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Discussions

Chemical and physical transformations of mercury in the ocean: a review

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Abstract

Mercury is well known as a dangerous neurotoxin enriched in the environment by human activities. It disperses over the globe, cycling between different environmental media. The ocean plays an important role in the global mercury cycle, acting both as a dispersion medium and as an exposure pathway. In this paper, we review the current knowledge on the major physical and chemical transformations of mercury in the ocean. This review describes the mechanisms and provides a compilation of available rate constants for the major processes in seawater, including oxidation and reduction reactions under light and dark conditions, biotic and abiotic methylation/demethylation, and adsorption by particles. In perspective, these data could be useful for the development of transport models describing processes undergone by mercury in the ocean and in air–seawater exchange.

1 Introduction

The role of the ocean in the biogeochemical cycling of mercury (Hg) is critical (Mason and Sheu, 2002; Sunderland and Mason, 2007; Strode et al., 2010). As estimated by Sunderland and Mason (2007), ocean waters contain 1750 Mmol (3.5×10^8 kg) of Hg, whereas the atmospheric reservoir contains 28 Mmol (5.6×10^6 kg). Ocean emissions contribute approximately 30–40 % of the current Hg input to the atmosphere, which includes anthropogenic sources, as well as evasion from soils and activities of hydrothermal vents and volcanoes (Sunderland and Mason, 2007; Pirrone et al., 2009). However, wet and dry deposition from the atmosphere is the greatest source of mercury in the oceans (90 %) (Mason et al., 1994; Andersson et al., 2011).

Once it enters the ocean water, mercury is subject to various biogeochemical processes that include association and dissociation with various ligands, precipitation and dissolution as minerals (e.g., mercury sulfide), oxidation and reduction reactions, methylation and demethylation, adsorption and desorption to suspended particulate

matter (SPM), sedimentation and resuspension, leaching and transport to groundwater, and uptake by aquatic biota (Stein et al., 1996; Haitzer et al., 2003; Fitzgerald et al., 2007; Liu et al., 2012).

Investigators have devoted keen attention to methylation because of its influence on human health; methylmercury, which is bioaccumulated in fish, is a potent neurotoxin (Mergler et al., 2007). Furthermore, increased exposure to methylmercury during gestation may result in neurobehavioral disorders in children (Grandjean et al., 1997; Van Oostdam et al., 2005; Selin, 2011). Thus, studies on the transformations of mercury in the ocean are an important part of research in the global cycle of mercury and its adverse impact on human health and the environment.

At present, there are many reports on the behavior of mercury in the ocean. However, measurement data on the levels of different mercury species as well as concentration profiles of these species in the water column are still limited. Consequently, estimates of mercury concentrations in the ocean and the ocean-atmosphere exchange have relied on a variety of models (e.g., Rajar et al., 2000; Mason and Sheu, 2002; Sunderland and Mason, 2007; Selin et al., 2008; Soerensen et al., 2010; Strode et al., 2010; Sunderland et al., 2010). To develop reliable models, processes occurring in the ocean water need to be understood, and data that include parameters characterizing the kinetics of these processes need to be acquired.

In Sect. 2 of this paper a review of mercury species in the ocean water is presented. Section 3 contains description of mercury reduction/oxidation reactions affected by solar radiation and occurring under dark conditions. Adsorption processes by particles and colloidal materials are discussed in Sect. 4. Section 5 considers biotic and abiotic methylation/demethylation reactions. The review includes description of the mechanisms and a compilation of available rate constants for the major processes of mercury transformations in seawater. This information can be useful for modelling of mercury behaviour in the sea and ocean water.

2 Mercury speciation in the ocean

Poissant et al. (2002) classified marine environments into three compartments: coastal zones, areas of upwelling, and open oceans. For these three zones, wet and dry deposition from the atmosphere is among the most significant sources of mercury. River systems are sources of mercury in specific coastal zones. Upwelling and sea currents may play a significant role in mercury transport to open oceans. Reactive mercury can be transported via particles from the upper layers of the ocean to deep ocean areas where the oxygen content is lower (Poissant et al., 2002). Deep ocean sediments, as well as estuarine and shelf sediments, are the most probable locations of methylmercury production, but methylation of mercury can also take place in the ocean water column (Whalin et al., 2007). Mercury cycle in the ocean is schematically shown in Fig. 1.

Mercury exists in different chemical and physical forms in the ocean waters (Hines and Brezonik, 2004). Bioavailability and toxicity of mercury in the ocean depend on its speciation in water (Bloom, 1992; Benoit et al., 2001a; Choe et al., 2003; O'Driscoll et al., 2003a, b).

Total mercury in the ocean includes dissolved species of bivalent mercury (Hg(II)), dissolved gaseous mercury (DGM), and particulate mercury species (Hg(P)). DGM is mainly composed of dissolved elemental mercury (Hg(0)) in the surface ocean. Elemental mercury is relatively volatile and it is the main form of mercury found in the atmosphere, whereas Hg(II) is the predominant form found in water and is bound to various organic and inorganic ligands (O'Driscoll et al., 2005, 2006). DGM may also include methylmercury, dimethylmercury, and ethylmercury, but concentrations of these forms is not significant in surface waters; however, the quantity of the methylated forms is relatively large at greater depths in the ocean (Amyot et al., 1997; Gill, 2008; Morel et al., 1998). A list of published DGM and total mercury concentrations in sea and ocean water is presented in Tables S1 and S2 (Supplement).

Many investigations have found differences in mercury concentrations among ocean basins (Laurier et al., 2004; Mason and Gill, 2005). For instance, in the Atlantic Ocean (Dalziel, 1995; Mason et al., 1998; Mason and Sullivan, 1999), mercury concentrations on average are higher than in the Pacific Ocean (Gill and Fitzgerald, 1988; Mason and Fitzgeraldt, 1991, 1993; Laurier et al., 2004) but lower than in the Mediterranean Sea (Cossa et al., 1997, 2004; Sunderland and Mason, 2007). Concentrations of total mercury in coastal waters and in the open ocean are on the order of 1 pM (Sunderland and Mason, 2007; Gill, 2008). Total mercury concentrations vary from 1 to 10 pM, whereas concentrations of DGM range from 0.05 to 0.25 pM. In general, concentrations of Hg(0) are higher near the air–water interface, whereas levels of methylmercury are higher near the sediments (Morel et al., 1998).

Hg(II) is a relatively reactive species in the environment. In seawater, Hg(II) is not present as a free ion, but rather mainly as inorganic and organic complexes. The concentration of the free metal ion (Hg^{2+}) is exceedingly small in seawater systems ($< 1 \times 10^{-18}$ M) (Mason and Fitzgeraldt, 1996). Consequently, the level to which Hg may transform between its different oxidation states and forms, is defined by the reactivity of the inorganic and organic complexes of Hg(II) (Whalin et al., 2007).

