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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 CH_3Hg and $(CH_3)_2Hg$. 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

RÉSUMÉ

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 CH_3Hg et $(CH_3)_2Hg$. 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.

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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(Hg^0), mercurous ion (Hg_2^{2+}) and mercuric ion (Hg^{2+}) which have a strong affinity for many inorganic and organic ligands as inorganic mercury (HgL_i) 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 bioavaibility, 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, CH_3Hg and $(CH_3)_2Hg$, 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 ($SO4^{2-}$) is a weak ligand ($K = 10^{1.3}$) whereas sulfide (S^{2-}) 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 S^{2-}, but the importance of mercury-hydroxide complexes ($Hg(OH^+)$, $Hg(OH)_2$, and $Hg(OH)_3{}^-$), and mercury-chloride complexes ($HgCl^+$, $HgClOH$, $HgCl_2$, $HgCl_3{}^-$, and $HgCl_4{}^{2-}$) 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].

$$Hg^{2+} + SH^- \leftrightarrow HgS_{aq}{}^0 + H^+ \qquad K_f = 26.5$$

$$Hg^{2+} + SH^- \leftrightarrow HgS_{(s)} + H^+ \qquad K_f = 36.5$$

$$Hg^{2+} + SH^- \leftrightarrow HgSH^+ \qquad K_f = 30.5$$

$$Hg^{2+} + 2SH^- \leftrightarrow Hg(HS)_2{}^0 \qquad K_f = 37.5$$

$$Hg^{2+} + 2SH^- \leftrightarrow HgS_2H^- + H^+ \qquad K_f = 32.0$$

$$Hg^{2+} + 2SH^- \leftrightarrow HgS_2{}^{2-} + 2H^+ \qquad K_f = 23.5$$

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 (NH_2). Sulfur groups also exist in different oxidation states (R–SH, and R–SO_3 H), 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