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Review

Particles-involved photochemical processes: A review for the case of mercury reduction in relation to aquatic mercury cycling

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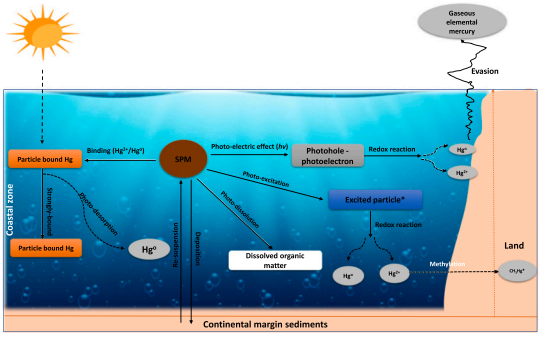
HIGHLIGHTS

- Comprehensive review of potential particle involvement in aquatic Hg photoreaction.
- Critical mechanistic insights of particle-mediated Hg photoreduction pathways.
- Implications of particle involvement in Hg redox reaction and aquatic Hg cycling.

GRAPHICAL ABSTRACT



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ABSTRACT

Mercury (Hg) is one of the toxic metals of global and environmental concern, with aquatic Hg cycling being central in determining the production of highly toxic methylmercury and the air-water Hg exchange influencing the long-range intercontinental atmospheric Hg transport. Both inorganic and organic forms of Hg can be bound by suspended particles, including inorganic minerals (in particular metal oxides/sulfides) and particulate organic matter. Photochemical transformation is a critical process in surface water, and the role of suspended particles in Hg redox photoreactions has increasingly emerged, albeit in limited studies in comparison to extensive studies on aqueous (homogeneous) photoreactions of Hg. The lack of understanding of what roles suspended particles play might result in inaccurate estimation of how Hg species transform and/or cycle in the environment. In view of this gap, this paper critically reviews and synthesizes information on the studies conducted on different natural surface waters with respect to the potential roles of suspended particles on Hg photo-redox reactions. It robustly discusses the various possible pathways and/or mechanisms of particle-mediated Hg (II) reduction, in enhancing or lowering the production of dissolved gaseous mercury. These processes include photo hole-electron pair formation and reactive oxygen species generation from particle excitation and their involvement in Hg photo-reduction, in addition to the light attenuation effect of particles. This paper highlights the necessity of future studies exploiting these particles-mediated Hg photoreactions pathways and the implications of including these

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heterogeneous photoreactions (together with particulate elemental Hg species) on the air-water Hg exchange estimation.

1. Introduction

Natural water bodies are populated with particles, conveniently known as suspended particulate matter (SPM) or otherwise referred to as aquatic particles, generally characterized as being greater, in size, than 0.45 μm (Hart, 1982). Suspended particles can be separated into biotic and abiotic categories. Biotic suspended particles refer to bacteria and phytoplankton (aquatic plants) while abiotic includes both inorganic and organic particulates (Tipping, 1981). In terms of composition, aquatic particles consist mainly of silica and clay substrates covered with oxides of metals and organic matter. Particulate organic matter (POM) is formed due to fragmentation of some chemically refractory polymeric compounds obtainable from plants. For example, POM consists of proteins, lipids, carbohydrate, chlorophyll, which are acid-unhydrolyzable fibres (Çoban-Yildiz et al., 2000; Cotrufo et al., 2013). Comparatively, with respect to bed sediments, suspended particles in shallow lakes and fluvial systems exhibit similar characteristics.

Suspended particles often act as carriers/ligands, allowing other metals or molecules to bind on their surfaces, creating complexes with new physicochemical properties. The presence of these particles, and their subsequent complexes impact the overall properties of the aquatic system as well. Suspended particles, in the form of suspended inorganic particulate minerals (lithogenic and authigenic) and POM, have been found to be effective at scavenging and transporting metal ions in marine environment (Lamborg et al., 2016). Fe and Mn (hydro)oxide are common examples of authigenic minerals whereby metal ions are scavenged (Rosati et al., 2018). Moreover, organic particulate complexes, binds and/or interacts with metals, among other molecules, in a series of chemical processes.

Suspended particles are often inherently light-sensitive (Zafiriou et al., 1984). Coined photochemistry, the study of chemical reactions that result from irradiation with light, has since revealed that these suspended particles react under light, typically visible and UV radiation from the sun (Turro and Lamola, 1977; Wang et al., 2020). Under illumination, the suspended particles behave frequently in a semiconducting fashion, and there is an induced charge separation that ultimately initiates photo-redox reactions (Vinodgopal and Kamat, 1992). These particles can serve as catalysts in the photolysis of other compounds within the interface; among these particles are often oxides of metal(loids) (Zhang, 2006). These properties make suspended particles an essential area of study, as they are crucial in understanding the complex mechanisms in which metals within the aquatic interface transform.

Of all metals, mercury (Hg) is of a global concern due to its high toxicity, especially for methylmercury (MeHg), and long-range atmospheric transport tendency of elemental Hg (Hg^0) with an estimated atmospheric residence time of 0.8 years to 1.7 years (Ariya et al., 2015). Its uniqueness is also embedded in its ability to exist in liquid state at room temperature, amalgamation with other metals, and inherent ability to exist as monomer in the vapor state. A large number of studies have been conducted on the homogeneous photoreactions of Hg in aquatic environment while few reported the impacts of suspended particles on Hg photoreactions, without exploring the possible mechanisms involved and assessing the environmental implication of these reactions (Gonzalez-Raymat et al., 2017). Fig. 1 shows the various pathways through which suspended particles can play roles in aquatic environment using Hg as an example.

Despite previous reviews on Hg in aquatic ecosystems, such as aqueous photoreactions of Hg (Luo et al., 2020), unique properties and fate of Hg^0 (Gonzalez-Raymat et al., 2017), factors influencing Hg

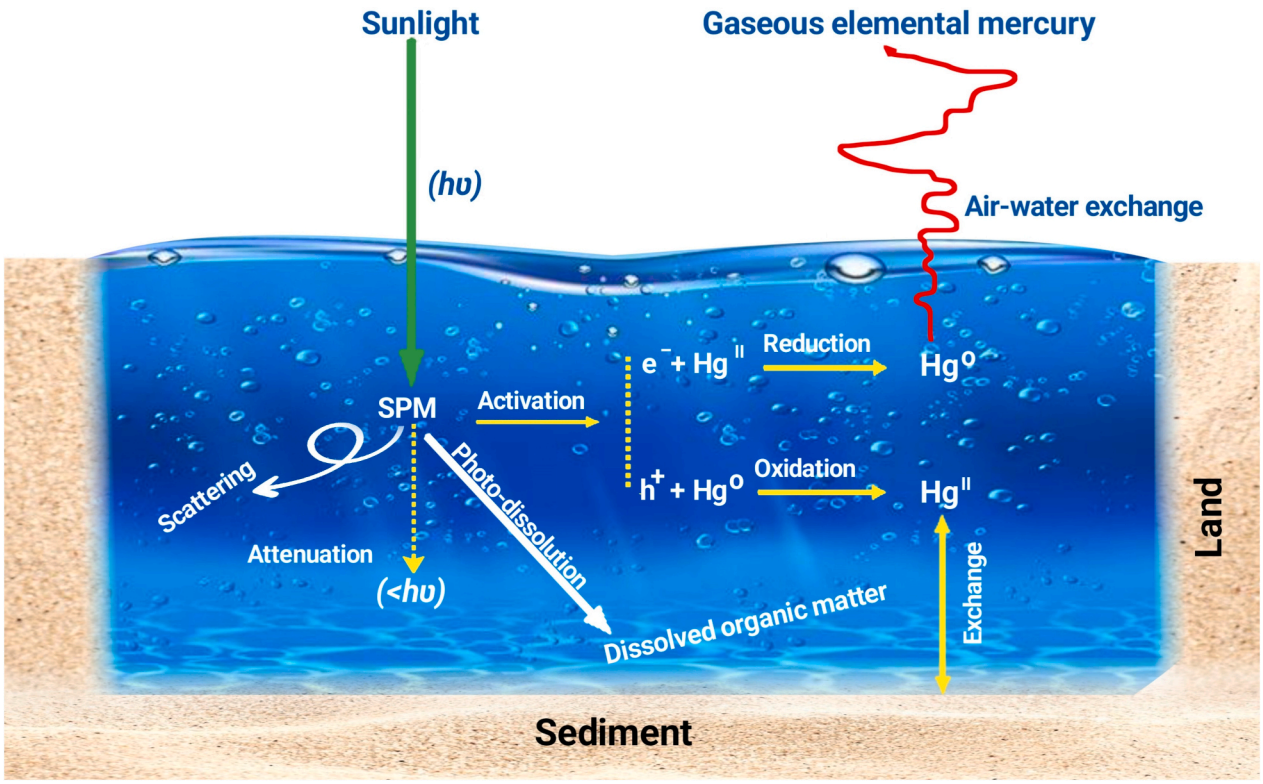

Fig. 1. Conceptual diagram illustrating the interaction of suspended particles with mercury species.

methylation (Ullrich et al., 2001), and Hg transport and fate models (Zhu et al., 2018), a review on the emerging role of SPM in Hg photoreactions is absent. The lack of understanding of the roles suspended particles play could lead to inaccurate estimation of the extent of Hg(II) reduction, Hg^0 oxidation, air-water exchange of Hg^0 and the bioavailability of Hg(II) for methylation in aquatic environment. Further, an in-depth understanding of mechanism of transformation and/or cycling of Hg species in the environment is germane in order to accurately provide data on biogeochemical cycling of Hg species. Sequel to this, the primary aim of this review is to understand the roles played by suspended particles in the photoreactions of Hg species under the influence of sunlight and to explore the possible mechanisms of particle-mediated photochemical reactions, in order to understand the air-water gaseous elemental Hg exchange and the overall contribution of particles in the cycling of Hg species.

