposited at the water/ bottom sediment interface, leading to a temporary increase in mercury concentration in the near surface layers of sediments [68]. For example, in the anaerobic conditions from the Saguenay Fjord as much as 70% of total mercury bound with sediment was extracted with 1N HCl. A strong correlation between the reactive iron and manganese (extracted with 1N HCl) and mercury extracted with 1N HCl points to a very important role of iron and manganese hydroxides in binding the mercury coming from the water column and its accumulation in bottom sediments [17].

Effect of Redox Conditions on Mercury Speciation

It is supposed that the surface layers of the bottom sediments (with oxidising conditions) make a geochemical barrier for diffusion of methylmercury from the deeper layers (with reducing conditions) to the water column [16, 17]. If so, in aerobic conditions, methylmercury can be transformed to dimethylmercury and evaporate to the water column and then to the atmospheric air [41]. Another process, which can be catalysed perhaps by iron and manganese hydroxides, is the demethylation of mercury in aerobic conditions [69]. Hg (II) coming from the demethylation of methylmercury can be bound by organic matter, or in aerobic conditions by iron and manganese hydroxides [45]. A significant flow of mercury from the sediment to the water column was observed at the surface layer of the bottom sediments, characterised by strongly reducing conditions [16]. According to another interpretation, the migration of methylmercury from the sediments with redox conditions, through the surface aerobic layer to the water column, can be facilitated by benthos activity [16].

The redox conditions also strongly affect the speciation of mercury bound with the suspension. The suspension,

coming from the water zone of aerobic conditions, in the process of sedimentation getting onto the bottom sediment characterised by reducing conditions, relatively quickly undergoes degradation /mineralisation under the effect of micro-organism activity. In this way mercury bound with the suspension can be transformed into soluble species appearing as a result of dissolution of iron and manganese hydroxides or carbonates. The mercury species dissolved in this way can undergo methylation both in the bottom sediment and in the water column.

With regard to the above-mentioned processes, many authors have questioned the suitability of examination of the sediment-cores for the analysis of mercury inflow to the sediments in the historic perspective. Nevertheless, results of the measurements of mercury content in the dated sediments agreed with the historical data on the amounts of mercury released from the anthropogenic point- sources [70].

Effect of pH on Mercury Release from the Environmental Matrix

At low pH heavy metals are usually released from bottom sediments. As far as mercury is concerned, the data on the mobility of this element at different pH are diverse. Some authors reported that low pH favours the release of mercury from the bottom sediments [71], while others claim that the sorption of mercury on the sediment increases at low pH [72-74]. For example, in different soils analysed, the adsorption of Hg(II) increased with pH increasing from 2.5 to 5.5, then significantly decreased at about pH 5.5. For the same Hg(II) concentration and the same pH (range 2.5-5.5 pH), the greater adsorption of Hg(II) was observed for soils with higher content of organic matter [73]. The observed release of mercury with decreasing pH was the result of a release of humus substances together with the mercury it contained [74]. In contrast to the findings for other metals, the amount of mobile mercury decreased at pH <3 and pH >12 [74]. As follows from the laboratory study of Wallschlager *et al.* [74], the mercury polluted soil, which was flooded by the Elba River, released only 1% of the mercury it contained as a result of extraction by water of pH close to of the river Elba water. The mercury released from the samples studied came almost exclusively from the fraction bound with humic acids. Even though the soil was flooded with water of pH 1, mercury was not released from the humic acids. This indicates the great ion-exchange capacity of humus substances in the soil. Similar results were obtained in the experiment on the river bottom sediments treated with distilled water, in which the amount of mercury released from sediment was also less than 1% [75].

It is supposed that the processes of sorption/desorption of mercury at different pH depends on the kind of mercury species. The values of pH seem to affect the mobility of methylmercury more than Hg(II). This supposition has been formulated on the basis of the data on the release of methylmercury from bottom sediment at different pH and the mobility mercury species from catchments to water reservoirs, which suggest a strong increase in the

methylmercury solubility with decreasing pH [52].

In fresh waters a positive correlation was found between the Hg⁰ concentration and pH of the water sample [76, 77]. Therefore, in the water of higher pH a greater amount of mercury is transformed to the elementary mercury and a smaller amount of Hg(II) is available for methylation. Moreover, at higher pH, the processes of mercury demethylation are favoured [14, 41, 75]; hence, the formation of methylmercury is favoured in acidic conditions at a relatively high concentration of mercury [78]. However, Matilainen & Verta [42] have reported that the pH of water ranging from 4,9-6,9 had no effect on mercury methylation.

