Occurrence and speciation of arsenic and mercury in alluvial and coastal sediments

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Abstract
Among potential toxic elements (PTEs), arsenic (As) and mercury (Hg) are well known for the toxicity of their different chemical species and diffusion in the environment via several anthropic sources (i.e., industrial settlements, mining activity). Bottom sediments often become a repository for As and Hg, although they may be considered a potential secondary source of these elements into the water column depending on their speciation and mobility. Focusing on the most recent studies (since 2019) on the occurrence of As and Hg in contaminated aquatic sediments, the aim of this review is to give an overview of the current understandings on the complex biogeochemical cycle of these elements in this environmental media. The main biogeochemical factors governing the transformations of As and Hg among their different chemical species were synthesized, highlighting those driving the formation of more mobile and/or bioavailable forms. Additionally, the most advanced analytical techniques for the determination of the different chemical species of As and Hg in sediments are briefly presented.

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Mercury and Arsenic: natural and anthropogenic sources

Mercury (Hg) is a potential toxic element (PTE) well known for its toxicity, especially as a neurotoxin, naturally released in the environment through volcanic activity and rock weathering. Currently, however, natural emissions of Hg are only a small fraction compared with those related to human activities.

Anthropogenic sources of Hg include mining, coal combustion, various industrial processes, and Hg-added product disposal [1,2]. Once released, Hg can reach aquatic environments through atmospheric depositions, direct discharges, and runoff and erosion of contaminated layers [3,4]. Here it is effectively scavenged by particles and settles on the bottom sediments, which act as a sink of anthropogenic pollution [5] and, especially near point-sources, can reach Hg concentrations (Table 1) several orders of magnitude higher than the natural background [6]. Thanks to the implementation of the Minamata Convention, the characterization of these sites is receiving growing worldwide attention [7] as a tool to assess the possible Hg dispersion patterns and exposure risk for humans and wildlife, mostly related to the formation of methylmercury (CH_3Hg^+) [6].

Mining activities still represent a widely recognized source of Hg for downstream sediments [8,9], particularly historic Hg mining [7,10,11], while there is an increasing interest in evaluating its impact on surrounding environments of Hg use in artisanal small-scale gold mining in developing countries [12−15]. With regard to industrial activities, chlor-alkali plants and chemical factories which use Hg represent notable pollution sources [16,17], but the release of this metal can occur via a wide range of anthropic activities, for example, metal smelting [18], oil refining [5], coal combustion [4], industrial and domestic wastewaters discharge [19] (Table 1).

Arsenic (As) is a toxic and carcinogenic metalloid whose natural sources are related to mineral dissolution, volcanic emissions, and geothermal activity [26]. Large amounts of anthropogenic As have also reached the environment from past mining activities, pharmaceutical and glass industries, metal smelting, pesticide and herbicide production, manufacturing of leather and wood preservatives along with the use of fossil fuels [26].

Contamination of soil, sediments (Table 2), and surface and groundwaters [27,28] are mainly due to the leaching of As from mine residues as the legacy of the historical extraction not only of sulfides, such as primary As-

Table 1

Results of recent studies on Hg occurrence in worldwide contaminated sediments.