2. Aquatic photochemistry

2.1. A brief overview of aquatic photochemistry

Photons are regarded as energy source that drives photochemical processes (Chowdhury et al., 2014). These processes include photolysis, photodegradation, photocatalysis, and photo-redox reactions, and other means - which can occur directly and indirectly. Direct photochemical processes occur when the compound in question directly absorbs energy from photon, thereby undergoing a chemical reaction (Zeng and Arnold, 2013). Photolysis and photodegradation describes the dissociation of a molecule or compound when irradiated with natural or artificial photons of energy greater than the chemical bonding in the molecule or compound (Arnold and McNeill, 2007; Luo et al., 2020; Zhang, 2006). During photocatalysis, photon-absorbing specie(s), otherwise known as photosensitizer or photocatalyst, absorbs the photon energy to become electronically excited via photo-induced bandgap excitation to photogenerate hole, electron and/or reactive oxygen species (ROS) required for photo-redox reactions (Chen et al., 2023; He et al., 2021; Serpone et al., 1987). Typical instances of direct photochemical processes are photolysis and/or photodegradation of mercuric hydroxide to produce elemental mercury and water (Nriagu, 1994). However, most photochemical reactions proceed through indirect pathways, such as in photocatalysis, where photosensitizers other than the compounds of interest are excited by the absorption of photons, producing reactive intermediates that then transform the molecule of interest (Lam et al., 2003). Some photosensitizers in natural waters comprise of dissolved organic matter (DOM), nitrate, nitrite, carbonate, and iron ions, among other metal ions, organic compounds as well as natural oxide minerals (Lam et al., 2003; Luo et al., 2020; Vost et al., 2011). The most common reactive intermediates involved in indirect photochemical processes are free radicals and ROS such as oxygen free radicals, peroxyl radicals, hydroxyl radicals, nitrate radicals, carbonate radicals and singlet oxygen transients (Lam et al., 2003; Zhang, 2006). ROS especially drives a large portion of indirect photooxidative reactions.

2.2. Heterogeneous photochemistry

Photoactive suspended particles in water are often photosensitizers with a tendency to ultimately produce ROS (Mayer et al., 2006). Suspended particles could exist as potential reactive species involved in indirect photochemical processes, and these heterogeneous photochemical reactions generally occur on surfaces exposed to (photolytic) solar irradiation (Vähätalo, 2009). Some oxides and sulfides of metals (loids), which are usually major components of suspended particles, can produce ROS by acting as photosensitizers or photocatalysts (Rani et al., 2022). A list of reactions showing photo-induced production of ROS via hematite, as a model semi-conducting material, is given as follows (Felizzetti et al., 1990):

$$\propto -Fe_2O_3 + h\nu \rightarrow \propto -Fe_2O_3\ \left(h^+_{VB}, e^-_{CB}\right) \quad (1)$$

$$O_2 + e^-_{eq} \rightarrow O_2^{\cdot -} \quad (2)$$

$$O_2^{\cdot -} + H^+ \rightarrow HO_2^{\cdot} \quad (3)$$

$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \quad (4)$$

$$HO_2^{\cdot} + O_2^{\cdot -} \rightarrow HO_2^- + O_2 \quad (5)$$

$$HO_2^- + H^+ \rightarrow H_2O_2 \quad (6)$$

$$H_2O_2 + e^-_{eq} \rightarrow {}^{\cdot}OH + {}^{-}OH \quad (7)$$

$$H_2O_2 + O_2^{\cdot -} \rightarrow {}^{\cdot}OH + {}^{-}OH + O_2 \quad (8)$$

$$H_2O_2 + h\upsilon \rightarrow 2\,{}^{\cdot}OH \quad (9)$$

When irradiated, the photoactive metal oxides or metalloids produce photo-holes and photo-electrons that interact with surface trapped water to produce different ROS. A few examples of particles that can act as photocatalysts or photosensitizers are clay, minerals, zinc oxide as zincite, titanium dioxide as titania, iron oxides, etc. A number of metal chalcogenides and oxides can be found in natural aquatic environment with semi-conducting properties, which can be activated via solar irradiation (Pelizzetti and Calza, 2002). Some minerals or oxides which occur naturally in aquatic environment possess characteristic semiconducting features, as presented in Table 1.

However, in a circumstance whereby non-semiconducting suspended particles become coated with organic matters (OM), the OM may act as light trapping part of the coated particle whereby various chemical reactions, leading to formation of ROS, can take place. These formed radicals then react with chemical substances that are within the proximity of the irradiated OM-coated particles and ultimately transforming the chemical substances of interest (Appiani and McNeill, 2015; Pham et al., 2020). For instance, based on previous studies (Appiani and McNeill, 2015; Carlos et al., 2012; Hu et al., 2022; Lee et al., 2023; Pham et al., 2020), the interactions of light with organic matter coated particles can be likely expressed as:

$$\mathrm{OM-coated\ particle} + h\upsilon \rightarrow [\mathrm{OM-coated\ particle}]^+ + e^-_{eq} \quad (10)$$

Studies on photochemical reactions related to OM-coated particles and even POM are limited, despite extensive studies on DOM photochemistry. Based on these previous studies, we speculate that the irradiation of a coated substrate may photoactivate the particle and induces photo(catalytic) degradation of the OM to CO_2 and water, but these reactions could depend on the thickness of the coating (Fig. 2). When organic matter layer on photoactive particles is thin, it is more likely that sunlight penetrates, photoactivates and generates charge carriers (Fig. 2a), unlike a thickly coated photoactive particles that ultimately results in photo-dissolution of the OM on the particles (Fig. 2b) (Geller,

Table 1
Bandgap energies (E_g) for some naturally occurring metal oxide/chalcogenide semiconductors (Felizzetti et al., 1990). Reproduced with permission from (Felizzetti et al., 1990). Copyright (1990) Elsevier.

Semi-conductor	Bandgap (eV)	Wavelength of light equivalent to bandgap (nm)
α-Fe_2O_3	2.3	530
TiO_2	3.0–3.3	376–413
β-MnO_2	0.26	4770
ZnO	3.3	376
PbO_2	1.7	729
$BaTiO_3$	3.3	376
CdS	2.4	517
β-HgS	0.54	2300

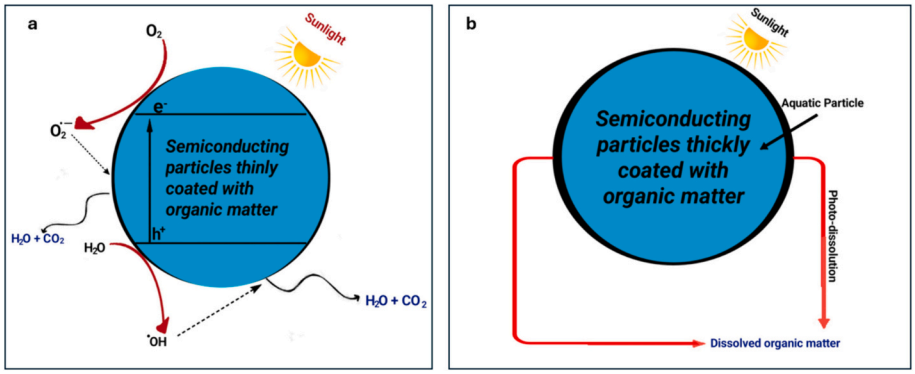

Fig. 2. Hypothetical outcomes of irradiation of OM-coated (semiconducting) particles for (a) thinly-coated and (b) thickly-coated particles.

1985; Hu et al., 2021; Lee et al., 2019; Mayer et al., 2006, 2012). Moreover, it is important to mention that the energy of irradiation must be greater than or equal to E_g of the photoactive particles to be capable of generating e^- and h^+ pairs.

The photo-generated ROS can contribute to heavy metal cycling in the aquatic environment. Hydroxyl radical is one of the most reactive of ROS (Parrino et al., 2020). In aquatic environment, hydroxyl radical has a concentration of 10^{-7} M (Moffett and Zika, 1987) in surface seawater and it is capable of initiating reduction and/or oxidation of metals. Hydrogen peroxide is another reactive intermediate closely related to hydroxyl radical generation and can also be involved in metal redox reactions. Examples of reactions of hydrogen peroxide with iron (Fe) and copper (Cu) by acting as either oxidant or reductant are generalized (with M denoting metals) below (Barb et al., 1949; Haber et al., 1934; Pham et al., 2013; Tacu et al., 2021). These mechanisms have been suggested for different types of aqueous chemical and biochemical systems and are perhaps effective in seawater and other natural waters (Moffett and Zika, 1987).

For oxidation:

$$M^{n+} + H_2O_2 \rightarrow M^{(n+1)+} + OH^- + {}^{\cdot}OH \text{ (slow)} \quad (11)$$

$$M^{n+} + {}^{\cdot}OH \rightarrow M^{(n+1)+} + OH^- \text{ (fast)} \quad (12)$$

