Some Aspects of Speciation of Mercury in a Water Environment

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Abstract

Extreme toxicity of some species of mercury, the ability of this element to bioaccumulate in particular in fish meat, and the known cases of lethal poisoning by mercury have drawn particular attention to this element's presence in the natural environment. Due to the relatively long time of its presence in the air, elemental mercury can be transported over large distances, hence the presence of mercury of anthropogenic origin is detected practically all over the world. Apart from the elemental mercury, the main species of mercury in water are Hg(II) and mercury-organic species, in particular methylmercury. The latter undergoes strong bioaccumulation in living organisms and concentration in the trophic chains. That is why the relative concentration of mercury in organisms is determined by its presence in water. The concentration of mercury in water is related to the processes of methylation and demethylation, influenced by biotic and abiotic factors such as the activity of microogranisms, access to oxygen, illumination, temperature, pH and others. Despite intense studies, full and reliable recognition of the ecological and health effects of pollution by this toxic metal is still impossible. The aim of this paper is to present the problems related to speciation of mercury, and describe some conversion and migration processes of mercury in the water environment.

Keywords: mercury, concentration, speciation, water, environmental transformation, fluxes.

Introduction

Mercury was one of the first elements whose speciation has been studied. The main incentive of the studies was the serious poisoning by mercury which polluted the waters of Minamata Bay, Japan, where it occurred as methylmercury and dimethylmercury [1, 2]. The phenomena pointed not only to different toxicities of different compounds of the same element but also to the possibility of conversions of these compounds in the environment, in this case to mercury methylation by microogranisms.

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The mercury species occurring in the environment can be divided into volatile ($Hg°$, $(CH_3)_2Hg$), easily water soluble (Hg^{2+}, $HgCl_2$, $Hg(NO_3)_2$) and hardly soluble organic complexes (CH_3Hg^+, CH_3HgS), [3, 4]. Mercury can form compounds not only with a methyl group but also with other alkyl groups [5, 6]. Distribution of mercury compounds depends to a significant degree on red-ox conditions. In the oxidising conditions the dominant forms are Hg^{2+}, Hg_2^{2+}, etc., while in the reducing conditions the dominant are sulphur-mercury compounds HgS, HgS_2^{2-}, CH_3HgS^-, etc., and in the intermediate conditions the most often met are alkyl mercury compounds [3, 7]. Mercury species occurring in the natural environment can be also divided according to their reactivity. The most reac-

Table 1. Concentrations of mercury (ng/L) in water from various parts of the world.

	Hg (total)	Hg (total dissolved)	DGM	Hg (reactive)	MeHg	Hg (particulate)	Refe-rences
Sea Water							
Baltic Sea	0.6 ± 0.2				~20% Hg(total)		[12]
Gulf of Gdańsk	277-630						[11]
Gulf of Finland	10-140						[11]
Bothnian Bay	2-40						[11]
Gulf of Riga	10-40						[11]
Matsalu Bay (Baltic Sea)	5-130						[11]
North Sea	0.56 ± 0.24						[24]
North Sea	0.5-200						[73]
Mediterranen Sea (Tunisia)	990-27060						[74]
Northeastern Atlantic	2.7						[23]
Sepetiba Bay (Brazil)		0.12-0.67	0.032-0.082	0.11-0.36	< 0.020-0.55		[25]
River Water							
Ebro Delta (Spain)	1-18						[75]
Gösku Delta (Turkey)	156-1502						[76]
Rivers inflowing to Onondaga Lake (USA)	1.0-104						[41]
Rivers inflowing to Narragansett Lake (USA)	7.2-69.2						[77]
Rivers in Wisconsin-industrial area (USA)	1-43						[78]
Tapajos River (Brazil)	0.28-13.3						[79]
St. Lawrence River (Canada)	0.08-2.0						[80]
Indrija River (Slovenia)	2.77-322	0.43-39.23			< 4.52		[13]
Madeira River (Brazil)	2.25-20.05	0.28-8.06			0.61-1.825		[13]
Carson River (USA)	4-7585	0.2-88			0.3-7.2		[13]
Rivers inflowing to Michigan Lake	0.98-21.9				0.050-0.360		[16]
St. Lawrence Estuary	0.4-1.5			< 20% Hg(total)			[81]
Various estuaries in Florida (USA)	3-7.4				<0.002-2.3		[82]
Chattahoochee River (USA)		0.12-3.174				8-18*	[42]
Various streams in Southern USA	< 2100				< 0.8		[83]
Gironde Estuary (France)	< 250	< 3.0			< 1.8	< 60*	[84]
Scheld Estuary (Belgium/Netherlands)	< 150	< 2.4			< 1.4	< 24*	[84]
Rhine Estuary (Netherlands)	< 20	< 2.0			< 0.1	< 10*	[84]
Lake Water							
Lake Michigan (USA)	0.56-182						[85]
Lake Michigan (USA)	0.32 ± 0.05						[86]
Lake Michigan (USA)	0.32				0.005-0.042**	0.64-0.16	[87]
Lake Michigan (USA)	0.30 (0.2-0.4)	0.204 (0.11-0.31)			0.0075 (0.0075-0.014)		[88]
Lake Michigan (USA)					0.0047 (0.0054-0.011)**		[88]
Various water reservoirs (Canada)						200-600*	[89]
Interstitial Water							
Sepetiba Bay (Brazil)			< 2.6	0.2-32.2	0-246		[90]
St. Lawrence Estuary	3.3-15.6			< 30% Hg (total)	1.0-2.8		[81]

