



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. These data could be useful for the development of transport models describing processes undergone by mercury in the ocean.

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 seawater, 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 neurobehavioural 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 into the global cycle of mercury and its adverse impact on human health and the environment.

At present, there are many studies on the behaviour of mercury in the ocean (e.g. Fitzgerald et al., 2007; Gill, 2008; Mason et al., 2012). 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, 2007; Mason and Sheu, 2002; Sunderland and Mason, 2007; Zagar et al., 2007, 2014; Selin et al., 2008; Soerensen et al., 2010; Strode et al., 2010; Sunderland et al., 2010). To develop reliable models, current knowledge on processes occurring in seawater need to be summarized, and data that include parameters characterizing the kinetics of these processes need to be brought together.

In Sect. 2 of this paper a review of mercury species in seawater is presented. Section 3 contains a 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 seawater.

2 Mercury speciation in the ocean

Wet and dry deposition of mercury from the atmosphere is among the most significant sources of mercury in marine environments (Poissant et al., 2002). For example, Zagar et al. (2014) estimated that atmospheric deposition contributes about 45 % of total mercury input to the Mediterranean Sea. On a global basis, this proportion is higher and contribution of atmospheric deposition can exceed 75 % (Sunderland and Mason, 2007; Mason et al., 2012; Amos et al., 2013). River systems are sources of mercury in specific coastal zones. Upwelling and ocean currents may play a significant role in mercury transport to open oceans. Divalent 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). The most probable location of methylmercury production in open-ocean environments is the water column, whereas mercury methylation processes in sediments are important in estuarine and shelf zones (Lehnher et al., 2011; Kirk et al., 2012; Whalin et al., 2007). The mercury cycle in the ocean is schematically shown in Fig. 1.

Mercury exists in different chemical and physical forms in seawater (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 divalent 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 (Mason et al., 2012). Elemental mercury is relatively volatile and is the main form of mercury found in the atmosphere, whereas Hg(II) is the generally predominant form found in water, but surface seawater is supersaturated with respect to Hg(0) (Castelle et al., 2009) and its concentration could be comparable with the amount of divalent mercury (O'Driscoll et al., 2005, 2006). DGM may also include monomethylmercury, dimethylmercury, and ethylmercury, but concentrations of these forms are not significant in surface waters. However, the quantity of the methylated forms is relatively large at greater depths in the ocean (Amyot

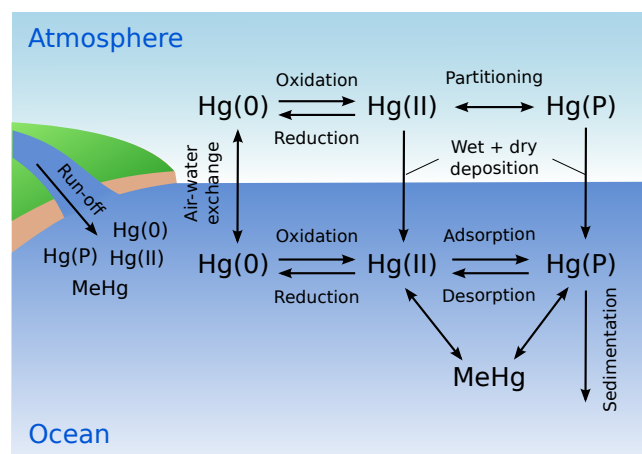


Figure 1. General scheme of mercury transformations in the ocean.

et al., 1997; Morel et al., 1998; Gill, 2008) and amount to 70 % of DGM (Cossa et al., 2011). A list of published DGM and total mercury concentrations in seawater 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 Fitzgerald, 1991, 1993; Laurier et al., 2004) but lower than in the Mediterranean Sea (Cossa et al., 1997, 2004; Sunderland and Mason, 2007). Total mercury concentrations in the open ocean vary from 0.4 to 3 pM (Lamborg et al., 2012; Mason et al., 2012), whereas concentrations of DGM range from 0.05 to 0.25 pM. As was shown by Fantozzil et al. (2007), the concentration of the DGM depends on the intensity of light radiation, the Hg(II) concentration, and the particular fraction of the dissolved organic matter (DOM). In general, concentrations of Hg(0) are higher near the air-water interface in comparison with concentrations of Hg(0) in deeper layers (Mason et al., 2012). However, sometimes, for example in the Southern Ocean, Hg(0) concentrations can increase in the water column to maximum values at 100–200 m as was shown by Cossa et al. (2011). Concentrations of monomethylmercury are low in the surface mixed layer and increase with depth to an intermediate maximum and then remain constant or decrease (Cossa et al., 2011). In coastal areas levels of MeHg are commonly higher near the sediments (Morel et al., 1998).

