



Account/Revue

Some aspects of speciation and reactivity of mercury in various matrices



Quelques aspects de la spéciation et de la réactivité du mercure dans diverses matrices

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ABSTRACT

Speciation of mercury compounds in environmental and biological samples requires different techniques and different approaches. This speciation is mandatory to explain the toxicity, the reactivity and the bioavailability of mercury. It is dominated by inorganic mercury species Hg(II) and Hg(0), and the organic mercury species CH₃Hg and (CH₃)₂Hg. In this paper, some aspects of mercury speciation are presented in terms of:

- mercury reactivity (Hg(II) complexation and reduction),
- mercury species distribution in the main compartments of the environment

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R É S U M É

La spéciation du mercure dans les échantillons environnementaux et biologiques nécessite différentes techniques et différentes approches. Cette spéciation permet d'expliquer la toxicité, la réactivité et la biodisponibilité du mercure. Elle est dominée par les espèces de mercure inorganique Hg(II) et Hg(0) et les espèces organiques CH₃Hg et (CH₃)₂Hg. Dans cet article, quelques aspects de la spéciation du mercure sont présentés en termes de :

- réactivité du mercure (complexation et réduction de Hg(II)),
- distribution des espèces du mercure dans les principaux compartiments de l'environnement.

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1. Introduction

Mercury (Hg) is considered as one of the most toxic metals found in the environment and has no known

essential biological function [1]. Moreover, unlike many heavy metals, Hg participates in a variety of biogeochemical processes with a complex cycle characterized by exchanges between different compartments of the ecosphere: atmosphere, hydrosphere, and biosphere. In the natural environment, mercury occurs in three oxidation states (0, +I and +II) and can exist in several different chemical forms. The three most important known chemical forms of Hg in the environment are: elemental mercury

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(Hg⁰), mercurous ion (Hg₂²⁺) and mercuric ion (Hg²⁺) which have a strong affinity for many inorganic and organic ligands as inorganic mercury (Hg_L) and organic mercury (HgX_i). All these forms have different chemical properties and are potentially toxic.

The determination and quantification of Hg species, it is to say speciation [2], is fundamental for environmental studies because it has now been recognized that its bioavailability, toxicity and mobility depend on its chemical forms [3,4]. Speciation can provide information about the bioavailability, mobility and toxicity of an element in a system [5–8] but also a better understanding of reactivity including the process of a reaction [5]. The organic mercury compounds, of which methyl-mercury is the most common, are of special concern because of their great toxicity. These compounds can accumulate in living organisms and damage their central nervous system [9,10]. So, a better knowledge of mercury biogeochemical cycle is required in order to understand well the biogeochemical cycle of mercury necessary to predict its fate and its transport.

The importance of speciation of mercury is reflected by the publication of numerous studies and the constant progress realized in analysis [11–19]. Several books and reviews about mercury speciation have been published [20–26].

In this paper, a brief summary of mercury speciation is presented in terms of the importance of Hg(II) complexation, Hg(II) reduction and distribution of the inorganic mercury species of Hg(II) and Hg(0), and the organic ones, CH₃Hg and (CH₃)₂Hg, in the environment.

2. Mercury reactivity

2.1. Mercury complexation

In the natural environment, the presence of ligands (organic and inorganic) and mercury can lead to the formation of mercury complexes [27]. The complexing properties depend on the nature of the ligands and their characteristics, the concentrations of both, mercury and ligands.

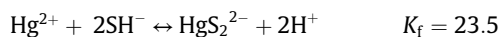
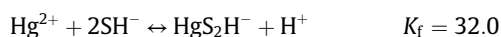
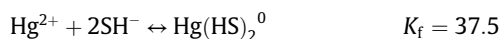
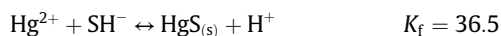
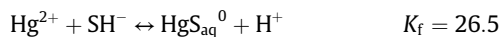
Hg(II) is a B-type cation with different affinities (weak, moderate or strong) depending on whether the inorganic or organic ligands contain oxygen, nitrogen or sulfur atoms. For example in the case of inorganic ligands, sulfate (SO₄²⁻) is a weak ligand ($K = 10^{1.3}$) whereas sulfide (S²⁻) is extremely strong ($K = 10^{52.4}$) [28]. Among the organic ligands, sulfur functional groups (cysteine, and mercaptoacetate) bind mercury much more strongly than those oxygen-containing functional groups. In addition, in sulfur functional groups, thiol sites exhibit very strong interactions, whereas oxidized sulfur groups are extremely weak.