As shown by Morel et al. (1998), inorganic complexes of Hg(II) in natural aquatic systems include complexes with variable amounts of hydroxide ($[Hg(OH)]^+$, $Hg(OH)_2$, and $[Hg(OH)_4]^{2-}$), and of chloride ions ($[HgCl]^+$, $HgCl(OH)$, $HgCl_2$, $[HgCl_3]^-$, and $[HgCl_4]^{2-}$) depending on the pH and chloride concentration. For seawater, the most typical complexes are $[HgCl_3]^-$ and $[HgCl_4]^{2-}$. Complexes with bromide ions are also significant in seawater. Mercury hydroxide $Hg(OH)_2$ is the least stable of the known dissolved complexes of mercury. More stable complexes are those formed with the halides chloride and bromide. Stronger complexes are formed with organic matter and sulfides. Even in oxic surface waters, some Hg(II) may be bound to sulfides (S^{2-} and HS^-), which occur at nanomolar concentrations in surface seawater (Luther and Tsamakis, 1989; Morel and Hering, 1993; Morel et al., 1998; Whalin, 2005). Among the organic complexes of Hg(II), the most prevalent are complexes with humic acids. The reactions of ionic

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mercury are relatively fast, and it is believed that various species of Hg(II), including those in the particulate phase, are at equilibrium with each other. Reaction of mercury with particulate matter can lead to storage of the metal in the complex, or reactions may continue if the complex is surficial (Morel et al., 1998; Whalin, 2005).

Primarily, inorganic mercury in seawater occurs as Hg(II), but Hg(II) can undergo reduction to elemental mercury Hg(0). Complexes of mercury in the intermediate oxidation state Hg(I) are not stable; an exception is the dimer Hg_2^{2+}, but its concentration in seawater is inappreciable (Morel et al., 1998; Whalin et al., 2007).

In addition to the redox transformations, Hg(II) can be taken up by microorganisms, some of which methylate the Hg(II) complexes, forming methylmercury $[CH_3Hg]^+$, in which the oxidation state of Hg is still Hg(II). In organometallic species of mercury, the carbon-metal bonds are stable in water because they are partly covalent and because the hydrolysis reaction, which is thermodynamically favorable (and thus renders the organometallic species of most other metals unstable), is kinetically hindered. As a result, the dimethylmercury species, $(CH_3)_2Hg$, is unreactive. The monomethylmercury species, $[CH_3Hg]^+$, is usually present as chloro and hydroxo complexes (CH_3HgCl and CH_3HgOH) in oxic waters (Morel et al., 1998; Whalin et al., 2007). Methylmercury rather than inorganic mercury is bioconcentrated because it is better retained by organisms at various levels in the food chain. The relative efficiencies of the methylation and demethylation processes control the methylmercury concentration in water, and so determine the concentration of mercury in the biota. Anoxic waters and sediments are an important source of methylmercury in the ocean because of the methylating ability of sulfate-reducing bacteria (SRB). Methylmercury may be transported from anoxic layers to surface waters. Methylmercury may also be formed in the surface waters through biological or chemical processes. Demethylation occurs both photochemically and biologically (Morel et al., 1998).

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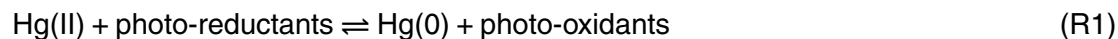Full Screen / Esc

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3 Mercury reduction and oxidation processes in the ocean

Redox reactions of mercury are significant parts of the mercury cycle in the ocean (see Fig. 1). Reduction results in the production of dissolved elemental mercury Hg(0) from bivalent forms of mercury. Elemental mercury can then volatilize to the atmosphere, thereby decreasing the levels of mercury in the ocean. This process is facilitated by wind and surface layer disturbances (O'Driscoll et al., 2003a, b; Orihel et al., 2007; Vost et al., 2012). Reduction of mercury can be both photochemical (Amyot et al., 1994, 2004; Zhang and Lindberg, 2001) and biotic (Mason et al., 1995; Siciliano et al., 2002).

Not all Hg(II) in natural waters is present in an easily reducible form (Strode et al., 2007). O'Driscoll et al. (2006) estimated that reducible mercury in freshwater lakes account for about 40 % of the total mercury. One of their hypotheses is that in order for mercury reduction to occur, Hg(II) must be complexed with dissolved organic matter (DOM), reduction subsequently occurs by electron transfer from the organic ligand to mercury (Allard and Arsenie, 1991; Spokes and Liss, 1995; Gårdfeldt and Jonsson, 2003). This process is inhibited by the presence of ligands such as chlorides, which may compete with organic matter for binding with mercury (Allard and Arsenie, 1991). The size of the reducible fraction is dependent on the incident wavelengths and the intensity of radiation. The most important types of radiation for mercury redox reactions are ultraviolet A (UV-A), which comprises wavelengths ranging from 315 to 400 nm, and ultraviolet B (UV-B) with wavelengths of 280–315 nm. More mercury is in the reducible form under UV-B radiation than under UV-A radiation. Under higher radiation intensities, the amount of reducible mercury has been observed to increase (Qureshi et al., 2010).

The oxidation of Hg(0) is one of the least understood parts in the mercury biogeochemical cycle. Oxidation decreases the concentration of DGM in aquatic environments and increases the concentration of Hg(II), which is the substrate for methylation (Lin et al., 2012). Oxidation of elemental mercury can also be both photochemical

(Voughan and Blough, 1998; Lalonde et al., 2001, 2004) and biotic (Siciliano et al., 2002).

Mercury oxidation can result in the formation of Hg(II) species, which then could be reduced (Whalin and Mason, 2006; Whalin et al., 2007). Some investigators believe that mercury oxidation can also result in production of nonreducible forms of Hg(II), which would imply that mercury redox reactions follow a three-species pathway (Qureshi et al., 2010) rather than a two-species pathway, as commonly believed (Whalin and Mason, 2006; Whalin et al., 2007).

3.1 Photochemical redox processes

3.1.1 Photochemical reduction

Photochemical reduction processes are characterized by high reduction rates that are in positive correlation with solar irradiance (Whalin, 2005). For example, in experiments by Amyot et al. (1994, 2000) a positive correlation was found between production of DGM and level of UV radiation. Furthermore, maximum evasion of Hg(0) over both seawater and river surfaces was observed during daylight hours (Gårdfeldt et al., 2001; Whalin et al., 2007).

Many experiments showed that Hg(II) reduction in natural waters is correlated with the DOM content (Allard and Arsenie, 1991; Xiao et al., 1995; Cossa and Liss, 1999). DOM behaves as a photosensitizer because it contains chromophores that can absorb light, and each photon it absorbs can initiate reactions (Spokes and Liss, 1995; Whalin, 2005; Whalin et al., 2007).

Hg(II) forms strong complexes with DOM. The estimated value of the stability constants (given as $\log K$) for these complexes is between 10.6 (Benoit et al., 2001b) and 24 (Lamborg et al., 2002). If these values are correct, then the majority of Hg(II) in freshwater and coastal seawater is organically complexed (Spokes and Liss, 1995; Whalin, 2005).

There are two hypothesized mechanisms that explain the correlation between DOM levels and mercury reduction (Whalin et al., 2007). The first mechanism is ligand-metal charge transfer by chromophoric material, in other words, the direct reduction of Hg(I) or Hg(II) (Allard and Arsenie, 1991; Spokes and Liss, 1995). The second is through the formation of reactive intermediate reductants such as $HO_2^\bullet$, which are formed through photolysis of DOM (Voelker et al., 1997; Zhang and Lindberg, 2001). Gårdfeldt et al. (2003), however, concluded that the latter mechanism is impossible under natural conditions and that the likely reaction mechanism for reduction is ligand-metal charge transfer.