In seawater, Hg(II) is present as inorganic and organic complexes rather than as a free ion. The concentration of the free metal ion (Hg^{2+}) is exceedingly small in seawater systems ($< 1 \times 10^{-18}$ M) (Mason and Fitzgerald, 1996). Consequently, the level to which Hg may transform between its different oxidation states and forms is defined by the reactiv-

ity 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 ($[\text{Hg}(\text{OH})]^+$, $\text{Hg}(\text{OH})_2$, and $[\text{Hg}(\text{OH})_4]^{2-}$) and of chloride ions ($[\text{HgCl}]^+$, $\text{HgCl}(\text{OH})$, HgCl_2 , $[\text{HgCl}_3]^-$, and $[\text{HgCl}_4]^{2-}$), depending on the pH and chloride concentration. Complexes of mercury $[\text{HgCl}_3]^-$ and $[\text{HgCl}_4]^{2-}$ are predominant in seawater (Morel et al., 1998). Complexes with bromide ions are also significant in seawater. Mercury hydroxide $\text{Hg}(\text{OH})_2$ 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. 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 $[\text{CH}_3\text{Hg}]^+$, in which the oxidation state of Hg is still Hg(II) (Monperus et al., 2007). 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 favourable (and thus renders the organometallic species of most other metals unstable), is kinetically hindered. The monomethylmercury species, $[\text{CH}_3\text{Hg}]^+$, 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 (Morel et al., 1998). 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. Methylmercury in the ocean is predominantly derived from in situ production in the ocean water column through biotic and abiotic pathways (Lehnherr et al., 2011; Blum et al., 2013). Demethylation also occurs both photochemically and biologically (Morel et al., 1998; Mason, 2012).

3 Mercury reduction and oxidation processes in the ocean

The mercury cycle in the ocean includes redox reactions of mercury (see Fig. 1). Reduction results in the production of dissolved elemental mercury Hg(0) from divalent forms of mercury. Elemental mercury can then volatilize to the atmosphere, thereby decreasing the levels of mercury in the ocean (Andersson et al., 2011; Ci et al., 2011; Soerensen et al., 2013). 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 (Qureshi et al., 2010). O'Driscoll et al. (2006) estimated that reducible mercury in freshwater lakes accounts for about 40 % of the total mercury. Allard and Arsenie (1991) found that in order for mercury photoreduction to occur, Hg(II) must be complexed with DOM, reduction subsequently occurs by electron transfer from the organic ligand to mercury. This hypothesis was supported in other studies (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 (Qureshi et al., 2010). 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) plays an important role in the mercury biogeochemical cycle. Oxidation decreases the concentration of Hg(0) 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).

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

Location	Rate constant, s ⁻¹	Comments	Reference
Baie Saint-Paul	1.6×10^{-4}	Net (UV-B, 0.4 W m^{-2})	Lalonde et al. (2001)
Patuxent River and Brigantine Island	1.2×10^{-3}	Gross (visible, 240 W m^{-2})	Whalin and Mason (2006)
Chesapeake Bay	6.5×10^{-4}	Gross (visible, 240 W m^{-2})	Bash and Cooter (2008)
Chesapeake Bay	$(4.3 \pm 1.1) \times 10^{-4}$	Gross (natural light, isotope ²⁰² Hg)	Whalin et al. (2007)
Chesapeake Bay	$(8.7 \pm 4.0) \times 10^{-4}$	Gross (natural light, isotope ¹⁹⁹ Hg)	Whalin et al. (2007)
Chesapeake Bay, estuarine waters	$(6.5 \pm 2.6) \times 10^{-4}$	Gross (midday sun)	Whalin et al. (2007)
Chesapeake Bay, coastal waters	$(6.5 \pm 1.5) \times 10^{-4}$	Gross (midday sun)	Whalin et al. (2007)
Chesapeake Bay, coastal shelf waters	$(0.29\text{--}3.7) \times 10^{-5}$	Net (surface waters, May 2005)	Whalin et al. (2007)
Chesapeake Bay, coastal shelf waters	$(0.67\text{--}1.8) \times 10^{-6}$	Net (deep waters, May 2005)	Whalin et al. (2007)
Chesapeake Bay, coastal shelf waters	$(0.01\text{--}2.9) \times 10^{-4}$	Net (surface waters, Jul 2005)	Whalin et al. (2007)
Open Atlantic Ocean	$(0.42\text{--}2.58) \times 10^{-4}$	Gross (UV-A, 0.15 W m^{-2}) Gross (UV-B, $0.4\text{--}0.9 \text{ W m}^{-2}$)	Qureshi et al. (2010)
Used for modelling	min: $< 1.0 \times 10^{-7}$ max: 8.7×10^{-4}		Soerensen et al. (2010)