2.1.1. Mercury – inorganic ligand complexes

Chloride, hydroxide and sulfide are considered as important inorganic ligands in controlling mercury speciation in aquatic systems [29]. Mercury has a strong tendency to build complexes with Cl⁻, OH⁻, and S²⁻, but the importance of mercury-hydroxide complexes (Hg(OH)⁺, Hg(OH)₂, and Hg(OH)₃⁻), and mercury-chloride complexes

(HgCl⁺, HgClOH, HgCl₂, HgCl₃⁻, and HgCl₄²⁻) depends on pH, salinity and the chloride concentration [30,31].

Under anaerobic conditions, mercury combines with sulfide to form HgS_(s) (cinnabar) or soluble aqueous complexes depending on sulfide concentrations [32]. Benoit et al, and Dyrssen and Wedborg [33,34] have shown the existence of neutral dissolved Hg complexes in sulfidic solutions. The following reactions have been presented by Benoit et al. [33].



Among various inorganic ligands, sulfur plays an important role in mercury complexation, and thus, it controls mercury speciation in anaerobic environments.

The stability constants of various complexes between mercury and inorganic ligands have been tabulated elsewhere [28,35,36].

2.1.2. Mercury – DOM complex

It is well known that dissolved organic matter (DOM) has a strong interaction with mercury and other trace metals affecting their speciation, mobility and toxicity [37]. In the recent decade many studies have been published regarding the ability of DOM to complex with Hg in various natural environments [27,38–43]. The comprehensive review on interaction between mercury and DOM, including the nature of DOM, binding constants of Hg–DOM complexes and the role of DOM in mercury speciation under sulfidic environments are given by Ravichandran [28] but the information about this interaction is still limited and incomplete seen the numbers of recent publications in this area.

Mercury-DOM associations are complex, influenced by several factors especially the heterogeneous character of DOM [44]. DOM contains several molecular organic compounds of different weights, solubilities and reactivities and a large number of hydrophilic functional groups: carboxylic (COOH), phenolic and/or alcoholic (OH), carbonyl (C=O) and amine groups (NH₂). Sulfur groups also exist in different oxidation states (R–SH, and R–SO₃H), but organic sulfur reduced compounds containing the thiol group, –SH, are the most active form [45]. These different fractions can interact with mercury, and influence differently the DOM-mercury interaction. The research on DOM continues to improve the understanding of the DOM composition and its interaction with mercury.

The strong binding between mercury and DOM is generally attributed to many reduced sulfur (sulfide, and

thiol) sites, contained in organic matter [28,46]. The importance of reduced organic sulfur associated with natural organic matter is now well recognized, and although these ligands are less abundant compared to other binding functional groups in DOM, they play an important role in DOM–mercury complexes because of their stronger binding capability with metal ions in general and mercury (II) in particular [47,48].

• Mercury – DOM – sulfide systems

The use of an X-ray absorption near-edge structure (XANES) spectroscopy method has shown the strong interaction of mercury with reduced sulfur groups [49,50]. Moreover, geometry, coordination number and bond distance in mercury- DOM- sulfide systems have been determined by extended X-ray absorption fine structure (EXAFS) spectroscopy [50,51]. Gerbig et al. [51] have indicated that in the absence of sulfide, mercury bonds with an average of 2.4 sulfur atoms with a bond length typical of mercury-organic thiol ligands (2.35 Å). However, in the presence of sulfide, mercury- sulfur bonds with longer interatomic distances (2.51–2.53 Å) similar to the mercury – sulfur bond distance in meta-cinnabar (2.53 Å) are observed.

Taking into account the importance of HgS(s) in mercury methylation, the system (mercury – DOM – sulfide) has been the subject of several research studies [39,52–54] due to the limited understanding of the effects of DOM on the reaction between Hg_{aq} and S(–II) and on the stability of HgS(s). The studies of Ravichandran et al. [54] were the first to quantify how DOM affects the reactivity of mercury toward S(–II). They concluded that dissolved thiol and hydrophobic organic ligands can inhibit the formation and the particle growth of HgS(s). In 2009, Deonarine and Hsu-Kim [47,53,54] showed that increasing concentrations of DOM can progressively slow the growth, but cannot inhibit the formation of HgS(s). Recently, Gerbig et al. [51] showed a positive correlation between the Hg:DOM ratio and sulfur coordination number, suggesting the progressive increase of particle size with increasing abundance of mercury with respect to DOM, therefore, nanocolloidal species may form.