For reduction of copper (II) and iron (III), the following mechanism was proposed (Barb et al., 1949):

$$H_2O_2 \rightleftharpoons H^+ + HO_2^- \text{ (fast)} \quad (13)$$

$$M^{(n+1)+} + HO_2^- \rightarrow M^{n+} + HO_2 \text{ (slow)} \quad (14)$$

$$HO_2 \leftrightarrow H^+ + O_2^{\cdot-} \text{ (fast)} \quad (15)$$

$$M^{(n+1)+} + O_2^{\cdot-} \rightarrow M^{n+} + O_2 \text{ (fast)} \quad (16)$$

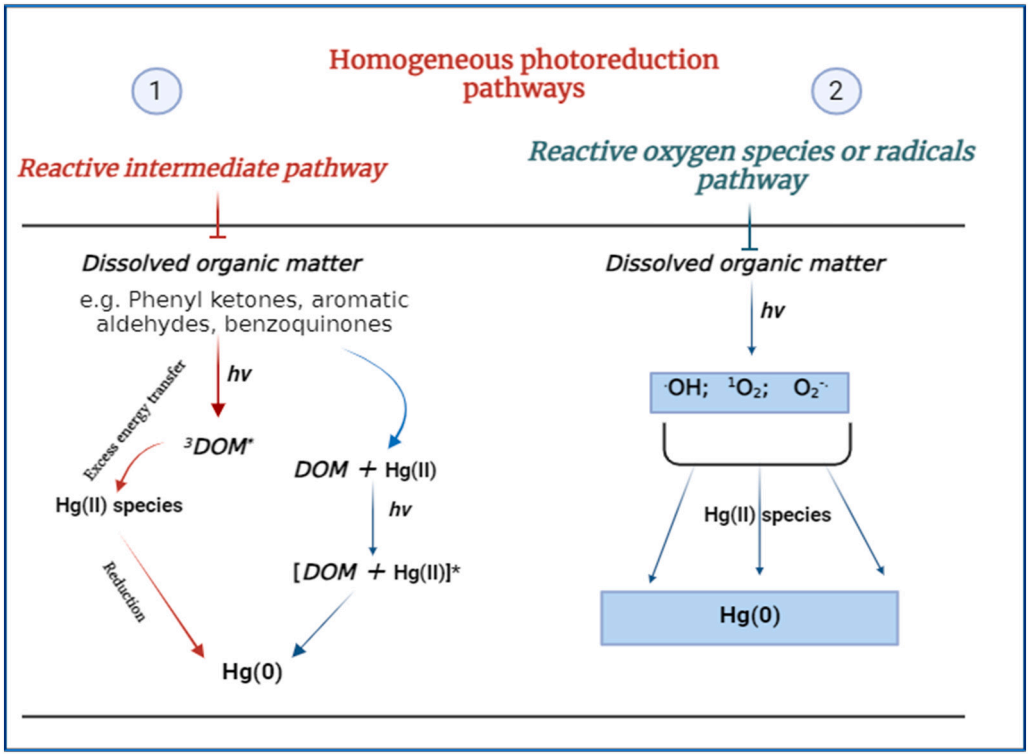

Fig. 3. Homogeneous photoreduction pathways for Hg(II).

3. Aquatic photochemistry of mercury

3.1. Homogeneous photoreactions of Hg in aquatic environments

Most previous studies on Hg photochemical transformation concerned homogeneous Hg photoreactions in the dissolved phase, where DOM seemed to play a major role. The interaction of DOM with Hg(II) occurs in various ways, thereby influencing the bioavailability, transport, and transformation of Hg(II). In its role as transforming agent, researchers have suggested ROS (Wen et al., 2023; Yang et al., 2023) and photochemically excited reactive intermediates from DOM (Nriagu, 1994) as two important mechanisms for the photoreduction of Hg(II) to Hg^0. Fig. 3 shows the mechanisms and/or pathways of homogeneous photoreduction of Hg(II).

DOM can be photochemically excited and then, loses its energy by reducing Hg(II) to Hg^0. In the excitation process, photons of light energetically induce the excitation of DOM to excited state (DOM*), which is capable of transferring this energy to nearby species like Hg(II) and then return to ground state (DOM) (Ravichandran, 2004). The excited energetic donor atom in the DOM transfers its energy to Hg(II) to induce reduction to Hg^0. The chromogenic nature and solar radiation interaction pattern of proteins, flavins, humic acids, and other organic compounds (as DOM components) in natural water has made this mechanism a suitable pathway for Hg(II) conversion to Hg^0. On the other hand, these chromogenic DOM may form complex with Hg(II) in natural water. As soon as the complex is irradiated, it becomes excited and later loses its energy by internal transfer of electron to Hg(II) to form Hg^0. The photo-induced reduction by excited DOM* intermediate and/or excited complex formed can be depicted by the following equations:

$$\mathrm{DOM}\rightarrow\{\mathrm{DOM}\}^{*}\xrightarrow{h\nu}\{\mathrm{DOM}^{+}+\mathrm{e}^{-}\}^{*}+\mathrm{Hg}^{2+}_{\mathrm{complexed}}\rightarrow\mathrm{DOM}^{+}+\mathrm{Hg}^{0} \quad (17)$$

$$\mathrm{DOM}+\mathrm{Hg}^{2+}\xrightarrow{h\nu}\{\mathrm{DOM}-\mathrm{Hg}^{2+}\}^{*}\rightarrow\mathrm{DOM}^{+}+\mathrm{Hg}^{0} \quad (18)$$

The complexation between DOM and Hg, which is usually strong, may affect photochemical reactions of Hg. A stronger complexation between Hg and DOM could hinder an efficient Hg(II) photoreduction when Hg(II) binds to the thiol functional group on DOM (Jiang et al., 2015; Luo et al., 2020). The following reactions provides information on how functional groups might influence the complexation stability constant and photoreduction of Hg(II) (Jiang et al., 2015; Skyllberg, 2008).

$$2\mathrm{SH}^{-}+\mathrm{Hg}^{2+}\rightleftharpoons\mathrm{Hg(SH)}^{o}_{2(aq)}\ \mathrm{Log\ K}=37.7 \quad (19)$$

$$2\mathrm{OH}^{-}+\mathrm{Hg}^{2+}\rightleftharpoons\mathrm{Hg(OH)}^{o}_{2(aq)}\ \mathrm{Log\ K}=22.2 \quad (20)$$

$$\mathrm{OH}^{-}+\mathrm{SH}^{-}+\mathrm{Hg}^{2+}\rightleftharpoons\mathrm{HOHgSH}^{o}_{(aq)}\ \mathrm{Log\ K}=30.3 \quad (21)$$

Moreover, ROS have been suggested to be involved in other pathways for effective photoreduction of Hg(II) to Hg^0 (He et al., 2014; Nazhat and Asmus, 1973). For instance, the formation of organic free radicals during photolysis may be responsible for photoreduction of Hg (II) (He et al., 2012). Hydrogen peroxide and superoxide anion, which can be formed from the sunlight-involved transformations of DOM in natural waters (Schroeder et al., 1991), are suitable example of ROS for Hg(II) photoreduction (Leenheer, 1994). Similarly, the presence of organic acids like formate, acetate and oxalate in natural waters can photochemically form hydroperoxyl (HO_2) radicals (Barth et al., 1990; Pehkonen and Lin, 1998), which can reduce Hg(II) via a two-step mechanistic reduction pathway involving unstable Hg(I) (Pehkonen and Lin, 1998). Other photosensitive intermediates, such as carboxyl radical anion produced from photolysis of Fe(III)-organic complexes, may also promote photoreduction of Hg(II) (Ababneh et al., 2006).

3.2. Suspended particle-involved photoreactions of Hg species

The tendency of Hg species partitioning on particles in aquatic environments has long been known, as both inorganic and organic forms of Hg(II) compounds can be bound by suspended particles, including inorganic minerals and POM (Nriagu, 1994; Stein et al., 1996). The importance of inorganic minerals and organic matter in determining particulate Hg speciation can vary, depending heavily on the nature of the solid particles and the chemical speciation of Hg, among many other factors (Ullrich et al., 2001). The formation of particulate Hg(II) for inorganic minerals, particularly metal (hydr)oxides, may occur through the complexation of hydroxylated Hg species with hydroxyls on the mineral surfaces (≡S-OH) (Jung et al., 2015; Walcarius et al., 1999). The organic matter fraction of suspended particles can form OM-bound particulate Hg through Hg complexation with various S-, O-, and N-containing functional groups (Skyllberg, 2008; Skyllberg et al., 2006; Skyllberg and Drott, 2010). As a result, particles serve as a vehicle that is responsible for the transport of Hg in natural aquatic systems (Jędruch et al., 2017; Turritto et al., 2018) as well as reaction medium for Hg transformation.

Although previous studies have extensively investigated aqueous phase Hg photochemical reactions, particles-involved Hg photochemical transformation has received limited attention, despite the prevalence of particle-bound Hg species. There are a few studies attempted to examine the role of SPM photoreduction of Hg(II) through the comparison between filtered and unfiltered natural water samples, mainly considering the light attenuation effect of SPM. These studies have reported conflicting results of enhancing or inhibitory effect of SPM on Hg^0 generation, with enhanced, decreased or non-significantly changed Hg^0 production in filtered lake water samples (Beucher et al., 2002; Garcia et al., 2005a; Whalin et al., 2007). It is important to note that the reports of previous studies on magnitude of Hg^0 production by comparing filtered and unfiltered water lacked information and/or data on particulate Hg^0 (Beucher et al., 2002; Garcia et al., 2005b; O'Driscoll et al., 2018; Washburn et al., 2019). Hg^0could be bound by SPM to form potentially non-purgeable particulate Hg^0, and thus the quantification of Hg^0in the bulk liquid phase alone will present an inaccurate estimation of Hg^0 generated. A high fraction of particulate Hg^0, after photoreduction experiment, was found on SPM through thermal desorption (Wang et al., 2015, 2023). The controversies in the effect of filtration on Hg(II) reduction and the presence of particulate Hg^0 that was often not quantified and included in the data interpretation of Hg(II) photoreduction suggest that SPM may play roles beyond merely attenuating light in photochemical reactions of Hg species. The possible pathways for particles to mediate Hg photochemical transformation are shown in Fig. 4 and discussed below. Fig. 4 shows the conceptual diagram detailing the various possible photoreactions particle-bound Hg undergoes in natural waters. These pathways include 1) particle-bound Hg as an intact Hg species could become excited on absorption of light and then release Hg^0 through the electron transfer between particulate and Hg; 2) the particle itself could be photoexcited and generate electron-hole pairs inducing Hg redox reactions; and 3) ROS could be produced on the particle surface upon light irradiation and mediate Hg redox reactions.