3.1 Photochemical redox processes

3.1.1 Photochemical reduction

Photochemical reduction processes are characterized by high reduction rates in comparison with reduction rates under dark conditions (see Tables 1 and 3), and the rates of photochemical reduction 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; Ci et al., 2011).

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 and 40 (Benoit et al., 2001b; Lamborg et al., 2002; Ravichandran, 2004). If these values are correct, then most 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

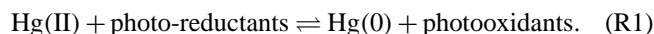
(Whalin et al., 2007). The first mechanism is ligand–metal charge transfer by chromophoric material; in other words, the direct reduction of Hg(I) or Hg(II) (Allard and Arsenie, 1991; Spokes and Liss, 1995). The second is through the formation of reactive intermediate reductants such as HO₂[•], which 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 seawater. 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 is 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 seawater (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 DOM is unlikely 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 (O'Driscoll et al., 2006):



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 (Morel et al., 1998; O'Driscoll et al., 2006). 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 seawater are 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:



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).

b. Pathway II:



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) are expected to differ from the value of the rate constant k_1 in Pathway I.

For all samples and radiation intensities, it was found that k_1 or $k'_1 > k_{\text{red}} > k_2$ 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 approach offered by Qureshi et al. (2010) could be more accurate for mercury redox chemistry and requires further investigation. Nevertheless, the two-species pathway is also often used for describing mercury redox processes (Morel et al., 1998; O'Driscoll et al., 2006).

3.1.2 Photochemical oxidation

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 in comparison to oxidation rates under dark conditions (Lalonde et al., 2004; Whalin, 2005).

Many studies suggest that the dominant oxidant of mercury in natural waters is the hydroxyl radical (OH*) (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 found that halides such as chloride and bromide may also be involved in the processes of Hg(0) oxidation 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*, which results in formation of additional oxidants such as [OCl][−], [OBr][−], or Br₂[−] (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) showed that if hydroxyl radical is the main oxidant of mercury, then mercury oxidation may be dependent on the availability and concentration of OH* radicals. The estimated concentration of OH* radicals in seawater is low (10^{-17} – 10^{-18} M) because of its very short life-

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

Location	Rate constant, s ⁻¹	Comments	Reference
Baie Saint-Paul	$(1.9 \pm 0.28) \times 10^{-4}$	Net (UV-B, 0.49 W m ⁻²)	Lalonde et al. (2001)
Patuxent River and Brigantine Island	7×10^{-4}	Gross (visible, 240 W m ⁻²)	Whalin and Mason (2006)
Chesapeake Bay	7.2×10^{-4}	Gross (visible, 240 W m ⁻²)	Bash and Cooter (2008)
Chesapeake Bay	$(4.7 \pm 1.2) \times 10^{-4}$	Gross (natural light, isotope ²⁰² Hg)	Whalin et al. (2007)
Chesapeake Bay	$(9.7 \pm 4.5) \times 10^{-4}$	Gross (natural light, isotope ¹⁹⁹ Hg)	Whalin et al. (2007)
Chesapeake Bay, estuarine waters	$(7.2 \pm 2.9) \times 10^{-4}$	Gross (midday sun)	Whalin et al. (2007)
Chesapeake Bay, coastal waters	$(4.1 \pm 0.89) \times 10^{-4}$	Gross (midday sun)	Whalin et al. (2007)
Gulf of Mexico, coastal waters	$(0.25-0.28) \times 10^{-4}$	Net (natural light)	Amyot et al. (1997)
Open Atlantic Ocean	$(1.11-5.28) \times 10^{-4}$	Gross (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)

time (Mopper and Zhou, 1990). However, the rates of OH^{*} production are around 10 nMh⁻¹ (0.24 μMd⁻¹) in the open ocean surface water and around 100 nMh⁻¹ (2.4 μMd⁻¹) in coastal surface water (Mopper and Zhou, 1990) and are much greater than the supply of mercury involved in the reaction. Therefore, pseudo-first-order kinetics can be used 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 9.7×10^{-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 than that in freshwater (Lalonde et al., 2001, 2004; Whalin et al., 2007), perhaps because of the production of aqueous halogen radicals, which are additional oxidants, through the reaction of hydroxyl radicals with halides (Cl⁻ and Br⁻) (Zafirou 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 seawater, 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, but 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:

$$k(\lambda) = k_{\text{ref}} \frac{I(\lambda)}{I(\lambda)_{\text{ref}}}, \quad (1)$$