Although, numerous studies have been published on DOM-mercury interaction, all is not yet well understood concerning the reaction mechanisms. The characteristic of DOM is a difficulty in this study; its composition varies according to space, time and matrix. A better knowledge of this interaction is very important for understanding mercury biogeochemistry and its speciation that should help us to assess the environmental and health effects of mercury.

• Mercury – DOM complex and the stability constant

The conditional stability constant is a parameter generally used to characterize and quantify the strength of DOM–mercury interactions. Numerous studies are devoted to the measurement of mercury complexation parameters by using natural organic ligands [42,50,55–58]. The methods used and conditional stability constants of mercury-binding organic ligands, previously mentioned, are summarized in Table 1. It shows that values of the

Table 1

Conditional stability constants of mercury-organic complexes (K_{cond}) reported.

Method	Sample type	Log K	Reference
Anodic stripping voltammetry	Natural water	9.7–10.8	[141]
Ion Exchange	DOM isolates	21.9–31.6	[56]
Reducible Hg titrations	DOM isolates	<14	[62]
Gel filtration chromatographic	Sediment	22.6–24.6	[48]
Hg sorption modeling	water/sediment	18–21.1	[142]
	DOM	22.8; 23.2	[60]
	Costal and estuarine waters	26.5–29.0	[38]
	Natural water	29.9–33.5	[61]
	wastewater	log $K > 30$	[143]
Equilibrium dialysis	Soil	22.6–38.3	[41]
ligands exchange	Water	22.5–23.5	[59]
Potentiometric method	Water	10,37	[144]
Competitive complexation	Soil	20.6–23.9	[145]
Specific ion electrodes	Soil	4.86–5.08	[146]
	Soil	4.7	[147]

conditional stability constants for DOM–mercury complexes given in Table 1 vary from 10^4 to 10^{38} . A number of factors could explain this difference and the difficulty of measuring accurate binding constants for Hg–DOM complexes. One of the factors is the heterogeneity of DOM depending on the environmental compartment from which it was taken (soil samples, sediment samples, and aquatic samples) [56]. Recently, the influence of different DOM fractions according to their hydrophobicity has been studied by Muresan et al. [42]. It appeared that, for Hg complexation the distinction between DOM of different origins was more fundamental than that resulting from the use of a fractionation method. According to the results of Haitzer et al. [59], the DOM from different environments may have slightly different strengths (different stability constants) but the lower values of stability constants would be due to the additional binding of mercury to oxygen-containing functional groups which are weaker in nature. Han et al. [58] determined two classes of natural ligands associated with dissolved organic matter in surface waters of Galveston Bay: a strong class (Ls), ranging from 19 to 93 pM with an average conditional stability constant (KHgLs) of 10^{28} , and a weak class (Lw) ranging from 1.4 to 9.8 nM with an average KHgLw of 10^{23} . Generally, the stability constants of DOM–mercury complexes in the order of 10^{22} to 10^{30} are considered consistent with binding by thiols [58,60,61]. In addition to the nature of DOM, the mercury concentration, analytical methods, stability constant calculations and experimental conditions are also at the origin of this large difference of stability constants [28]. Jarrod et al., [62] have shown that stability constant values could depend on the method used. They have obtained better results with Competitive Ligand Exchange–Solid Phase Extraction (CLE-SPE) (log $K = 25–30$) while an ion exchange method has been limited by its detection window, which constrains the method, to stability constants with log K values less than about 14. The comparison of stability constant values is not judicious, because in calculations of log K values, various methods and/or binding models are used and different assumptions are formulated.

