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Elsa Ramalhosa^a; Susana Río Segade^b; Maria Eduarda Pereira^c; Carlos Vale^d; Armando Duarte^c

^a Centro de Investigação de Montanha (CIMO), ESA-Instituto Politécnico de Bragança, 5301-855 Bragança, Portugal ^b EVEGA - Estación de Viticultura e Enoloxía de Galicia, 32427-Ourense, Spain ^c CESAM & Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal ^d IPIMAR - Instituto de Investigação das Pescas e do Mar, 1400 Lisboa, Portugal

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Monomethylmercury behaviour in sediments collected from a mercury-contaminated lagoon

Elsa Ramalhosa^{a*}, Susana Río Segade^b,
Maria Eduarda Pereira^c, Carlos Vale^d and Armando Duarte^c

^aCentro de Investigação de Montanha (CIMO), ESA-Instituto Politécnico de Bragança, Campus de Santa Apolónia, Apartado 1172, 5301-855 Bragança, Portugal; ^bEVEGA – Estación de Viticultura e Enoloxía de Galicia, Ponte San Clodio s/n, Leiro, 32427-Ourense, Spain; ^cCESAM & Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal; ^dIPIMAR-Instituto de Investigação das Pescas e do Mar, Av. Brasília, 1400 Lisboa, Portugal

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Surface sediments and sediment cores were collected in a mercury (Hg)-contaminated lagoon, namely Largo do Laranjo – Ria de Aveiro, Portugal and analysed in order to establish the monomethylmercury (MeHg) behaviour in this kind of environment. In surface sediments, this compound was only detected in one place (13.2 ng g^{-1} (dry weight)). In this site, it was determined one of the lowest redox potentials (22 mV), indicative of oxic/anoxic conditions, which favours Hg methylation by enhancing the sulphate-reducing bacteria activity. However, the MeHg percentage obtained was low, namely less than 0.1% of the total Hg. This is probably due to Hg deposition with organic matter and iron oxyhydroxides, decreasing Hg availability to methylation. At the deeper layers, MeHg was also determined, reaching 46.4 ng g^{-1} (dry weight) and representing less than 0.1% of the total Hg. The higher MeHg percentages were observed near the surface, where Hg seems to be faster methylated as a result of the lower sulphide concentrations that render bioavailable the inorganic Hg. At depth the low MeHg percentages obtained are due to the formation of HgS and to the adsorption of Hg to iron monosulphides.

Keywords: monomethylmercury; total mercury; acid volatile sulphides; organic matter; iron species; Portugal

1. Introduction

Biochemical processes involving Hg compounds in the aquatic environment are of great importance, especially in those areas where Hg inputs are particularly high. The conversion of inorganic Hg to MeHg is a critical process, as this last form is one of the most toxic and it can be bioaccumulated in organisms. The main factors that determine the exposure of coastal organisms to MeHg are: (1) the amount of inorganic Hg in the sediments that can be converted to MeHg; and (2) the geochemical conditions that affect the activity of methylating bacteria and the availability of inorganic Hg for uptake and methylation, as referred by Sunderland *et al.* [1] and Hammerschmidt *et al.* [2]. To better

*Corresponding author. Email: elsa@ipb.pt

establish correction actions to be implemented in areas contaminated with Hg, both factors should be understood and known.

Several studies have been performed in order to evaluate the chemical speciation of Hg and the physicochemical conditions that control Hg cycling and consequent bioavailability in sediments. For example, Gagnon *et al.* [3] suggested that the superficial oxic sediment layer serves as a geochemical barrier to the diffusion of dissolved MeHg accumulated in anoxic sediments to the overlying waters, which is a significant advantage as the dissolved MeHg in the anoxic layers accounts for up to 30% of the total dissolved Hg. In terms of particulate fraction, less than 1% of the total Hg on particles is MeHg [3]. In the Yatsushiro Sea, Tomiyasu *et al.* [4] verified that the Hg-enriched sediments near Minamata Bay are still being redistributed, causing an increase in the surface Hg concentrations at remote sites, even though 30 years have passed since the shutdown of the discharge of the Hg-contaminated effluent. The predominant species in the sediments is inorganic Hg, with organic Hg composing approximately 1% of the total Hg. Sunderland *et al.* [1], in a macrotidal estuary located at the mouth of Fundy Bay, verified that MeHg production occurs throughout an active surface layer around 15 cm thick. Heyes *et al.* [5] verified that, in the Hudson River Estuary, the Hg methylation is active throughout the upper 25 cm, resulting in a large pool of MeHg in the estuarine turbidity maximum. However, the fraction of the total Hg that is MeHg was smaller than the observed in less contaminated systems. Sunderland *et al.* [6] reported that to the highest sulphide concentrations in sediments from the Bay of Fundy, Canada corresponded an elevated fraction of Hg in methylated form, suggesting higher net methylation rates in these sediments. Besides, this relationship is strong in sediments that are moderately impacted by organic enrichment, but weak in less impacted aerobic sediments [6].

Recently, in Thau Lagoon (France), Muresan *et al.* [7] verified that MeHg represents a small fraction of total Hg (0.02–0.80%) in the solid phase of sediments, and the amorphous oxyhydroxides played a major role in controlling total and MeHg mobility throughout the sediment-water interface. On the contrary, Hammerschmidt *et al.* [2] in the New York/New Jersey Harbor reported that organic material largely controls the geographical distribution of inorganic Hg and MeHg, stating that organic matter and dissolved sulphide inhibit MeHg production in those sediments. Moreover, they stated a considerable variation in solid phase concentrations of Hg(II) and MeHg among sampling locations and periods, with MeHg being 0.20–1.65% of the former. Canário *et al.* [8] also observed in Tagus Estuary (Portugal) that MeHg varied spatially and had a similar distribution to that for total Hg, MeHg representing 0.02 to 0.4% of the total.