3.2.1. Photoreactions of Hg species in relation to Hg adsorption on SPM

Depending on SPM composition and type, the adsorption of Hg onto SPM may vary which subsequently influences Hg photochemistry. POM is an efficient candidate for Hg adsorption and pronounced photoreactivity (Helms et al., 2014; Southwell et al., 2010) and can result in a range of effects on photoreduction of Hg(II) (Ravichandran, 2004). POM can absorb in the UV and visible region of the spectrum, depending on their composition and other factors (Appiani and McNeill, 2015; Mayer et al., 2006). Metal-ligand complexes are often formed during Hg (II) adsorption onto POM (Ravichandran, 2004; Soto Cárdenas et al., 2018). The strength of the bond depends on the hard-soft acid base

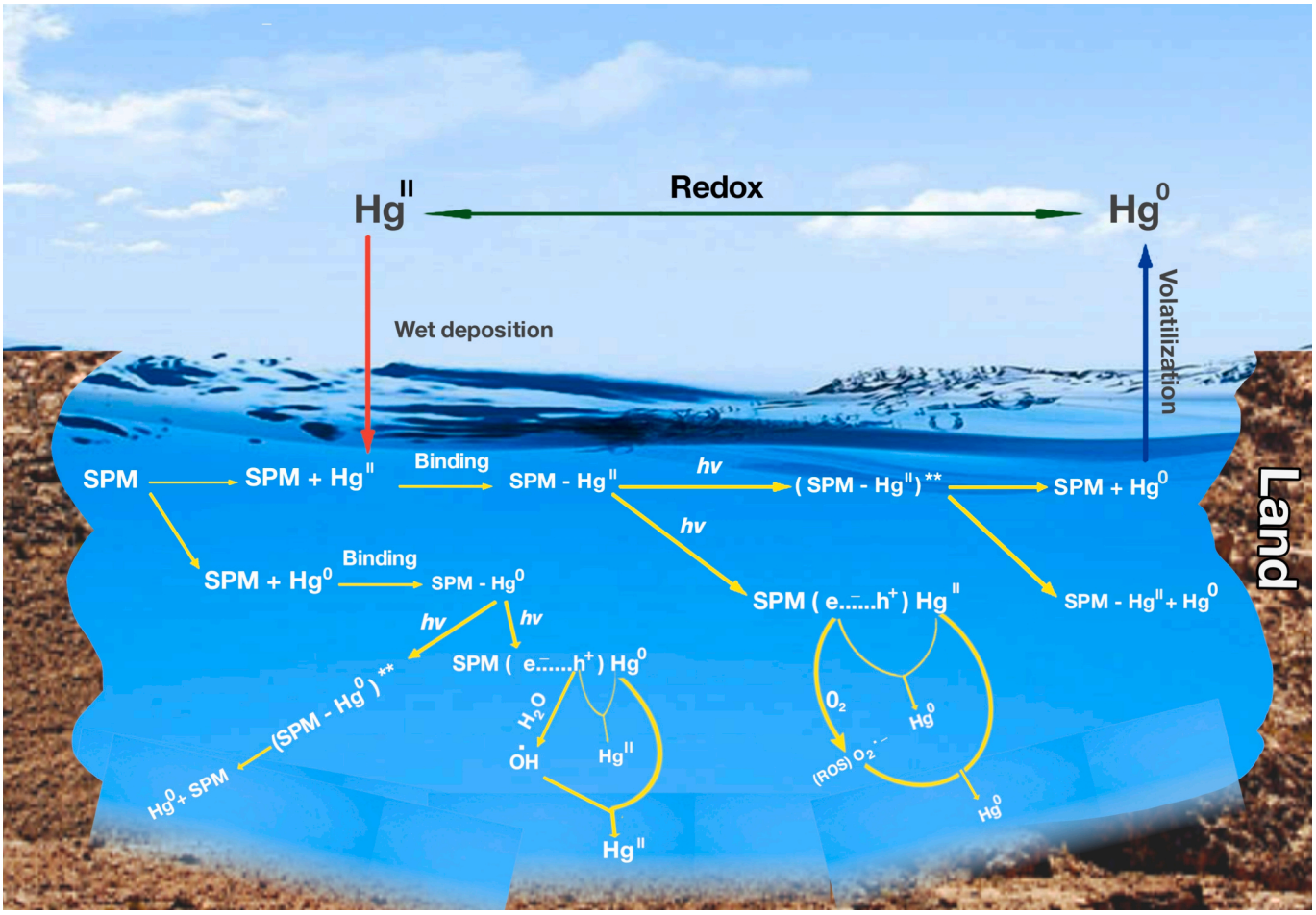

Fig. 4. Conceptual diagram detailing the various photoreactions SPM bound Hg (SPM—Hg) undergoes in natural waters.

theory. It is opined that POM–Hg bonds typically have energies consistent to the 200–800 nm and that the transfer of energy within the POM-Hg complex during irradiation can lead to photo-redox reactions (Billing, 1997; Schiebel et al., 2015), as it was observed that Hg(II) species bound to POM could release Hg^0 during photo-excitation (Hu et al., 2020; Pham et al., 2020).

For suspended inorganic particles, the sorption of Hg(II) will takes place via either physisorption or chemisorption (Eq. (22)), which can be differentiated using standard free energy of (ad)sorption. For instance, $\Delta G_{ads} > -20$ kJ/mol, $\Delta G_{ads} < -40$ kJ/mol, and $-20 > \Delta G_{ads} > -40$ kJ/mol are usually used to indicate physisorption, chemisorption and mixed adsorption, correspondingly (Chen et al., 2022). Physisorption involves weaker bond and Hg may be more easily dissociated by the use of lower energy – presumptively as Hg(II) species, in the presence of light (Archer and Blum, 2018; Xia et al., 2019). Photoreaction of chemisorbed Hg on particles may depend on the energy of the light to cleave the oxygen/sulfur-Hg bond to release Hg^0 through the potential pathways below that we reason could occur (Eqs. (23)–(24) and Fig. 4). In any of the proposed pathways, each exhibits different relationships with surrounding variables.

$$2FeO(OH) + Hg^{2+} \rightarrow 2FeOOHg + 2H^+ \quad (22)$$

$$FeOOHg \xrightarrow{hv} 2FeOOHg^* \quad (23)$$

$$2FeOOHg^* \rightarrow 2FeO + O_2 + 2Hg^0 \quad (24)$$

3.2.2. Photo-induced electron-hole pairs and Hg redox reactions

Semiconducting minerals and oxides (α-Fe_2O_3, β-MnO_2, ZnO, PbO_2, CdS, M-sulfides (M, metal), etc) are often present in aquatic environment (Litter et al., 1991). Upon exposure to light of equal or greater energy than the bandgap, photoholes and photoelectrons may be generated (Eq. (25)) (Litter et al., 1991; Mills and Le Hunte, 1997; Nriagu, 1994; Zhang, 2006). The minerals (metal sulfide, metal oxide or mixture) and the irradiated form are expressed as M_aY_b and M_aY_b ($electron^-$.....$hole^+$), respectively. M_a *and* Y_b represent metal and oxygen or sulfur atom(s) while e^-_{CB} and h^+_{VB} are photoelectrons and photoholes generated on surfaces of the semiconducting minerals/oxides, respectively.

$$M_aY_b + hv(> E_g) \rightarrow M_aY_b\ (electron^- \ldots hole^+) \rightarrow e^-_{CB} + h^+_{VB} \quad (25)$$

The photoelectron generated often has potential of +0.5 eV to −1.5 eV with sufficient energy to reduce Hg(II) (Eq. (26)) while the holes created in the valence band (VB) with +1.0 to 3.5 eV is strongly oxidizing (Eq. (27)), possibly inducing redox reactions of Hg as shown in Eqs. (26)–(27) and Fig. 5. For reduction of Hg(II) to Hg^0, it is most likely to occur when Hg(II) binds to the surface of the photo-activated particles as the diffused photoelectrons are more likely to react with abundant dissolved molecular oxygen than to reduce aqueous Hg(II) in bulk natural water, since electron lack selectivity in its reaction with other chemical species (Nriagu, 1994). Eqs. (28) and (29) depict photoreactions of titanium dioxide-sorbed Hg, as an example of mineral-Hg complex (Nriagu, 1994):

$$2e^-_{CB} + Hg^{2+} \rightarrow Hg^0 \quad (26)$$

$$2h^+_{VB} + Hg^0 \rightarrow Hg^{2+} \quad (27)$$

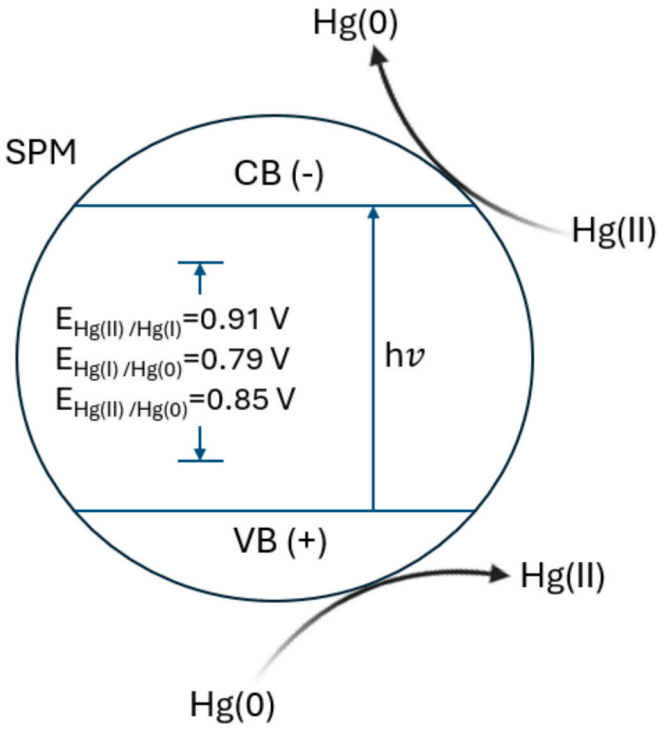

Fig. 5. Possible Hg redox reactions on particle surface induced by photoelectron and photo-hole.

$$TiO_2 + Hg^{2+} \rightarrow [TiO_2 - Hg]^{2+} \quad (28)$$

$$[TiO_2 - Hg]^{2+} \overset{h\nu}{\rightarrow} \left[TiO_2\ 2e^-_{CB} \ldots 2h^+_{VB} - Hg\right]^{2+} \rightarrow \left[TiO_2 \ldots 2h^+_{VB}\right] + Hg^0 \quad (29)$$

Furthermore, where charge recombination is feasible, irradiated semiconducting minerals will be inefficient at carrying out photoreactions of Hg species. Kinetic and thermodynamic factors play roles in circumventing the unwanted recombination reactions of electron-hole pairs. Thermodynamically, separation of photo-generated carriers occurs when the Fermi levels of semi-conducting particle and the neighboring water are in thermodynamic equilibrium, causing semiconductor interfacial band bending and potential difference gradient (Gerischer, 1979; Langford and Carey, 1987). In the electrical field induced by the band bending, photoelectrons usually travel in opposite path from holes (Stumm, 1992). Kinetically, this depends on the rate of either thermal reaction or photoreaction. Although, the main factors are the extent of overlap of the distribution of energy levels of solute species as well as the degree of exergonicity of the interfacial electron transfer (Gerischer, 1979).

