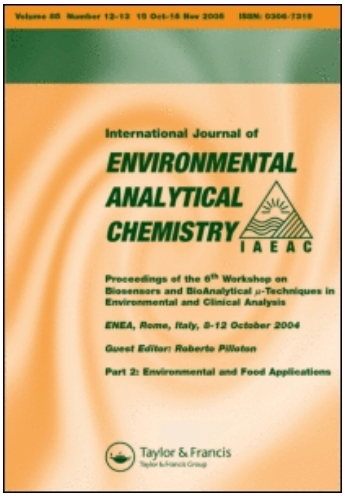

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Use of Partial Extractions to Study Mercury Partitioning on Natural Sediment Particles—A Cautionary Note

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USE OF PARTIAL EXTRACTIONS TO STUDY MERCURY PARTITIONING ON NATURAL SEDIMENT PARTICLES—A CAUTIONARY NOTE

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Inorganic and organic mercury forms ($^{203}HgCl_2$ and $CH_3{}^{203}HgCl$) were added to a natural sediment maintained in dilute suspension under oxic conditions, and partitioning was followed over time with the aid of phase separation techniques (centrifugation—filtration) and chemical extractions (1 N HCl; 0.1 N NaOH; 30% H_2O_2). Sorption of inorganic Hg onto the suspended sediment was essentially complete (>99% of the added $HgCl_2$ was associated with the sediment particles) and very rapid ($t_{1/2}$<< 1 d). The nature of the Hg-particle association, as probed by partial extractions with HCl or NaOH, showed no discernible time trend (t = 1, 3, 8, 16, 32 d). Partitioning of $CH_3{}^{203}HgCl$ also favoured the particulate phase, but the relative amounts present in the dissolved phase (3-5%) and in the HCl extract were higher than with $HgCl_2$. Results obtained with hydrogen peroxide, a reagent often used in the past to oxidize sedimentary organic matter and solubilize the Hg associated with this sink, proved unreliable. Under the extraction conditions the H_2O_2 acts not only as an oxidizing agent for the organic matter, but also as a reducing agent for the mercury, leading to volatilization and loss of the metal, presumably as Hg^o.

KEY WORDS: Mercury, sediment, partitioning, extraction, hydrogen peroxide.

INTRODUCTION

Mercury introduced into the aquatic environment tends to accumulate at the sediment-water interface. In this zone of intense microbial activity and steep redox gradients, it is subject to a variety of oxidation/reduction transformations as well as methylation/demethylation reactions[1]. The reactivity of Hg in this environment, and its bioavailability to benthic organisms, will be determined in large measure by its chemical speciation and its partitioning between the interstitial water and a variety of particulate forms, e.g., adsorbed at particle surfaces (Fe/Mn oxides; clays; humic flocs); present in lattice positions in secondary minerals or occluded in amorphous Fe/Mn oxides; associated with organic matter (living micro-organisms; freshly deposited detritus; refractory organic material).

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Experimental determinations of Hg partitioning in sediments fall naturally into two classes: (i) procedures developed to extract methyl-Hg present in sediments, often involving organic solvents[2–4]; and (ii) partial extractions designed to evaluate the distribution of (inorganic) Hg among various solid sorbents (for a recent review, see NRCC[5]). Among the commoner extractants used in this connection are dilute acids[3, 6, 7], dilute bases[3, 6, 8] and oxidizing reagents such as H_2O_2[3,8–10]. Despite the widespread use of these reagents, however, relatively little effort has been devoted to evaluating their analytical performance.

As part of an ongoing study of the bioaccumulation and trophic transfer of mercury in a multicompartment laboratory model (water/natural sediment/biota)[11–13], we have undertaken a complementary investigation of the equilibrium partitioning of mercury ($HgCl_2$ and CH_3HgCl) between sediment and water. The original aim of the study was simply to compare the partitioning of the organic and inorganic Hg forms under controlled conditions, but mass balance problems led us to evaluate the analytical performance of the various extractants.

