



Sulfur speciation in mercury-contaminated sediments of a coastal lagoon: the role of elemental sulfur

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Chemical equilibrium studies have predicted that elemental sulfur (S^0) could play a crucial role in mercury mobility in salt marsh sediments. This prompted us to consider the occurrence of S^0 in conjunction with the degree of contamination in sediments of a coastal wetland (Pialassa Baiona, Italy) impacted by inputs of mercury derived from past industrial activity. The distribution of S^0 , total Hg, soluble sulfates and acid-soluble sulfides was studied in five sediment cores collected in two ponds of the lagoon. Sulfides, sulfates and S^0 exhibited vertical profiles typical of salt marsh systems, with concentrations declining with depth. Mercury enrichment ($2\text{--}23\text{ mg kg}^{-1}$) was detected at the surface strata where the highest concentrations of sulfides and S^0 were found (up to 1.70 and 0.9 g kg^{-1} , respectively). The effect of elevated levels of sulfides and elemental sulfur on the fate of mercury in the lagoon is discussed.

Introduction

Sulfur exists as a variety of species in sediments (sulfates, sulfides, elemental sulfur, organic sulfur compounds), which are involved to various degrees in the biogeochemistry of toxic metals. Sulfides are considered to be a key binding phase involved in the biogeochemical cycling of heavy metals in anoxic sediments. The amount of sulfide that reacts with aqueous acids at room temperature to release gaseous H_2S , *e.g.* acid-volatile sulfide (AVS), is a sediment property which may control the biological impact of toxic metals.^{1,2} Both forms of solid mercury sulfides, cinnabar (red HgS) and metacinnabar (black HgS), are extremely insoluble and, for this reason, HgS is considered to be an important sink of mercury in anoxic sediments. However, the solubility of HgS strongly depends on the chemical composition of the sediment. Natural organic matter, especially humic acids, favours the dissolution or inhibits the precipitation of HgS .^{3,4} The dissolution process may be promoted by ligand–metal interactions, and recent studies on complexes of $Hg(II)$ with humic substances have demonstrated the relevance of reduced sulfur functional groups in the coordination of the metal.⁵

The solubility of HgS can be augmented by high sulfide concentrations through the formation of dissolved $Hg(II)$ sulfur species,⁶ such as the neutral complex HgS^0 and ions such as HgS_2^{2-} . Dissolved species can be taken up by sulfate-reducing bacteria capable of producing the highly toxic methylmercury. The Hg methylating activity of bacteria has been shown to occur when the sole source of mercury in the aqueous phase is solid HgS ,⁷ and in sulfidic waters seems to be controlled by the occurrence of the neutral complex HgS^0 .⁸ The concentration of methylmercury in sediments is determined by the balance of its formation and degradation and, as both processes are influenced by the levels of sulfates and sulfides, these two sulfur species play a pivotal role in the toxicology of mercury in aquatic environments.^{9–11}

Elemental sulfur (S^0) is another relevant sulfur species in aquatic sediments, but its role in the cycling of mercury has been less investigated. Elemental sulfur can exist in a variety of different forms (*e.g.* allotropes) and molecular species (*e.g.*

cyclo-S, polycatena-S); the stable solid form in environmental conditions is orthorhombic α -sulfur consisting of cycloocta-S molecules.¹² In addition to elemental sulfur, other classes of sulfur compound occurring in the sedimentary environment contain catenated zero-valent sulfur atoms: sulfanes (H_2S_n), hydropolysulfides (HS_n^{1-}), polysulfides (S_n^{2-}), polythiosulfates ($S_nO_3^{2-}$) and polythionates ($S_nO_6^{2-}$).^{13,14} The importance of S^0 for mercury availability has been stressed by Paquette and Helz,¹⁵ who have demonstrated that S^0 increases the solubility of cinnabar. This effect has been attributed to the formation of complexes between mercury and polysulfides, the latter in turn formed by the reaction of S^0 with sulfides. The enhanced dissolution of cinnabar by S^0 has recently been confirmed by Jay *et al.*¹⁶

It is clear from the above discussion that sulfur cycling may control the behaviour of sediment as a source or sink of mercury, especially in marine-like environments. Prompted by recent results on the implication of S^0 for mercury mobility in salt marsh systems,^{15,16} we have investigated the sulfur speciation in Pialassa Baiona, a coastal lagoon contaminated by mercury. In this study, we report the distribution of S^0 and mercury, together with soluble sulfates and acid-soluble sulfides, in five sediment cores of the lagoon. To our knowledge, this is the first study addressing the distribution of mercury in connection with the occurrence of elemental sulfur in sediments.