Qureshi et al. (2010) hypothesized that if DOM is the main reductant, then mercury reduction might be dependent on both the nature and the total amount of DOM available in the ocean water. The nature of DOM could be estimated by observing the DOM fluorescence. Under UV-B radiation, changes in DOM characteristics are not significant (Lepane et al., 2003; O'Driscoll et al., 2006), and pseudo-first-order kinetics are valid. Changes in DOM composition under UV-A radiation are manifested by a decrease in DOM fluorescence (O'Driscoll et al., 2006). However, experiments showed that it is unclear whether and to what extent changes in DOM structure influence the reaction rate, results of these experiments confirm that a pseudo-first-order reaction of photochemical reduction occurs in natural waters (O'Driscoll et al., 2006; Whalin and Mason, 2006).

The DOM concentration in ocean water (40–100 µM; Ogawa and Tanoue, 2003) is much higher than the concentration of total mercury (1–10 pM; Mason et al., 2001). Qureshi et al. (2010) assumed that that DOM unlikely to be a limiting factor, even after considering the possibility that only part of the DOM concentration is involved in mercury reduction. Consequently, if DOM is the main reductant, then the reduction reaction has pseudo-first-order kinetics.

Thus, DGM production in natural waters can be described by the following equation (O'Driscoll et al., 2006):

$$Hg(II) + \text{photo-reductants} \rightleftharpoons Hg(0) + \text{photo-oxidants} \tag{R1}$$

This equation is often used in the elementary reaction method of determining the reduction rate constant. A list of published photoreduction rate constants in seawaters is presented in Table 1. As seen from the table the rate constants commonly range from 1.0×10^{-6} to $1.2 \times 10^{-3} \, \text{s}^{-1}$. Most researchers use a two-species pathway for describing mercury redox processes. In this pathway, two forms of mercury (Hg(0) and Hg(II)) participate in the redox reactions, and mercury reduction–oxidation is a simple reversible reaction.

Qureshi et al. (2010) disproved the assumption that mercury reduction–oxidation is a simple reversible reaction. In their experiments, DGM concentrations did not increase exponentially to a sustained maximum. Instead, the DGM concentrations reached a maximum usually within 1–5 h, and then decreased with time to a nonzero value after 24 h of irradiation. Thus, these results indicate that mercury reduction and oxidation in ocean water is not a simple two-species reversible reaction. Qureshi et al. (2010) proposed that along with Hg(0) and Hg(II), a new mercury species (Hg*) different from the reducible form of mercury Hg$_r$(II) is involved in mercury redox reactions. Hg* is produced by oxidation of Hg(0). They proposed two alternative reaction pathways involving Hg* that can be written as follows:

a. Pathway I:

$$\text{Hg}_r(\text{II}) \xrightarrow{k_{\text{red}}} \text{Hg}(0) \tag{R2}$$

$$\text{Hg}(0) \xrightarrow{k_1} \text{Hg}^* \tag{R3}$$

$$\text{Hg}^* \xrightarrow{k_2} \text{Hg}_r(\text{II}) \tag{R4}$$

where k_{red} is the photochemical reduction rate constant, k_1 is the rate constant for conversion of Hg(0) to Hg* in Pathway I and k_2 is the rate constant for conversion of Hg* to Hg$_r$(II).

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b. Pathway II:

$$Hg_r(II) \xrightarrow{k_{red}} Hg(0) \tag{R5}$$

$$Hg(0) \xrightarrow{k'_1} Hg^* \tag{R6}$$

$$Hg^* \xrightarrow{k'_2} Hg(0) \tag{R7}$$
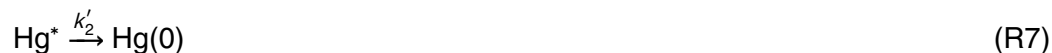
where k'_1 is the rate constant for conversion of Hg(0) to Hg* in Pathway II and k'_2 is the rate constant for conversion of Hg* to Hg(0). It should be noted, that values of the rate constant k'_1 in Pathway II evaluated by Qureshi et al. (2010) is expected to differ from the value of the rate constants k_1 in Pathway I.

For all samples and radiation intensities, it was found that k_1 or $k'_1 > k_{red} > k_2$ or k'_2. The presence or absence of microbes and colloidal phase did not appreciably influence mercury oxidation kinetics (Qureshi et al., 2010). It was also found that it is not possible to decide whether Pathway I or II provides a better description of the observations. The three-species pathways described by Qureshi et al. (2010) may be perspective for further investigating mercury redox chemistry. However, the two-species pathway has often been also considered as appropriate for describing mercury redox processes.

3.1.2 Photochemical oxidation

Mercury reduction has been described much earlier, and mercury oxidation has been considered to be a negligible process because of the "unreactive" nature of Hg(0). However, recent investigations (e.g., Whalin et al., 2007) showed that oxidation occurs in waters in many places, and that the rate constants for mercury oxidation are on the same order of magnitude as those for reduction. The rates of oxidation reactions are higher under solar irradiation.

Many studies suggest that the dominant oxidant of mercury in natural waters is the hydroxyl radical (OH$^\bullet$) (Gårdfeldt et al., 2001; Hines and Brezonik, 2004) which

is produced, for instance, by photolysis of nitrate/nitrite (Voughan and Blough, 1998) or Fe(III)-organic acid coordination compounds (Zhang and Lindberg, 2001).

Some investigators assumed that halides such as chloride and bromide may also be oxidants of Hg(0) in natural waters (Mason et al., 2001; Lalonde et al., 2001; Hines and Brezonik, 2004); various mechanisms have been hypothesized. The first is the reaction of halides (chloride or bromide) with $OH^\bullet$, which results in formation of additional oxidants such as $[OCl]^-$, $[OBr]^-$, or Br_2^- (Zafiriou et al., 1987; Whalin et al., 2007). Experiments have shown that this mechanism potentially occurs in simple artificial solutions (Mason et al., 2001), but is unlikely to occur in natural waters. Nevertheless, this mechanism is assumed to be acceptable for Hg(0) oxidation in aqueous solutions of the marine boundary layer (Lin and Pehkonen, 1999). The other proposed mechanism is formation of stable complexes of halides with mercury ions Hg(I) and Hg(II), which results in a decrease in the reduction rate and thereby contributes to greater net oxidation (Whalin et al., 2007).

Lalonde et al. (2004) observed that Hg(0) oxidation also appears to proceed in the presence of organic acids such as semiquinones in artificial saline water.

Qureshi et al. (2010) assumed that if hydroxyl radical is the main oxidant of mercury, then mercury oxidation may be dependent on the availability and concentration of $OH^\bullet$ radicals. The estimated concentration of $OH^\bullet$ radicals in seawater is approximately 10^{-17}–10^{-18} M (Mopper and Zhou, 1990), which can be accepted to be constant (Liu et al., 2007). This concentration is lower than that of mercury in ocean water. The rates of $OH^\bullet$ production are around $10\,nM\,h^{-1}$ ($0.24\,\mu M\,d^{-1}$) in the open ocean surface water and around $100\,nM\,h^{-1}$ ($2.4\,\mu M\,d^{-1}$) in coastal surface water (Mopper and Zhou, 1990). Thus, the total quantity of hydroxyl radicals obtained through supplying of $OH^\bullet$ during the reaction is much greater than the concentration of total mercury in the ocean water, and, therefore, pseudo-first-order kinetics can be assumed for oxidation reactions (Qureshi et al., 2010).