Dong et al. [56] determined the stability constants for four selected DOM isolates, the values varied slightly from 21.9 to 23.6 for 1:1 HgL complexes, and from 30.1 to 31.6 for 1:2 HgL₂ complexes. The results obtained in this study were compared to those of several authors (Lamborg et al. [47] and Black et al. [61] (1:1 complexes) and Khwaja [41] et al. and Haitzer et al. [59] (1:2 complexes)) and the values were found to be different. Some researchers have been also interested in the influence of pH and the Hg/DOM ratio on DOM–mercury complexation. Haitzer et al. [59] have measured the binding of Hg(II) to DOM in a wide range of Hg-to-DOM concentration ratios. The conditional coefficients determined by this group were strongly affected by the Hg/DOM concentration ratio. Very strong interactions were observed at low Hg/DOM ratios. The pH dependence on complexation has been analyzed by Kwadja et al. [41]. They suggested that two or more protons are released when one of the Hg²⁺ cations is bound. However, some results concerning DOM–mercury complexation are not always in direct agreement with those mentioned above. Haitzer et al. [59] do not find notable difference in complexation using seven aquatic humic materials derived from various sources.

Despite some differences in the values of binding constants, the strong binding of mercury with DOM is recognized as well as the involvement of thiol groups. Several studies assume that reactive thiols in DOM are the principal binding sites for Hg²⁺, particularly at relatively low Hg/DOM ratios.

2.2. Mercury reduction

Reduction of the mercuric ion Hg(II) to elemental mercury Hg(0) is a process critically important in the understanding of the mercury transformations, especially in bioavailability. The process of mercury reduction implies several compartments of the environment (air, water, and soil). In this process, two important aspects can influence mercury species distribution in aquatic systems. The volatilization process of Hg(0) from sediments, or soils, towards the atmosphere, where Hg(0) can be oxidized to different species, such as HgO, is a process which contributes to atmospheric deposition [63]. The second process is methylation/demethylation. In an anaerobic medium, Hg(0) can react with a carbanion for methylation [64,65], while it would also occur from the degradation of methylmercury. Monperrus et al. [66] have studied the processes of methylation, demethylation and reduction of mercury; their results show that methylation is taking place in oxic surface seawater (0.3–6.3% day⁻¹) and the demethylation rates are in the range of 6.4–24.5% day⁻¹. Moreover, these results evidence simultaneous methylation, demethylation, and reduction mechanisms involving various biogeochemical pathways such as sunlight induced processes, and/or autotrophic and heterotrophic micro-organisms activities. All of these reactions may affect the speciation of mercury and the availability of each species.

2.2.1. Photo reduction process

Usually, a photo-reduction process is considered as the main mechanism for reducing Hg(II) to Hg(0) at natural

levels of mercury [67–72] and the influence of light (intensity and wavelength) on the production of dissolved gaseous mercury (DGM) has been shown. Amyot et al. [73] investigated the effect of sunlight on DGM production in seawater. The results show that DGM production was only induced in the presence of sunlight, visible (400–700 nm), UVA (320–400 nm) and UVB (280–320 nm) radiation and that the contributions are respectively around 46, 31, and 23% of the total DGM production. Costa et al. [69] indicated that mercury reduction depends on the intensity and the type of light used and that the reaction efficiency is the greatest at UV wavelengths. The influence of UV wavelengths depends on water quality. Under UVB light, the production of DGM was higher in clear lakes than in humic saturated water, but the tendency of DGM production was to be higher in humic lakes in the UVA range [70]. O'Driscoll et al. [74] have realized irradiation experiments in freshwater under UVA and UVB radiation and have determined kinetic photo-reduction relative to radiation. The rate constants were higher for UVB irradiations (6·10⁻⁵ s⁻¹ and 4.4·10⁻⁴ s⁻¹) than those for UVA irradiations (5.26·10⁻⁵ s⁻¹ and 3.04·10⁻⁴ s⁻¹).

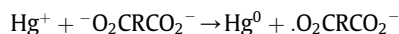
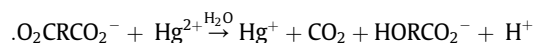
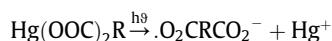
Recently, Ahn et al. [75] presented a result in contradiction with many previous studies showing that DGM concentrations were primarily controlled by a photo-reduction process. DGM concentrations in general depend on water temperatures rather than on solar radiation. They assumed that heterotrophic bacterial transformations reducing Hg(II) to Hg(0) were generally the dominant reduction processes. Several studies have also noticed the importance of bacterial or biological reduction [76–79]. For example, Deng et al. in 2010 [79] showed that the photo-reduction rate of Hg(II) increased with increasing concentrations of algae *Nitzschiahantzschiana*. These differences are difficult to analyze because the reaction mechanism of mercury photo-reduction is still not clear.