* ng/g; **measurements "dissolved" fraction of Hg; Hg(total) - total mercury; DGM-dissolved gaseous mercury; Hg(reactive) - "reactive" mercury; MeHg - monomethylmercury; Hg(particulate) - mercury bound with particles.

tive species are: Hg^{2+}, HgX^+, HgX_2, HgX_3^- HgX_4^{2-} (where X = OH^-, Cl^-, or Br), $Hg°$ bound to aerosol molecules and Hg^{2+} bound to organic acids (water-soluble). The unreactive species include CH_3Hg^+, CH_3HgCl, CH_3HgOH and other mercury-organic compounds, $Hg(CN)_2$, HgS and Hg^{2+} bound to sulphur in the humic substances [8]. Certain species belonging to the chemically unreactive ones (e.g. CH_3Hg^+) are bioavailable and can undergo bioaccumulation and biomagnification. Moreover, some chemically unreactive species can be converted to the reactive ones through biochemical transformations [4, 9, 10].

Speciation of Mercury in Hydro-Ecosystems

Concentrations of Mercury Species in Hydrosystems

In natural waters, especially in marine water, mercury occurs at very low concentrations, which causes many serious problems with their accurate determination. The literature data on the concentration of mercury in natural waters are unreliably diverse not only as a consequence of the natural variation of the species and concentrations of this metal in water (Table 1 and 2), but also because of analytical difficulties. For instance, the report of the Baltic Marine Environmental Protection Commission in Helsinki [11] says that the concentration of mercury in Gdansk Bay reaches from 227 to 630 ng/L, which is a value much higher than that reported for any other Baltic region. However, according to recent data the concentration of mercury in different regions of the Baltic Sea, Gdansk Bay included, is much lower - 0.6 ± 0.2 ng/L [12]. It has been estimated that the natural concentration of mercury in marine waters varies from 0.5 to 3.0 ng/L, while in estuaries and precipitation it varies from 2.0 to 15 ng/L [9]. In strongly polluted waters the concentration of total mercury reaches a few tens μg/L [4, 13, 14].

Reliable determination of methylmercury concentration in water is even more difficult than that of total mercury. It is estimated that the contribution of methylmercury in the concentration of total mercury in natural non-polluted waters is 3-6% in sea water and 26-53% in fresh water [15]. The data on the concentration of methylmercury in natural waters (and its contribution in the total mercury concentration) are characterised by significant ambiguity (Table 1 and 2). For instance, the contribution of methylmercury in the concentration of total mercury in unfiltered water from the non-polluted river Pere Merquette was determined as 5% [16], and was of the same order of magnitude as that determined for the water from Onondaga lake [17]. The contribution of methylmercury in the concentration of total mercury in the pore water from the same lake was 37% [17] and that in the pore water from the polluted Saquenay Fjord in Canada was smaller than 1% [18].

In surface waters mercury does not occur in the form of free Hg^{2+} ions but as a mixture of compounds in which mercury form a hydroxy- and chloro-complexes in proportions depending on pH and the concentration of chloride ions (Fig. 1 and 2). In marine water the dominant mercury compounds are chlorine complexes. The occurrence and migration of different mercury species in

Table 2. Concentrations of mercury (ng/L) in precipitation water from various parts of the world.

Precipitation Water	Hg(total)	Hg(reactive)	MeHg	References
Gardsjon Lake – (Sweden)			0.1-0.66	[91]
Halle/Leipzig/Bitterfold (Germany)	460	30		[92]
Mace Head (Ireland)	5.1-37.8	3.7-17.3		[92]
Langenbrugge – 200 km from industrial area (Germany)	45.7-58	3.1-5.7		[92]
Sylt Island – North Sea (Germany)	6.1-18.3	0.6-1.3		[92]
Zingst Penisula – Batic (Germany)	20-111	8.2-31.2		[92]
Scandinavia	5-40			[93]
Experimental Lakes Area – Ontario (Canada)	0.95-9.3		0.010-0.18	[94]
Quebec (Canada)	7.0			[95]
Florida (USA)	5-113			[96]
Chesaepake Bay (USA)	2-8			[44]
Michigan (USA)	1.2-60			[97]
Florida (USA)	9-26		< 0.005 – 0.020	[98]
Lake Superior (USA)	9			[99]
Wisconsin (USA)	8			[100]
Wisconsin (USA)	2.7-150			[101]
Wisconsin (USA)	10.5 ± 4.8		0.16 ± 0.07	[102]
Maine (USA)	8.9 ± 3.8		0.17 ± 0.08	[103]
Hoyama (Japan)	5-187			[104]