Experimental

Study site

The lagoon (10 km^2 , Fig. 1) is connected to the northern Adriatic Sea through the harbour of Ravenna (Italy) and consists of a system of interconnected man-made channels delimiting open reaches (ponds). For a few decades, the lagoon has been impacted by inputs of municipal, agricultural and industrial run-off, mainly from the Cupa channel located in the southern part. Although the inputs of pollutants declined significantly in the 1970s following environmental regulations,

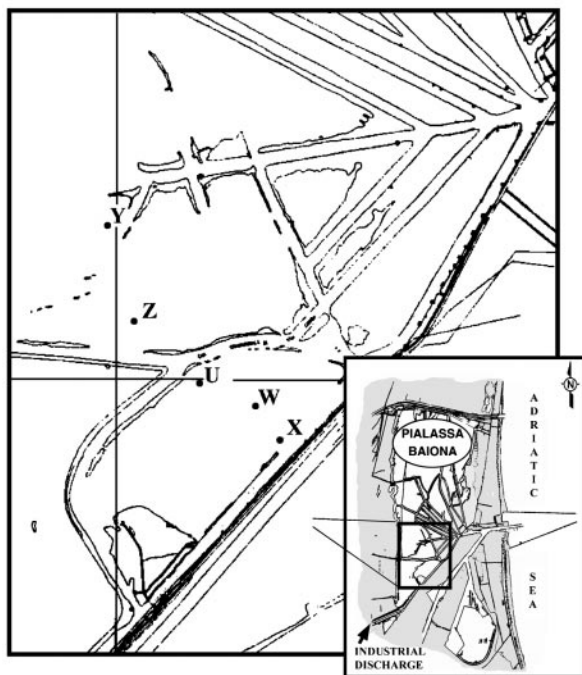


Fig. 1 Study area with sampling locations (filled circles).

sediments are still heavily contaminated by mercury,^{17–19} polycyclic aromatic hydrocarbons²⁰ and synthetic polymers.²¹

Sampling

Sediment cores were withdrawn in winter (February 25th 1999) during low tide from a boat using a manual corer (washed with 1% HNO₃ prior to sampling) at the following locations (Gauss-Boaga co-ordinates in parentheses): U (2301270E, 4928985N), W (2301480E, 4928910N), X (2301555E, 4928805N), Y (2300955E, 4919525N), Z (2301060E, 4929195N). The sites, shown in Fig. 1, were located in two different ponds in areas characterized by the absence of human interventions (*e.g.* dredging) in recent years. Water samples were also collected for the determination of sulfates. Once sampled, cores were sealed to maintain anoxic conditions and transported to the laboratory, where they were extruded and sectioned under a nitrogen atmosphere at 6 cm intervals. Samples were transferred to glass vials, sealed under nitrogen and stored at -18°C prior to analyses. An aliquot was added to water (twice the sample weight) for pH measurements.

Analysis

Sulfates were extracted in 10 mL of de-ionized water from 1 g of wet sediment sample by magnetic stirring at room temperature (10 min). After centrifugation, the aqueous solution was filtered through a 0.45 μm filter, brought to 100 mL and sulfates were analysed by ion chromatography using a Dionex DX100 under standard conditions.²² The reproducibility of the overall procedure was 6% (expressed as the relative standard deviation, RSD, of four replicate analyses of a sediment sample).