Ria de Aveiro is a coastal lagoon located in the north-western coast of Portugal that covers an area of 43 km² at low tide. In high tide the water column can reach the height of 1.0 to 1.5 m, with the exception of the navigation channel where values of 3.5 m have been measured. In low tide, mud depositional areas are observed. During more than four decades, a chlor-alkali industry discharged an effluent rich in Hg in a branch of the lagoon, namely Esteiro de Estarreja. Due to the severe contamination with Hg, several studies on sediments have been carried out in Ria de Aveiro [9–12]. However, to our knowledge, few data exist about the MeHg presence in this ecosystem.

In order to obtain more information on this species behaviour in the marine sediments, this paper reports, for the first time, the MeHg concentrations determined in surface sediments and sediment cores collected in this area, and it is inferred how this compound is related and controlled by other sediment variables, such as the total Hg, organic matter, iron species and acid volatile sulphides (AVS).

2. Experimental

2.1 Field operations

Surface sediments (around 1 cm layer) were collected with a grab sampler at 20 sites of the contaminated area of Largo do Laranjo – Ria de Aveiro in February 2000 (Figure 1). In June 2000, three sediment cores of approximately 50 cm were also collected in the site that presented higher MeHg concentrations in surface sediments, using hand-held PVC acid-cleaned tubes, which were transported vertically to the laboratory immediately after collection.

In the surface sediments, the pH (WTW 320) and redox potential (Mettler Pt 4805/S7, with an Ag/AgCl reference electrode) were determined *in loco*. These parameters were also determined in the sediment cores after arrival to the laboratory, where they were sectioned at 3 cm intervals.

2.2 Sample treatment

All sediment samples were processed in a nitrogen-filled glove bag to prevent oxidation reactions. The pore water samples were extracted from sediments by centrifugation at 6000 rpm, for 20 minutes (B. Braun Sigma 4–10). A portion of the supernatant was filtered through Millipore 0.45 µm porosity filters. The filtrate was collected in acid-cleaned glass bottles, preserved by acidification to pH < 2 with “Hg free” HNO₃ and stored at 4°C. Another portion of the supernatant was filtered through Gelman glass fibre filters to

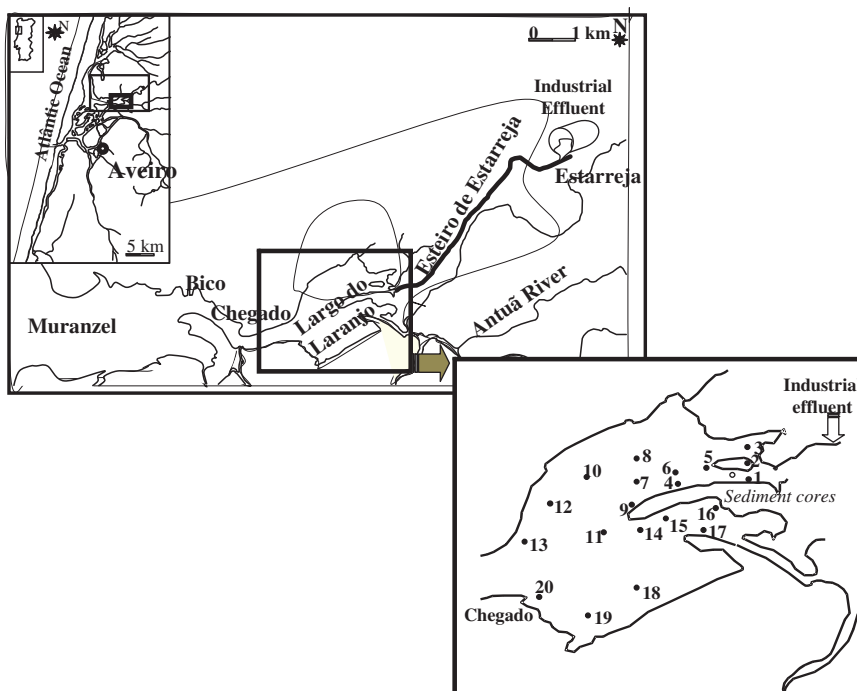


Figure 1. Detailed map of Ria de Aveiro, showing the location of the sampling stations of the surface sediments (●) and sediment cores (○). The Hg industrial discharge is also marked.

evaluate the dissolved organic carbon. Previously, the filters were cleaned by heating at 450°C during 24 hours. Identical volumes of ultra pure water were carried through the centrifugation and filtration stages, as a blank procedure. Portions of all sediments were freeze-dried (Christ Alpha 1–4) and sieved through 1 mm and 63 µm stainless sieves (Fritsch Analysette 3).