2.2.2. Mercury reduction by DOM

Some recent studies on DOM–mercury interaction have shown that, DOM plays an important role in mercury reduction [69,80–83]. Nevertheless, one of the research gaps concerning interaction between DOM and mercury species is probably the reduction of Hg(II) to Hg(0). Indeed, several studies published on this topic are contradictory. Some have shown that DOM has no significant influence on the mercury reduction process [73,75,84,85] whereas Watras et al., [84] have observed that an increasing DOC (Dissolved Organic Carbon) concentration was related to an exponential decrease in the ratio of DGM to total mercury and Matthiessen [86] has found that humic acid has no effect on mercury reduction. The decrease of DGM production would be due to the presence of DOM, which reduces the availability of UV radiation for direct photo-reduction of mercury according to Amyot et al. [73]. In the same order, recently, Ahn et al. [75] did not observe a consistent relationship between DOC and DGM production. While some researchers found a negative correlation between the DOC concentration and DGM production [73,84], others showed the increasing DGM production in the presence of DOC [69,80,81,83,86–88]. Despite the recognition of the importance of the DOC concentration in

mercury reduction by these authors, conclusions differ according to experimental conditions. As previously mentioned, the photo-reduction process is considered as the main way for reducing Hg(II) to Hg(0); this process is enhanced by the presence of DOM [89,90]. In dark environments, no observable Hg reduction occurs in the presence of humic acids at low total mercury concentrations [86], while Baohua et al. [83] and Zheng et al. [81] demonstrated that under anoxic dark conditions, DOM can rapidly convert Hg(II) to Hg(0) at very low DOM concentrations (up to ~70% at 0.2 mg/L). The importance of DOM concentrations was also observed by Zheng et al. [81] who suggested that reduction of Hg(II) occurs only when the DOC:Hg ratio is lower than a given threshold but depending on DOC used. For example, the DOC:Hg ratio is $\geq 20\,000$ for samples from Integrated Field Research Center – Fulvic Acid (IFRCFA, USA), and it is ≤ 5000 for other DOM samples.

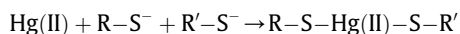
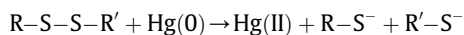
The effect of DOC characteristics has been also investigated [74,80,81,91,92]. The reduction of Hg(II) by aquatic humic substance fractions separated by tangential-flow multistage ultrafiltration is influenced by the molecule size and DOC structure [83]. They indicated also that, the degree of Hg(II) reduction is significantly influenced by the ratio of phenolic/carboxylic groups and by sulfur bound in these humic substance fractions. O'Driscoll et al. [74] observed a difference between carboxylic functional groups of DOM from lake water and sediment. Si and Ariya [93] suggested that the photo-reduction of Hg(II) was mediated by the complexes formed between Hg(II) and dicarboxylic acids. Their results also indicated that the presence of chloride ion significantly decreases the reduction rate by competing with the complexation of Hg(II) with dicarboxylic acids. They have also proposed a tentative of the reaction mechanism; the mechanism would be an intra-molecular process within the Hg–(OOC)₂R complex.



Zheng and Hintelmann [92] studied the effects of specific functional groups on mercury reduction by various low-molecular-weight organic compounds. The results showed that mercury reduction was dramatically different by two classes of organic compounds. They concluded that, this important difference is related to the fundamental nature of bonds between Hg(II) and the O:N ratio or reduced S donor groups. In another work, Zheng et al. [81] have given some details on reaction rates, and on mechanisms between organic compounds and Hg(II) or Hg(0). They indicated that reduced DOM is much more reactive than oxidized DOM. Moreover, they assumed that abundant electron-donating functional groups such as hydroquinones or semi-quinones contained in reduced DOM, able to reduce various metal ions, can explain the large percentage of Hg(II) reduced even at relatively low DOC:Hg

ratios. In 1974, Albert et al. [94] had already suggested that quinone or semi-quinone moieties in organic matter are involved in mercury reduction.