Sulfides were determined by a standard acid volatilization procedure under nitrogen.²³ The wet sediment was added to water (200 mL) in a distillation apparatus, concentrated sulfuric acid (10–20 mL) was added dropwise at room temperature and the evolved H₂S was stripped with N₂ for 90 min into gas scrubbing bottles containing 100 mL of zinc acetate solution (0.05 mol L⁻¹). The precipitated ZnS was determined by iodine titration using starch as indicator. This method measures acid-soluble sulfides and provides only a

semi-quantitative determination of very insoluble metal sulfides (HgS, CuS, SnS₂).²³

The measurement of S⁰ was accomplished using a procedure detailed elsewhere.²⁴ Briefly, 1 g of wet sediment was mixed with MgO and extracted three times with deoxygenated toluene (3 mL) by sonication (20 min) in a closed centrifuge tube. Aeration was minimized to avoid the oxidation of sulfur species. The extracted S⁰ was oxidized by bomb combustion to sulfate which was analysed by ion chromatography. The typical reproducibility (RSD), recovery and detection limit were 12%, 85% and 40 mg kg⁻¹, respectively.

The total sulfur content was determined using a Sulfanazo III instrument, in which the samples (5–10 mg) were combusted in an oxygen flask containing hydrogen peroxide as an absorbent. The flasks were then washed with distilled water and the solutions boiled to remove excess hydrogen peroxide. After cooling to room temperature, acetone and diphenylcarbazone (indicator) were added and the solutions were titrated with barium perchlorate. The reproducibility (RSD) and detection limit were 8% and 2 g kg⁻¹, respectively.

For the determination of total mercury, wet sediment samples (about 4 g) were digested with 10 mL of concentrated HNO₃ and 20 mL of concentrated H₂SO₄ for 3 h at 90 $^{\circ}\text{C}$. The digests were brought to 100 mL and an aliquot was analysed for total mercury by cold vapour atomic absorption spectrometry (CVAAS). Three replicate analyses of the Estuarine Sediment Reference Certified Material BCR-CRM 277 issued by the Commission of European Communities gave an Hg concentration of $1.63 \pm 0.16 \text{ mg kg}^{-1}$ (certified, $1.77 \pm 0.06 \text{ mg kg}^{-1}$). The detection limit was 0.03 mg kg⁻¹.

Concentrations are expressed on a dry weight basis (loss of weight at 105 $^{\circ}\text{C}$).

Results and discussion

Distribution of sulfur species

Data on elemental sulfur (S⁰), soluble sulfates, acid-soluble sulfides and total sulfur are presented in Table 1, together with mercury concentrations. Typical vertical profiles of sulfides, S⁰ and Hg are shown in Fig. 2 for cores U and W.

Sulfate concentrations in the uppermost surface strata range from 290 to 1060 mg kg⁻¹ (as S). The observed concentrations are related to the sea water-like conditions of the water body, which is dominated by tidal inputs from the Adriatic Sea. Indeed, sulfate concentrations in the column water fall in the 1.2–1.7 g L⁻¹ range ($n=5$) against 2.7 g L⁻¹ of mean sea water. Sulfate concentrations in sediments decrease rapidly within the surface layer and then flatten out below 15 cm of the sedimentary column.

Sulfides are abundant in the upper layers (660–1500 mg kg⁻¹), indicating that the oxic–anoxic boundary is located close to the sediment–water interface. Sulfide concentrations diminish with depth; a concentration peak is apparent only in core Z.

Similar to our observations for sulfates and sulfides, S⁰ occurs at higher levels in the top layer (350–890 mg kg⁻¹); its concentration then declines with increasing depth until values of less than 40 mg kg⁻¹ are reached (the limit of detection of the overall procedure).

Total sulfur vertical profiles are more variable, a behaviour observed in other salt marsh systems.^{25,26} From the data in Table 1, it appears that sulfides, S⁰ and sulfate represent a minor fraction of the total sulfur pool (generally less than 20%), the remaining part being accounted for by pyrite and organic sulfur which are the principal repository species in salt marsh sediments.^{25–27}

The observed trends in the vertical profiles of sulfur species are typically encountered in coastal and intertidal sediments.^{25–33} Sulfate is consumed by sulfate-reducing bacteria

Table 1 Concentrations of soluble sulfates, acid-soluble sulfides, elemental sulfur (S^0) and total sulfur (mg kg^{-1} dry weight as S) and total mercury (mg kg^{-1} dry weight) in sediment cores of Pialassa Baiona lagoon (n.d., not determined)