Site	Total Hg ($\mu g\ g^{-1}$)	CH_3Hg^+ ($ng\ g^{-1}$)	Main Hg source	Reference
	min ÷ max	min ÷ max		
EUROPE				
Paglia River (ITA)	0.1 ÷ 97.9 n = 102	–	Hg mining	[10]
Port of Monfalcone (ITA)	0.30 ÷ 13.5 n = 16	–	Hg mining	[11]
Krka River Estuary (HRV)	0.06 ÷ 12.36 n = 40	–	Shipbuilding and repairing	[20]
Ohre−Kossein−Roslau River System (GER)	0.4 ÷ 312 n = 91	–	Chemical industry	[17]
Asturias Estuary (ESP)	0.57 ÷ 5.01 n = 15	–	Hg mining, wastewater discharge	[21]
Union Canal (GBR)	21.9 ÷ 565 n = 8	–	Munitions manufacturing	[22]
ASIA				
Lugou River (CHI)	0.15 ÷ 4.4 n = 48	0.036 ÷ 7.8 n = 48	Coal mining	[8]
Giava River (IDN)	6.9 ÷ 11.8 n = 7	–	Artisanal Small-Scale Gold Mining (ASGM)	[14]
Kaosiung Harbor (TWN)	0.48 ÷ 2.34 n = 20	4.55 ÷ 23.2 n = 20	Industrial wastewaters (and domestic sewage)	[19]
Tagburos River-Pit Lake (PHL)	1.8 ÷ 454.1 n = n.d.	–	Hg mining	[7]
Honda Bay (PHL)	0.04 ÷ 731.6 n = n.d.	–	Hg mining	[7]
Jiehe River (CHI)	5.2 ÷ 51 n = 38	–	Gold mining	[9]
Jinzhou Bay (CHI)	0.43 ÷ 11.88 n = 6	0.67 ÷ 8.56 n = 6	Zinc smelter	[18]
AMERICA				
Cold Creek (USA)	4.30 ÷ 58.02 n = 3	3.91 ÷ 27.75 n = 3	Chlor-alkali plant (CAP)	[16]
The Cove (USA)	0.94 ÷ 2.84 n = 8	4.71 ÷ 6.50 n = 8	CAP	[16]
Alviso Slough (USA)	0.04 ÷ 10.4 n = 106	–	Hg mining	[23]
Galveston Bay (USA)	0.08 ÷ 51.27 n = n.d.	–	CAP, coal combustion, industrial wastewaters, agricultural and industrial runoff	[4]
East Fork Poplar Creek (USA)	16.1 (average) n = 57	2.11 (average) n = 57	Lithium isotope separation plant	[3]
Sagua la Grande River (CUB)	0.16 ÷ 5.07 n = 6	<2 ÷ 16 n = 6	CAP	[24]
San Juan mining ponds (COL)	0.04 ÷ 1.27 n = 27	<5 ÷ 138.33 n = 27	Artisanal Small-Scale Gold Mining (ASGM)	[13]
Todos os Santos Bay (BRA)	0.03 ÷ 0.38 n = 372	<10 ÷ 27 n = 372	CAP, lead smelter, oil refineries, shrimp farming	[5]
AFRICA				
Cote d'Ivoire ASGM sites (CIV)	0.02 ÷ 0.147 n = 13	0.03 ÷ 4.35 n = 13	Artisanal Small-Scale Gold Mining (ASGM)	[12]
Gambia River (SEN)	0.02 ÷ 2.4 n = 58	2.3 ÷ 8.0 n = 58	Artisanal Small-Scale Gold Mining (ASGM)	[25]
Tinkoto and Sabodala water ponds (SEN)	0.23 ÷ 9.26 n = 5	3.6 n = 5	Artisanal Small-Scale Gold Mining (ASGM)	[25]
Farvic Mines Streams (ZWE)	0.006 ÷ 1.54 n = 211	–	Artisanal Small-Scale Gold Mining (ASGM)	[15]

Table 2

Arsenic concentrations in worldwide contaminated sediments from the most recent studies.

Site	Total As (μg g^{-1})	Main As sources	Reference
	min ÷ max		
EUROPE			
Asturian coasts (ESP)	3.50 ÷ 55.30 n = 35	Geogenic, anthropogenic	[29]
ASIA			
Tibetan lakes (CHI)	10.26 ÷ 127.41 n = n.d.	Geogenic	[30]
Hunan province, rivers (CHI)	50-190 n = 3	Sb mining	[31]
Huangshui Creek (CHI)	120.12 ÷ 992.33 n = 5	As mining, hydrothermal and hot springs, urban runoff, sewage discharge	[32]
Xijiang River (CHI)	10.26 ÷ 4993.34 n = 18	Geogenic, industrial	[33]
Daya Bay (CHI)	8.98 ÷ 26.45 n = 9	Maricolture farms	[34]
Taiwan Strait (CHI)	2.7 ÷ 21.2 n = 187	Not defined	[35]
AMERICA			
Huautla district (MEX)	4.49 avg. n = 9	Ag, Pb mining	[27]
San Luis Potosí drainage basin (MEX)	39 ÷ 1500 n = 7	Pb–Ag and Au mining	[36]
Tundra Mine site lakes (CAN)	28 ÷ 1010 n = 124	Au mining	[37]
Long Lake (CAN)	2.2 ÷ 3420 n = 147	Au mining	[28]
Cobalt region lakes (CAN)	1.13 ÷ 6.70 n = 105	Ag, Co, Ni, As mining	[38]
AFRICA			
Lagos Lagoon (NGA)	0.21 ÷ 7.97 n = 45	Anthropogenic	[39]
OCEANIA			
Macleay River (AUS)	15 ÷ 207 n = n.d	Sb–As mining	[40]