3.2.3. Particle-induced ROS and Hg redox reactions

It is also feasible to have some ROS generated via the reaction of the e^-_{CB} and h^+_{VB} with water by redox reaction or interfacial electron transfer (Kisch, 2013; Nosaka and Nosaka, 2017). This photo-catalyzed transfer of electron mechanism may involve the removal of electron from the valence band to the conduction band of naturally occurring transition or non-transitional metal oxides and transfer it to O_2 with corresponding generation of superoxide anion radical, O_2^-. $^1O_2$ also has enough single-electron redox potential to compete with O_2 in accepting the photo-generated electron to produce superoxide radical, O_2^- (Buettner, 1993). Generally, the primary conditions under which superoxide anion radical is generated are direct-surface oxygen electron transfer, photo-induced electron transfer, the decomposition of hydrogen peroxide and surface intermolecular electron transfer (Georgiou et al., 2015). The photo-generated superoxide anion radical may be adsorbed on the surface of minerals where it could saturate their positively charged sites (Georgiou et al., 2015).

ROS, such as hydroperoxyl radical, has been found to play a major role in reduction of Hg(II) in water (Pehkonen and Lin, 1998; Vaughan and Blough, 1998; Zepp et al., 1987). The following series of reactions would be feasible in natural water environment owing to reduction of Hg(II) by ROS that would be formed:

$$Hg^{2+} + 2O_2^- \rightarrow Hg^0 + 2O_2 \quad (30)$$

$$Hg^{2+} + HO_2 \rightarrow Hg^+ + O_2 + H^+ \quad (31)$$

$$Hg^+ + HO_2 \rightarrow Hg^0 + O_2 + H^+ \quad (32)$$

3.2.4. Light attenuation effects of SPM affecting Hg photoreactions

An indirect way for SPM to play a role in Hg photochemistry lies with the effects on the quality and intensity of solar radiation (Costa, 2000) due to light absorption or scattering by particles (Castelle et al., 2009; Qureshi et al., 2010; Vost et al., 2011). Previous studies usually used the comparison between filtered and unfiltered samples to examine this light attenuating effect of SPM on photoreduction of Hg(II). It was noted that the Hg^0 production plateau was 30 % higher for filtered lake water samples (Garcia et al., 2005a), consistent with many other findings that lakes with greater SPM had lower rates of Hg^0 formation (Tseng et al., 2004), and thereby suggesting the radiation reducing effect of SPM. The similar effect was also reported for coastal shelf sites where lower Hg reduction rate constants were observed with higher total suspended solids (TSSs) (Whalin et al., 2007). The authors ascribed this reduction rate to high levels of TSSs in the water which reduced solar penetration. On the contrary, it was reported that filtration of water obtained from French Guyana had no impact on Hg(II) photoreduction in the presence of light, but decreased the formation of Hg^0 in the absence of light (Beucher et al., 2002).

Castelle and coworkers reported that a high level of SPM might be established as a significant factor affecting the Hg^0 generation in surface water by preventing penetration of light (Castelle et al., 2009). Light is needed for development of phytoplankton and thus, a reduced light penetration might lead to decreased development of phytoplankton that may be required in the biotic Hg reduction (Mason et al., 2012). The role of colloids and microbes on kinetics of gross photooxidation and photoreduction of Hg was investigated (Qureshi et al., 2010). It was found that neither colloids nor microbes noticeably impacted the oxidation and/or reduction kinetics as the pseudo-first order rate constants for gross reduction in filtered samples were similar to or slightly more than the rate constants for Hg reduction in unfiltered water samples (Mason et al., 1995; Strode et al., 2007). However, it was noted that abiotic Hg reduction is more than biotic reduction close to the surface of the ocean and it was ascribed to decreased penetration of light within the ocean column.

3.2.5. Methodological aspects in particles-involved Hg photochemistry

Using conventional filtration methods, a few studies have included experimental design to account for the role of SPM during Hg photochemistry experiments (Amyot et al., 1997, 2000; López-Muñoz et al., 2011; Luo et al., 2020; Mann et al., 2015; O'Driscoll et al., 2018; Wang et al., 2015). The filtration can enable the observation of the effects of SPM on Hg photoreactions when compared to unfiltered water samples, and in some cases amending the SPM concentrations in the ambient water by using the filtered particles could facilitate this observation (Wang et al., 2023). The filtration-separated particles could be analyzed for particulate Hg species, although there remain technical and experimental challenges in determining Hg(II) and/Hg^0 on the particles (Du et al., 2023; Mann et al., 2015; Wang et al., 2023). Since Hg^0 can be present in both purgeable and particle-bound (potentially non-purgeable) forms, with the former being used as a proxy of total Hg^0 in most previous studies due to the difficulties in determining the latter,

it is necessary to measure particulate Hg^0 as well. Thermal desorption analysis at different temperatures has been shown to be able to differentiate Hg^0 and Hg(II) bound to particles (Liu et al., 2006)(Hojdová et al., 2009; Wang et al., 2015, 2023; Windmller et al., 1996), but it might not be an accurate quantitative method due to the potential overlap in the Hg(II) and Hg^0 releasing temperatures.

Although filtration is useful for observing the effects of SPM on Hg photochemistry, it provides limited information on how SPM is involved in Hg photochemical reactions. To examine the exact role of SPM in Hg photoreactions, methods used in studies related to photocatalytic reduction of Hg(II) using synthetic catalysts (e.g., TiO_2) and photoreaction dynamics of other contaminants on oxide mineral surfaces could be useful. A hole scavenger (e.g., formic acid) is often used in Hg(II) photocatalytic reduction studies, since Hg(II) is presumably reduced by photoelectron in the system, and the enhanced Hg(II) reduction after hole scavenging could validate the role of electron (Wang et al., 2004). Instrumental monitoring of electron−hole charge carriers and ROS using molecular spectroscopies such as electron paramagnetic resonance spectroscopy and infrared spectroscopy and addition of individual ROS scavengers (e.g., isopropanol for ·OH and histidine for $^1O_2$) may help illustrate the reaction pathways (Schneider et al., 2014). It should be noted that these studies are often conducted under controlled conditions (e.g., low temperature) by using synthetic catalysts (sometimes well-defined single crystals), and the techniques used there may have limited applicability to studying natural aquatic particles.

4. Concluding remarks

Overall, the roles of suspended particles on Hg cycling are critical in process and at the same time somewhat complex. As indicated by the various mechanistic pathways of aquatic Hg(II) photoreduction, it is evident that heterogeneous photoreductions, and not only homogenous photoreductions, contribute to aquatic photochemistry of Hg species. Both inorganic minerals and organic or OM-coated particles could provide a consistent source of reactive intermediates following photoexcitation and photolysis, which may be able to mediate Hg photooxidation and photoreduction pathways. For particle bound Hg, irradiation could result in the formation of Hg^0 via photo hole-electron pair formation or internal transfer of electron. These plausible pathways imply that, in addition to playing a role of light attenuation, suspended particles have the capability of facilitating the reduction of Hg(II) in water, which warrants future studies.

Moreover, as a matter of emphasis, it is germane to consider particulate Hg^0 when studying the cycling of Hg species in aquatic environment, sequel to the various heterogeneous pathways highlighted in this paper. The absence of inclusion of particulate Hg^0 might affect the accuracy of magnitude of Hg^0 reported to have been produced from a typical Hg(II) photoreduction study. In addition, the presence of errors in the estimation of Hg^0 will have pronounced effect on the modelling of biogeochemical cycling data as inaccurately estimated Hg^0 will give rise to inaccurate model input data. Thus, considerations of the mechanistic pathways of photoreduction of aquatic Hg(II) highlighted in this article is important to obtain accurate data on Hg^0 production and Hg cycling in aquatic environment, in particular relevant to atmospheric-water surface Hg exchange.

CRediT authorship contribution statement

Peter Olusakin Oladoye: Writing – review & editing, Writing – original draft, Investigation, Formal analysis, Data curation. **Kang Wang:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Kate Aguilar:** Writing – original draft, Investigation, Data curation. **Guangliang Liu:** Writing – review & editing, Validation, Funding acquisition, Formal analysis, Conceptualization. **Yong Cai:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

Ababneh, F.A., Scott, S.L., Al-Reasi, H.A., Lean, D.R.S., 2006. Photochemical reduction and reoxidation of aqueous mercuric chloride in the presence of ferrioxalate and air. Sci. Total Environ. 367, 831–839. https://doi.org/10.1016/j.scitotenv.2006.02.018.

Amyot, M., Gill, G.A., Morel, F.M.M., 1997. Production and loss of dissolved gaseous mercury in coastal seawater. Environ. Sci. Technol. 31, 3606–3611. https://doi.org/10.1021/es9703685.

Amyot, M., Lean, D.R., Poissant, L., Doyon, M.-R., 2000. Distribution and transformation of elemental mercury in the St. Lawrence River and Lake Ontario. Can. J. Fish. Aquat. Sci. 57, 155–163. https://doi.org/10.1139/f99-248.

Appiani, E., McNeill, K., 2015. Photochemical production of singlet oxygen from particulate organic matter. Environ. Sci. Technol. 49, 3514–3522. https://doi.org/10.1021/es505712e.

Archer, D.E., Blum, J.D., 2018. A model of mercury cycling and isotopic fractionation in the ocean. Biogeosciences 15, 6297–6313. https://doi.org/10.5194/bg-15-6297-2018.