It is also reported that DOM plays a dual role in the mercury redox process [81,83]. DOM reduced in an anaerobic environment can simultaneously mediate both reduction and oxidation reactions of Hg. This process is important for mercury speciation and for its availability under these conditions:



where R-S-S-R' represents DOM with oxidized sulfur or disulfides. [83]

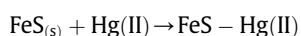
Among these different studies, influences of pH and competitive ions on mercury reduction have been also studied. The highest reaction rates were observed in systems free of both oxygen and chloride [89,93], while ferric iron dramatically increases DGM production [95,96]. However, some authors found that chloride ions do not influence mercury reduction [85,97]. Different results indicate that the mercury reduction reaction appears to be pH-dependent [79,94,98]. The influence of DOM on mercury reduction is still very complex and not well understood, in terms of DOM concentration, structure, and reaction mechanism.

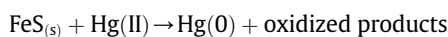
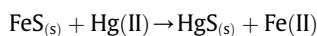
While the results on mercury reduction seem to be contradictory, literature data suggest that the production of DGM is affected by three essential factors: irradiation intensity and spectrum, the quantity and structure of DOM, and the presence of competitive ions. Ricardo et al. [91] have studied the reduction capacity of mercury(II) by humic substances from different soils. They concluded that humic substances extracted from different types of regions contribute in different ways in mercury reduction.

2.2.3. Mercury reduction by nanoparticles

Some nanoparticles such as hydrous ferric oxide (HFO) and iron sulfide are known for their ability to scavenge trace metal [99–101]. The interactions between aqueous Hg(II) and synthetic nanoparticles were studied under anaerobic conditions and show that the Hg(II) reaction with nanoparticles includes not only sorption, and precipitation as cinnabar (α -HgS) and/or metacinnabar (β -HgS) but also the formation of elemental mercury [102–104].

The interaction mechanism varies with the types of nanoparticles and geochemical conditions. In the reaction between Hg(II) and pyrrhotite, sorption is the main reaction [105]. Meta-cinnabar and cinnabar are the primary products of Hg(II) sorption on mackinawite [102–104], while cinnabar and Hg(0) are formed when Hg(II) interacts with pyrite and troilite [106]. However, the authors are not unanimous on sorption products and on the role of nanoparticles in the reduction of Hg. In fact, the mechanisms have been rarely analyzed. Jeong et al. [103] have proposed the following different mechanisms for Hg(II) sorption by iron sulfide





However, they have been unable to detect Hg(0) as well as numerous researchers who have investigated the reaction between Hg(II) and FeS [104]. Only one work has reported the reduction of mercury by iron sulfide [107]. This work concluded that Hg(0) was generated from the reduction of Hg(II)–S(–II) by FeS.

Recently, there is evidence that reduced iron species, such as magnetite, green rust, and iron sulfides can reduce Hg(II) to Hg(0) [107–110]. Fe(II) seems to play an important role in this reduction. Indeed, Wiatrowski et al. [108] have shown that the Hg(II) reaction with solid-phase Fe(II) is a kinetically favorable pathway for Hg(II) reduction with magnetite. However, there is not a consensus in the literature regarding the homogeneous or heterogeneous reduction of Hg(II) in the presence of Fe(II). Amirbahman et al. [110] have studied the homogeneous reduction of Hg(II) at different pH values and different total Fe(II) concentrations. They concluded that the Hg(0) production rate increased with increasing pH and Fe(II) concentrations. For some authors, aqueous solutions of Fe(II) are unreactive, but the adsorption of Fe(II) on the mineral surface created highly reactive sites for the reduction of Hg(II) [111,112], nevertheless the surface-catalyzed reduction depends on the mineral. HFO increases the Hg(0) production rate, while other minerals such as γ -alumina ($\gamma\text{-Al}_2\text{O}_3$) decrease the Hg(0) production rate [110].

For now, the reactivity of Fe(II) associated with minerals for the mercury reduction require more investigations mainly regarding the role of Fe(II)

3. Distribution of mercury species in the environment

The distribution of mercury in the environment is generally organized around five main species; elemental mercury (Hg^0), divalent inorganic mercury (Hg^{2+}), mono-methyl-mercury (MeHg), di-methyl-mercury (DMeHg), and mono-ethyl-mercury (EtHg). The determination and quantification of mercury species in water, soil, and sediment have been largely reported [113]. A number of studies have shown the importance of mercury distribution to obtain information on mercury levels, speciation, methylation rates, and mercury transport across water-sediment-air interfaces [114].