bearing minerals such as realgar (AsS), orpiment (As_2S_3) and arsenopyrite (FeAsS), but also of gold mining. Ore roasting processes may convert gold-bearing arsenopyrite to gold-bearing Fe oxides, from which gold can be extracted by cyanidation. The atmospheric release of the more bioaccessible As_2O_3 as a byproduct of ore-roasting operations can then lead to its aerial deposition in nearby terrestrial and aquatic environments [26].

Analytical determination and speciation techniques

A key aspect influencing the bioavailability and mobility of Hg in sediments is its speciation. Mercury can be present in three main forms: elemental mercury Hg(0), inorganic mercury Hg(I), Hg(II), and various forms of organic mercury such as CH_3Hg^+, dimethylmercury ($(CH_3)_2Hg$), ethylmercury ($EtHg^+$), phenylmercury ($PhHg^+$), which are characterized by different degrees of bioavailability and toxicity. To achieve accurate results with speciation, an analytical approach using precleaned and acid-treated PTFE (polytetrafluoroethylene) containers is recommended together with the analysis of the proper quality reference materials [41], in particular for CH_3Hg^+ determination (ERM-CC580, IAEA/433/158/456/405 estuarine, coastal, and marine sediments). Fractionation of Hg is commonly performed using single (i.e., alkaline, acid, or common distillation for CH_3Hg^+) or multiple-step extraction procedures [42] (i.e., for exchangeable fraction, acid soluble or carbonate associated, bound to metal oxides, organic and residual Hg fractions). Extractions, however, do have some disadvantages including being time-consuming, having low reproducibility, nonspecific removal of species, and the formation of artefacts [42]. Thus, nondestructive methods are often used such as X-ray absorption near-edge structure (XANES), X-ray absorption fine structure (EXAFS) [43,44], and thermo-desorption techniques [45,46].

More than 100 arsenic compounds are present in the environment and biological systems [47], which are speciated by sequential and nonsequential extraction procedures [40,48], DGT-probes [34], scanning electron microscopy (SEM)-based automated mineralogy [49] or, more commonly, by the coupling of chromatographic and spectroscopic techniques (GC-MS, HPLC-ICP-MS, HPLC-MS, HPLC-MS/MS, HPLC-HG-AFS, HPLC-HG-AAS [30,50–53] after the application of microextraction techniques to preconcentrate the compounds and based on solid sorbent, liquid phase, or combined techniques [54]. In this context, the importance of the proper collection, storage, and pretreatment of samples cannot be underestimated due to a possible parallel reaction, degradation, and loss of the analyte [55].

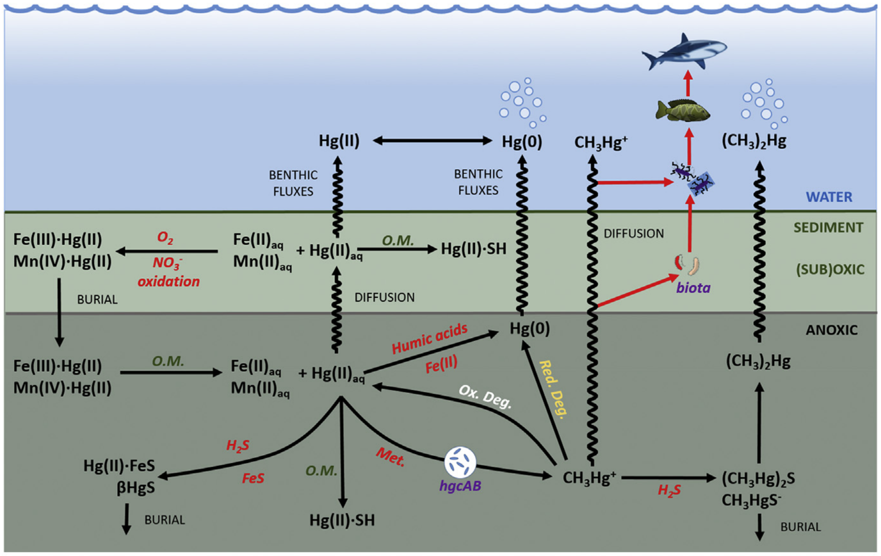
Mercury in sedimentary compartments and mobility