A list of published rate constants for photochemical oxidation in seawaters is presented in Table 2. The photooxidation rate constants range from 5.6×10^{-6} to

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$9.7 \times 10^{-4}\, s^{-1}$. According to these data, the rate of oxidation is equal to or greater than that of reduction in marine water.

The rate constant for mercury oxidation in marine water is greater relative to that in freshwater (Lalonde et al., 2001, 2004; Whalin et al., 2007; Soerensen et al., 2010), perhaps because of the production of aqueous halogen radicals, which are additional oxidants, through the reaction of hydroxyl radicals with halides (Cl^- and Br^-) (Zafiriou et al., 1987). This difference may also be due to the formation of stable Hg(II) complexes in marine water, which decrease the reduction rates and result in greater net oxidation (Whalin et al., 2007; Soerensen et al., 2010).

It must be noted that halogen ions, which occur in high concentrations in the ocean, are very important for mercury chemistry in the ocean water, because these ions may be ligands for mercury as well as photoreactants. Lalonde et al. (2001) and Qureshi et al. (2010) assumed that presence of chloride ions contributes to the stabilization of mercury ions in solution after oxidation; however, they believe that chloride ions are not oxidants of Hg(0).

3.1.3 Influence of radiation on photochemical redox reactions

Photochemical processes could be divided into three steps: (i) absorption of radiation of certain wavelengths resulting in the formation of an excited state; (ii) primary photochemical processes involving the transformation of the electronically excited state and its de-excitation; (iii) secondary reactions of various species that have been produced by the primary photochemical processes (Bonzongo and Donkor, 2003). Similar to that of other photochemical processes, the rate of photochemical redox reactions of mercury was also observed to be dependent on the intensity and type of radiation (Bash and Cooter, 2008; Qureshi et al., 2010).

O'Driscoll et al. (2006) and Bash and Cooter (2008) proposed that redox rates in surface waters could be calculated by taking account of the radiation intensity through

the following equation:

$$k(\lambda) = k_{ref} \frac{I(\lambda)}{I(\lambda)_{ref}} \tag{1}$$

where $k(\lambda)$ is the photoreduction or photooxidation rate as a function of radiation intensity $I(\lambda)$ at the wavelength λ; k_{ref} is the reference rate reported in the literature and $I(\lambda)_{ref}$ is the radiation intensity used in the measurement of k_{ref}.

As it was mentioned above Qureshi et al. (2010) proposed a three-species pathway for reduction and oxidation of mercury in ocean water. In this model, the mercury reduction rate constant at any intensity could be calculated through following equation: $k_{red}(I) = \alpha I$, where $\alpha = 0.12$ (0.10–0.15) $m^2 h^{-1} W^{-1}$.

The oxidation rate constants k_1 or k_1' increase with increasing radiation intensity of both UV-B and UV-A radiation:

$$k_1(I) = \beta I + k_{dark}, \tag{2}$$

where $\beta = 0.15$ (0.10–0.23) $m^2 h^{-1} W^{-1}$; $k_{dark} = 0.5$ (0.31–0.8) h^{-1};

$$k_1'(I) = \gamma I + k_{dark}', \tag{3}$$

where $\gamma = 0.15$ (0.10–0.23) $m^2 h^{-1} W^{-1}$; $k_{dark}' = 0.6$ (0.39–0.93) h^{-1}.

However, the rate constants k_2 and k_2' are independent of the intensity of radiation ($k_2 = 0.13$ (0.11–0.16) h^{-1}; $k_2' = 0.11$ (0.09–0.13) h^{-1}), and have similar values for both filtered and unfiltered water samples (Qureshi et al., 2010).

For the sake of simplicity (Soerensen et al., 2010) estimated that rate coefficients in mercury photochemical redox reactions could be calculated within observational confidence limits by the following equations, which are obtained on the basis of data reported by Qureshi et al. (2010):

$$k_{red} = 1.7 \times 10^{-6} I, \tag{4}$$

$$k_{ox} = 6.6 \times 10^{-6} I, \tag{5}$$

where k_{red} and k_{ox} (s^{-1}) are the photochemical reduction and oxidation rate constants; I (Wm^{-2}) is the average shortwave radiation intensity in the mixed layer.

3.2 Redox processes under dark conditions

3.2.1 Dark reduction

Investigations on mercury reduction in the dark showed that reduction does occur under dark conditions in unfiltered seawater, and that the rate constants are 2–20 times lower than those in the surface waters under solar light (Whalin et al., 2007). Since little oxidation or reduction was observed in filtered estuarine water in the dark, it was concluded that the dark reactions are microbially mediated. This conclusion is confirmed by others investigators. Therefore, Rolfhus and Fitzgeraldt (2004) estimated that about 20 % of the photoreduction reactions in Long Island Sound were microbially mediated. Mercury biotic reduction may be carried out, for example, by heterotrophic bacteria (Barkay et al., 1989; Mason et al., 1995; Siciliano et al., 2002) and by algae; thus, this process can play a role in detoxification (Ben-Bassat and Mayer, 1977, 1978; Whalin et al., 2007). A list of published reduction rate constants in seawaters under dark conditions is presented in Table 3. Dark reduction rate constants range from 2.8×10^{-8} to 8.3×10^{-5} s^{-1}.

For the modeling purposes Soerensen et al. (2010) assumed that the biotic reduction rate constant correlates with the net primary productivity (NPP, mgC m^{-2} d^{-1}), and that it could be described by the equation $k = 4.5 \times 10^{-6} \times$ NPP.

3.2.2 Dark oxidation

Amyot et al. (1997) found that in the coastal waters of the Gulf of Mexico, dissolved elemental mercury was oxidized under dark conditions (so-called dark oxidation), and the oxidation rate was estimated to be 0.1 to 0.4 h^{-1}. In similar experiments with river water, these authors showed that the oxidation rates are greater in the presence of

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high concentrations of chloride ions. The rate of mercury oxidation reaction was also found to depend on the presence of particles or colloids. However, results of these experiments may be insufficiently because of the loss of elemental mercury from solution through volatilization of Hg(0), adsorption of Hg(II) on the walls of containers used in the experiments, or both (Lalonde et al., 2001).

In a more recent study, Lalonde et al. (2001) found that the rate of oxidation of Hg(0) in a water sample from Baie Saint-Paul kept in the dark is significant, but about 10 times lower than that of the sample exposed to the light ($k = 0.06\,\text{h}^{-1}$ vs. $k = 0.58\,\text{h}^{-1}$), assuming first-order reaction. Additionally, in their investigation of waters from the St. Lawrence Estuary, Lalonde et al. (2004) observed no significant loss of Hg(0) under dark conditions. Amyot et al. (2005) concurred with previous authors; in their experiments, they found that dissolved Hg(0) did not rapidly oxidize in the presence of chloride ion or O_2 in the dark.