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 $I(\lambda)_{\text{ref}}$ is the radiation intensity used in the measurement of k_{ref} .

As mentioned above, Qureshi et al. (2010) proposed a three-species pathway for reduction and oxidation of mercury in seawater. In this model, the mercury reduction rate constant at any intensity could be calculated: $k_{\text{red}}(I) = \alpha I$, where $\alpha = 0.12$ (0.10–0.15) m² 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:

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

where $\beta = 0.15$ (0.10–0.23) m² h⁻¹ W⁻¹, $k_{\text{dark}} = 0.5$ (0.31–0.8) h⁻¹;

$$k'_1(I) = \gamma I + k'_{\text{dark}}, \quad (3)$$

where $\gamma = 0.15$ (0.10–0.23) m² h⁻¹ W⁻¹, $k'_{\text{dark}} = 0.6$ (0.39–0.93) h⁻¹.

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	Modelling value	Strode et al. (2007)
Chesapeake Bay and shelf	(5.5–19.4) × 10 ⁻⁷	Isotope amended deep water (< 5 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) × 10 ⁻⁴	O ₂ as the most likely oxidant	Amyot et al. (1997)
Open Atlantic Ocean	(0.86–2.22) × 10 ⁻⁴	For Pathway I	Qureshi et al. (2010)
Open Atlantic Ocean	(1.08–2.58) × 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)

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 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):

$$k_{\text{red}} = 1.7 \times 10^{-6} I \quad (4)$$

$$k_{\text{ox}} = 6.6 \times 10^{-6} I, \quad (5)$$

where k_{red} and k_{ox} (s⁻¹) are the photochemical reduction and oxidation rate constants, and I (W m⁻²) is the average short-wave 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 other investigators (Mason et al., 2012; Hu et al., 2013). Rolfhus and Fitzgerald (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 modelling purposes Soerensen et al. (2010) assumed that the biotic reduction rate constant correlates with the net primary productivity (NPP, mg C m⁻² d⁻¹), and that it could be described by the equation $k = 4.5 \times 10^{-6} \times \text{NPP}$.

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 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 insufficient 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 ($k = 0.06$ h⁻¹ vs. $k = 0.58$ 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. As distinct from the studies of previous authors, Amyot et al. (2005) in their experiments found that dissolved Hg(0) did not rapidly oxidize in the presence of chloride ion or O₂ 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). 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 its bioavailability, toxicity, and fate (Tessier and Turner, 1995; Choe et al., 2003).

It has been found that most of the particulate mercury is bound to 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 (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:

$$K_d = \frac{C_s}{C_d}, \quad (6)$$

where C_s is the sorbed Hg(II) concentration (expressed in mg of metal per kg of sorbing material) and C_d is the dissolved Hg(II) concentration (expressed in mg of metal per L of solution) (Allison and Allison, 2005). Although 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 a decrease of K_d as SPM concentration increases. This phenomenon is termed

the “particle concentration effect” (Benoit, 1995). 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 ($< \sim 20 \text{ mg L}^{-1}$), and increases more slowly than linearly with increasing SPM concentration. When the SPM concentration is high ($> 30 \text{ mg L}^{-1}$), 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 $\sim 1 \text{ nm}$ to $\sim 1 \mu\text{m}$. 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 significant attention recently (Benoit et al., 1994; Powell et al., 1996; Choe et al., 2003). The concentration of colloidal material depends on the SPM concentration:

$$[\text{colloid}] = k[\text{SPM}]^x, \quad (7)$$

where k is a constant, and x ranges between 0.5 and 1.0 (Benoit, 1995). Thus, the concentration of colloiddally 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:

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

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

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

The filter-passing fraction includes the dissolved and colloidal phases; consequently, K_p values are always 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 $x < 1$ in Eq. (7) 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 seawater could produce colloidal complexes with mercury species, and thereby reduce mercury adsorption on the noncolloidal particles and increase mercury

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

Location	$\log K_d, \text{L kg}^{-1}$	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 Fitzgerald (1993)
Marine environments	5.5	Chosen for modelling	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)

transport in the ocean. The presence of organic colloidal matter may increase or reduce mercury adsorption on the noncolloidal 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. Bioavailability of colloidal mercury depends on size and species of particles; for example, HgS nanoparticles could be bioavailable for bacteria that methylate inorganic mercury (Farrell et al., 1998; Hsu-Kim et al., 2013).