Core	Level/cm	Sulfates	Sulfides	S^0	Total S	Hg
U	3	556	876	380	11600	2.17
	9	244	1470	490	11600	2.28
	15	220	1260	410	2000	0.8
	21	300	775	270	4800	0.04
	27	141	324	140	n.d.	<0.03
	33	93	67	50	n.d.	<0.03
	39	84	14	<40	n.d.	<0.03
W	3	1060	1510	660	17500	19.6
	9	589	532	440	5500	20.2
	15	305	282	130	7000	1.76
	21	205	130	70	n.d.	0.03
	27	215	38	<40	n.d.	0.07
	33	249	9	<40	n.d.	0.04
X	3	540	659	350	7800	23.09
	9	197	117	60	<2000	0.47
	15	187	11	<40	n.d.	<0.03
	21	168	4	<40	n.d.	<0.03
Y	3	544	1140	620	5700	2.9
	9	434	1080	550	22100	4.06
	15	233	1280	400	9700	6.73
	21	232	887	370	10600	12.7
	27	228	854	380	n.d.	1.6
	33	260	71	40	n.d.	0.03
Z	3	281	183	<40	n.d.	<0.03
	9	771	1700	890	16500	8.2
	15	577	1150	540	14200	13.1
	21	483	329	150	14000	10.0
	27	309	102	60	n.d.	1.82
	33	216	831	150	n.d.	0.27
	39	201	43	<40	n.d.	0.04
	39	221	14	<40	n.d.	<0.03

to oxidize organic matter with the formation of sulfides that are rapidly deposited as FeS. In turn, FeS is transformed into the more stable pyrite (FeS_2) by reaction with S^0 , which is formed by the abiotic as well as microbially mediated oxidation of sulfides. High concentrations of S^0 (up to hundreds/thousands of mg kg^{-1}) can be found in salt marsh systems^{25,26,34} and coastal sediments.²⁹

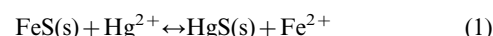
Correlation with mercury

The data in Table 1 show that mercury is mostly confined to the upper 20 cm. The distribution of Hg in the southern pond (cores U, W, Z) strongly parallels that of S^0 , as demonstrated by the excellent correlation coefficients for the linear regression curve ($r=0.82$, 0.92 and 0.96 for cores U, X and W, respectively). In fact, in these sites, mercury is concentrated within the upper 10 cm where S^0 concentrations are at a maximum. In cores Y and Z, located in the northern pond, Hg

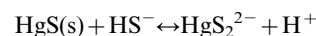
profiles exhibit a subsurface peak and the correlation with S^0 is poorer ($r=0.39$ and 0.66, respectively). However, considering the high levels of Hg, its distribution is probably caused mainly by the deposition/erosion dynamics of the sediments, rather than by bio/chemical processes. Whatever the causes of mercury distribution, given that the metal is found at those levels displaying the greatest values of both sulfides and elemental sulfur, it is likely that these sulfur species shape the mobility of Hg in the investigated area.

In the mercury-contaminated layers, acid-soluble sulfides are in large excess with respect to the total mercury concentration, the values of the sulfide/Hg ratio, expressed on a molar basis, being in the 100–19 000 range. Given the abundance of acid-leachable iron in these sediments (around 20 mg g^{-1} ; Mn was found at lower concentrations¹⁷), iron(II) monosulfides are thought to be the principal constituents of acid-soluble sulfides.

Iron monosulfides represent a pool of solid sulfur available for the precipitation of mercury, as they have higher solubility than mercury sulfides:^{35,36}

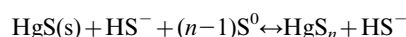


Therefore mercury is expected to occur mostly as HgS in the solid phase. In agreement, solid speciation studies performed on sediments collected in the southern pond have shown that mercury is predominantly associated with sulfides in this area.^{19,37} However, at high sulfide concentrations and alkaline pH, mercury can be mobilized from the solid to the aqueous phase in the form of sulfide complexes. For instance:⁶



Increased levels of dissolved Hg above those expected from HgS solubility have been found in sulfidic water and sediments.^{38,39}

In the presence of S^0 , the solubility of solid HgS is further increased through the formation of polysulfide complexes:¹⁵