Fig. 1. Dominance diagram of hydroxo- and chloro-complexes of Hg(II) as a function of pH and chloride concentrations [10].
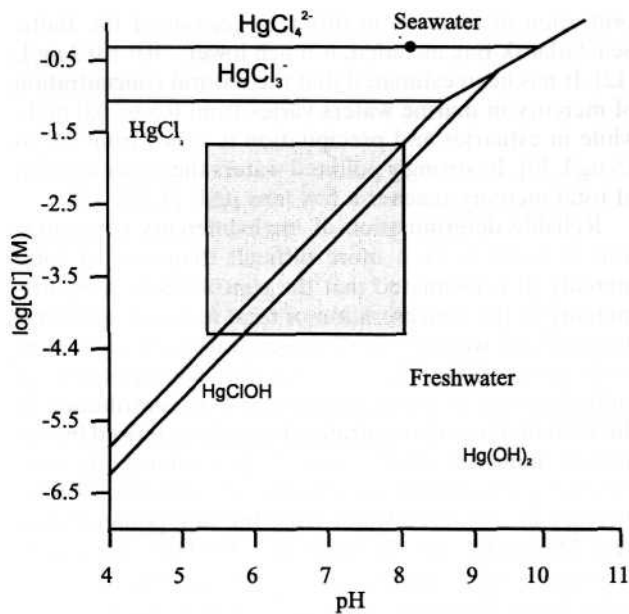

Fig. 2. Dominance diagram of hydroxo- and chloro-complexes of methylmercury as a function of pH and chloride concentrations [10].

water environment depends also to a great degree on the red-ox conditions and the content of dissolved organic carbon (DOC). In water of low pH, the dominant are the soluble mercury compounds, such as $HgCl_2$ and CH_3Hg^{2+}, whereas in mild alkaline conditions $Hg°$ and $(CH_3)_2Hg$ dominate. In the water of oxidative properties the dominant compounds are $HgCl_4^{2-}$ and $HgOH^+$, while in reductive conditions it is CH_3HgS^- and HgS_2^-, and in variable conditions we most often find CH_3HgCl and CH_3Hg^{2+} [3, 9, 10, 19-21]. In polluted waters, mercury compounds with phenyl groups were noted [21]. It has been estimated that the lifetime of mercury in water can last from a few minutes to many years, depending on the type of mercury species [22, 23].

Speciation of Mercury in the Suspended Phase

Mercury occurs in water in the dissolved phase as well as in the colloidal and suspended phases. The contribution of mercury in these two phases varies both in time (seasonal changes) and in space (e.g. bathymetric depth), and is also affected by living organisms (phytoplankton and bacteria) forming a kind of organic suspension. For example in the suspension from the North Sea, the contribution of methylmercury to total mercury was -6% [24]. In water from Sepetiba Bay the contribution of mercury in the suspended phase made about 70% of the total mercury concentration in water [25]. Although there is little data on the chemical species of mercury in the suspended phase, it is supposed that the mercury species bound to the organic suspension are dominant [26]. Organic matter, in particular in water rich in humic substances, is surrounded by iron and manganese hydroxides in the colloidal phase. The molecules undergo intense
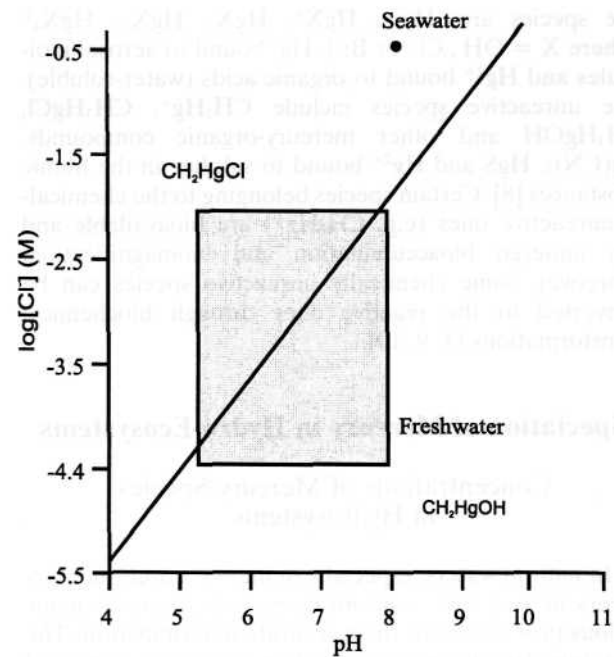
aggregation, which is the main mechanism of removal of heavy metals, including mercury, from bulk water to bottom sediments, especially in estuaries [27]. The predominant role of organic matter in migration of mercury in water environment is supported by a strong positive correlation between the concentration of total mercury and the content of organic matter in bottom sediments, established in different parts of the world [28-31]. In Puck Bay, a relatively homogeneous distribution of mercury in bottom sediments, after normalisation of the concentrations and their expression per units of organic matter, unambiguously indicates the sedimenting organic matter as the main source of this element in bottom sediments. At the same time it points to the atmosphere as the main source of this metal reaching the organic matter [31, 32]. The magnitude of the inflow of mercury from different parts of the world to the bottom sediments are given in Table 3. These magnitudes most often correspond to the inflow of mercury through the atmosphere to water reservoirs and illustrate the role of water suspensions in biogeochemical cycle of mercury.