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):

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

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, and M_{ic} (or M_{oc}) is the concentration of inorganic (or organic) colloids.

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 the phases (Liu et al., 2012).

5 Mercury methylation and demethylation processes

The most toxic mercury species commonly found in seawaters is monomethylmercury $[\text{CH}_3\text{Hg}]^+$, which is produced by the methylation of the reactive, ionic form, primarily Hg(II) (Morel et al., 1998; Driscoll et al., 2013). The toxicity of methylmercury is due to its easy bioaccumulation and biomagnification to significant concentrations inside living cells and tissues of aquatic organisms; therefore, $[\text{CH}_3\text{Hg}]^+$ 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 location of methylmercury production is the ocean water column (Lehnher et al., 2011; Mason, 2012; Blum et al., 2013). Inputs of $[\text{CH}_3\text{Hg}]^+$ from sediments and rivers could be comparable with water column production of methylmercury only in some specific zones such as estuaries and near-shore environments (Kirk et al., 2012; Driscoll et al., 2013). Mercury methylation occurs through biotic and abiotic pathways in the ocean (Ullrich et al., 2001; Boszke et al., 2002). Most investigators believe that most of the methylmercury production in aquatic environments occurs through biotic processes (Benoit et al., 2001a; Mason et al., 2012), and that abiotic methylation is less important, as shown below (Ullrich et al., 2001; Kemper, 2009; Mason, 2012).

Biotic methylation of mercury occurs in both anaerobic and aerobic conditions (Matilainen and Verta, 1995; Regnell et al., 1996). A significant role in methylmercury production in sediments and estuaries is played by sulfate-reducing bacteria (Leermakers et al., 1993; Matilainen, 1995; Benoit et al., 2001a; Harmon et al., 2007). Recent studies showed that in sediments mercury could be methylated also by other groups of bacteria, such as Fe-reducers in the genus *Geobacter* (Mason, 2012).

In sediments and estuaries the rate of $[\text{CH}_3\text{Hg}]^+$ formation may be affected by various environmental factors determining the supply of bioavailable Hg(II) and the activity of methylating microbes. In particular, methylmercury formation and accumulation depend 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

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

Location	Rate constant, s ⁻¹	Comments	Reference
Methylation			
South San Francisco Bay, California	6.4×10^{-8}	²⁰³ Hg(II)-methylation in sediments	Marvin-DiPasquale et al. (2007)
Mediterranean Sea	$(0.35\text{--}7.29) \times 10^{-7}$	In oxic surface seawater	Monperrus et al. (2007)
Chesapeake Bay and the mid-Atlantic continental margin	$(0.37\text{--}4.7) \times 10^{-5}$	In bottom sediments	Hollweg (2010)
Bay of Fundy	3.08×10^{-7}	In sediments	Heyes et al. (2006)
Canadian Arctic Archipelago	$(3.4\text{--}11.7) \times 10^{-8}$	In water column	Lehnerr et al. (2011)
Demethylation			
South San Francisco Bay, California	3.6×10^{-6}	Me ²⁰³ Hg-degradation in sediments	Marvin-DiPasquale et al. (2007)
Equatorial Pacific	10^{-8}	In deep waters	Mason and Fitzgerald (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	$(0.2\text{--}2.0) \times 10^{-5}$	(CH ₃) ₂ Hg-degradation in surface water	Mason and Sullivan (1999)
Monterey Bay, CA	1.3×10^{-7}	(CH ₃) ₂ Hg-photodegradation	Black et al. (2009)
Canadian Arctic Archipelago	$(3.1\text{--}5.2) \times 10^{-6}$	In water column	Lehnerr et al. (2011)

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 (Boszke et al., 2002).