Oxidation in the absence of light is also effected by hydroxyl radicals produced from photochemically produced hydrogen peroxide via the Fenton reaction (Zhang and Lindberg, 2001). Accordingly, the kinetics of oxidation reaction under dark conditions depends on the intensity and duration of prior light exposure (Krabbenhof et al., 1998; Lalonde et al., 2001; Zhang and Lindberg, 2001; Garcia et al., 2005; Qureshi et al., 2010). Some published oxidation rate constants in seawaters under dark conditions are given in Table 3.

4   Adsorption processes of mercury in the ocean

Adsorption of Hg(II) and methylmercury onto suspended particles and sediments is very important for the fate of mercury in the ocean. Phase speciation and size distribution of mercury in the ocean influence it bioavailability, toxicity, and fate (Tessier and Turner, 1995; Choe et al., 2003).

It has been assumed that most of the particulate mercury is bound to the organic suspensions (Bryan and Langston, 1992; Boszke et al., 2002). A strong positive correlation

was observed between the concentration of total mercury and the content of organic matter in bottom sediments, which were measured in different parts of the world (Degetto et al., 1997; Muhaya et al., 1997; Boszke et al., 2002).

Other investigators believe that both types of solid particles, namely, inorganic minerals (e.g., metal oxides such as manganese or iron), and organic matter (e.g., humic substances), take part in mercury adsorption (Stein et al., 1996).

Mercury adsorption is usually a fast process. This conclusion was suggested by several experiments estimating rate of mercury adsorption (Lockwood and Chen, 1973; Baeyens et al., 1982).

4.1 Water-particle distribution coefficient

A fundamental parameter describing the distribution of a chemical species between the dissolved and solid phases in mercury adsorption is the distribution coefficient (or partition coefficient) K_d ($\mathrm{L\,kg}^{-1}$) (Stumm, 1992; Allison and Allison, 2005). The K_d for mercury is the ratio of adsorbed mercury concentration to the dissolved mercury concentration at equilibrium:

$$K_d = \frac{C_s}{C_d},\tag{6}$$

where C_s is the sorbed Hg(II) concentration (expressed in mg of metal per kg of sorbing material); C_d is the dissolved Hg(II) concentration (expressed in mg of metal per L of solution) (Allison and Allison, 2005). Despite that K_d is not a true thermodynamic parameter, it is widely used to describe adsorption processes because of its simplicity (Stordal et al., 1996; Wen et al., 1999; Leermakers et al., 2001).

The method of calculating K_d leads to negative value of the proportionality of K_d to the SPM concentration; this phenomenon is termed as the "particle concentration effect" (Benoit, 1995). For example, experiments by Choe et al. (2003) showed that the contribution of particulate mercury to the total mercury in unfiltered samples is small when the SPM concentration is low ($< \sim 20\,\mathrm{mg\,L}^{-1}$), and increases nonlinearly with

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increasing SPM concentration. When the SPM concentration is high ($> 30\,\mathrm{mg\,L^{-1}}$), Hg exists predominantly ($> 90\,\%$) in the particulate phase (Choe et al., 2003).

K_d depends on the nature of suspended solids or sediment and key geochemical parameters of the water, which primarily include the pH of the system and the nature and concentration of sorbents. Table 4 shows K_d values for mercury in natural environments.

4.2 Mercury adsorption on colloidal particles

A colloid is the phase defined as inorganic or organic material in the size range of $\sim 1\,\mathrm{nm}$ to $\sim 1\,\mathrm{\mu m}$. Since the colloidal phase in natural aquatic systems is characterized by a short residence time (Baskaran et al., 1992; Moran and Buesseler, 1992) and strong reactivity with trace metals (including mercury) (Honeyman and Santschi, 1989), colloidal materials have received considerable more attention recently (Benoit et al., 1994; Powell et al., 1996; Choe et al., 2003). The concentration of colloidal material depends on the SPM concentration:

$$[\text{colloid}] = k[\text{SPM}]^x, \tag{7}$$

where k is a constant, and x ranges between 0.5 and 1.0 (Benoit, 1995). Thus, the concentration of colloidally associated mercury increases as SPM concentration increases (Benoit, 1995; Quemerais et al., 1998; Benoit and Rozan, 1999).

Similar to the case of describing mercury adsorption on particles, variations of particle-water K_d can be developed:

$$K_d = \frac{[\text{particulate Hg (pM\,kg^{-1})}]}{[\text{filter-passing Hg (pM\,L^{-1})}]}, \tag{8}$$

$$K_p = \frac{[\text{particulate Hg (pM\,kg^{-1})}]}{[\text{dissolved Hg (pM\,L^{-1})}]}, \tag{9}$$

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$$K_c = \frac{[\text{colloidal Hg (pM kg}^{-1})]}{[\text{dissolved Hg (pM L}^{-1})]}, \tag{10}$$

The filter-passing fraction includes the dissolved and colloidal phases; consequently, K_p values are always be greater than K_d values. If K_p values are greater than K_c values, then particulate matter is a more important carrier phase of mercury than is colloidal matter (Choe et al., 2003). However, if $x < 1$ and concentrations of colloidal material and SPM are small then colloids could be more important.

Colloids significantly influence mercury adsorption on the noncolloidal particles and mercury transport in the ocean. Inorganic colloids in the ocean water could produce colloidal complexes with mercury species, and thereby reduce mercury adsorption on the noncolloidal particles and increase mercury transport in the ocean. The presence of organic colloidal matter may increase or reduce mercury adsorption on the non-coloidal particles, depending on the nature of organic colloids and particles, and on other geochemical factors (Sigleo and Means, 1990; Bengtsson and Picado, 2008; Liu et al., 2012).

Although both truly dissolved and colloidal mercury are present in solution, the mobility, reactivity, and bioavailability of these mercury fractions may be different. Colloidal mercury can undergo transport in the ocean but it is poorly bioavailable (Farrell et al., 1998).

The effect of colloids on the distribution of mercury species between the solution and solid phases could be accounted for when calculating K_d (Liu et al., 2012):

$$K_d = \frac{K_p}{1 + K_{ic}M_{ic} + K_{oc}M_{oc}}, \tag{11}$$

where K_p is the partition coefficient of mercury between the solid and truly dissolved phases; K_{ic} (or K_{oc}) is the distribution coefficient of mercury between the inorganic (or organic) colloidal and truly dissolved fractions; M_{ic} (or M_{oc}) is the concentration of inorganic (or organic) colloids.

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Thus, when studying mercury adsorption on solids in the presence of colloids, it may be necessary to differentiate mercury into particulate, colloidal, and truly dissolved phases, and then to calculate various distribution coefficients of mercury species between two phases (Liu et al., 2012).

5 Mercury methylation and demethylation processes

The most toxic mercury species commonly found in ocean waters is monomethylmercury $[CH_3Hg]^+$, which is produced by the methylation of the reactive, ionic form, primarily Hg(II) (Morel et al., 1998). The toxicity of methylmercury is due to its easy bioaccumulation and biomagnification to significant concentrations inside living cells and tissues of aquatic organisms; therefore, $[CH_3Hg]^+$ is hazardous to aquatic ecosystems and human populations (Lawson and Mason, 1998; Lawrence and Mason, 2001; Sunderland et al., 2006). Table 5 lists published rate constants for the methylation and demethylation processes in seawaters discussed below.