Mercury is strongly adsorbed and retained in sediments; therefore, total Hg concentrations along sediment cores represent a reliable archive to track the temporal variation of anthropogenic contamination [20] but can also be used as a reliable proxy for past volcanic activity [56]. Moreover, the recently developed Hg-stable isotope analysis provides a useful tool to discriminate the source of Hg stored in sediments and also to track its transformations and bioaccumulation (e.g. Ref. [16]).

In general, sites impacted by industrial activities are characterized by a greater proportion of soluble and mobile forms of Hg than mining sites, where the majority of Hg usually exists as insoluble cinnabar (α-HgS) [17,43]. Divalent Hg (Hg(II)) usually represents the predominant form of this metal in sediments (Figure 1), where it forms associations with different fractions depending on geochemical conditions and the availability of the host phases [56], namely organic matter, sulphides, and iron (Fe) and manganese (Mn) oxyhydroxides [13]. Because of the high affinity of Hg for sulphur, thiol groups of organic matter, and inorganic sulphides play a crucial role in strong Hg adsorption in sediments, for example, through the precipitation of insoluble metacinnabar (β-HgS), stable under anoxic conditions, but also complexes of Hg with Fe sulphides can be present [43,44]. Moreover, under reducing conditions (Figure 1), large amounts of Hg(0) can occur due to the reduction of Hg(II) mediated by humic acids or Fe(II): this species is weakly adsorbed by sediment constituents and is easily released into the atmosphere [43]. Conversely, in oxic layers of sediments (Figure 1) where oxidation of organic matter occurs Hg forms complexes with Fe and manganese (Mn) oxyhydroxides [57]. However, particularly in contaminated sites, high supplies of Hg can saturate the binding capacity of organic matter and sulphides resulting in a greater abundance of Hg weakly bound to sediment matrix [22,58]. The presence of bioavailable forms of Hg is a relevant factor influencing the formation of CH_3Hg^+, which represents a key issue for environmental and human health due to the neurotoxicity and bioaccumulation potential of this organic form, even at low concentrations [24]. CH_3Hg^+ is usually formed in sediments under anaerobic conditions (Figure 1) through the activity of mainly sulphate-reducing bacteria and, to a lesser extent, iron-reducing bacteria, methanogens, and syntrophs that possess the *hgcAB* genes [59].

In addition to microbial methylation, abiotic pathways for the formation of CH_3Hg^+ in the presence of methyl donors (e.g., methylcobalamin, humic materials, methyltin) have also been identified in controlled experiments, but their exact role under natural environmental conditions is still unclear [1]. Biotic methylation is strongly influenced not only by the bioavailability of inorganic Hg, related to the speciation of this metal in sediments [6], but also by the composition of the microbial community and multiple environmental parameters including organic matter concentration and quality, speciation of sulfur compounds, and redox conditions and associated amounts of terminal electron acceptors (e.g., sulphates, Fe^{2+}, Mn^{4+}) [6,60]. As an example, lower CH_3Hg^+ production under high sulphide conditions could be caused not only by a smaller pool of bioavailable Hg due to its

Figure 1



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Schematic representation of Hg cycle in sediments. O.M. = organic matter, Met. = methylation, Ox. Deg. = oxidative demethylation, Red. Deg. = reductive demethylation, hgcAB = methylating microorganisms.