Mercury speciation has been determined in numerous matrices, including environmental matrices (air, water, soil, sediment, fish, and plant) [19,115] and biological materials (blood, urine, tissues, and hair) [116–119]. The speciation of mercury in water, soil, and sediment has been described in different reviews [29,36,120].

3.1. Mercury species in water

Mercury speciation in aquatic environments is of particular importance for understanding the global Hg cycle as well as health risk assessments due to the consumption of fish by human. Generally, mercury species are

present at very low levels in natural waters, especially in marine water and their determination is still a challenge in analytical chemistry. For example the reliable determination of the methyl-mercury concentration is very difficult; its contribution to the total mercury concentration in natural non-polluted waters is 3–6% in seawater and 26–53% in fresh water [120] and it is present in ocean waters at very low concentrations at picoM levels [121–123].

In natural water, mercury behavior depends on the characteristics of the system. Some parameters such as environmental parameters (physicochemical parameters, and pH), biological activities of aquatic micro-organisms and the presence of organic and inorganic ligands determine the species forms of mercury [123]. In water samples, the partition of mercury is realized between the following different phases: dissolved, colloidal, and particulate [36,121]. Temporal and spatial variations affect strongly the distribution of mercury in each of the phases. Usually, mercury speciation in water includes the determination of total mercury (THg), dissolved gaseous mercury (DGM), reactive mercury (RHg) defined as all Hg species that are readily available for reduction with SnCl_2 solution, volatile Hg species, particulate mercury (PHg), mono-methyl-mercury (MeHg) or di-methyl-mercury (DMeHg). In water from the Mediterranean Sea, a significant fraction of Hg was present as RHg (average value 0.33 ± 0.32 picoM), DGM represented a proportion of 20%, (0.23 ± 0.11 picoM), but DMeHg has not been found in surface waters down to the depth of 40 m [124]. Laurier et al. [115] studied the distribution, the partition and the speciation of mercury in water and they found that Groundwater in the karstic coastal zone of the Pays de Caux was characterized by high RHg:THg ratios in the dissolved phase (44–95%), and very low total mono-methyl-mercury concentrations ($\text{MMHg} < 8 \text{ pg L}^{-1}$). In general the concentrations of MeHg are higher near the sediments, the highest DMHg concentrations were found in deep waters, while near the air-water interface, the concentration of Hg(0) is higher [36]. Concerning the divalent mercury, it is not present in the free form in surface water, but complexed with hydroxide, chloride, sulfide or DOM depending on water characteristics (pH, chloride concentration, and anaerobic or aerobic conditions) [125].

The contribution of different species in the concentration of total mercury varied according also to the type of waters, the seasons and the years, showing thereby the influence of environmental parameters on mercury speciation. Mercury speciation in the Mediterranean Sea was done during different years, resulting in different concentrations of THg, RHg, DGM or MMHg (THg: 1.2 and 2.5 picoM [122]; 1.35 picoM, [123]; 1.7 and 2.5 picoM [126]; 1.46 and 1.21 picoM) [124]. Moreover, average values for THg (1.3 picoM) in the Mediterranean Sea are lower than those found in the Atlantic Ocean (2.4 picoM) [121] and South and equatorial Atlantic (2.9 picoM) [127], and nearly to those of the North Pacific Ocean (1.15 picoM) [115]. Concerning the influence of seasons, Kotnik et al. [124] found that the average MeHg concentration was significantly higher during the spring (0.28 ± 0.12 picoM; $25 \pm 10\%$) than during the summer (0.16 ± 0.1 picoM; $14 \pm 9.1\%$). Recently, Zhijia et al. [11] investigated the phase distribution of mercury (Hg) in yellow seawater (China) and

they found that particulate mercury was the dominant phase in unfiltered water samples (%PHg/THg = $70 \pm 11\%$) while in the dissolved phase RHg accounted for the dominant fraction of THg (range: 42–124%, average: $86 \pm 16\%$). They studied also the influence of seasons on mercury concentrations, and have found that the concentrations of mercury species showed no significant seasonal variation over the year.

Generally, the RHg fraction represents the substantial part of the total mercury [115,123,124,127]. This fraction is important in different transformations such as photo-induced transformations, methylation and demethylation on surface layers.