Mercury was added to a natural sediment maintained in dilute suspension under oxic conditions, and partitioning was followed over time with the aid of phase separation techniques (centrifugation—filtration) and chemical extractions. Although this experimental design differed from that employed in the ecotoxicological model (where the sediments were allowed to settle), it did allow us to study the "behaviour" of the two Hg compounds in the presence of natural sediments, while maintaining a stricter control over the environmental factors known to affect metal partitioning (e.g., concentration of particles in suspension, redox potential, pH, amount of metal)[5, 14].

MATERIALS AND METHODS

Sediment—water partitioning

Sediment, identical to that used in our ecotoxicological models, was taken from the banks of the Garonne River, upstream from Bordeaux, France. A very homogeneous silt, rich in clays (75–80%), this sediment has a low total organic carbon content (ave. 1.2%) and a background level of total mercury of 0.124 ± 0.012 mg Hg·kg^{-1} (fresh weight).

Twenty-four reactors (Erlenmeyer flasks, 2 L capacity) were set up, each containing 870 mL of spring water (Ca : 20 mg·L^{-1}, Mg : 5 mg ·L^{-1}, HCO_3^{-1}: 161.0 mg·L^{-1}, pH = 7.2), 1.5 g of sediment (dry weight), 3.6 µg of total Hg ($HgCl_2$ or CH_3HgCl), 0.136 mCi of $^{203}HgCl_2$ for inorganic mercury reactors (15) and 0.088 mCi of $CH_3{}^{203}HgCl$ for organic mercury reactors (9). The reactors were stirred continuously under ambient light (neon tubes) at 24°C. The pH was regularly monitored throughout the experiment but did not change appreciably (pH ≈ 7.5 at the end of the experiment).

The partitioning of $HgCl_2$ was studied after 1, 3, 8, 16 and 32 d, while that of methylmercury was determined after 1, 3 and 8 d (longer incubations would have favoured demethylation). At each sampling time 3 replicate reactors were sacrificed, with 4 sub-samples (150 mL) being withdrawn from each reactor (Fig. 1). The first sub-sample (A1) was used for determination of total and dissolved mercury. After centrifugation at 13,000 rpm for 10 min, Hg was determined in the sediment pellet and in the supernatant (before and