2.3 Mercury, iron and organic carbon determinations in the pore waters

The pore waters were analysed for acid-labile Hg, using the procedure described in Bonzongo *et al.* [13] with slight modifications, namely by cold vapour atomic fluorescence spectrophotometry (Cold Vapour Generator PSA 10.003, associated to a Merlin PSA 10.023 detector), using SnCl₂ (2% (w/v) in HCl 10% (v/v)), as the reducing agent. This fraction includes mostly ionic (Hg²⁺) plus dissolved gaseous Hg, but also the Hg fraction weakly bound to the inorganic and organic dissolved complexes [14] that are displaced by protons during acidification of the sample to pH ~1 [13]. The detection limit for the dissolved Hg was calculated from data obtained by 44 calibration curves in the range of 2 to 20 ng dm⁻³, varying from 0.22 to 1.8 ng dm⁻³. The detection limit was calculated as the intercept plus three times the standard deviation of the signal. The relative standard deviation ($n = 5$) for a 20 ng dm⁻³ inorganic Hg standard was less than 5%. No peak was observed when the blanks were analysed. The total dissolved Hg concentrations were determined using the same methodology, after oxidation with K₂S₂O₈ (saturated solution) and ultra-violet radiation (1000 W), as described by Mucci *et al.* [15]. The dissolved iron was determined by flame atomic absorption spectrophotometry (Perkin Elmer, Analyst 100), using the method D1068-84 [16]. The concentration of the dissolved organic carbon was assessed by the wet persulfate/ultra-violet oxidation method ('Method 415.3' of EPA).

2.4 Mercury, iron, organic matter and acid volatile sulphides determinations in the sediments solid fraction

The solid fraction of sediments was analysed for total Hg, MeHg, organic matter, iron oxyhydroxides and amorphous monosulphides, and AVS. The total Hg concentrations were determined by cold-vapour atomic absorption spectrophotometry (Perkin Elmer 3030B), after SnCl₂ reduction (5% (w/v) in HCl 10% (v/v)), following the procedure of Pereira *et al.* [10] involving an acid digestion with HNO₃. The accuracy and precision of the method were evaluated using the estuarine standard reference material, CRM 277, certified by BCR, as described in Table 1. The determined values were in good agreement (*t*-test and *F*-test at $\alpha = 0.05$) with the certified value. The MeHg concentrations were determined by the procedure described in Ramalhosa *et al.* [17], consisting of an extraction

Table 1. Quality control of the results.

Certified material	Species	Certified value \pm CI*	Determined value \pm CI*	Unities
CRM 277	Hg _{Total}	1.77 \pm 0.06	1.73 \pm 0.03 ($n = 10$)	µg g ⁻¹ dry weight
BCR 580	MeHg ⁺	75.5 \pm 3.7	69.5 \pm 8.8 ($n = 3$)	ng g ⁻¹ dry weight
IAEA 356	MeHg ⁺	5.46 \pm 0.39	5.53 \pm 0.21 ($n = 3$)	ng g ⁻¹ dry weight

Note: *CI –*t*-test 95% confidence interval.

of the organic Hg species from the sediments (involving a microwave-assisted alkaline digestion), followed by its separation and determination in an analytical system composed by an high-performance liquid chromatographer (Chromatographic column: Supelco, Nucleosil C18; HPLC pump: Knauer, Mini Star K-500) – ultra-violet post column oxidation system – cold vapour (PSA 10.003) and atomic fluorescence spectrophotometer (PSA, Merlin 10.023). The MeHg detection limit of this method was 11 ng g^{-1} (dry weight), calculated by the intercept plus three times the standard deviation of the signal. Two certified reference materials of sediment containing different amounts of MeHg, BCR 580 and IAEA 356, were analysed in order to evaluate the accuracy and precision of the method. As a consequence of the very low level of MeHg in the IAEA 356 reference material, the analysis required the treatment of four 0.15 g portions of this reference material, following the extraction procedure described before, and the mixing of the organic extracts (dichloromethane) obtained for each portion. Using this procedure, it was possible to determine concentrations lower (around 5 ng g^{-1} (dry weight)) than the detection limit reported previously. It is important to reinforce that an identical procedure was used with natural samples containing MeHg concentrations lower than the detection limit reported before. The determined values of MeHg concentration of these two reference materials were in good agreement (*t-test* and *F-test* at $\alpha=0.05$) with the certified values (Table 1). The organic matter in the sediments was determined by weight loss on ignition at 550°C for 4 h. Iron oxyhydroxides, as well as, the amorphous monosulphide forms, were determined after extraction with hydroxylaminum hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$): 0.5 g of sediment were treated with 20 cm^3 of 0.1 mol dm^{-3} $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution at pH 2 (obtained by adding CH_3COOH), during 16 h. The suspension was filtered through Millipore $0.45 \mu\text{m}$ porosity filters and the filtrate was analysed for iron by flame atomic absorption spectrophotometry (Perkin Elmer Analyst 100). AVS were determined by polarography (PAR 264A) with a Hg electrode (PAR 303A), according to the procedure described by Casas and Crecelius [18].

3. Results and discussion

3.1 Surface sediments

3.1.1 Total mercury and monomethylmercury contents

In Largo do Laranjo surface sediments, the total Hg concentrations varied between 0.146 and $22.7 \mu\text{g g}^{-1}$ (dry weight), the higher values being determined in the nearest area of Esteiro de Estarreja, which corresponds to the Hg source. MeHg was only detected in one location also close to the Hg source (station 1), in a concentration of 13.2 ng g^{-1} (dry weight), corresponding to less than 0.1% of the total Hg. This percentage is in accordance with other values reported in several works (Table 2). It must be inferred that higher MeHg percentages, such as 3%, can be encountered in Largo do Laranjo. In fact it should be noted that MeHg percentage in this ecosystem can be higher if, in sites with the lowest total Hg concentrations (around $0.15 \mu\text{g g}^{-1}$ (dry weight)), MeHg concentrations equal to $4\text{--}5 \text{ ng g}^{-1}$ (dry weight) exist. As the proposed methodology only allows the determination of concentrations higher than 5 ng g^{-1} (dry weight), after joining the organic extracts, with accuracy and precision, the determined MeHg percentage may be slightly underestimated.