The solubility of S^0 in water is low owing to its hydrophobic character ($2 \times 10^{-8} \text{ mol kg}^{-1}$ as S_8).⁴⁰ Accordingly, porewaters contain low levels of dissolved S^0 , although values larger than $10^{-6} \text{ mol L}^{-1}$ are generally found in marine sediments,⁴¹ and concentrations of colloidal sulfur close to $10^{-3} \text{ mol L}^{-1}$ have been reported for some sulfidic waters.⁴² Given the high concentrations of S^0 in our sediments, it is likely that interstitial waters are saturated or even oversaturated with respect to S^0 . Laboratory experiments have shown that, in solutions saturated with S^0 , and at the pH values typical of our sediments (between pH 8 and 9.5), the concentration of dissolved mercury in equilibrium with cinnabar falls in the $1\text{--}10 \text{ } \mu\text{mol L}^{-1}$ interval.¹⁵ Concentrations could be even higher in water oversaturated with S^0 . Thus, a significant partitioning of Hg into water promoted by S^0 is expected in our sediments, in spite of the fact that Hg is mainly trapped as solid HgS. In fact, there are several pieces of evidence indicating the bioavailability of the metal in the investigated area: (i) active biomonitoring experiments using transplanted mussels have indicated that mercury is capable of entering the food chain;¹⁸ (ii) significant concentrations of methylmercury have been detected in sediments;³⁷ (iii) high levels of mercury have been found in macroalgae.³⁷

The bioavailability of mercury is not solely related to its porewater concentration, but is also dependent on the nature and distribution of chemical species occurring in the dissolved phase. At least for methylating bacteria, mercury bioavailability has been related to the occurrence of hydrophobic species capable of passive diffusion across the lipid cell membrane. In particular, it would be governed by the

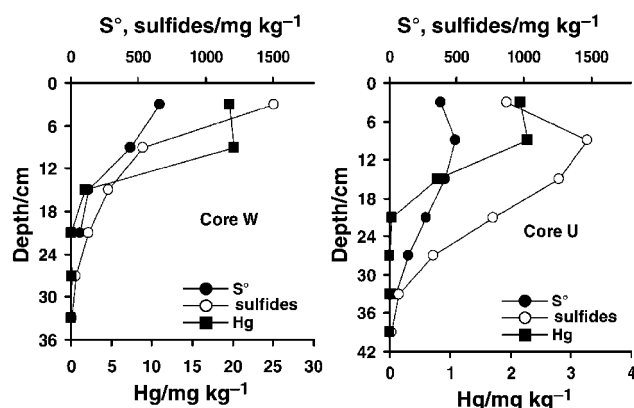


Fig. 2 Concentrations of elemental sulfur (S^0), acid-soluble sulfides and total mercury versus depth in sediment cores: W (left) and U (right).

abundance of the neutral complex HgS^0 in sulfidic waters.⁸ In the presence of S^0 , other neutral species could be involved, for instance the neutral mercury polysulfide HgS_5 .¹⁶ Thus, an increased partitioning of mercury into porewater promoted by S^0 does not necessarily mean an increase in mercury bioavailability.

Moreover, in sediments, S^0 could be involved in chemical processes (e.g. pyritization, sulfurization of organic matter) which might counteract the enhanced mobility of mercury expected from the formation of polysulfide complexes. Mercury can be precipitated and adsorbed on authigenic pyrite.⁴³ This process could be active in our sediments given the significant pyritization observed in surface layers, probably linked to the high levels of S^0 . However, pyritized Hg may be potentially available if the pyrite is oxidized, for instance by sediment resuspension.⁴³ S^0 is also involved in the sulfurization of organic matter,^{26,44,45} and solid organosulfides may strongly bind mercury limiting its mobility.⁸

Conclusions

The principal aim of the present study was to draw attention to elemental sulfur as an important sulfur species capable of shaping the fate of mercury in salt marsh sediments. In the investigated area, mercury occurs in the surface zone where bioturbation may continuously supply reactive organic matter, inducing high rates of sulfate reduction and correspondingly high levels of sulfides. In this active zone, incomplete oxidation of sulfides produces abundant S^0 which promotes chemical processes potentially capable of affecting mercury mobility (formation of polysulfides, organosulfides, pyrite). The determination of zero-valent sulfur species, together with mercury, in the aqueous phase is required in order to understand the contribution of S^0 to mercury availability in polluted areas.

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