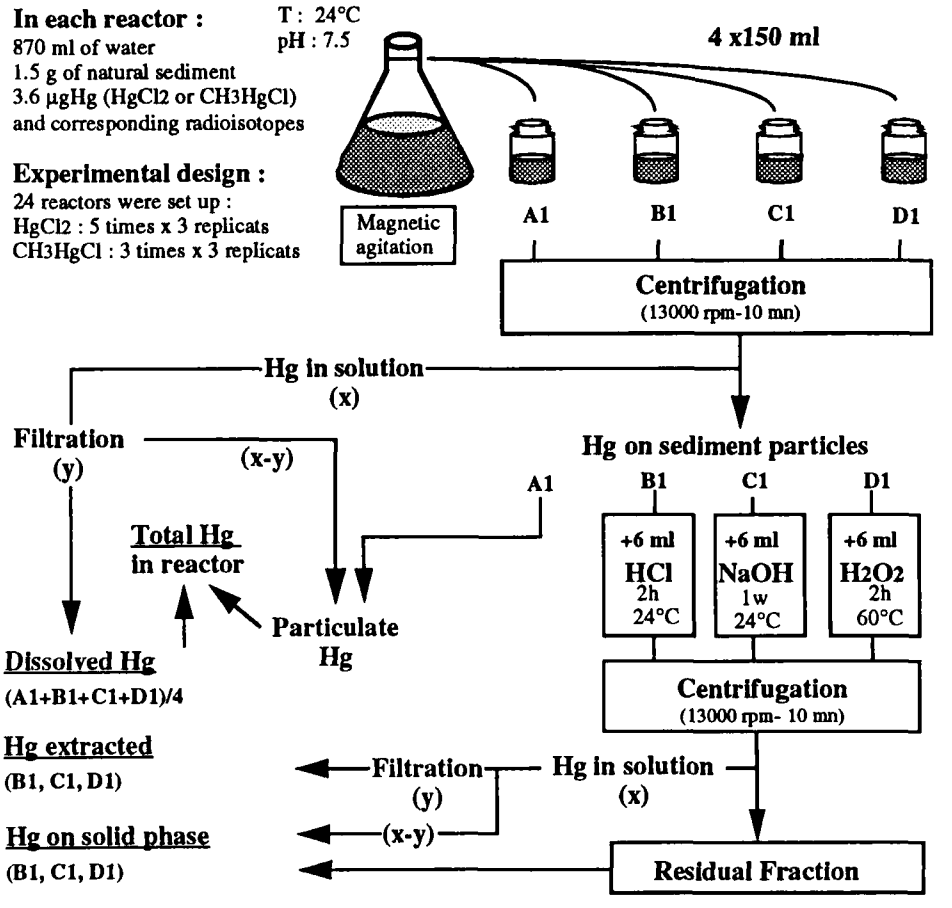

Figure 1 Experimental design and separation scheme for the partial extraction of Hg from the sediment suspension samples in each reactor.

after filtration through a 0.4 µm Nuclepore polycarbonate membrane); analytical results were summed to give the total amounts of Hg in each unit. The other three sub-samples (B1, C1 and D1) were used to determine Hg partitioning in the particulate phase (see below).

Sediment extractions

A variety of chemical extractants have been employed to determine Hg partitioning among sediment components[5]. We chose three reagents that have been widely used[3,6]: HCl (1 N), to solubilize Hg associated with amorphous Fe and Mn oxyhydroxides; NaOH (0.1 N), to extract sedimentary humic and fulvic acids and their associated Hg; H_2O_2 (30%), to oxidize

sedimentary organic matter. Each sub-sample (B1, C1, D1) was centrifuged, the supernatant discarded, and an extractant solution (6 mL) added to the residual pellet. After the appropriate extraction time (HCl—2 h, 24°C, with agitation; NaOH—1 week, 24°C, with agitation; H_2O_2—2 h, 60°C, with agitation), the samples were again centrifuged. As before, Hg was determined in the supernatant before and after filtration, and in the residue.

Appreciable losses of Hg were noted during the H_2O_2 extraction step (see Results). It seemed likely that Hg was being lost by volatilization during extraction, caused by either the temperature of the reaction (60°C) or the chemical reagent used. The action of these two factors was studied separately, with Garonne sediment that had been equilibrated with $^{203}HgCl_2$ for 72 h. The labelled sediment was collected by centrifugation and introduced into a closed Pyrex flask. The flask was kept at a temperature of 60°C and joined by a glass tube to a test tube containing a permanganate solution ($KMnO_4$, 5 $mg \cdot L^{-1}$) to trap any volatile mercury. In order to assist gaseous exchanges, a constant flow of nitrogen was maintained through the two compartments, i.e. swept over the suspended sediment in compartment #1 and bubbled through the permanganate solution. After 2 h the "trapping" solution was replaced with fresh $KMnO_4$ and hydrogen peroxide (30% H_2O_2; 6 mL) was introduced into the first compartment, containing the sediment sample. After a second 2 h reaction period at 60°C, the permanganate solution was again removed and counted.

Similar extraction trials with H_2O_2 were also run with a sediment richer in organic matter (2.4% organic C) that had been collected from Lake St-Joseph, a small mesotrophic lake located ≈ 40 km northwest of Quebec City, and labeled with $^{203}HgCl_2$. In addition, to determine whether mercury in a "naturally" contaminated sediment behaved in a manner similar to the radioactive spike, we extracted sediments from Reality Lake, Oak Ridge, Tennessee (6.7% organic carbon; 90 mg $Hg \cdot kg^{-1}$ dry wt) and checked for mercury volatilization.