Table 2. Total Hg (ng g⁻¹ dry weight) and MeHg (ng g⁻¹ dry weight) contents of some surface sediments collected on estuaries.

Site (Sediment depth)	Concentration range		MeHg (%)	Reference
	Hg _{Total} (ng g ⁻¹ (dry weight))	MeHg (ng g ⁻¹ (dry weight))		
Loire Estuary		0.19 ± 0.08	0.2 ± 0.1	[19]
Scheldt Estuary (0–10 cm)	143.8–1192	0.80–5.70	0.4–1.2	[20]
Patuxent River Estuary (0–4 cm)	around 55–165	0.1–0.8	0.1–0.5	[21]
Lavaca Bay (0–1 cm)	5.1–789	0.028–10.34	0.65 0.34	[22]
Tagus Estuary (0–5 cm)	8.0–49.3 × 10 ³	0.310–34.5	0.02–0.4	[8]
Haihe River (0–5 cm)	60.8–2279.5	0.7–21.7	0.1–2.2	[23]
Dagu Drainage River (0–5 cm)	55.4–8779.1	0.8–7.7	0.1–2.4	
Thau Lagoon (0–12 cm)	3.4 × 10 ² –4.6 × 10 ²	0.075–2.749	0.02–0.80	[7]

3.1.2 Monomethylmercury and total mercury behaviours

In some studies, for example, Benoit *et al.* [21] and Drott *et al.* [24], the existence of a positive correlation between total Hg and MeHg is reported, suggesting that both Hg species (inorganic Hg and MeHg) were co-deposited or the *in situ* MeHg production was a function of total Hg concentration. In Largo do Laranjo, on the contrary, there were places with total Hg concentrations higher than those determined in site 1 and where MeHg was not detected. As described in the previous section, the total Hg concentrations determined in the solid fraction of the sediments varied between 0.146 and 22.7 μg g⁻¹ (dry weight), with the higher Hg concentrations being observed in the sediments located near to the anthropogenic source. This Hg spatial distribution in surface sediments of Largo do Laranjo may be due to the transport of small particles enriched with Hg inside the lagoon. In fact, surface sediments are composed of fine particles (< 63 μm) in a range of 12–41%, increasing their percentage towards the upper zone of Largo do Laranjo, near to the Hg anthropogenic source [25]. These small particles rich in Hg can easily be transported by the tide to other places farther away from the Hg source, contributing to the Hg dispersion inside the lagoon.

Largo do Laranjo surface sediments have pH values between 6.4 and 7.0, showing that sediments are weakly acid or almost neutral. The pH values increase in the direction of Cais do Chegado because this zone is more subjected to seawater, which presents higher pH values than estuarine waters.

Due to the fact that MeHg has only been detected in one place and at a low percentage, as suggested by the results obtained, it means that Hg is not available to be methylated or the sedimentary conditions do not favour Hg methylation and/or do enhance MeHg demethylation. In terms of the redox potential, the values encountered in Largo do Laranjo sediments collected in the 20 sites studied varied between 8.0 and 292 mV, indicating that the present conditions are typically oxic and suboxic, this characterisation having been suggested by Suffet *et al.* [26], who established anoxic conditions when the redox potential is less than -350 mV and oxic conditions when the redox potential is superior to 200 mV. The organic matter content of these surface sediments varied between 0.76 and 10.1%, which can be considered high and not a restriction for bacterial activity. However, these values can be overestimated. In fact, in clay rich sediments, a considerable

Table 3. Total Hg ($\mu\text{g g}^{-1}$ (dry weight)), MeHg (ng g^{-1} (dry weight)) and organic matter (%) concentrations, as well as redox potential (mV) values, determined on the solid fraction of the sixth most contaminated surface sediments collected on Largo do Laranjo – Ria de Aveiro.

Site	[Hg] Total ($\mu\text{g g}^{-1}$ (dry weight))	[MeHg] (ng g^{-1} (dry weight))	Organic matter (%)	Eh (mV)
1	14.7	13.2	7.98	22
2	22.7	ND	9.81	136
3	20.5	ND	10.1	157
4	22.7	ND	7.23	142
5	16.1	ND	9.45	195
6	19.7	ND	9.17	176

Note: ND – Not detected (less than the detection limit of the method).

amount of hydrated minerals may lose its water during loss on ignition, which is a drawback of this method. This water is not removed during drying procedures.

As stated in Table 3, site 1 (the only station in Largo do Laranjo where MeHg was detected) presented an intermediate organic matter content (7.98%), but the lowest redox potential (22 mV), when compared to the sixth most contaminated surface sediments also collected in the studied area. This greater anoxic character of the sediments seems to be essential to the occurrence of Hg methylation. In fact it is in this oxic/anoxic layer of the sediments that it is expected the highest activity of sulphate-reducing bacteria, which are the most important methylators for Hg, in a similar way as that observed by Drott *et al.* [24] for sediments collected in several contaminated places. In this layer, bacteria are able to compete with respect to electron acceptors (such as O_2 , Fe(III)) and have access to energy-rich organic matter (electron donor).