5.1 Methylation

Methylmercury in the ocean is derived predominantly from in situ production (Mason and Benoit, 2003; Mason et al., 2012). The most important locations of methylmercury production are estuarine and shelf sediments, deep ocean sediments, and the ocean water column (Whalin et al., 2007). Many natural biotic and abiotic processes in the ocean methylate Hg(II) (Ullrich et al., 2001; Boszke et al., 2002). Most investigators believe that most of the methylmercury production in aquatic environments occurs through biotic processes, and that abiotic methylation may be of secondary importance (Ullrich et al., 2001; Kempter, 2009). The methylation process is influenced by many factors, such as availability of inorganic Hg(II), activity of microorganisms, redox conditions, pH, temperature, salinity, and organic matter content (Stein et al., 1996; Morel et al., 1998; Ullrich et al., 2001; Boszke et al., 2002).

5.1.1 Biotic methylation

Biotic methylation of mercury occurs mainly in anaerobic conditions (e.g., in sediments), but it can also occur, although more weakly, in aerobic conditions (Matilainen and Verta, 1995; Regnell et al., 1996). In anaerobic conditions, methylcobalamin acts as a donor of methyl groups (Hamasaki et al., 1995; Hobman et al., 2000). In aerobic methylation, a significant role is played by sulfate-reducing bacteria (Leermakers et al., 1993; Matilainen, 1995; Benoit et al., 2001a), whose involvement in the process can be described as follows (Benoit et al., 2001a; Harmon et al., 2007):

$$SO_4^{2-} + OM \xrightarrow{SRB} S^{2-} + \text{products} \tag{R8}$$

$$Hg(II) \xrightarrow{S^{2-}} HgS \tag{R9}$$

$$HgS \rightleftharpoons Hg\text{-Ligand} \tag{R10}$$

$$Hg\text{-Ligand} \xrightarrow{\text{enzymes}} [CH_3Hg]\text{-Ligand}, \tag{R11}$$

where OM is organic matter. It should be noted that Reactions (R11) and (R11) occur in bacteria cells. In addition, some methylmercury in the ocean can be formed in aerobic conditions via conversion of dimethylmercury from deeper layers (Boszke et al., 2002).

The rate of $[CH_3Hg]^+$ formation may be affected by various environmental factors determining the supply of bioavailable Hg(II), the activity of methylating microbes, or both. In particular, methylmercury formation and accumulation depends on Hg(II) concentrations, sulfide concentrations, total organic carbon, and redox potential (Compeau and Bartha, 1984; Baeyens et al., 1998; Benoit et al., 1999, 2001c; Mason and Lawrence, 1999; Stoichev et al., 2004; Sunderland et al., 2006). In addition, the rate of methylation decreases with increasing salinity, most probably because of the inhibitory influence of chlorine complexes. The concentration of methylmercury was observed to increase in proportion to the concentration of free sulfide ions. However, the concentration of $[CH_3Hg]^+$ could subsequently decrease, most probably because of the formation of

dimethylmercury (Boszke et al., 2002):

$$2[CH_3Hg]^+ + H_2S \rightarrow (CH_3)_2Hg + HgS + 2H^+, \tag{R12}$$
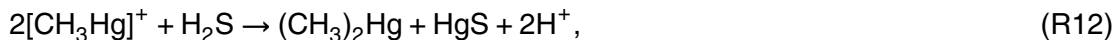
At excessively high concentration of sulfide ions, the concentration of dissolved Hg(II) is too low for methylation because of the formation the sparingly soluble HgS, which limits the availability of HgS to sulfate-reducing bacteria (Hammerschmidt and Fitzgerald, 2006; Kempter, 2009).

Altogether, methylation appears to depend largely on the initial characteristics of a specific ecosystem that limit the biotic production of methylmercury, such as bioavailable Hg(II) or other factors that affect microbial activity (Sunderland et al., 2006). The relative rates of production of monomethyl- and dimethylmercury are influenced by the mercury concentration and pH of the environment. Monomethylmercury is produced more easily in acidic environments at a relatively high mercury concentration, whereas dimethylmercury is produced more easily 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 (Galvin, 1996; Ullrich et al., 2001). It was estimated that the rate of monomethylmercury formation is about 6000 times higher than that of dimethylmercury formation; thus, only 3 % of organic mercury in the natural environment occurs as dimethyl species (Bryan and Langston, 1992). The production of dimethylmercury by microorganisms and its liberation to the environment is assumed to be a detoxification mechanism (Leermakers et al., 1993; Hobman et al., 2000).

Although Monperrus et al. (2007) observed that the most suitable conditions for methylation are in sediments, they showed that methylmercury formation may occur in oxic surface seawater via heterotrophic organisms (mainly phyto- and bacterioplankton). In surface coastal regions, methylation rates range from 0.008 to $0.063\,d^{-1}$; in open seawater, methylation rates range from 0 to $0.005\,d^{-1}$ (Monperrus et al., 2007; Kempter, 2009). Mercury methylation varies seasonally: high methylation rates are observed when water temperatures are high and nanoplanktons are present in sufficient amount (Monperrus et al., 2007).

In coastal surface water, high net methylation rates occur during periods of high primary production and biological turnover; and methylation rates increase when metabolic activities of phytoplankton (autotrophic) and pelagic bacteria (heterotrophic) are high. Therefore, mercury methylation is primarily a biotic process (Monperrus et al., 2007).

In the open ocean, the highest methylation rates were observed under dark conditions for samples with high nanoplanktonic activities. Nanoplanktons, which consist predominantly of autotrophic organisms, are located in the deeper euphotic zone, where photosynthetic active radiation is present only from 0.1 % to 1 % values of this radiation at the sea surface (Monperrus et al., 2007).

5.1.2 Abiotic methylation

In the marine environments, abiotic mercury methylation is of minor importance; nevertheless, it can occur (Fitzgerald et al., 2007; Kempter, 2009). One of the most substantial abiotic sources of methylmercury in the open ocean is the activity of hydrothermal vents and submarine volcanoes (Kempter, 2009). Information on methylmercury concentrations in the deep ocean suggest that methylmercury, which is produced by hydrothermal fluids, may deposit in sediments or decompose and then transfer to the ocean surface (Lamborg et al., 2006; Kempter, 2009).

The abiotic processes of methylation may or may not involve irradiation (Hamasaki et al., 1995). In reactions involving irradiation, the donors of methyl groups may be acetic acid, propionic acid, methanol, and ethanol, whereas reactions without irradiation include those with methylcobalamin, methylated tin compounds (in transmethylation), and those with humic substances (Hamasaki et al., 1995). Methylated tin and lead compounds can also be potential reagents in abiotic methylation of mercury, especially in tin- and lead-polluted regions (Ceratti et al., 1992; Weber, 1993; Ebinghaus et al., 1994). It is suggested that humic substances are most important methylating agents for mercury because of their relatively high concentration in aquatic environments as well as the comigration of mercury in water (Weber, 1993; Boszke et al., 2002).