Speciation of Mercury in the Dissolved Phase

In the dissolved phase mercury can occur in the form of many species: elemental mercury ($Hg°$) volatile and relatively unreactive, ionic [Hg(II)] in a number of compounds, organic - mainly methylmercury (CH_3Hg^+) or dimethylmercury ($(CH_3)_2Hg$). In strongly stratified water ecosystems elemental mercury is mainly found in surface layers, whereas the total mercury (in dissolved phase and suspended phase) and methylmercury are determined in higher concentrations in the bottom layer [33]. There is

Table 3. Inflow of mercury (ng/m^2/day) to bottom sediments from different parts of the word.

	Inflow of total mercury to bottom sediments	Inflow of MeHg to bottom sediment	References
Europe			
Batic Sea	44		[105]
Baltic Proper	41		[105]
Gulf of Botnian	112		[105]
Gulf of Bothnian	90		[106]
Bothnian Sea (Baltic)	16		[105]
Bothnian Sea (Baltic)	88		[106]
Gulf of Finland	112		[105]
Gulf od Riga	47		[105]
Central Norway	28		*vide* [107]
North America			
Onondaga Lake (USA)	8500-13400		[108]
Lake Michigan (USA)	57.4	1.0	[88]
Lake Michigan (USA)	90 ± 52 – 274 ± 238 (23-876)		[45]
Lakes in Wisconsin (USA)	126-305		[109]
Lakes in Midwest USA	34.2		[110]
Fjord Sequenay (Canada)	537		[18]
Imitavik Lake (Canada) – 1980's – 1990's	34 49		[107]

also the easily-reducible fraction of mercury (dissolved and suspended phases) undergoing reduction upon treatment by a solution of SnCl$_2$. This fraction includes the species easily reducible also in natural conditions and most probably made of inorganic compounds. Investigation of mercury species in vertical water columns revealed an increase in the concentration of divalent gaseous mercury (DGM) in the surface layers relative to that in bottom layer, most probably due to a greater reduction and demethylation in accordance with greater primary production and microbial activity in the surface layers [25]. In the water from Sepetiba Bay the concentration of total reactive mercury in the surface layer varied from 55% to 90% of total soluble mercury, while the organic dissolved Hg made 10% - 83% of total soluble mercury. In general, reactive Hg occurred in higher concentrations in the regions with high concentration of the suspension [25]. In water from the North Sea the contribution of reactive Hg to total Hg was ~30%, while the contribution of mercury in the suspended phase to the concentration of total mercury varied from 13% to 82% [24]. The concentration of total mercury in the dissolved phase in the river Ochleckonee and its estuary (the USA) varied from 0.6 to 6.0 ng/L, while in water from the northern Atlantic - from 0.1 to 0.5 ng/L. The contribution of mercury in the colloidal fraction (>1 kD) in the water from

the estuary was 35% - 87% of total mercury in the dissolved phase (at a low salinity it was 79% - 87%) and in water from the northern Atlantic it was 10% - 50% [34].

Speciation of Mercury in Water Catchments

Some amount of divalent mercury is bound to humic acids, estimated to contain 50% - 90% of dissolved organic carbon (DOC). The fraction of divalent mercury bound to DOC has been estimated at 95% [35]. The strong affinity of divalent mercury [Hg(II)] to organic matter plays a very important role in transportation of mercury from catchment to water reservoirs [36-40]. The laboratory tests of Wallschlager et al. [36] proved that soil polluted with mercury and flooded by water from the river Elba released only 1% of mercury contained in the soil upon their treatment with water of pH close to natural. The mercury liberated from the samples was almost completely bound to the humic acids, which points to a large ion-exchange capacity of the humic substances contained in the soil [36]. The magnitude of mercury outflow with water in different parts of the world is given in Table 4. The estimated outflow of mercury with the river water expressed per m^2 of catchment area varies from 2.2 to 66 ng/m^2/day. Of course, greater loads of the mercury out-

Table 4. Outflow of mercury with the rivers water (ng/m^2/day) expressed per m^2 catchment area in various parts of the world.

	Area of catchment (1000 x m^2)	Outlow of total mercury with river waters	Outflow of MeHg with river waters	References
Europe				
Iso Lake (Finland)	39	4.1-4.7		[111]
15 various catchments (Sweden)		2.2-16		[112]
Gardson Lake (Sweden)	37	6.3-9.6		[91]
Tiveden National Park (Sweden)	14	9.3		[113]
Catchment in South Sweden	50	4.2	0.33	[49]
North America				
Chesapeake Bay (USA)	16x10^7	2.6		[44]
Catchments in Wisconsin (USA)		5-14		[78]
Onondaga Lake (USA)	6.9x10^5	14-66		[108]