In terms of Hg, in the surface sediments an exponential association between the total Hg and organic matter ($r=0.883$, $p=0.01$, $n=20$) was observed, as represented in Figure 2a, showing the importance of this parameter over the transport and deposition of Hg in this aquatic system. This was also stated in a previous work performed in Esteiro de Estarreja [10], where a significant correlation between Hg concentration and organic matter content of the sediments was observed. In fact, in Esteiro de Estarreja, which ends in Largo do Laranjo, several urban and industrial effluents are discharged, increasing the organic matter load on that area [10]. This explains the higher concentrations determined. The present work also suggests that iron oxyhydroxides, the main species extracted by the hydroxylaminum hydrochloride solution, have an important role in Hg deposition, as stated in Figure 2b ($r=0.919$, $p=0.01$, $n=20$). The iron oxyhydroxides content varied between 0.29 and 2.81 mg g^{-1} (dry weight). All these results point up the possibility of two kinds of particles existing in Largo do Laranjo. Those that are richer in Hg seem to be richer in organic matter and iron. However, further comparative studies on the nature of the particles that circulate on Largo do Laranjo, as well as those that come from Esteiro de Estarreja (channel with the most contaminated sediments in Hg), should be carried out. The exponential relationships obtained may be due to the mixing of those distinct particles.

Looking at the behaviour of Hg in pore waters, which composition is indicative of the type and extension of the reactions of the present compounds in the sediment particles

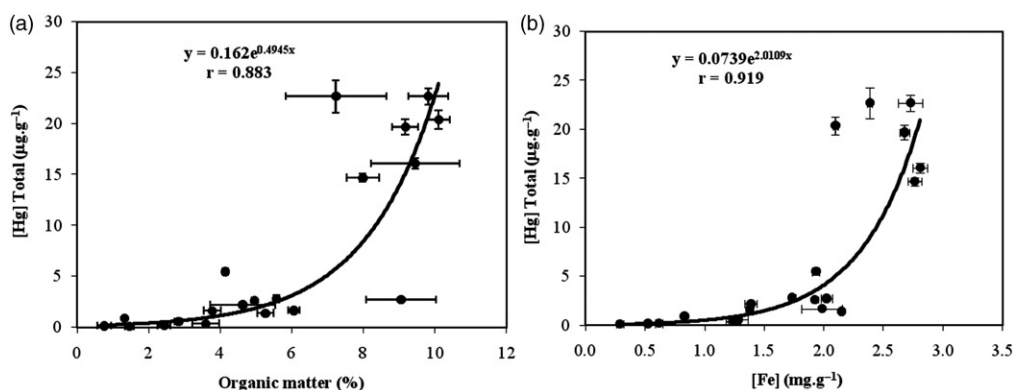


Figure 2. Total Hg concentrations ($\mu\text{g g}^{-1}$ (dry weight)) determined in the solid fraction of the surface sediments collected in Largo do Laranjo in February 2000, in function of: (a) Organic matter content (%); (b) Iron extracted with hydroxylaminum hydrochloride (mg g^{-1} (dry weight)).

and the aqueous phase, significant positive correlations were observed between acid-labile Hg and dissolved organic carbon ($r=0.690$, $p=0.01$, $n=18$), as well as between acid-labile Hg and dissolved iron ($r=0.601$, $p=0.01$, $n=17$). These results suggest that the Hg species extracted as acid-labile Hg species correspond to Hg complexed with dissolved organic carbon or Hg bound to iron oxides that suffered solubilisation.

The acid-labile Hg concentrations varied between 3.45 and 37.7 ng dm^{-3} . The highest concentrations were observed in the zone near to the Hg source and the lower were measured in the locations that were farther away. The dissolved organic carbon and dissolved iron concentrations varied between 1.2 and 17 mmol dm^{-3} , and 0.044 and 1.4 mmol dm^{-3} , respectively. However, the acid-labile Hg found in the pore waters represents only 3.7 to 21% of the total Hg, being the lowest percentages observed in the locations nearby the Hg source. These results are important because they suggest that the quantity of Hg available for methylation, Hg(0) formation and other conversion processes is low, taking into account the definition of acid labile mercury described by Mason and Fitzgerald [27].

3.2 Sediment cores

3.2.1 Monomethylmercury content

MeHg was also detected and its concentration varied between 5.84 and 46.4 ng g^{-1} (dry weight), as depicted in Figure 3a, representing less than 0.1% of the total Hg (Figure 3b). MeHg in the solid phase increased with depth until a maximum value located at 21–24 cm, which corresponds to the maximum concentration of total Hg. On contrary, the highest MeHg percentage was found in the upper 0–3 cm of the cores, decreasing rapidly with depth.

3.2.2 Influence of other sediment variables over mercury availability

Largo do Laranjo sub-surface sediments presented redox potentials of 49 to -134 mV , being the highest values observed at the surface. The pH values varied between 6.3 and 7.8,