Ariya, P.A., Amyot, M., Dastoor, A., Deeds, D., Feinberg, A., Kos, G., Poulain, A., Ryjkov, A., Semeniuk, K., Subir, M., Toyota, K., 2015. Mercury physicochemical and biogeochemical transformation in the atmosphere and at atmospheric interfaces: a review and future directions. Chem. Rev. 115, 3760–3802. https://doi.org/10.1021/cr500667e.

Arnold, W.A., McNeill, K., 2007. Transformation of pharmaceuticals in the environment: photolysis and other abiotic processes, pp. 361–385. https://doi.org/10.1016/S0166-526X(07)50011-5.

Barb, W.G., Baxendale, J.H., George, P., Hargrave, K.R., 1949. Reactions of ferrous and ferric ions with hydrogen peroxide. Nature 4148, 692–694. https://doi.org/10.1038/163692a0.

Barth, T., Borgund, A.E., Riis, M., 1990. Organic acids in reservoir waters—relationship with inorganic ion composition and interactions with oil and rock. Org. Geochem. 16, 489–496. https://doi.org/10.1016/0146-6380(90)90064-7.

Beucher, C., Wong-Wah-Chung, P., Richard, C., Mailhot, G., Bolte, M., Cossa, D., 2002. Dissolved gaseous mercury formation under UV irradiation of unamended tropical waters from French Guyana. Sci. Total Environ. 290, 131–138. https://doi.org/10.1016/S0048-9697(01)01078-6.

Billing, R., 1997. Optical and photoinduced electron transfer in ion pairs of coordination compounds. Coord. Chem. Revie 159, 257–270.

Buettner, G.R., 1993. The pecking order of free radicals and antioxidants: lipid peroxidation, α-tocopherol, and ascorbate. Arch. Biochem. Biophys. 300, 535–543. https://doi.org/10.1006/abbi.1993.1074.

Carlos, L., Cipollone, M., Soria, D.B., Sergio Moreno, M., Ogilby, P.R., García Einschlag, F.S., Mártire, D.O., 2012. The effect of humic acid binding to magnetite nanoparticles on the photogeneration of reactive oxygen species. Sep. Purif. Technol. 91, 23–29. https://doi.org/10.1016/j.seppur.2011.08.028.

Castelle, S., Schäfer, J., Blanc, G., Dabrin, A., Lanceleur, L., Masson, M., 2009. Gaseous mercury at the air-water interface of a highly turbid estuary (Gironde estuary, France). Mar. Chem. 117, 42–51. https://doi.org/10.1016/j.marchem.2009.01.005.

Chen, M.F., Chen, Y., Jia Lim, Z., Wah Wong, M., 2022. Adsorption of imidazolium-based ionic liquids on the Fe(100) surface for corrosion inhibition: Physisorption or chemisorption? J. Mol. Liq. 367, 120489 https://doi.org/10.1016/j.molliq.2022.120489.

Chen, Z., Tang, T., Ni, B., Bai, M., Qi, Y., Yang, X., Jia, T., Wang, D., Wu, J., Lin, J., 2023. Amorphous TiO_2 doped with carbon for visible light photocatalytic oxidation of