5.2 Demethylation

Methylmercury is relatively stable and water-soluble in deeper ocean waters. It may therefore be transported through long distances from its site of methylation to its site of bioaccumulation (Mason and Fitzgeraldt, 1993; Mason et al., 1999, 2001; Whalin et al., 2007). However, in surface waters, methylmercury is relatively unstable. Demethylation may also occur in the water column and in sediments, and it is a very important process because it results in the decrease in the levels of toxic methylmercury (Kempter, 2009).

Experiments by Whalin et al. (2007) on methylmercury degradation in seawater demonstrated that the rate of this process is within analytical variability ($< 10\%$ loss) during incubation for several days; this corresponds to degradation rates of $< 10^{-7}\,s^{-1}$, which are much less than that for freshwater. However, experiments by Chen et al. (2003) showed that the rates of demethylation were similar in the presence or absence of Cl^- in experiments at high methylmercury concentrations ($3 \times 10^{-5}\,M$) under artificial light conditions. Accordingly, it is not clearly understood whether Cl^- enhances or hinders demethylation and other degradation pathways such as degradation in the presence of hydroxyl radicals (Chen et al., 2003).

Demethylation readily occurs in the sediments; rate constants for demethylation are estimated to be higher than those for methylation (Heyes et al., 2004, 2006; Sunderland et al., 2004; Kim et al., 2006; Whalin et al., 2007). The range for demethylation rates in aquatic systems is relatively wide (see Table 5). Demethylation can be mediated by both biological (through microorganisms) and abiotic routes (Hobman et al., 2000; Boszke et al., 2002).

5.2.1 Biotic demethylation

Biotic demethylation of mercury is a slow process, it is most effective against methylation in aerobic conditions (Boszke et al., 2002). Matilainen and Verta (1995) demonstrated that demethylation involves microorganisms, as evidence by the large influence of decreasing temperature on the rate of demethylation and cessation of demethylation

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in sterilized samples of water. Demethylation may require hydrolysis of the mercury-carbon bond along with the formation of Hg^{2+} and methane. Thereafter, Hg^{2+} may be reduced to volatile elementary mercury and released to the atmosphere, where it undergoes further conversions (Stein et al., 1996):

$$[CH_3Hg]^+ \rightarrow Hg^{2+} \rightarrow Hg(0) \tag{R13}$$

In sediments, there are two predominant pathways for demethylation: reduction and oxidation. The reduction mechanism is believed to proceed by activity of bacteria that exhibit the mer operon (a genetic resistance to mercury), and to therefore represent a detoxification process. The oxidation mechanism occurs through C_1 (one carbon) metabolism of bacteria. It must be noted that reductive demethylation may be predominant in sediments (Marvin-DiPasquale et al., 2000).

5.2.2 Abiotic demethylation

Abiotic demethylation is suggested to be predominantly a photochemical process. For example, Monperrus et al. (2007) suggested that demethylation in coastal and marine surface waters is mainly photochemically driven. Photochemical demethylation has been shown to occur in freshwater systems and in marine waters (Sellers et al., 1996; Whalin et al., 2007). Whalin et al. (2007) found that demethylation rates under high-illumination conditions are increased compared with those under low-illumination conditions. Since demethylation also occurs in samples incubated under dark conditions, demethylation in the oceanic water column probably has abiotic as well as biotic components.

Dimethylmercury is relatively rapidly degraded in the presence of light (2×10^{-4} to $2 \times 10^{-5}\,s^{-1}$) (Mason and Sullivan, 1999; Whalin et al., 2007). Dimethylmercury can be decomposed to methyl radicals and elemental mercury by photolysis, or oxidized by hydroxyl radical (Stein et al., 1996):

$$(CH_3)_2Hg + h\nu \rightarrow Hg(0) + 2CH_3^\bullet \tag{R14}$$

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$$(CH_3)_2Hg + OH^\bullet \rightarrow CH_3HgOH + CH_3^\bullet \tag{R15}$$

In the ocean, degradation of dimethylmercury to monomethylmercury was found to be primarily an abiotic process, whose rate increases in the presence of light (Mason, 1991; Mason and Sullivan, 1999).

The results reported by Whalin et al. (2007) and earlier studies confirm that demethylation rates are lower in saline waters. The absence of a large difference between samples incubated in the light and dark suggests the process that in saline waters is not strongly mediated by sunlight.

The results presented by Whalin et al. (2007) and Mason (1991) suggest that methylmercury is relatively stable in ocean waters. The stability of methylmercury in seawater is a very important parameter for estimating the quantity of methylmercury released from sediments, which may be transported to the water column and then to offshore regions where it may be accumulated in the food chain. If the stability is as high as demonstrated by Whalin et al. (2007), then coastal waters may be an important source of methylmercury for open ocean waters and the food chain.

6 Conclusions

In our study, we have reviewed the processes of physical and chemical transformations of mercury in the ocean. The ocean processes are tightly coupled with processes in the atmosphere and the air-water exchange. We have compiled values of available parameters for the dominant processes of the mercury cycle in the ocean, including photochemical reduction and oxidation rate constants, the mercury redox rate constants under dark conditions, biotic and abiotic methylation and demethylation rate constants, and values of the partition coefficients, which define mercury adsorption processes. In perspective, these data can be used for the development of transport models describing mercury processes in the ocean as well as air–seawater exchange.

Supplementary material related to this article is available online at http://www.ocean-sci-discuss.net/11/1/2014/osd-11-1-2014-supplement.pdf.

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Table 1. Rate constants of mercury photochemical reduction in seawater.

Location	Rate constant, s^{-1}	Comments	Reference
Baie Saint-Paul	1.6×10^{-4}	UV-B, $0.4\,\mathrm{w\,m^{-2}}$	Lalonde et al. (2001)
Patuxent River and Brigantine Island	1.2×10^{-3}	Visible, $240\,\mathrm{w\,m^{-2}}$	Whalin and Mason (2006)
Chesapeake Bay	6.5×10^{-4}	Visible, $240\,\mathrm{w\,m^{-2}}$	Bash and Cooter (2008)
Chesapeake Bay	$(4.3 \pm 1.1) \times 10^{-4}$	Natural light, isotope ^{202}Hg	Whalin et al. (2007)
Chesapeake Bay	$(8.7 \pm 4.0) \times 10^{-4}$	Natural light, isotope ^{199}Hg	Whalin et al. (2007)
Chesapeake Bay, estuarine waters	$(6.5 \pm 2.6) \times 10^{-4}$	Midday sun	Whalin et al. (2007)
Chesapeake Bay, coastal waters	$(6.5 \pm 1.5) \times 10^{-4}$	Midday sun	Whalin et al. (2007)
Chesapeake Bay, coastal shelf waters	$(0.29–3.7) \times 10^{-5}$	Surface waters, May 2005	Whalin et al. (2007)
Chesapeake Bay, coastal shelf waters	$(0.67–1.8) \times 10^{-6}$	Deep waters, May 2005	Whalin et al. (2007)
Chesapeake Bay, coastal shelf waters	$(0.1–29) \times 10^{-5}$	Surface waters, Jul 2005	Whalin et al. (2007)
Open Atlantic Ocean	$(0.42–2.58) \times 10^{-4}$	UV-A, $0.15\,\mathrm{w\,m^{-2}}$ UV-B, $0.4–0.9\,\mathrm{w\,m^{-2}}$	Qureshi et al. (2010)
Used for modelling	min: $< 1.0 \times 10^{-7}$ max: 8.7×10^{-4}		Soerensen et al. (2010)

Table 2. Rate constants of mercury photochemical oxidation in seawater.