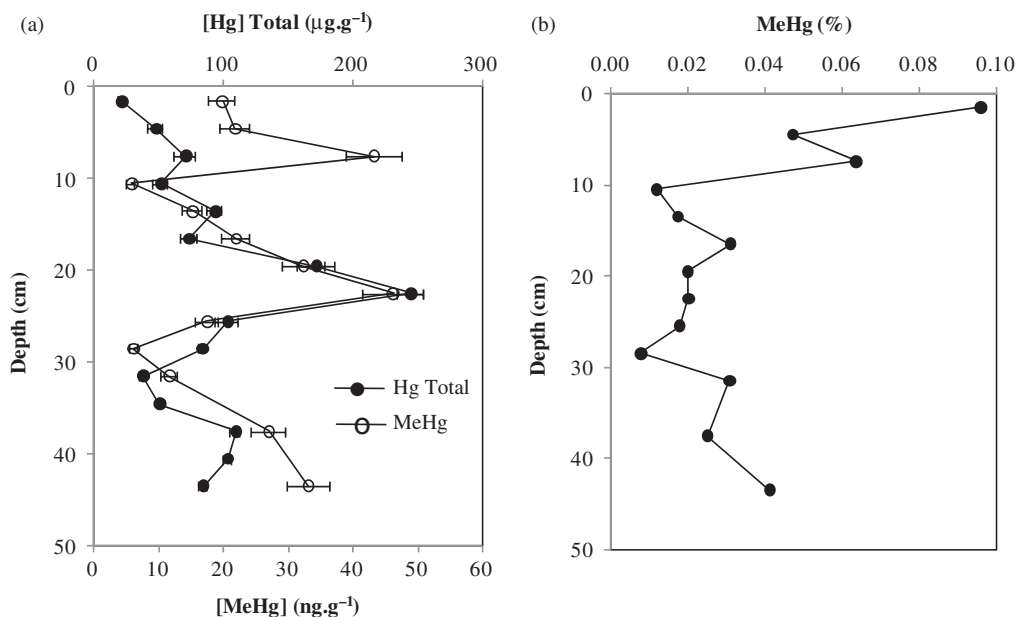


Figure 3. Profiles obtained in the sediment cores (around 50 cm) for: (a) Total Hg ($\mu\text{g.g}^{-1}$ (dry weight)) and MeHg (ng.g^{-1} (dry weight)); (b) MeHg percentage (%).

being the lowest values determined in the first 10 cm, probably attributable to organic matter decomposition processes, increasing afterwards. The total Hg concentrations varied between 21.3 and 245 $\mu\text{g.g}^{-1}$ (dry weight), the maximum incorporation being observed at 21–24 cm depth. The total Hg profile is represented in Figure 3a. The AVS concentrations varied between 15.0 and 273 $\mu\text{mol.g}^{-1}$ (dry weight), the lowest concentrations being determined in the surface layers. Until 27 cm depth, the profile of total Hg was similar to that corresponding to AVS (Figure 4a). This indicates the formation of Hg sulphide or its coprecipitation with iron sulphides. It would be expected that Hg will form its own discrete mineral before the iron sulphide formation [28]. However, as the concentrations of unbound or ionic Hg^{2+} are normally very small in natural systems due to its strong association with dissolved ligands, such as organic matter, iron sulphides can form before mercury sulphide solids. This phenomenon reduces the Hg reactivity towards sulphides, allowing Hg adsorption onto FeS minerals [29].

Until the sediment depth of 15 cm, the total Hg profile is similar to the one obtained for the iron extracted by hydroxylaminum hydrochloride, as shown in Figure 4b, and which concentrations varied between 2.6 and 5.6 mg.g^{-1} (dry weight). Near the surface, the iron species that can be present is FeOOH, although in the deeper layers, the iron amorphous monosulphide forms will predominate. The formation of the latter explains the observed increase in the concentration of iron extracted by the hydroxylaminum hydrochloride at the deeper layers of the sediment, as these species are also co-extracted with this reagent.

In terms of MeHg, some similarities between the profile of this Hg species and organic matter were observed (Figure 5a), as well as between MeHg and AVS (Figure 5b). For all depths, a linear relationship was encountered between MeHg and organic matter

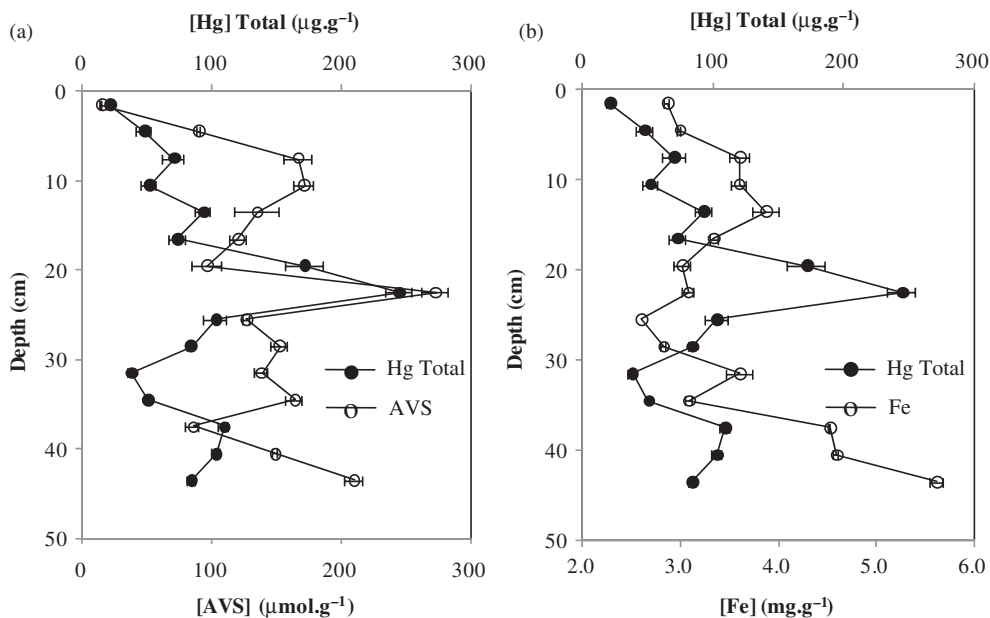


Figure 4. Profiles obtained in the sediment cores (around 50 cm) for: (a) Total Hg ($\mu\text{g g}^{-1}$ (dry weight)) and AVS ($\mu\text{mol g}^{-1}$ (dry weight)); (b) Total Hg ($\mu\text{g g}^{-1}$ (dry weight)) and iron extracted by hydroxylaminum hydrochloride (mg g^{-1} (dry weight)).