3.2. Mercury species in sediment and soil

In aquatic environments, sediments are considered as a reservoir for metals and they can provide historical input records of metals [128–130]. Evaluating the concentration and the distribution of mercury in sediment is the most effective way to know the degree of environmental pollution and this explains the numerous and recent publications in this field [13,15,17,19,131,132].

The behavior of mercury in soil or sediment depends on matrix parameters and environmental conditions. The reactions, shown to exist for the water system, may also occur in sediments and soils such as methylation/demethylation, complexation, and reduction. These reactions can occur in biotic or abiotic conditions, according to the composition of sediment/soil, quantity of organic matter, concentration of mercury, and physicochemical conditions (pH, competitive ions...) [133].

In sediment and soil, Hg(II) is the dominant species of mercury but it can be complexed with different ligands and methylated into methyl mercury. As indicated in Section 2, mercuric ion exhibits extremely high affinity for sulfide and organic matter, so the speciation is dominated by these properties (organic and inorganic complex) [134]. In a study on mercury speciation in sediment and soil, two phases can be distinguished: the aqueous phase and solid phase. The total concentration of Hg(II) in the aqueous phase of soils and sediments is normally in the range of 5–100 pM, and solid phase concentrations are often in the range of 50–500 ng/g (250–2500 pM/g) [134]. Usually, the speciation of mercury in sediment and soil include the determination of the total mercury and methyl-mercury concentrations, where MeHg contributes in general to 0.1–10% of the total Hg in solid phases and 5–80% of total Hg in aqueous phases of soil and sediment [134]. Lamertsson et al. [135] examined the MeHg concentration in an unpolluted estuarine sediment, the contribution of which to the total mercury concentration was relatively high (MeHg/THg = 4–13%). Alessandro et al. [19] found that MeHg constitutes on average 0.08% of THg in Marano and Grado Lagoon (northern Adriatic Sea).

The MeHg content in the sediment is very low in general but it is influenced by environmental conditions. The process of methylation or demethylation reported in the literature can explain why the concentration of MeHg is not strictly related to the total Hg concentration in sediments [67,136]. Sulfide and sulfate play an important role in these

reactions. Under sulfidic conditions, Hg interacts with sulfur to form dissolved Hg–S complexes that may control the bioavailability of Hg, and bacterial methylation [33].

The bacterial methylation is known to be a main process of methylation in the environment in particular in sediment [137]. However, it has been reported that bacterial activities are influenced by the presence of sulfur (a high concentration of sulfur increases the formation of complexes, $\text{Hg}_3\text{S}_4^{2-}$, non assimilable by bacteria), by temperature and by organic matter (limits the activities of bacteria).

On the other hand, the speciation of mercury in soil and sediment depends also on the process of adsorption/desorption. Hg(II) and MeHg are able to bind on particles or colloids [29,138–140]. For example clay is negatively charged and can interact with mercury species positively charged. The sedimentary particles rich in Mn, Fe, and Al constitute adsorbent sites for hydroxide, allowing thus the formation of mercury-hydroxide complexes [29]. The distribution of mercury species in environmental compartments is affected by temporal, and spatial variability, matrix type, and environmental conditions.

4. Conclusion

Despite considerable work in recent years, the fate of mercury in the environment remains a serious problem. Because mercury is present in the environment in different forms, and since it can be very toxic, the knowledge of mercury speciation and of its biogeochemical cycle is critically important. However, the processes of mercury transformations and reactivity are not well understood.

It is well known that the photo-reduction is the main process of mercury reduction but the mechanism of this process is still not clear. The reduction of mercury by DOM is affected by several factors, and the influences of these factors are not known in detail. In addition, the process of this reaction depends on the DOM characteristics (the structure, origin, and state of oxidation). This makes it difficult to propose a reaction as well as a comprehensive model for the mercury–DOM interaction.

There are still some limitations in the understanding of the exact mechanisms by which mercury–DOM interactions occur, but the literature has shown that DOM plays an important role in mercury speciation via the complexation, reduction of mercury(II) and oxidation of mercury(0). The complexation would be due to the reaction with reduced sulfur (S) or thiolate functional groups of DOM, while mercury is assumed to be reduced by hydro-quinones or semi-quinones contained in reduced DOM. Moreover, according to recent studies, in addition to reduction, DOM could oxidize mercury(0) to mercury(II) especially at a high DOM:Hg ratio under the same reducing environment.

Further investigations are required to confirm the previous results and to determine the reaction mechanisms.

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