Radioanalysis

Radioactive ^{203}Hg was measured in a gamma particle counter (LKB Wallac 1282 Compugamma, NaI (T1) well type) between 158 and 171 nm, where emitted energy was maximal. All solid samples were digested with hot concentrated HNO_3 for 24 h before counting; samples were placed in 10 mL polystyrene test tubes for counting. Correction was made for radioactive decay ($t_{1/2}$=47 d) and for background radiation, which was determined from several blank samples (deionized water) with a standard deviation (SD) < 0.7%. Sample counting times were adjusted in order to obtain a relative counting error (SD) of < 2%; only net values exceeding the mean blank plus 2 SD (alpha = 0.05) were retained.

Chemical analysis

In the extraction trials run with the contaminated sediments from Reality Lake, total mercury in the H_2O_2 extract and in the $KMnO_4$ trap solution was determined by reduction with stannous chloride and gas-phase detection of Hg^0 by cold vapour atomic fluorescence, after a two-stage gold amalgamation step[15,16,17]. Before reduction with stannous chloride, water

samples were first treated with bromine[18]. To determine total mercury initially present in the sediments, sub-samples of the sediment were first digested with a mixture of sulfuric and nitric acids (1:2.5, v/v) at 90°C for 6 h; total mercury in the digestion solution was then analyzed as described above.

RESULTS AND DISCUSSION

Mercury partitioning was determined according to the separation scheme indicated in Figure 1, after variable equilibration periods (Table 1). Values calculated after the first centrifugation step gave the *total* amounts of Hg present in the reactors (dissolved + particulate, Table 1) and served as a reference from which to calculate percentages of Hg found in the different extracts. *Particulate* Hg is defined as that present in the residue obtained after centrifugation plus Hg that was retained on the 0.4 µm membrane used to filter the supernatant. The amounts of mercury "lost" after each extraction were calculated from the mass balance.

Hg partitioning between water/sediment

Virtually all (>99%) of the added $^{203}HgCl_2$ was associated with the particulate phase. Sorption onto the suspended sediment was rapid, there being no appreciable change in the amounts of dissolved Hg recovered after 1, 3, 8, 16 or 32 d (Figure 2A; ave. 0.2% Hg_T). Note that the total amount of mercury introduced into the reactors varied little from one replicate to another (inter-replicate scattering less than 2.6%) and over time (inter-replicate scattering less than 3.2% between day 1 and day 32).

The partitioning of $CH_3{}^{203}HgCl$ also favoured the particulate phase, but the relative amounts recovered from the dissolved phase were considerably higher than with $HgCl_2$. The percentage of dissolved Hg decreased over the period studied (Figure 2A), indicating that the association of methyl-Hg with the particulate phase is somewhat slower than that of inorganic Hg.

These results for the partitioning of the two Hg forms between the dissolved and particulate phases are consistent with our earlier observations on the experimental model "water/sediment/*Hexagenia rigida*", where, for comparable Hg_T concentrations in the sediments, Hg levels in *H. rigida* larvae were up to 60 times higher with the organic form of the metal than for inorganic Hg[13]. The higher proportion of organic Hg in the aqueous phase obviously contributes to its greater bioavailability.