flow with river waters are observed in industrialised areas - 14-66 ng/m^2/day than in rural parts - 2.2-6.8 ng/m^2/day as in the industrialised areas the deposition of atmospheric mercury and the concentration of mercury in waters are usually greater [41, 42]. In general, inflow of total mercury through natural waterways is smaller than the deposition of atmospheric mercury [43]. In Chesapeake Bay [44] and Lake Michigan [45] direct deposition of mercury from the atmosphere is an important source of this element. In these two water reservoirs the contribution of mercury deposited from the atmosphere has been estimated at 50% of all mercury flowing into these reservoirs from all sources. Total mercury of atmospheric origin is strongly bound in the soil and water suspension. It has been estimated that 90% of total mercury coming from the atmosphere is captured in the catchment area [44]. For the take of comparison, the contribution of mercury mass flowing into Onondaga Lake from the catchment area in total mass of mercury flowing into the lake has been estimated as -25% [41]. Unfortunately, information on the behaviour of total mercury cannot be used to infer about the behaviour of methylmercury [16, 39, 40, 43, 46]. In Chesapeake Bay the dominant inflow of methylmercury comes from waterways (25-50 mol/year) and not from the atmosphere (~7 mol/year). The mass of methylmercury deposited from the atmosphere in the Bay catchment area (80 mol/ year) is of a similar order of magnitude as that flowing into the Bay from the waterways. This fact indicates that methylmercury is produced in the catchment area, even if we assume that methylmercury is to a lesser degree bonded to the suspension and soil [44]. When there are no point sources of methylmercury, the main source of this toxic species is precipitation falling directly on the bay water and on the catchment area, the inflow through surface waterways (methylmercury deposited in the catchment area and not captured there, and methylmercury produced in the area), production of methylmercury in the water column or bottom sediments [41,43, 46]. The contribution of these sources is different and depends on the magnitude of atmospheric deposition, type of water res-

ervoir (type of lake) and the size of the wetlands within the catchment area. According to St Louis et al. [43], the wetlands are a source of methylmercury (a net source) and the size of production depends on the type of ground (swamps or peat bogs) and the hydrological conditions there. A smaller production of methylmercury was observed in wetlands of river valleys, where water interaction was restricted to a peat layer and did not reach the mineral substrate. The production of methylmercury was greater at the sites where infiltration water was in contact with the mineral substrate. In the area without wetlands, with aerobic soils, the concentration of methylmercury in the water coming from the waterways is much lower. This finding can be explained by a stronger bonding of methylmercury in these conditions and by greater demethylation taking place on access to oxygen [43]. Therefore, it is obvious that the contribution and distribution of methylmercury depends on the contribution of wetlands in the catchment area. It has been estimated that wet grounds undergoing flooding can produce from 26 to 79 times more methylmercury than the non- flooded grounds [46]. The presence of forests also affects the inflow of mercury to water reservoirs. For instance, in the catchment area of the river Marquette (non-polluted river) forests occupy about 71% of the area and 8% are taken by wetlands. The mean concentration of methylmercury in the water from this river was of the same order of magnitude as that in the river Monistique, whose catchment area is 70% occupied by wetlands [16]. Another factor influencing the presence of methylmercury is the size of precipitation. The greater the amount of the precipitation the greater the outflow of methylmercury from the wetlands [43]. Moreover, the production of methylmercury in natural reservoirs were the same as the amount of methylmercury flown in with the water from the waterways [43]. In artificial water reservoirs the internal production of methylmercury is of greater importance [46]. According to the estimations made by Porvari & Verta [47], the internal production of methylmercury is more important for seepage lakes (up to 67% of total intake) than for drainage lakes (35% of total intake). The same

authors reported that for drainage lakes, whose catchment comprises 10% of wetlands, the contribution of methylmercury flowing in from the catchment is significant and reaches 67% of the total inflow of methylmercury to the lake. For seepage lakes only 5% of methylmercury comes from the catchment area, even when the contribution of wetlands in the catchment area reaches 100% [47].

The effect of the type of catchment on the inflow of methylmercury into the water reservoirs is evidenced by a positive correlation between the concentration of methylmercury in the plankton and the colour of water, the size of the catchment and the contribution of the flooded grounds in the catchment area [48]. The same authors reported a negative correlation between the concentration of methylmercury in the plankton and pH of the water. In brown reservoirs there is in general a higher concentration of methylmercury in fish meat [46]. The study by Petersson et al. [49] also revealed a strong positive correlation between the concentration of methylmercury flowing out of the catchment and the concentration of humic substances.

## Chemistry of Mercury Species in Hydrosystems

Biotic Methylation of Mercury

Methylation of mercury takes place mainly in bottom sediments and in soils, but it can also take place in water. The process can occur by biotic and abiotic pathways and is affected by many factors such as availability of inorganic Hg(II), activity of microorganisms, red-ox conditions, pH, temperature, salinity, content of organic matter (often described by the colour of water) [4, 9,10]. The biotic methylation takes place mainly in anaerobic conditions, but it can also occur, although more weak, in aerobic conditions [33, 50]. In the biotic methylation of mercury in anaerobic conditions, methylcobolamine acts as a donor of methyl groups [15, 51]. Of key importance in the aerobic process are the sulphate reducing bacteria (SRB) [52-54], with whose involvement in the process can be described as:

$$Hg^{2+} + RCH_3 -» CH_3Hg^+ + R' \qquad (1)$$
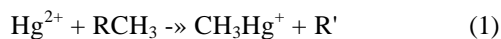
Monomethylmercury forms easier in the acidic environment, at a relatively high concentration of mercury (Breteler et al., 1981 vide [26]), although Matilainen & Verta [33] reported no effect of pH in the range 4.9 - 6.9 on the methylation of mercury in lake waters. It is believed that in rivers, the optimum temperature of the process is 35°C (Callister & Winfrey, 1986 vide [26]). As far as the effect of salinity is concerned, it has been established that the rate of methylation decreases with increasing salinity, most probably because of the inhibitory influence of chlorine-complexes [55]. The rate of methylation also seems to increase in anaerobic bottom sediments. It has been observed that the amount of methylmercury increased in proportion to the concentration of free sulphide ions (maximum 1.8 mg S^{2-}/ g of sediment). Above this point, the concentration of CH_3Hg^+ decreased, most probably because of the formation of vol-

atile dimethylmercury (reaction 4) [56]. At a too high concentration of sulphide ions, the concentration of Hg(II) in the solution is too low for methylation to occur and a hardly soluble HgS forms [57]. The mechanisms of mercury methylation in water have not been fully recognised yet, but it is assumed that they involve microorganisms, similarly as in bottom sediments [10]. For instance it is assumed that in lakes methylmercury found in surface layers is transported there by diffusion and currents from the deeper anaerobic layers. In oceans it is supposed that some methylmercury can be formed in aerobic conditions as a result of conversion of dimethylmercury coming from deeper layers. The reactions involving microorganisms lead to the formation not only of monomethylmercury but of dimethylmercury [4, 9]:

$$2CH_3Hg^+ + H_2S -> (CH_3)_2Hg + HgS + 2H^+ \qquad (2)$$
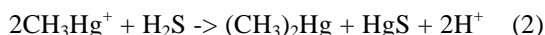
The rate of formation of these species depends on the concentration of mercury and pH of the environment. Monomethylmercury forms easier in acidic environments, at a relatively high concentration of mercury, while dimethylmercury in neutral or alkaline conditions, at a relatively low concentration of mercury and in the presence of relatively strong complexing reagents such as H_2S [4, 21]. The rate of monomethylmercury formation is about 6000 times higher than that of dimethylmercury formation, so in the natural environment only 3% of organic mercury occurs as dimethyl species (Regnell, 1990 vide [26]). It is assumed that the formation of dimethylmercury by microorganisms and its liberation to the environment is a detoxication mechanism [51, 52].

Abiotic Methylation

The abiotic pathways of methylation can be divided in two groups: those involving and not involving irradiation [15]. In reactions involving irradiation the donors of methyl groups can be acetic acid, propionic acid, methanol and ethanol, whereas the reactions without irradiation include those with methylcobalamine, trasmethylation (methylated tin compounds) and those with humic substances [15]. The role of these agents in methylation of mercury taking place in the natural environment has not been fully determined [57]. Methylkobalamine is a derivative of vitamin B12, in which the terminal ligand CN is substituted with a CH_3 group. A strong correlation has been found between the concentrations of methylmercury and methylcobalamine in bottom sediments [50]. Methylated tin and lead compounds can also be potential reagents in abiotic methylation of mercury, especially in tin and lead-polluted regions [57-59]. The compound CH_3J, occurring at a relatively high concentration in natural waters and produced by algae, had also been supposed to be involved in direct methylation of mercury. However, experimental data excluded this hypothesis. Nevertheless, CH_3J can be indirectly involved in methylation of mercury taking part in methylation of tin compounds in water environment [58]. Weber [57] suggested that in marine water CH_3J can methylate trace amounts of Hg(I) (Hg_2^{2+}). From among the methylating agents the most important seems to be humic substances,

Table 5. Concentration of mercury (ng/g dry weight) in bottom sediments from different parts of the world.

	Hg(total)	MeHg	References
Sea			
Baltic Sea	2-340		[12]
Baltic Proper	100 ± 50		[105]
Baltic Proper	20-360		[114]
Aland Sea (Baltic)	180 ± 60		[105]
Bothnia Sea (Baltic)	100 ± 30		[105]
Bothnian Bay	400 ± 240		[105]
Gulf of Gdańsk	3.5-160		[115]
Gulf of Gdańsk	310 ± 310		[114]
Puck Bay	0.74-5.7		[115]
Puck Bay	2.8-180		[32]
Danish Strait	60-220		[114]
Bosex Area (Baltic)	140-190		[114]
Southern Baltic	30 ± 10		[114]
Gulf of Riga	30-790		[116]
Mediterranen Sea (Israel)	10-900		[117]
Ninety Mile Beach, Victoria (Australia)	< 290		[118]
Mediterranen Sea (Italy)	100-5330		[119]
China Sea (Malaysia)	20-127	0.01-0.053	[66]
La Zacatecana Dam (Mexico)	38-790		[120]
The Beagle Channel (Argentina)	10-410		[121]
Cagliari Bay (Italy)	50-2700		[29]
Rivers and estuaries			
Motława River (Poland)	6-892		[122]
Vistula (Poland)	2.3	0.042	[66]
Odra River (Poland)	3.2-32	0.032-0.16	[66]
Odra River (Poland)	200-3900		[123]
Elba River (Germany)	110-12000		[59]
Ebro Delta (Spain)	14-185		[75]
Nile Delta (Egypt)	< 822		[124]
Göksu Delta (Turkey)	594-1152		[76]
Cato Ridge River (South Africa)	30-1764000		[125]
Newark Estuary (USA)	380-29600		[126]
Vistula Estuary (Poland)	54	0.08	[66]
Anadyr Estuary (Russia)	83-2100	0.055-0.62	[66]
Scheldt Estuary (Belgium)	30-1756		[52]
Brunswick Estuary (USA)	1000-27000		[127]
Newark Bay (USA)	100-9800		[128]
Scheldt Estuary (Belgium)	144-1192	0.80-4.81	[30]
Various rivers in USA	100-2100	0.2-0.8	[83]
Florida-various estuaries (USA)	20 (1-219)	0.078 (< 0.49)	[82]
Lakes			
Obozin Lake (Poland)	11	0.16	[66]
Various lakes (Poland)	3.6-390		[129]
Lakes in Quebec (Canada)	3-267	0.14-1.48	[130]
Hydroelectric reservoirs (Canada)	40-106	0.1-1.6	[131]
Lake Michigan (USA)	78 (2-260)	2.2 (0.78-2.34)	[88]
Cima Lake (Brazil)	113-239		[132]