Thermal Effect (Kinetic Processes)

The transformations of mercury in the bottom sediments, in particular the processes of methylation and demethylation, are temperature dependent. Supposedly, the rate of mercury methylation in the bottom sediments is higher at high temperatures, which is related to an enhanced activity of micro-organisms in such conditions [79]. In the summertime (because of higher temperatures, lower oxygen content and increased primary production), the methylation of mercury is usually higher. The optimum temperature of mercury methylation is between 33 and 45°C. As has been established, the optimum temperature of mercury methylation is between 33-45°C, and with further temperature increase the rate of methylation decreased and the process ceased at 55°C [80]. Temperature also affects the process of demethylation. The rate of demethylation increases at higher temperatures [42]. It seems that with increasing temperature, the rate of methylation increases more than that of demethylation [2]. Moreover, Matilainen & Verta [42] have shown that the process of demethylation was less effective at lower temperatures and it did not occur in sterilised samples. This may imply that biological processes are responsible for methylation.

Temperature also affects the kinetics of the mercury sorption from the soil components and the bottom sediments. It has been found that the concentration of inorganic fraction of mercury Hg(II) in the solution increased with increasing temperature, probably due to an increase in the concentration of dissolved organic carbon (DOC). The solubility of Hg(II) strongly depends on the formation of complexes with the soluble organic matter, whereas the solubility of methylmercury depends rather on ion-exchange [81]. This can explain why no similar correlation has been noted for the methylmercury CH₃Hg(I).

The Effect of Salt

In the marine and estuary sediments, the contribution of methylmercury in the concentration of total mercury is ~ 0.5%, whereas in the fresh water sediments it usually reaches 1-1.5% [10, 11]. One of the reasons for a smaller contribution of methylmercury in the marine and estuary

sediments is that the chlorine ions affect the processes of mercury methylation and demethylation [80, 82, 83]. The rate of mercury methylation decreases with increasing concentration of salt, which is most probably a result of the inhibitory effect of chlorine-complexes. The divalent mercury in compounds endowed with negative charge (e.g. HgCl_3^- or HgCl_4^{2-}) is hardly available for the biotic methylation in comparison with the neutral species of Hg(II) such as HgCl_2 or Hg(OH)_2 [80, 82]. It is supposed that the processes of mercury demethylation are more effective in the marine ecosystems with relatively high salinity than in the fresh waters [10, 84].

In the bottom sediments, which do not contain salt, the adsorption of mercury depends on the pH of the sediment. The increase in concentration of the desorbed mercury was noted only at the salt concentration of ~30 per milles. Hg(II) is mostly bound with the organic matter and clay minerals, which controls the amount of mercury available to the organisms in the water environments [85].

The presence of salt is also important for oxidation processes of Hg^0 to Hg(II). In the past, these processes were considered rather insignificant or non-occurring in the natural water reservoirs. On the contrary, the recent data proved their occurrence, particularly in marine waters, where chlorine ions are present [61, 86]. Another interesting finding is that the oxidation of elementary mercury is significantly lower in distilled water than in marine water [86]. Besides, the oxidation of elementary mercury to Hg(II) is stimulated not only by the presence of NaCl, but also KCl, MgCl and HCl. The oxidation processes are believed to be more effective in the waters of coastal regions, where the concentrations of suspension are higher [61]. In aerobic conditions the elementary mercury can be oxidised by other agents mainly such as: oxygen, nitrates, nitrites, iron hydroxides, iron phosphates, sulphides and carbon dioxide [75].

Summary

The bottom sediments are the main reservoirs of mercury and the sensitive indicators of the aquatic ecosystems pollution with this element. The behaviour of mercury in the bottom sediments strongly depends on the kind of its chemical species present in this matrix. This paper summarises knowledge on the mercury species distribution and the transformation processes in the bottom sediments, which are controlled by various physical, chemical and biological factors. On the basis of some laboratory and *in situ* experiments on mercury, it has been shown that the main factors controlling the behaviour of this element are micro-organisms, inorganic sulphides, organic matter, iron and manganese hydroxides, red-ox potential, chlorides and temperature in the bottom sediments.

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