Hg partitioning in the solid phase (HCl; NaOH)

The Garonne sediments were contaminated with $^{203}HgCl_2$, equilibrated for 1 to 32 d, and extracted with 1 N HCl or 0.1 N NaOH. Recoveries of Hg with the HCl extraction were only about 6% (6 ± 3%) while those with NaOH were somewhat higher (15 ± 3%); in neither

Table 1 Quantity (CPM ± SD, n = 3) and percentage (%) of mercury recovered from dissolved and particulate phases after each extraction procedure. The quantity of mercury lost is also indicated {% of Hg lost = 100-(% dissolved mercury + % extracted Hg + % remaining in particulate phase)}.

		day 1		*day 3*		*day 8*		*day 16*		*day 32*	
$HgCl_2$		CPM	%	CPM	%	CPM	%	CPM	%	CPM	%
Dissolved		64± 36	0.2%	34± 28	0.1%	98± 37	0.3%	39± 7	0.1%	30± 20	0.1%
Particulate		31490± 625	99.8%	32510± 584	99.9%	33840± 542	99.7%	31380± 1260	99.8%	31470± 1300	99.9%
HCl (1 N)	Solution	1685± 280	5.3%	1880± 155	5.8%	775± 190	2.3%	2085± 633	6.6%	3045± 1150	9.7%
	Particulate	26650± 594	84.5%	29970± 211	92.1%	31940± 681	94.1%	25580± 745	90.1%	26000± 659	82.5%
			10.0%		2.0%		3.3%		3.1%		7.7%
NaOH (0.1 N)	Solution	4540± 370	14.4%	5180± 490	15.9%	5960± 635	17.5%	4520± 244	14.4%	4130± 157	13.1%
	Particulate	22250± 255	70.5%	22120± 915	67.9%	24450± 958	72.0%	22750± 290	72.4%	24350± 254	77.3%
			14.9%		16.1%		10.2%		13.0%		9.5%
H_2O_2 (30%)	Solution	105± 83	0.3%	686± 19	2.1%	723± 188	2.1%	637± 426	2.0%	507± 125	1.6%
	Particulate	3240± 2040	10.3%	20160± 533	61.9%	16430± 817	48.4%	21780± 1420	69.3%	18250± 3130	57.9%
			89.2%		35.9%		49.2%		30.3%		40.4%
CH_3HgCl											
Dissolved		662± 56	4.9%	429± 42	3.1%	246± 151	1.8				
Particulate		12710± 1070	95.1%	13490± 1090	96.9%	(7520± 847)[a]	-				
HCl (1 N)	Solution	6880± 226	51.4%	6050± 287	43.4%	5670± 263	40.8%				
	Particulate	5060± 420	37.8%	1390± 51	9.9%	2570± 69	18.5%				
			5.9%		43.6%		40.7%				
NaOH (0.1 N)	Solution	2610± 212	19.5%	1870± 12	13.4%	2100± 53	15.1%				
	Particulate	5220± 131	39%	5470± 281	39.2%	7460± 350	53.6%				
			26.6%		43.3%		31.3%				
H_2O_2 (30%)	Solution	1740± 286	12.9%	421± 215	3%	332± 40	2.4%				
	Particulate	7510± 259	56.2%	3510± 537	25.1%	3110± 97	22.3%				
			26.0%		68.8%		75.3%				

[a] Suspect value. Distribution percentages were estimated from total Hg present in the reactors after 3 days.