taking into regard its relatively high concentration in water environment and co-migration with mercury in water [57]. Monomethylmercury is relatively stable and water-soluble, therefore it is absorbed by organisms and concentrated in the trophic chain, while dimethylmercury evaporates into the atmosphere where it can be decompose to methane and elemental mercury by photolysis or oxidised by hydroxyl radical [9, 51]:

$$(CH_3)_2Hg \rightarrow Hg° + 2CH_3 \qquad (3)$$

$$(CH)_2Hg + OH \rightarrow CH_3HgOH + CH_3 \qquad (4)$$
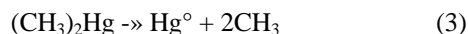
Reduction/Oxidation Reactions

The processes controlling conversion of elemental mercury into its ionic or organic forms determine the amount of mercury in the elemental state so the rate of mercury evaporation and the amount of total mercury remaining in water [4, 10, 60]. The reduction of mercury in ionic form Hg(II) to elemental mercury can proceed by biological and chemical processes. On the basis of experimental data some authors indicate the biological processes (with involvement of bacteria from the genus Pseudomonas and other microorganisms) as the most important, while others suggest that photochemical reactions play the dominant role [10, 21, 61-63]. According to other authors Hg(II) can be reduced by humic substances under the influence of solar radiation or without this radiation [57, 62-64]. The mechanisms of these conversions have not been well recognised yet.

As far as the process of oxidation of Hg° to Hg(II) is concerned, till recently it was considered negligible or not occurring in natural waters; however, in view of new data the process is possible, especially in marine water containing chlorine ions [61]. The oxidation processes are believed to be more important in waters close to shores where the concentration of suspension is the highest. In waters with good access to oxygen elemental mercury can be relatively quickly oxidised by different reagents - mainly oxygen but also nitrates, nitrites, iron hydroxides, iron phosphates, sulphates, sulphur, carbon dioxide [9]

Demethylation of Mercury

Demethylation of mercury-organic compounds is an important process taking place in natural waters. Demethylation of methyl-mercury, stable in water environments, can proceed by a biological route (through microorganisms) and a photochemical route (as a result of irradiation) [51]. Biological demethylation of mercury is a slow process and in contrast to methylation is most effective in aerobic conditions (Gilmour & Henry, 1991 vide [9]). The results reported by Matilainen & Verta [33] have indicated that demethylation takes place only with the involvement of microorganisms, because of a great influence of decreasing temperature on the rate of demethylation and cessation of demethylation in sterilised samples of water. The same authors reported that the rate of demethylation in the surface lake water was < 13.2% daily. The process of demethylation demands hydrolysis of mercury-carbon bond accompanying the formation of Hg^{2+} and methane. Then Hg^{2+} is reduced to volatile elementary mercury and released to the atmosphere where it undergoes further conversions [9]:

$$CH_3Hg^+ \rightarrow CH_3 + Hg^{2+} \qquad (5)$$

$$Hg^{2+} \rightarrow Hg° \qquad (6)$$
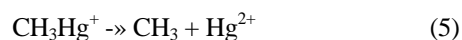
Speciation of Mercury in Bottom Sediments

A good indicator of water contamination with mercury is its content in bottom sediments, which can store large amounts of this metal and be a site of its many conversions [9, 20, 65]. There are significant differences in the concentration of mercury in bottom sediments of different origin (Table 5). Very high concentrations have been found in sediments from the water reservoirs in polluted regions and from estuaries of some rivers.

It is assumed that a natural concentration of total mercury in bottom sediments varies from 10 to 200 ng/g dry mass [20]. Kannan & Falandysz [66] suggested that a ratio of the concentration of total mercury to that of methylmercury could be used as an index describing the pollution status of a given reservoir. In Gdansk Bay methylmercury, occurring at a mean concentration of 0.65 ng/g dry mass, made up less than 0.5% of total mercury [66]. According to the same authors, in non-polluted regions this index takes values lower than 1; for Gdansk Bay this was 0.02 to 2.27. From among the samples studied the highest index found was for bottom sediments of the harbour in Hamburg and the rivers Elba and Mulde, for which the index varied from 2.5 to 9.7 [5, 67].