elemental mercury. Chem. Phys. Lett. 831, 140860 https://doi.org/10.1016/j.cplett.2023.140860.
Chowdhury, P., Elkamel, A., Ray, A.K., 2014. Photocatalytic processes for the removal of toxic metal ions. In: Heavy Metals in Water. Royal Society of Chemistry, pp. 25–43. https://doi.org/10.1039/9781782620174-00025.
Çoban-Yildiz, Y., Chiavari, G., Fabbri, D., Gaines, A.F., Galletti, G., Tugrul, S., 2000. The chemical composition of Black Sea suspended particulate organic matter: pyrolysis-GC/MS as a complementary tool to traditional oceanographic analyses. Mar. Chem. 69, 55–67. https://doi.org/10.1016/S0304-4203(99)00093-6.
Costa, M., 2000. Photoreduction and evolution of mercury from seawater. Sci. Total Environ. 261, 125–135. https://doi.org/10.1016/S0048-9697(00)00631-8.
Cotrufo, M.F., Wallenstein, M.D., Boot, C.M., Denef, K., Paul, E., 2013. The microbial efficiency-matrix stabilization (MEMS) framework integrates plant litter decomposition with soil organic matter stabilization: do labile plant inputs form stable soil organic matter? Glob. Chang. Biol. 19, 988–995. https://doi.org/10.1111/gcb.12113.
Du, H., Yin, X., Gu, X., Wang, D., Pierce, E.M., Gu, B., 2023. Dissolved elemental mercury [Hg(0) aq] reactions and purgeability in the presence of organic and inorganic particulates. Environ. Sci. Technol. Lett. 10, 691–697. https://doi.org/10.1021/acs.estlett.3c00275.
Felizzetti, E., Minero, C., Maurino, V., 1990. The role of colloidal particles in the photodegradation of organic compounds of environmental concern in aquatic systems. Adv. Colloid Interface Sci. 32, 271–316. https://doi.org/10.1016/0001-8686(90)80021-Q.
Garcia, E., Amyot, M., Ariya, P.A., 2005a. Relationship between DOC photochemistry and mercury redox transformations in temperate lakes and wetlands. Geochim. Cosmochim. Acta 69, 1917–1924. https://doi.org/10.1016/j.gca.2004.10.026.
Garcia, E., Poulain, A.J., Amyot, M., Ariya, P.A., 2005b. Diel variations in photoinduced oxidation of Hg0 in freshwater. Chemosphere 59, 977–981. https://doi.org/10.1016/j.chemosphere.2004.09.107.
Geller, A., 1985. Light-induced conversion of refractory, high molecular weight lake water constituents. Swiss J. Hydrol. 47, 21–26. https://doi.org/10.1007/BF02538181.
Georgiou, C.D., Sun, H.J., McKay, C.P., Grintzalis, K., Papapostolou, I., Zisimopoulos, D., Panagiotidis, K., Zhang, G., Koutsopoulou, E., Christidis, G.E., Margiolaki, I., 2015. Evidence for photochemical production of reactive oxygen species in desert soils. Nat. Commun. 6, 1–11. https://doi.org/10.1038/ncomms8100.
Gerischer, H., 1979. Solar photoelectrolysis with semiconductor electrodes. In: Seraphin, B.O. (Ed.), Solar Energy Conversion. Topics in Applied Physics. Springer, Berlin, Heidelberg, Berlin, Heidelberg, pp. 115–172. https://doi.org/10.1007/3-540-09224-2_4.
Gonzalez-Raymat, H., Liu, G., Liriano, C., Li, Y., Yin, Y., Shi, J., Jiang, G., Cai, Y., 2017. Elemental mercury: its unique properties affect its behavior and fate in the environment. Environ. Pollut. 229, 69–86. https://doi.org/10.1016/j.envpol.2017.04.101.
Haber, F., Weiss, J., A, P.R.S.L, 1934. The catalytic decomposition of hydrogen peroxide by iron salts. Proc. R. Soc. London. Ser. A - Math. Phys. Sci. 147, 332–351. https://doi.org/10.1098/rspa.1934.0221.
Hart, B.T., 1982. Uptake of trace metals by sediments and suspended particulates: a review. Hydrobiologia 91–92, 299–313. https://doi.org/10.1007/BF02391947.
He, F., Zheng, W., Liang, L., Gu, B., 2012. Mercury photolytic transformation affected by low-molecular-weight natural organics in water. Sci. Total Environ. 416, 429–435. https://doi.org/10.1016/j.scitotenv.2011.11.081.
He, F., Zhao, W., Liang, L., Gu, B., 2014. Photochemical oxidation of dissolved elemental mercury by carbonate radicals in water. Environ. Sci. Technol. Lett. 1, 499–503. https://doi.org/10.1021/ez500322f.
He, J., Cheng, J., Lo, I.M.C., 2021. Green photocatalytic disinfection of real sewage: efficiency evaluation and toxicity assessment of eco-friendly TiO_2-based magnetic photocatalyst under solar light. Water Res. 190, 116705 https://doi.org/10.1016/j.watres.2020.116705.
Helms, J.R., Glinski, D.A., Mead, R.N., Southwell, M.W., Avery, G.B., Kieber, R.J., Skrabal, S.A., 2014. Photochemical dissolution of organic matter from resuspended sediments: impact of source and diagenetic state on photorelease. Org. Geochem. 73, 83–89. https://doi.org/10.1016/j.orggeochem.2014.05.011.
Hojdová, M., Navrátil, T., Rohovec, J., Penížek, V., Grygar, T., 2009. Mercury distribution and speciation in soils affected by historic mercury mining. Water Air Soil Pollut. 200, 89–99. https://doi.org/10.1007/s11270-008-9895-5.
Hu, B., Wang, P., Bao, T., Shi, Y., 2020. The photochemical release of dissolved organic matter from resuspended sediments: insights from fluorescence spectroscopy. Chemosphere 257, 127161. https://doi.org/10.1016/j.chemosphere.2020.127161.
Hu, B., Wang, P., Bao, T., Qian, J., Wang, X., 2021. Mechanisms of photochemical release of dissolved organic matter and iron from resuspended sediments. J. Environ. Sci. 104, 288–295. https://doi.org/10.1016/j.jes.2020.12.002.
Hu, B., Wang, P., Wang, C., Bao, T., 2022. Photogeochemistry of particulate organic matter in aquatic systems: a review. Sci. Total Environ. 806, 150467 https://doi.org/10.1016/j.scitotenv.2021.150467.
Jędruch, A., Kwasigroch, U., Bełdowska, M., Kuliński, K., 2017. Mercury in suspended matter of the Gulf of Gdańsk: origin, distribution and transport at the land–sea interface. Mar. Pollut. Bull. 118, 354–367. https://doi.org/10.1016/j.marpolbul.2017.03.019.
Jiang, T., Skyllberg, U., Wei, S., Wang, D., Lu, S., Jiang, Z., Flanagan, D.C., 2015. Modeling of the structure-specific kinetics of abiotic, dark reduction of Hg(II) complexed by O/N and S functional groups in humic acids while accounting for time-dependent structural rearrangement. Geochim. Cosmochim. Acta 154, 151–167. https://doi.org/10.1016/j.gca.2015.01.011.
Jung, J.-E., Geatches, D., Lee, K., Aboud, S., Brown, G.E., Wilcox, J., 2015. First-principles investigation of mercury adsorption on the α-Fe_2O_3 ($11\bar{2}0$) surface. J. Phys. Chem. C 119, 26512–26518. https://doi.org/10.1021/acs.jpcc.5b07827.
Kisch, H., 2013. Semiconductor Photocatalysis—mechanistic and synthetic aspects. Angew. Chemie Int. Ed. 52, 812–847. https://doi.org/10.1002/anie.201201200.
Lam, M.W., Tantuco, K., Mabury, S., 2003. PhotoFate: a new approach in accounting for the contribution of indirect photolysis of pesticides and pharmaceuticals in surface waters. Environ. Sci. Technol. 37, 899–907. https://doi.org/10.1021/es025902.
Lamborg, C.H., Hammerschmidt, C.R., Bowman, K.L., 2016. An examination of the role of particles in oceanic mercury cycling. Philos. Trans. R. Soc. A Math. Phys. Eng. Sci. 374 https://doi.org/10.1098/rsta.2015.0297.
Langford, C.H., Carey, J.H., 1987. Photocatalysis by Inorganic Components of Natural Water Systems A brief inventory of aquatic components potentially active as photocatalysts includes colloidal and sedimentary oxides and sulfides, metal complexes of organic ligands, and certain metal io. In: Zika, R.G., Cooper, W.J. (Eds.), Photochemistry of Environmental Aquatic Systems. American Chemical Society, pp. 225–239.
Lee, H.-S., Hur, J., Lee, M.-H., Brogi, S.R., Kim, T.-W., Shin, H.-S., 2019. Photochemical release of dissolved organic matter from particulate organic matter: spectroscopic characteristics and disinfection by-product formation potential. Chemosphere 235, 586–595. https://doi.org/10.1016/j.chemosphere.2019.06.127.
Lee, H.S., Hur, J., Shin, H.S., 2023. Photochemical and microbial transformation of particulate organic matter depending on its source and size. Sci. Total Environ. 857, 159506 https://doi.org/10.1016/j.scitotenv.2022.159506.
Leenheer, J.A., 1994. Chemistry of Dissolved Organic Matter in Rivers, Lakes, and Reservoirs. In: Baker, L.A. (Ed.), Environmental Chemistry of Lakes and Reservoirs. American Chemical Society, pp. 195–221. https://doi.org/10.1021/ba-1994-0237.ch007.
Litter, M.I., Baumgartner, E.C., Urrutla, G.A., Blesa, M.A., 1991. Photodissolution of Iron oxides. 3. Interplay of photochemical and thermal processes in Maghemite/carboxylic acid systems. Environ. Sci. Technol. 25, 1907–1913. https://doi.org/10.1021/es00023a011.
Liu, G., Cabrera, J., Allen, M., Cai, Y., 2006. Mercury characterization in a soil sample collected nearby the DOE Oak Ridge Reservation utilizing sequential extraction and thermal desorption method. Sci. Total Environ. 369, 384–392. https://doi.org/10.1016/j.scitotenv.2006.07.011.
López-Muñoz, M.J., Aguado, J., Arencibia, A., Pascual, R., 2011. Mercury removal from aqueous solutions of $HgCl_2$ by heterogeneous photocatalysis with TiO2. Appl. Catal. Environ. 104, 220–228. https://doi.org/10.1016/j.apcatb.2011.03.029.
Luo, H., Cheng, Q., Pan, X., 2020. Photochemical behaviors of mercury (Hg) species in aquatic systems: a systematic review on reaction process, mechanism, and influencing factor. Sci. Total Environ. 720, 137540 https://doi.org/10.1016/j.scitotenv.2020.137540.
Mann, E.A., Mallory, M.L., Ziegler, S.E., Tordon, R., O'Driscoll, N.J., 2015. Mercury in Arctic snow: quantifying the kinetics of photochemical oxidation and reduction. Sci. Total Environ. 509–510, 115–132. https://doi.org/10.1016/j.scitotenv.2014.07.056.
Mason, R.P., Morel, F.M.M., Hemond, H.F., 1995. The role of microorganisms in elemental mercury formation in natural waters. Water Air Soil Pollut. 80, 775–787. https://doi.org/10.1007/BF01189729.
Mason, R.P., Choi, A.L., Fitzgerald, W.F., Hammerschmidt, C.R., Lamborg, C.H., Soerensen, A.L., Sunderland, E.M., 2012. Mercury biogeochemical cycling in the ocean and policy implications. Environ. Res. 119, 101–117. https://doi.org/10.1016/j.envres.2012.03.013.
Mayer, L.M., Schick, L.L., Skorko, K., Boss, E., 2006. Photodissolution of particulate organic matter from sediments. Limnol. Oceanogr. 51, 1064–1071. https://doi.org/10.4319/lo.2006.51.2.1064.
Mayer, L.M., Thornton, K.R., Schick, L.L., Jastrow, J.D., Harden, J.W., 2012. Photodissolution of soil organic matter. Geoderma 170, 314–321. https://doi.org/10.1016/j.geoderma.2011.11.030.
Mills, A., Le Hunte, S., 1997. An overview of semiconductor photocatalysis. J. Photochem. Photobiol. A Chem. 108, 1–35. https://doi.org/10.1016/S1010-6030(97)00118-4.
Moffett, J.W., Zika, R.G., 1987. Reaction kinetics of hydrogen peroxide with copper and Iron in seawater. Environ. Sci. Technol. 21, 804–810. https://doi.org/10.1021/es00162a012.
Nazhat, N.B., Asmus, K.D., 1973. Reduction of mercuric chloride by hydrated electrons and reducing radicals in aqueous solutions. Formation and reactions of mercury chloride (HgCl). J. Phys. Chem. 77, 614–620. https://doi.org/10.1021/j100624a010.
Nosaka, Y., Nosaka, A.Y., 2017. Generation and detection of reactive oxygen species in photocatalysis. Chem. Rev. 117, 11302–11336. https://doi.org/10.1021/acs.chemrev.7b00161.
Nriagu, J.O., 1994. Mechanistic steps in the photoreduction of mercury in natural waters. Sci. Total Environ. 154, 1–8. https://doi.org/10.1016/0048-9697(94)90608-4.
O'Driscoll, N.J., Vost, E., Mann, E., Klapstein, S., Tordon, R., Lukeman, M., 2018. Mercury photoreduction and photooxidation in lakes: effects of filtration and dissolved organic carbon concentration. J. Environ. Sci. 68, 151–159. https://doi.org/10.1016/j.jes.2017.12.010.
Parrino, F., Livraghi, S., Giamello, E., Ceccato, R., Palmisano, L., 2020. Role of hydroxyl, superoxide, and nitrate radicals on the fate of bromide ions in photocatalytic TiO_2 suspensions. ACS Catal. 10, 7922–7931. https://doi.org/10.1021/acscatal.0c02010.
Pehkonen, S.O., Lin, C.-J., 1998. Aqueous photochemistry of mercury with organic acids. J. Air Waste Manage. Assoc. 48, 144–150. https://doi.org/10.1080/10473289.1998.10463661.

Pelizzetti, E., Calza, P., 2002. Photochemical processes in the euphotic zone of sea water: Progress and problems. In: Antonio, G., Pelizzetti, Ezio, Sammartano, S. (Eds.), Chemistry of Marine Water and Sediments. Springer Berlin, Heidelberg, Berlin, Heidelberg, pp. 83–103. https://doi.org/10.1007/978-3-662-04935-8_3.

Pham, A.N., Xing, G., Miller, C.J., Waite, T.D., 2013. Fenton-like copper redox chemistry revisited: hydrogen peroxide and superoxide mediation of copper-catalyzed oxidant production. J. Catal. 301, 54–64. https://doi.org/10.1016/j.jcat.2013.01.025.

Pham, P., Rashid, M., Cai, Y., Yoshinaga, M., Dionysiou, D.D., O'Shea, K., 2020. Removal of as(III) from water using the adsorptive and photocatalytic properties of humic acid-coated magnetite nanoparticles. Nanomaterials 10, 1–18. https://doi.org/10.3390/nano10081604.

Qureshi, A., O'Driscoll, N.J., Macleod, M., Neuhold, Y.M., Hungerbühler, K., 2010. Photoreactions of mercury in surface ocean water: gross reaction kinetics and possible pathways. Environ. Sci. Technol. 44, 644–649. https://doi.org/10.1021/es9012728.

Rani, B., Nayak, A.K., Sahu, N.K., 2022. Fundamentals principle of photocatalysis. In: Sahu, Arpan Kumar, Nayak and Niroj, K. (Eds.), Nanostructured Materials for Visible Light Photocatalysis. Elsevier Inc., pp. 1–22. https://doi.org/10.1016/B978-0-12-823018-3.00009-9

Ravichandran, M., 2004. Interactions between mercury and dissolved organic matter - a review. Chemosphere 55, 319–331. https://doi.org/10.1016/j.chemosphere.2003.11.011.

Rosati, G., Heimbürger, L.E., Melaku Canu, D., Lagane, C., Laffont, L., Rijkenberg, M.J.A., Gerringa, L.J.A., Solidoro, C., Gencarelli, C.N., Hedgecock, I.M., De Baar, H.J.W., Sonke, J.E., 2018. Mercury in the Black Sea: new insights from measurements and numerical modeling. Global Biogeochem. Cycles 32, 529–550. https://doi.org/10.1002/2017GB005700.

Schiebel, H.N., Wang, X., Chen, R.F., Peri, F., 2015. Photochemical release of dissolved organic matter from resuspended salt marsh sediments. Estuar. Coasts 38, 1692–1705. https://doi.org/10.1007/s12237-014-9893-3.