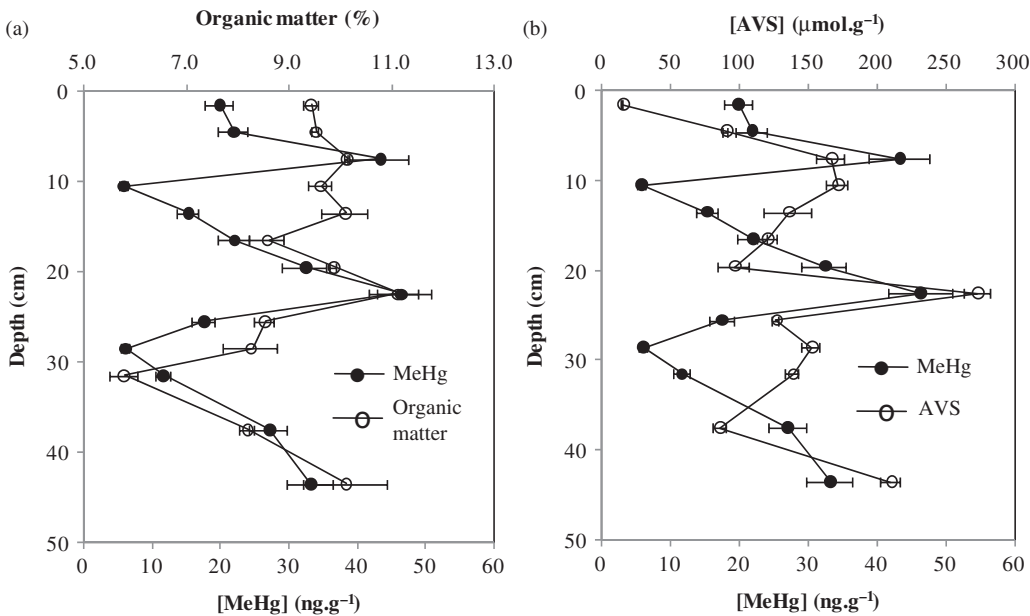


Figure 5. Profiles obtained in the sediment cores (around 50 cm) for: (a) MeHg (ng g^{-1} (dry weight)) and organic matter (%); (b) MeHg (ng g^{-1} (dry weight)) and AVS ($\mu\text{mol g}^{-1}$ (dry weight)).

($r=0.578, p=0.05, n=13$). The correlation increases to 0.821 ($p=0.05, n=8$), when the first five points are discarded. Between MeHg and AVS, no significant linear relationship was determined. However, when observing the profiles in detail, the highest similarities between AVS and MeHg profiles were encountered in the first sediment layers. After the 15 cm depth, MeHg had a more similar behaviour to organic matter. Besides, the maximums of the three components were all determined at the 21–24 cm depth.

These results indicate that the accumulation and biomethylation of Hg must be related to the presence of organic substrates and to some extent to the presence of sulphate-reducing bacteria (microorganisms responsible for sulphide production) mainly in the first 10 cm. In terms of percentage, MeHg represents less than 0.1% of the total Hg, being the higher percentages of the methylated form of the total Hg observed in the first 10 cm, as shown in Figure 3b. The first 5 cm of sediment are the less reducing, with the lowest sulphide content. This fact probably increases Hg availability for methylation. It must be emphasised that the highest MeHg concentrations are detected in the deeper layers; however, the associated MeHg percentages are low. As referred to above, the AVS peak ($273 \mu\text{mol g}^{-1}$ (dry weight)) is observed around the 21–24 cm depth, the maximum values of the organic matter (11.1%), total Hg ($245 \mu\text{g g}^{-1}$ (dry weight)) and MeHg (46.4 ng g^{-1} (dry weight)) being also detected. However, this represents only 0.02% of the total. These results indicate that under reducing conditions the availability of Hg (II) ions for Hg methylation is reduced. Hg will be in the form of HgS or co-deposited with iron monosulphides. Besides, in the presence of high dissolved sulphide concentrations, charged complexes of Hg-S will be present. These species are less bioavailable than neutral ones to methylating bacteria due to their difficult transport through cellular membranes [30–32].

These preliminary results also show that further studies must be performed over Hg transformation activities, namely methylation/demethylation, as the production of MeHg depends on these opposite reactions. Furthermore, special attention must be given to their variation along time and with depth because these factors influence both rates. Hines *et al.* [32] stated, for example, that methylation and demethylation rates vary seasonally, as well as with depth [32,33].

4. Conclusion

The results obtained in this study point out that the MeHg behaviour in sediments of Largo do Laranjo is influenced by several factors. In surface sediments the content of MeHg depends on the existence of favourable conditions for occurring Hg methylation, having the redox potential, an important role. In Largo do Laranjo surface sediments, MeHg was only detected in the site that presented the lowest redox potential (22 mV), when compared to the sixth most contaminated locations. This greater anoxic character of the sediments seems to be essential to the occurrence of Hg methylation. The redox potential can influence the activity of sulphate-reducing bacteria, which are the most important methylators recognised up to now. It was observed and it is known that under oxic/anoxic conditions, the activity of these microorganisms is higher.

At depth, MeHg represents less than 0.1% of the total Hg, the lowest percentages being observed in the deeper layers. Our results point out that Hg must be in stable forms, namely in HgS form or co-deposited with iron monosulphides, and probably unavailable to be methylated by microorganisms. This fact has practical importance because it warns the environmental agencies for the risk of performing dredging activities without the

minimum control of the storage conditions of the sediments. Uncontrolled actions can indeed favour the occurrence of Hg methylation.