Information on the methylating microbes is still limited for methylmercury production in the water column (Mason, 2012). Mercury methylation in the water column is correlated with the decomposition of organic matter (Sunderland et al., 2009). In Arctic and Antarctic regions concentrations of methylated mercury correlate with chlorophyll a concentrations, therefore [CH₃Hg]⁺ and (CH₃)₂Hg have a biogenic origin (Kirk et al., 2012). In addition, some methylmercury in the ocean can be produced from dimethylmercury (Lehnerr et al., 2011).

The relative rates of production of monomethylmercury 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 H₂S (Galvin, 1996; Ullrich et al., 2001). Bryan and Langston (1992) estimated that only 3% of organic mercury in the natural environment occurs as dimethylmercury. However, it was shown that concentrations of dimethylmercury (subpicomolar) can be higher than concentrations of monomethylmercury (less than 0.05 pM) in intermediate and deep waters (Black et al., 2009). The production of dimethylmercury by microorganisms and its liberation to the

environment are supposed to be a detoxification mechanism (Leermakers et al., 1993; Hobman et al., 2000).

Monperrus et al. (2007) observed that mercury methylation in the surface seawater varies seasonally: high methylation rates are observed when water temperatures are high and nanoplankton are present in sufficient amount. 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.

In the open ocean, the highest methylation rates were observed under dark conditions for samples with high nanoplanktonic activities. Nanoplankton, 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).

Abiotic methylation is not generally important in the natural environment (Mason, 2012). 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 suggests that methylmercury produced by hydrothermal fluids may deposit in sediments (Lamborg et al., 2006; Kempter, 2009). However, contribution of such sources is only significant locally. For instance, supply of methylmercury from hydrothermal fluids average 1–2% of all sources of methylmercury in the ocean (Mason et al., 2012).

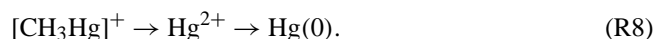
In abiotic methylation processes involving irradiation, the donors of methyl groups may be acetic acid, propionic acid, methanol, and ethanol, whereas reactions without irradiation include those with methylcobalamin, methylated tin compounds (in transmethylation), and those with humic substances (Hamasaki 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 could be important methylating agents (Weber, 1993; Boszke et al., 2002).

5.2 Demethylation

Processes of mercury demethylation in the water column influence the possibility of the transport of methylmercury through long distances from its site of methylation to its site of bioaccumulation. Lehnher et al. (2011) conclude that 90 % of $[\text{CH}_3\text{Hg}]^+$ in a particular water mass is demethylated during the water mass travelling over 20–200 km. Experiments by Blum et al. (2013) also demonstrate that mercury demethylation processes do not allow methylmercury to be transported through long distances since the rates of degradation and bioaccumulation are greater than vertical and horizontal fluxes of methylated mercury forms. Other recent studies (e.g. Driscoll et al., 2013) show that methylmercury should not persist over timescales of decades because of its rapid demethylation.

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 under light and dark conditions (Hobman et al., 2000; Boszke et al., 2002).

Matilainen and Verta (1995) demonstrated that demethylation involves microorganisms, as evidenced by the large influence of decreasing temperature on the rate of demethylation and cessation of demethylation in sterilized samples of water. Probably, in many cases biotic demethylation of mercury is a detoxifying process, but some organisms can use the low molecular weight methyl compounds as a carbon source (Mason, 2012). 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):



There are two hypothesized pathways for demethylation: reduction and oxidation (Mason, 2012). The reduction mechanism is believed to proceed in contaminated environments by activity of bacteria that exhibit the mer operon (a genetic resistance to mercury), and to therefore represent a detoxification process. Major products of reductive demethylation processes are CH_4 and $\text{Hg}(\text{II})$. The oxidation mechanism occurs in uncontaminated environments through C_1 (one car-

bon) metabolism of bacteria accompanied by the production of CO_2 as the major carbon product (Marvin-DiPasquale et al., 2000).

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. 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.

Mason and Sullivan (1999) have found that dimethylmercury could relatively rapidly degrade to monomethylmercury in the presence of light (2×10^{-4} to $2 \times 10^{-5} \text{ s}^{-1}$). However, more recent experiments by Black et al. (2009) showed that dimethylmercury is stable in natural seawater and the rate of its photodegradation is about $1.3 \times 10^{-7} \text{ s}^{-1}$. Dimethylmercury can be decomposed to methyl radicals and elemental mercury by photolysis, or oxidized by hydroxyl radical (Stein et al., 1996).

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. These data can be used for the development of transport models describing mercury processes in the ocean.

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