Location	Rate constant, s^{-1}	Comments	Reference
Baie Saint-Paul	$(1.9 \pm 0.28) \times 10^{-4}$	UV-B, $0.49\,\mathrm{w\,m^{-2}}$	Lalonde et al. (2001)
Patuxent River and Brigantine Island	7×10^{-4}	Visible, $240\,\mathrm{w\,m^{-2}}$	Whalin and Mason (2006)
Chesapeake Bay	7.2×10^{-4}	Visible, $240\,\mathrm{w\,m^{-2}}$	Bash and Cooter (2008)
Chesapeake Bay	$(4.7 \pm 1.2) \times 10^{-4}$	Natural light, isotope ^{202}Hg	Whalin et al. (2007)
Chesapeake Bay	$(9.7 \pm 4.5) \times 10^{-4}$	Natural light, isotope ^{199}Hg	Whalin et al. (2007)
Chesapeake Bay, estuarine waters	$(7.2 \pm 2.9) \times 10^{-4}$	Midday sun	Whalin et al. (2007)
Chesapeake Bay, coastal waters	$(4.1 \pm 0.89) \times 10^{-4}$	Midday sun	Whalin et al. (2007)
Gulf of Mexico, coastal waters	$(0.25\text{–}0.28) \times 10^{-4}$	Natural light	Amyot et al. (1997)
Open Atlantic Ocean	$(1.11\text{–}5.28) \times 10^{-4}$	UV-A and UV-B	Qureshi et al. (2010)
Used for modelling	min: 5.6×10^{-6} max: 9.7×10^{-4}		Soerensen et al. (2010)

Table 3. Rate constants of mercury dark reduction and oxidation in seawater.

Location	Rate constant, s^{-1}	Comments	Reference
Dark reduction			
Open Atlantic Ocean	2.8×10^{-8}		Strode et al. (2007)
Chesapeake Bay and shelf	$(5.5–19.4) \times 10^{-7}$	Isotope amended deep water ($< 5\,\mathrm{m}$ from sediments)	Whalin et al. (2007)
Used for modelling	min: 3.5×10^{-7} max: 8.3×10^{-5}	Biotic reduction rate constant	Soerensen et al. (2010)
Dark oxidation			
Gulf of Mexico, coastal waters	$(0.25–0.33) \times 10^{-4}$	O_2 as the most likely oxidant	Amyot et al. (1997)
Open Atlantic Ocean	$(0.86–2.22) \times 10^{-4}$	For Pathway I	Qureshi et al. (2010)
Open Atlantic Ocean	$(1.08–2.58) \times 10^{-4}$	For Pathway II	Qureshi et al. (2010)
St. Lawrence estuary	1.67×10^{-5}		Lalonde et al. (2004)
Used for modelling	1×10^{-7}		Soerensen et al. (2010)

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Table 4. Coefficients of mercury water-particle partition in seawater.

Location	$\log K_d$, L kg^{-1}	Comments	Reference
San Francisco Bay estuary	5.64 ± 0.16	Sep/Oct 2000	Choe et al. (2003)
San Francisco Bay estuary	5.46 ± 0.30	Mar 2001	Choe et al. (2003)
North Atlantic	5.04		Mason et al. (1998)
Equatorial Pacific	6.0		Mason and Fitzgeraldt (1993)
Marine environments	5.5		Soerensen et al. (2010) and references therein
Literature survey	5.3 (4.2–6.9)	For suspended matter/water	Allison and Allison (2005)
Literature survey	5.3 (5.3–5.6)	For dissolved organic carbon/water	Allison and Allison (2005)
Literature survey	4.9 (3.8–6.0)	For sediment/water	Allison and Allison (2005)
Chosen for box diffusion model	6.08		Strode et al. (2010)

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Table 5. Rate constants of mercury methylation and demethylation in seawater.

Location	Rate constant, s^{-1}	Comments	Reference
Methylation			
South San Francisco Bay, California	6.4×10^{-8}	^{203}Hg(II)-methylation rate constant	Marvin-DiPasquale et al. (2007)
Mediterranean Sea	$(0.35–7.29) \times 10^{-7}$	In oxic surface seawater	Monperrus et al. (2007)
Chesapeake Bay and the mid-Atlantic continental margin	$(0.37–4.7) \times 10^{-5}$	In bottom sediments	Hollweg (2010)
Bay of Fundy	3.08×10^{-7}	In sediments	Heyes et al. (2006)
Demethylation			
South San Francisco Bay, California	3.6×10^{-6}	Me^{203}Hg-degradation rate constant	Marvin-DiPasquale et al. (2007)
Equatorial Pacific	10^{-8}		Mason and Fitzgeraldt (1993)
Chesapeake Bay	$< 10^{-7}$	In surface water	Whalin et al. (2007)
Bay of Fundy	6.67×10^{-5}	In sediments	Heyes et al. (2006)
South and equatorial Atlantic, Deep Sea	$(0.2–2.0) \times 10^{-5}$	$(CH_3)_2$Hg-degradation in the presence of light	Mason and Sullivan (1999)
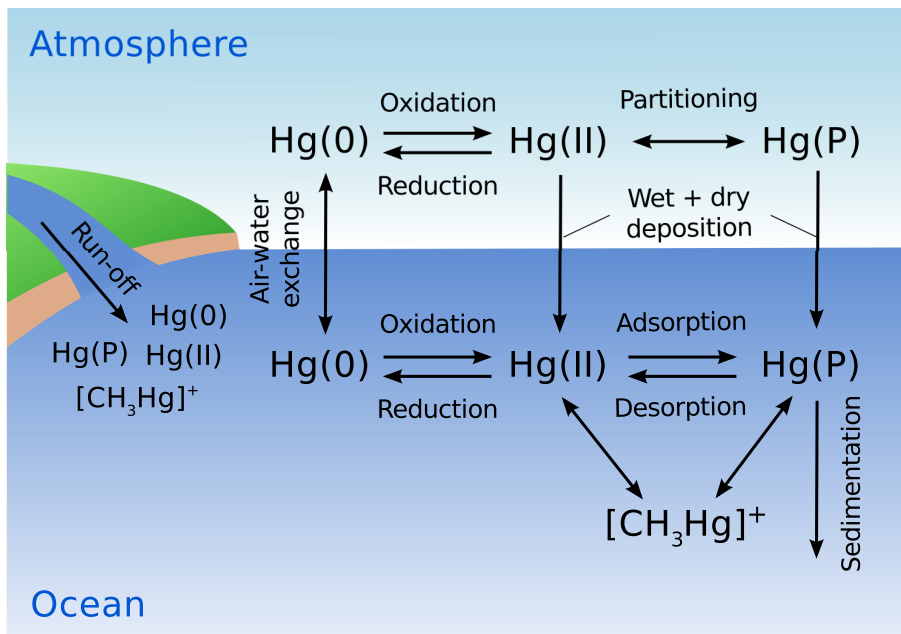
Fig. 1. General scheme of mercury transformations in the ocean.