precipitation as insoluble β-HgS [44], but also by shifts in relative abundance and diversity of the methylating population [61]. Furthermore, Hg methylation can also be subject to seasonal changes mainly driven by temperature, which is conducive to microbial activity [19]. In marine environments, where large quantities of organic matter are accumulated, the volatile form $(CH_3)_2Hg$ can also be formed and released to the water column [41,57], but its exact formation pathways are still unknown [62]. In the water column, $(CH_3)_2Hg$ can represent a source of CH_3Hg^+ through degradation mediated by dissolved sulphides [63] or, thanks to its volatility, contribute to the evasion of Hg to the atmosphere when occurring in surface waters, for example, in upwelling zones [62]. Particularly at contaminated sites, it is important to identify the variables controlling methylation [6]; indeed, spatial patterns of CH_3Hg^+ concentrations in sediments can differ from those of total Hg, with higher CH_3Hg^+ levels occurring where conditions are optimal for methylation [25]. However, under certain conditions CH_3Hg^+ can be degraded through both biotic and abiotic processes because methylation and demethylation coexist in the environment, the net CH_3Hg^+ production is the result of the balance between these processes. Two main mechanisms of biotic demethylation have been identified, reductive and oxidative, leading to the production of Hg(0) and Hg(II), respectively, whereas abiotic processes include the physical and chemical degradation of CH_3Hg^+ [64].

Sediments (Figure 1) can represent a source of both Hg(II) and CH_3Hg^+ for the water column through porewater diffusion after the oxidation of the sedimentary adsorptive phases [19,57]. However, under oxic conditions, Hg mobility in porewaters is influenced by the presence of Fe and Mn oxyhydroxides, which can promote the adsorption of Hg on solid surfaces through the formation of Hg—O bonds and therefore limiting the amount of Hg released to the water column [43,57]. Hg mobility in porewaters (Figure 1) is generally lower under reducing conditions, where it can be limited by the co-precipitation of Hg with sulphide minerals [65]. On the other hand, physical remobilization of sediments can potentially reintroduce large amounts of buried contaminants in aquatic environments, which may then be redistributed to nearby and downstream environments posing a serious risk to the health of the ecosystem [23]. Remobilization of sediments frequently occurs not only due to anthropogenic activities such as dredging [21], trawling [5], maritime traffic [22], or wetland restoration [23], but also due to natural erosion caused by currents [23], enhanced during intense flooding events (e.g., Ref. [10]). As the frequency of intense storm events increases with ongoing climate change, it is expected that resuspension of contaminated sediments due to flooding events will be a key aspect in managing legacy contamination, particularly at urbanized estuaries [4].

Arsenic in sedimentary compartments and mobility

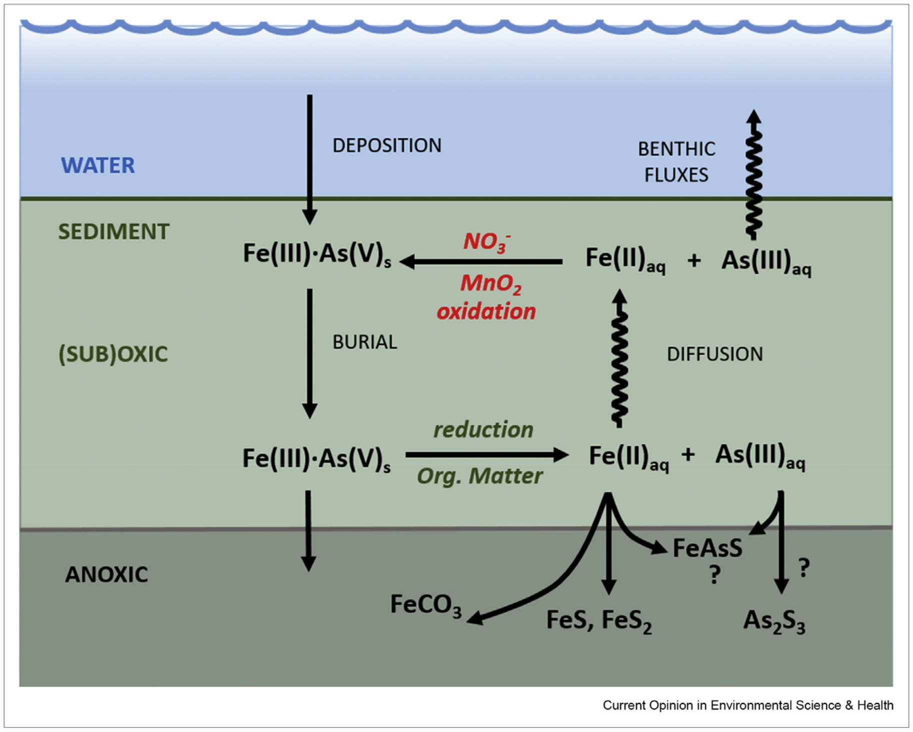
Arsenic can enter into the environment thanks to the oxidation of different mineral species, which causes As to become soluble [66] and being transported to the surroundings through drainage waters. In the Huautla mining district (Southern Mexico), during wet periods when erosion or water transportation may be enhanced, the suspended particulate matter from mines and springs were found to be highly contaminated by As and other trace elements. Thermodynamic calculations also demonstrated that the release of dissolved As from the dissolution of sulfides and subsequent As sorption/desorption processes onto oxyhydroxides or clays may constitute a serious health hazard for inhabitants living downstream [27].