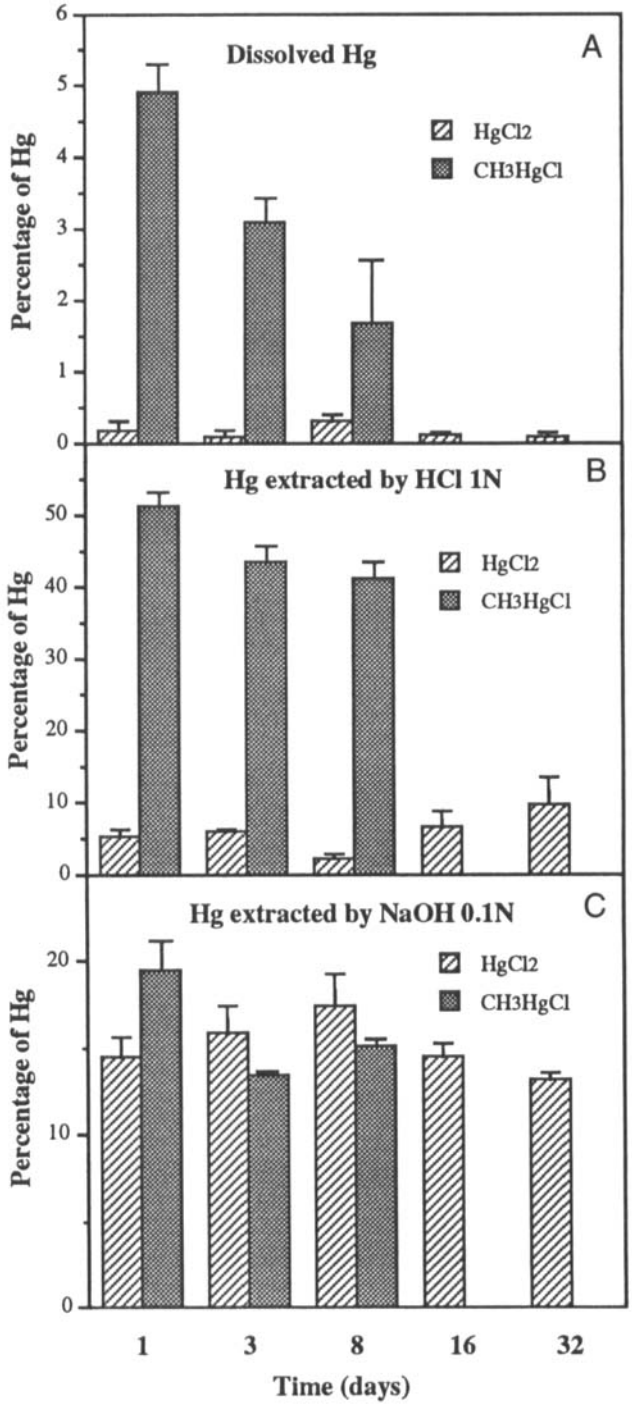

Figure 2 Percentage of Hg in the dissolved phase, extracted with HCl (1 N) or extracted with NaOH (0.1 N). Results expressed as a function of time for the two chemical forms of mercury initially introduced into the reactors ($HgCl_2$; CH_3HgCl).

case did the partitioning show a discernible time trend (Figures 2B, 2C). Mass balance calculations show negligible Hg losses after extraction with HCl (5% on average) and only slightly more after extraction with NaOH (13% on average) (Table 1). Coefficients of variation were low, an indication of the replicability of the methods used. Comparable partitioning results have been reported by Langston[3] for estuarine sediments in the U.K. (ave. 6.5% Hg_T extracted with 1 N HCl; ave. 14.4% with 0.1 N NaOH; N=36) and by Breteler and co-workers[6] for sediments from a salt marsh in Massachusetts (9±12% Hg_T extracted with 0.5 N HCl; 19±10% with 0.5 N NaOH; N=4).

When the sediments were spiked with $CH_3{}^{203}HgCl$, Hg extracted with 1 N HCl represented 45±6% of the total Hg introduced into the reactors, i.e. much higher values than for $HgCl_2$. Values decreased slightly over the 8 days of equilibration (from 51% to 41%—Figure 2B). With NaOH (0.1 N) recoveries were similar to those obtained with the inorganic spike (16±3%), and as with $HgCl_2$ the partitioning did not show a clear time trend (Figure 2C). Mercury losses during extractions were considerably greater than observed with inorganic $HgCl_2$, especially when NaOH was used as the partial extractant (7 d extraction time). These losses may be due to the inherent volatility of methyl-Hg, resulting in significant losses by volatilization during the extraction.