References

- [1] E.M. Sunderland, F.A.P.C. Gobas, A. Heyes, B.A. Branfireun, A.K. Bayer, R.E. Cranston, and M.B. Parsons, *Mar. Chem.* **90**, 91 (2004).
- [2] C.R. Hammerschmidt, W.F. Fitzgerald, P.H. Balcom, and P.T. Visscher, *Mar. Chem.* **109**, 165 (2008).
- [3] C. Gagnon, E. Pelletier, A. Mucci, and W.F. Fitzgerald, *Limnol. Oceanogr.* **41**, 428 (1996).
- [4] T. Tomiyasu, A. Nagano, N. Yonehara, H. Sakamoto, Rifardi, K. Oki, and H. Akagi, *Sci. Total Environ.* **257**, 121 (2000).
- [5] A. Heyes, C. Miller, and R.P. Mason, *Mar. Chem.* **90**, 75 (2004).
- [6] E.M. Sunderland, F.A.P.C. Gobas, B.A. Branfireun, and A. Heyes, *Mar. Chem.* **102**, 111 (2006).
- [7] B. Muresan, D. Cossa, D. Jézéquel, F. Prévot, and S. Kerbellec, *Estuar. Coast Shelf Sci.* **72**, 472 (2007).
- [8] J. Canário, C. Vale, and M. Caetano, *Mar. Pollut. Bull.* **50**, 1142 (2005).
- [9] M.F. Lucas, M.T. Caldeira, A. Hall, A.C. Duarte, and C. Lima, *Water Sci. Technol.* **18**, 141 (1986).
- [10] M.E. Pereira, A.C. Duarte, G.E. Millward, S.N. Abreu, and C. Vale, *Water Sci. Technol.* **37**, 125 (1998).
- [11] E. Ramalhosa, P. Monterroso, S. Abreu, E. Pereira, C. Vale, and A. Duarte, *Wetlands Ecol. Manage.* **9**, 311 (2001).
- [12] E. Ramalhosa, S.R. Segade, E. Pereira, C. Vale, and A. Duarte, *Water Res.* **40**, 2893 (2006).
- [13] J.C. Bonzongo, K.J. Heim, J.J. Warwick, and W.B. Lyons, *Environ. Pollut.* **92**, 2, 193 (1996).
- [14] W.F. Fitzgerald and R.P. Mason, in *Biogeochemical Cycling of Mercury in the Marine Environment*, edited by A. Sigel and H. Sigel (Marcel Dekker, New York, 1997), p. 53.
- [15] A. Mucci, M. Lucotte, S. Montgomery, Y. Plourde, P. Pichet, and H. VanTra, *Can. J. Fish. Aquat. Sci.* **52**, 2507 (1995).
- [16] Annual book of ASTM Standards. *Water and Environmental Technology*, edited by USA: ASTM (1984), Vol. 11.01 Water (I).
- [17] E. Ramalhosa, S.R. Segade, E. Pereira, C. Vale, and A. Duarte, *J. Anal. At. Spectrom.* **16**, 643 (2001).
- [18] A.M. Casas and E.A. Crecelius, *Environ. Toxicol. Chem.* **13**, 529 (1994).
- [19] M. Coquery, D. Cossa, and J. Sanjuan, *Mar. Chem.* **58**, 213 (1997).
- [20] B.B. Muhaya, M. Leermakers, and W. Baeyens, *Water, Air, Soil Pollut.* **94**, 109 (1997).
- [21] J.M. Benoit, C.C. Gilmour, R.P. Mason, G.S. Riedel, and G.F. Riedel, *Biogeochemistry* **40**, 249 (1998).
- [22] N.S. Bloom, G.A. Gill, S. Cappellino, C. Dobbs, L. Mcshea, C. Driscoll, R. Mason, and J. Rudd, *Environ. Sci. Technol.* **33**, 7 (1999).
- [23] J. Shi, L. Liang, G. Jiang, and X. Jin, *Environ. Int.* **31**, 357 (2005).
- [24] A. Drott, L. Lambertsson, E. Björn, and U. Skyllberg, *Environ. Sci. Technol.* **42**, 153 (2008).
- [25] E. Ramalhosa, *Mercúrio na Ria de Aveiro: associações, reactividade e especiação*. Ph. D. thesis. University of Aveiro, p. 352 (2002).
- [26] I.H. Suffet, L.L. Williams, C.T. Jafvert, J. Kukkonen, M.R. Servos, A. Spacie, and J.A. Noblet, in *Bioavailability: Physical, Chemical and Biological Interactions*, edited by J.L. Hamelink, P.F. Landrum, H.L. Bergman, and W.H. Benson (Lewis Publishers, Boca Raton, USA, 1994), p. 98.
- [27] R.P. Mason and W.F. Fitzgerald, *Nature* **347**, 457 (1990).

- [28] J.W. Morse and G.W. Luther III, *Geochim. Cosmochim. Acta* **63**, 3373 (1999).
- [29] M.M. Hyland, G.E. Jean, and G.M. Bancroft, *Geochim. Cosmochim. Acta* **54**, 1957 (1990).
- [30] J.M. Benoit, C.C. Gilmour, R.P. Mason, and A. Heyes, *Environ. Sci. Technol.* **33**, 951 (1999).
- [31] J.M. Benoit, C.C. Gilmour, and R.P. Mason, *Environ. Sci. Technol.* **35**, 127 (2001).
- [32] M.E. Hines, J. Faganeli, I. Adatto, and M. Horvat, *Appl. Geochem.* **21**, 1924 (2006).
- [33] M.E. Hines, M. Horvat, J. Faganeli, J.C.J. Bonzongo, T. Barkay, E.B. Major, K.J. Scott, E.A. Bailey, J.J. Warwick, and W.B. Lyons, *Environ. Res. A* **83**, 129 (2000).