Moving through terrestrial runoff and groundwater discharge to the water bodies, like other contaminants As tends to sink to the sediments [33,40]. Especially in mining areas, As concentrations in freshwater sediments can reach up to thousands of mg kg^{-1} ([26] and references therein; [67]) (Table 2). However, speciation and environmental factors (Eh, pH, water composition, physical disturbance, and microbial activity) may control As mobility from the sediments to the water column [32].

Speciation analyses may help depict the occurrence of the arsenate, As(V), or arsenite, As(III), species, and the toxic effects of As related to its oxidation state [30]. The chemical fractionation of As in the sediments (Figure 2) is often dominated by the residual fraction and the Fe (Mn, Al) (oxyhydr)oxides [33]. However, the relative proportion of As(III) concentration with respect to As(V) concentration varies widely depending on the redox conditions in the geological environment. A majority of As is in the form of As(III) in the aquatic sediments (Figure 2) as much as in groundwaters, since As(V) is reduced to As(III), enhancing As mobility, under reducing conditions [40]. Indeed, the same authors observed that in the Macleay River system (eastern Australia), legacy mining activities have caused As(V) to become strongly retained in the solid phase and widely dispersed in sediments across the entire active channel-zone favored by the (mainly) oxic nature of the river system. At this site, secondary Fe(III) (oxyhydr)oxides are recognized to play a role in hosting As in stream sediments. Only localized and dynamic redox driven shifts in speciation strongly influence the mobility and partitioning in the hyporheic zone, where local reducing/sulfidogenic conditions may enhance the aqueous mobility of As(III).

The effects of both seasonal changes and microbial community structure on As speciation and flux from sediments to freshwaters in a mining-affected river system were investigated in Huangshui Creek (Hunan province, China) [32]. The river has been severely

Figure 2



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Schematic representation of As cycle in sediments (redrawn from Ref. [68]).

impacted by long-term historic realgar extraction and its stream sediments contain both arsenate and arsenite, and relative proportions of these varied seasonally. Experimental results demonstrated that As release from sediments is high at high temperature but also suggested that As cycling is also controlled by adsorption/precipitation processes and by microbial and hydrophyte activity. In extreme environments such as subarctic lakes close to point sources of legacy mining emissions (Northwest Territories, Canada), As concentrations of surface water remain high because sediments are a persistent source of As to overlying waters that are seasonally recycled following ice-cover development [69]. The notable increase of As in the lake waters after the onset of anoxic conditions occurred in parallel with redox-sensitive elements such as iron (Fe) and manganese (Mn), suggesting the coupling of As mobility with Fe and Mn cycling. In the cold arid Tibetan plateau lakes [30], the labile As mobilization is primarily controlled by low Eh values in the sediments and HCO_3^- concentrations in the surface water through reductive dissolution of As-bearing Fe (hydr)oxides mediated by bacteria and oxyanion competition for As adsorption sites. The effects of indigenous microbes on the As redox cycling during the oxic-anoxic transitions were investigated by Ye et al. [31] on incubated sediment samples collected near an active antimony mining area located in Xikuangshan (Hunan province, China). Oxidized As(III/V)-hosting phases were the primary As species in the solid, and no As sulfides were formed. Arsenic mobility in sediments was mainly attributed to the formation of soluble thioarsenate with biogenic sulfide due to the activity of sulfate reducing bacteria. Conversely, the transformation of Fe species made a limited contribution to As release due to the low Fe(III) reductive dissolution and minor changes in the Fe-bearing solid phases. The algal bloom decay in shallow lakes was also found to generate strong anoxic conditions affecting the dynamics of labile As, Fe, Mn, and S from sediment [70].