Partial extractions with hydrogen peroxide

Extraction with H_2O_2 has often been used to evaluate the partitioning of Hg in sediments[3,9,10,19–21]. In such studies it is generally assumed that any Hg extracted with H_2O_2 was originally strongly associated with sediment organic matter. In the present case, when Garonne sediments were contaminated with $^{203}HgCl_2$ and extracted with H_2O_2, recovery of labelled ^{203}Hg in the supernatants was very low (ave. 2%: Table 1). For methyl-^{203}Hg, recovery was initially somewhat higher but decreased from day 1 (13%) to day 8 (3%) (Table 1). These partitioning results, though considerably lower than those reported in the literature (Table 2), were not initially surprising, given the low organic carbon content of the Garonne sediments. However, determinations of the amount of ^{203}Hg remaining with the sediments after extraction showed that very large and variable Hg losses had occurred. With $HgCl_2$ the "missing" Hg varied from 30 to 90% (ave. 49±24%; Table 1).

To determine whether Hg was being lost by volatilization during the treatment with H_2O_2, the extraction was carried out in a closed system. Raising the temperature to 60°C in the absence of H_2O_2 did not cause any appreciable loss of Hg; after 2 h only 0.2% of the initial radioactivity had been trapped in the permanganate solution. However, after a second 2 h treatment at 60°C with H_2O_2, about 50% of the Hg initially introduced was recovered from the permanganate solution (Table 3). Thus, under our experimental conditions the peroxide acts as an oxidizing agent for the organic matter and as a reducing agent for the mercury, leading to volatilization of the metal, presumably as $^{203}Hg^0$.

$$H_2O_2 + Hg^{2+} = O_2 + 2H^+ + Hg^0$$

An identical test was carried out with a sediment sample richer in organic matter, from Lake St-Joseph, to check whether Hg volatilization was affected by the peroxide:organic

Table 2 Typical recoveries of Hg after the partial extraction of aquatic sediments with hydrogen peroxide—values from the literature.

Extractant	*Sediment sample*	*% Hg extracted*	*Reference*
H_2O_2 (10%) (20°C)	St-Lawrence estuary Quebec, Canada (N=18)	45–90[a] ave 73	Loring[20]
H_2O_2 (3–30%) (pH 2; 85°C)	Palos Verdes coast California, USA (N=14)	<1–50 ave 17	Eganhouse *et al.*21
H_2O_2	Puget Sound estuary Washington, USA	>82[a]	Crecelius *et al.*[10]
H_2O_2 (30%) (60°C)	U.K. estuaries (N=5)	47–71[a] ave 63	Langston[3]
H_2O_2 (30%) KCl (10%)	Lake Michigan Michigan, USA (N=6)	10–85 ave≈50	Cline *et al.*[9]
H_2O_2 (30%) (60°C)	Garonne River, France (spiked $^{203}HgCl_2$)	<1–2	(this work)

[a]In at least three examples (as determined from the original paper[20], or by contacting the authors for additional experimental details[3,10]), the Hg extracted by the H_2O_2 reagent was not determined analytically but rather calculated *by difference*. In such cases, any losses of inorganic Hg due to reduction and volatilization would contribute to this difference and thus lead to an overestimation of "organic" mercury.

carbon ratio. Volatilization of Hg was slightly less (39% instead of 49%) but still appreciable (Table 3). Our initial hypothesis, that perhaps the Garonne sediment was atypically low in organic carbon and rich in clays, and that in the such a sediment the hydrogen peroxide might be "more available" to react with and reduce Hg(II), appears untenable.

A second and perhaps more pertinent observation is that all the earlier studies[3, 9, 10, 20, 21] reported in Table 2 were performed on mercury-contaminated natural sediments, whereas in our two experiments we had spiked the relatively uncontaminated Garonne and St-Joseph

Table 3 Percentage of mercury volatilized under the action of hydrogen peroxide, from two sediment suspensions contaminated with $^{203}HgCl_2$.