The high affinity of mercury ions to sulphides determines the chemistry of mercury in anaerobic regions of waters and bottom sediments. In anaerobic conditions, the dominant mercury species are: HgS, HgS_2H_2, HgS_2H^- and HgS_2^{2-} (Fig. 4), whereas from among the mercury-organic species the most important is CH_3HgS^- (Fig. 3). Mercury sulphide HgS is hardly water-soluble, is deposited in bottom sediments, and determines the solubility of Hg(II) in anaerobic waters. It seems that HgS deposition accompanies organic matter or iron oxide molecules [18]. The solubility of HgS can increase in the presence of increasing amounts of sulphide ions in the water (Fig. 4), appropriate to form soluble sulphide complexes with mercury. This property has a key importance at high concentrations of dissolved mercury noted in anaerobic regions of water ecosystems [20]. For example, in the bottom sediments from polluted Tokuyama Bay in Japan, organic species of mercury were not detected. Of the total mercury present at concentrations of 10,900 to 22,200 ng/g dry mass, the majority was bound to sulphides 50-90%, the rest occurred in the form of free ions and elemental mercury [68]. Although HgS is strongly bound to sediment, it can be partly dissolved as a result of conversions with the use of bacteria or under the effect of oxidising conditions (e.g. due to bioturbation) [18, 69-71]. The inflow of mercury from deeper layers of the sediment to near-surface layers, as a result of molecular diffusion, was estimated as 3% of the mercury inflow
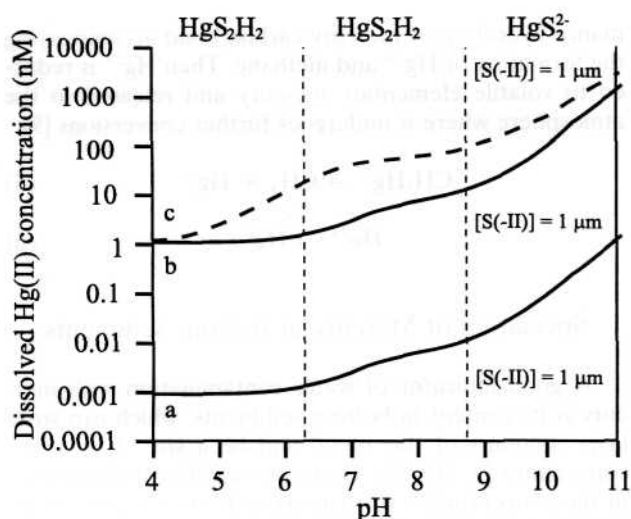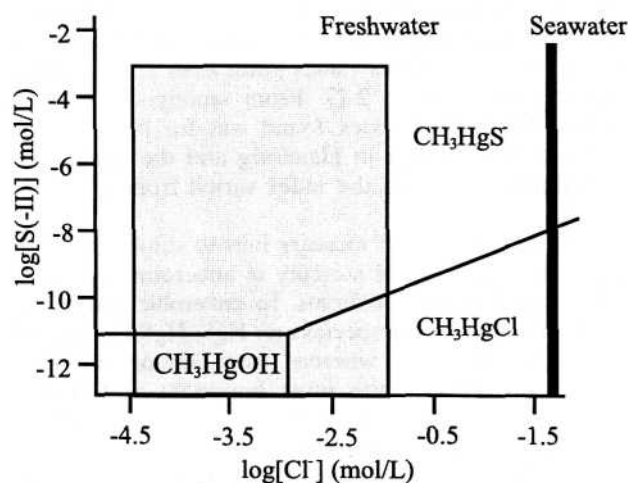
Fig. 3. Calculated dissolved Hg(II) concentrations at equilibrium with HgS in the presence of added sulphides, (a) and (b): no elemental sulphur is present, (c): the solution is at equilibrium with S° [10].

Fig. 4. Dominance diagram of hydroxo-, chloro and sulphide complexes of methylmercury at pH = 7 as a function of chloride and total sulphide concentration [10].

from water to the sediment by Gobeil & Cossa [71], and as 7% - by Gagnon et al., [72]. According to Rutgers van der Loeff et al., [70], the size of redeposition of mercury from the sediment to water taking place thanks to the activity of benthos organisms was from 2 to 10 times greater than the redeposition from the sediment to water as a result of diffusion. It seems that the surface layer of the bottom sediments in which there are oxidising conditions make a geochemical barrier for diffusion of methylmercury from the near surface layer of the bottom sediments with reducing conditions to bulk water [18, 72].

Conclusion

Mercury is one of the most hazardous contaminants occurring in aquatic environments, but its behaviour in hydro-systems strongly depends on the actual kind of chemical species present. Species distribution and transformation processes in natural aquatic systems are controlled by various physical, chemical and biological factors. Depending on the environmental condition, mercury species may be converted to very toxic forms (e.g. methylmercury and dimethylmercury). Recent development of analytical methods of determining mercury species in the natural environment has stimulated much effort towards the recognition of the behaviour of mercury species in the natural environment. Despite considerable literature devoted to this subject, the behaviour of mercury, processes of its conversion and distribution in natural aquatic environments are still poorly recognised.

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