Schneider, J., Matsuoka, M., Takeuchi, M., Zhang, J., Horiuchi, Y., Anpo, M., Bahnemann, D.W., 2014. Understanding TiO_2 Photocatalysis: mechanisms and materials. Chem. Rev. 114, 9919–9986. https://doi.org/10.1021/cr5001892.

Schroeder, W.H., Yarwood, G., Niki, H., 1991. Transformation processes involving mercury species in the atmosphere — results from a literature survey. Water Air Soil Pollut. 56, 653–666. https://doi.org/10.1007/BF00342307.

Serpone, N., Ah-You, Y.K., Tran, T.P., Harris, R., Pelizzetti, E., Hidaka, H., 1987. AM1 simulated sunlight photoreduction and elimination of Hg(II) and CH_3Hg(II) chloride chloride salts from aqueous suspensions of titanium dioxide. Sol. Energy 39, 491–498. https://doi.org/10.1016/0038-092X(87)90056-9.

Skyllberg, U., 2008. Competition among thiols and inorganic sulfides and polysulfides for Hg and MeHg in wetland soils and sediments under suboxic conditions: illumination of controversies and implications for MeHg net production. J. Geophys. Res. Biogeo. 113 https://doi.org/10.1029/2008JG000745.

Skyllberg, U., Drott, A., 2010. Competition between disordered iron sulfide and natural organic matter associated thiols for mercury(II)—an EXAFS study. Environ. Sci. Technol. 44, 1254–1259. https://doi.org/10.1021/es902091w.

Skyllberg, U., Bloom, P.R., Qian, J., Lin, C.-M., Bleam, W.F., 2006. Complexation of mercury(II) in soil organic matter: EXAFS evidence for linear two-coordination with reduced sulfur groups. Environ. Sci. Technol. 40, 4174–4180. https://doi.org/10.1021/es0600577.

Soto Cárdenas, C., Diéguez, M. del C., Queimaliños, C., Rizzo, A., Fajon, V., Kotnik, J., Horvat, M., Ribeiro Guevara, S., 2018. Mercury in a stream-lake network of Andean Patagonia (southern volcanic zone): partitioning and interaction with dissolved organic matter. Chemosphere 197, 262–270. https://doi.org/10.1016/j.chemosphere.2018.01.048.

Southwell, M.W., Kieber, R.J., Mead, R.N., Brooks Avery, G., Skrabal, S.A., 2010. Effects of sunlight on the production of dissolved organic and inorganic nutrients from resuspended sediments. Biogeochemistry 98, 115–126. https://doi.org/10.1007/s10533-009-9380-2.

Stein, E.D., Cohen, Y., Winer, A.M., 1996. Environmental distribution and transformation of mercury compounds. Crit. Rev. Environ. Sci. Technol. 26, 1–43. https://doi.org/10.1080/10643389609388485.

Strode, S.A., Jaeglé, L., Selin, N.E., Jacob, D.J., Park, R.J., Yantosca, R.M., Mason, R.P., Slemr, F., 2007. Air-sea exchange in the global mercury cycle. Global Biogeochem. Cycles 21, 1–12. https://doi.org/10.1029/2006GB002766.

Stumm, W., 1992. Chemistry of the Interface Processes at the Mineral-Water, 1st ed. New York. John Wiley and Sons Inc, New York.

Tacu, I., Kokalari, I., Abollino, O., Albrecht, C., Malandrino, M., Ferretti, A.M., Schins, R. P.F., Fenoglio, I., 2021. Mechanistic insights into the role of Iron, copper, and carbonaceous component on the oxidative potential of ultrafine particulate matter. Chem. Res. Toxicol. 34, 767–779. https://doi.org/10.1021/acs.chemrestox.0c00399.

Tipping, E., 1981. The adsorption of aquatic humic substances by iron oxides. Geochim. Cosmochim. Acta 45, 191–199. https://doi.org/10.1016/0016-7037(81)90162-9.

Tseng, C.M., Lamborg, C.H., Fitzgerald, W.F., Engstrom, D.R., 2004. Cycling of dissolved elemental mercury in Arctic Alaskan lakes. Geochim. Cosmochim. Acta 68, 1173–1184. https://doi.org/10.1016/j.gca.2003.07.023.

Turritto, A., Acquavita, A., Bezzi, A., Covelli, S., Fontolan, G., Petranich, E., Piani, R., Pillon, S., 2018. Suspended particulate mercury associated with tidal fluxes in a lagoon environment impacted by cinnabar mining activity (northern Adriatic Sea). J. Environ. Sci. (China) 68, 100–113. https://doi.org/10.1016/j.jes.2017.12.009.

Turro, N.J., Lamola, A.A., 1977. Photochemistry. In: Smith, K.C. (Ed.), The Science of Photobiology, in: The Science of Photochemistry. Springer, Boston, MA, pp. 63–86. https://doi.org/10.1007/978-1-4684-1713-5_3.

Ullrich, S.M., Tanton, T.W., Abdrashitova, S.A., 2001. Mercury in the aquatic environment: a review of factors affecting methylation. Crit. Rev. Environ. Sci. Technol. 31, 241–293. https://doi.org/10.1080/20016491089226.

Vähätalo, A.V., 2009. Light, photolytic reactivity and chemical products. Encycl. Inl. Waters 761–773. https://doi.org/10.1016/B978-012370626-3.00110-1.

Vaughan, P.P., Blough, N.V., 1998. Photochemical formation of hydroxyl radical by constituents of natural waters. Environ. Sci. Technol. 32, 2947–2953. https://doi.org/10.1021/es9710417.

Vinodgopal, K., Kamat, P.V., 1992. Environmental photochemistry on surfaces. Charge injection from excited fulvic acid into semiconductor colloids. Environ. Sci. Technol. 26, 1963–1966. https://doi.org/10.1021/es00034a013.

Vost, E.E., Amyot, M., O'Driscoll, N.J., 2011. Photoreactions of mercury in aquatic systems. In: Yong Cai, N.O. (Ed.), Guangliang Liu, Environmental Chemistry and Toxicology of Mercury. Wiley, pp. 193–218. https://doi.org/10.1002/9781118146644.ch6.

Wang, X., Pehkonen, S.O., Ray, A.K., 2004. Photocatalytic Reduction of hg (II) on Two Commercial TiO 2 Catalysts 49, pp. 1435–1444. https://doi.org/10.1016/j.electacta.2003.10.030.

Wang, Y., Li, Y., Liu, G., Wang, D., Jiang, G., Cai, Y., 2015. Elemental mercury in natural waters: occurrence and determination of particulate Hg(0). Environ. Sci. Technol. 49, 9742–9749. https://doi.org/10.1021/acs.est.5b01940.

Walcarius, A., Devoy, J., Bessiere, J., 1999. Electrochemical recognition of selective mercury adsorption on minerals. Environ. Sci. Technol. 33, 4278–4284. https://doi.org/10.1021/es990525v.

Wang, Y., Kong, L., He, M., Ouyang, W., Lin, C., Liu, X., 2020. Influences of particles and aquatic colloids on the oxidation of Sb(III) in natural water. ACS Earth Sp. Chem. 4, 661–671. https://doi.org/10.1021/acsearthspacechem.0c00035.

Wang, K., Liu, G., Cai, Y., 2023. Effects of natural particles on photo-reduction of divalent mercury in everglades waters. Environ. Pollut. 323, 121327 https://doi.org/10.1016/j.envpol.2023.121327.

Washburn, S.J., Blum, J.D., Donovan, P.M., Singer, M.B., 2019. Isotopic evidence for mercury photoreduction and retention on particles in surface waters of Central California, USA. Sci. Total Environ. 674, 451–461. https://doi.org/10.1016/j.scitotenv.2019.04.145.

Wen, X., Yang, X., Wang, T., Li, Z., Ma, C., Chen, W., He, Y., Zhang, C., 2023. Photoreduction of Hg(II) by typical dissolved organic matter in paddy environments. Chemosphere 327, 138437. https://doi.org/10.1016/j.chemosphere.2023.138437.

Whalin, L., Kim, E.-H., Mason, R., 2007. Factors influencing the oxidation, reduction, methylation and demethylation of mercury species in coastal waters. Mar. Chem. 107, 278–294. https://doi.org/10.1016/j.marchem.2007.04.002.

Windmller, C.C., Wilken, R.-D., Jardim, W.D.F., 1996. Mercury speciation in contaminated soils by thermal release analysis. Water Air Soil Pollut. 89, 399–416. https://doi.org/10.1007/BF00171644.

Xia, M., Chen, Z., Li, Y., Li, C., Ahmad, N.M., Cheema, W.A., Zhu, S., 2019. Removal of Hg(II) in aqueous solutions through physical and chemical adsorption principles. RSC Adv. 9, 20941–20953. https://doi.org/10.1039/C9RA01924C.

Yang, X., Ma, C., Li, Z., Wang, T., Wen, X., He, Y., Chen, W., Shi, X., Zhang, C., 2023. The fate of photoreduction of Hg(II) in aqueous solution by aged microplastic particles and their leached DOM. Sci. Total Environ. 891, 164513 https://doi.org/10.1016/j.scitotenv.2023.164513.

Zafiriou, O.C., Joussot-Dubien, J.J., Zepp, R.G., Zika, R.G., 1984. Photochemistry of natural waters. Environ. Sci. Technol. 18, 358A–371A. https://doi.org/10.1021/es00130a001.

Zeng, T., Arnold, W.A., 2013. Pesticide photolysis in prairie potholes: probing photosensitized processes. Environ. Sci. Technol. 47, 6735–6745. https://doi.org/10.1021/es3030808.

Zepp, R.G., Holgne, J., Bader, H., 1987. Nitrate-induced photooxidation of trace organic chemicals in water. Environ. Sci. Technol. 21, 443–450. https://doi.org/10.1021/es00159a004.

Zhang, H., 2006. Photochemical redox reactions of mercury. Struct. Bond. 120, 37–79. https://doi.org/10.1007/430_015.

Zhu, S., Zhang, Z., Žagar, D., 2018. Mercury transport and fate models in aquatic systems: a review and synthesis. Sci. Total Environ. 639, 538–549. https://doi.org/10.1016/j.scitotenv.2018.04.397.