The association of As with the exchangeable phases is also very common in subsurface deltaic sediments such as in the Vietnamese-side of the Mekong Delta [48] or the Mississippi deltaic plain in the USA [71]. Huyen et al. [48] observed that As release may be controlled by sorption-desorption reactions with clays/phyllosilicates, where As is in competition for sorption sites with dissolved Si and dissolved organic carbon (DOC), depending on pH. Arsenic mobility was more extensive in acidic conditions via the reductive dissolution of Fe-oxyhydroxides, and oxidation of pyrite associated with peat layers. The mobility of As may be further stimulated under acidic conditions in the presence of chloride

(Cl^-), connected to the saltwater intrusion due to uncontrolled pumping of the groundwaters or to soil flooding/inundation episodes, by forming more soluble iron-chloride surface complexes on pyrite.

In situ incubated experiments in aquifers have revealed the elevated efficiency of biogenic and poorly crystalline Fe(III) minerals (i.e., ferrihydrite) in As sorption compared with abiogenic minerals and their preeminent availability to more easily release As in dissolved form under reducing conditions by (Fe(III)-reducing) microorganisms [72].

In coastal areas, sediments may be potential sources of As in the water column mainly due to dissolution/desorption reactions of Fe-oxyhydroxides (Figure 2) and should be carefully monitored. Liu et al. [34] investigated the *in situ* As speciation and the release kinetics by separate diffusive gradients in thin film (DGT) technique the Daya Bay (South China Sea). The authors noticed that mariculture farms were the most important contributors to As(V) contamination in surface sediments with the potential risk of As(V) release into the overlying water, whereas labile As(III) was the dominant speciation in the deep layers of sediments. The effect of sediment resuspension and the subsequent remobilization and redistribution of As and Hg species were investigated through a mesocosm experiment (simulated resuspension under controlled conditions) in selected estuaries of the Asturian coast (northern Spain) impacted by decommissioned Hg and As mines and periodically subjected to dredging activities [21]. Pre-resuspension conditions were restored a few hours after resuspension, but at the Nalòn estuary, the release of dissolved As(V) and CH_3Hg^+ appeared to be favored during resuspension and can be considered an important issue to be taken into account when dredging is deemed necessary. The highest As(V) and SO_4^{2-} concentrations detected in porewaters at the Nalón estuary may be evidence of a scarce sulphate reduction, which usually inhibits the reduction of As(V). Moreover, the low rates of sulphate reduction could also explain the pronounced increase in CH_3Hg^+ at the same sites.

Future perspectives

Mercury and As are emitted and released to air, land and water by both natural and anthropogenic sources. When introduced in the environment the two elements undergo complex biogeochemical cycling, which also affect the aquatic compartments (oceans, lakes, and rivers). Sediments are vast reservoirs and act as both sinks and secondary sources of As and Hg. Arsenic and Hg cycling in sediments, including, for instance, the production of the highly toxic MeHg, are strongly influenced by biogeochemical conditions, especially those connected with S and Fe (Mn) cycling. Despite considerable work to date, the main outcome from this review is that the current understanding of Hg and As dynamics in sediments, to predict their mobility through speciation (i.e., As(III) and As(V)) and evaluate production/degradation of organic forms (i.e., MeHg), is still limited. More research is needed, for instance, on the effects of sediment resuspension induced by dredging operations or changing of redox conditions following the translocation of contaminated sediments for salt marsh restoration in coastal lagoon environments, which could affect the fate of As and Hg in the aquatic compartment and their transfer to the trophic chain.

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 article.

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* of special interest
* * of outstanding interest

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