	Sediment[a]	
	Garonne River	*Lake St-Joseph*
Initial radioactivity in closed flask	20,370	176,660
Final radioactivity in closed flask	5,380	86,280
Final radioactivity in the $KMnO_4$ trap	10,060	69,620
$\%^{203}Hg$ volatilized and trapped	49	39
$\%^{203}Hg$ missing	24	12

[a]Note: Sediment organic carbon content—Garonne River, 1.2%; Lake St-Joseph, 2.4%.

Table 4 Extraction of mercury from a naturally contaminated sediment (Reality Lake, Oak Ridge, TN) by hydrogen peroxide[a].

Run	*Initial Hg (μg)*	*Peroxide extract (%)*	*Volatilized (%)*
1	15	1.3	40
2	11	1.3	25
3	11	1.6	43

[a]Note: The naturally contaminated sediment (0.29–0.48 g) was treated with H_2O_2 in a closed flask joined by a glass tube to a test tube containing a permanganate solution, as described in the Materials and Methods section.

sediments with radio-tracer. Clearly the time available for reaction of the mercury with the sediment is very different in the two cases—years in the case of a "naturally" contaminated sediment, hours (72) in the case of the artificially spiked sediment. The nature of the ^{203}Hg-particle association, as monitored by partial extractions with HCl or NaOH, did not change over 32 days in our experiments. However, after much longer times in natural sediments, under the influence of sediment diagenesis, the Hg-particle association might indeed be different from that in our spiked sediments—and this different partitioning might in principle explain the divergent results in Table 2.

To verify this point we extracted highly contaminated natural sediments from Reality Lake with H_2O_2 and checked for possible Hg volatilization as in the earlier experiments with the radio-labeled sediments. As indicated in Table 4, the treatment with hydrogen peroxide removed 25 to 43% of the mercury initially present in the Reality Lake sediment. Note, however, that less than 2% of the mercury showed up in the peroxide extract—*the majority of the mercury removed from the sediment had in fact been volatilized and trapped in the permanganate solution.* In other words, the behaviour of mercury in the naturally contaminated sediment was comparable to that observed in the spiked sediments.

This observation may explain some of the high values for peroxide-extractable mercury reported in Table 2. In at least three examples[3, 10, 20], the Hg extracted by the H_2O_2 reagent was not determined analytically but rather calculated *by difference*. In such cases, any losses of inorganic Hg due to reduction and volatilization would contribute to this difference and thus lead to an overestimation of "organic" mercury.

Finally, it is intriguing that four of the five earlier studies reported in Table 2 were performed on estuarine or coastal sediments[3, 10, 20, 21], and the fifth[9] was carried out in the presence of added KCl. Given the known influence of chloride ion on the speciation of inorganic Hg(II), it is conceivable that the chloride concentration might affect the fate of sediment-bound mercury in the presence of H_2O_2.

Concluding remarks

The results of the present study are relevant both to environmental analytical chemists and to geochemists.

– The ability of hydrogen peroxide to act both as an oxidizing and as a reducing agent, though perhaps self-evident, has not been fully appreciated by workers in the field. Though restricted to two freshly spiked freshwater sediments and one naturally contaminated freshwater sediment, the present results do suggest that analyte losses may occur when H_2O_2 is used to oxidize sedimentary organic matter and to solubilize the Hg associated with this sink.

– Inorganic $^{203}HgCl_2$ sorbed rapidly and very strongly onto the suspended sediments, despite the relatively low levels of organic carbon in the sediment (> 99% of the added Hg was associated with the sediment particles). Sorption was essentially complete in < 24 h and the nature of the Hg-particle association, as probed by partial extractions with HCl or NaOH, showed no discernible time trend (t = 1, 3, 8, 16, 32 d). Recoveries of inorganic Hg after extraction with 1 N HCl were only about 6% (6±3%) while those with 0.1 N NaOH were somewhat higher (15±3%); very similar recoveries have been reported in the literature for natural sediments[3,6]. The nature of the solid phases responsible for binding inorganic Hg so tightly remains to be elucidated.

– Partitioning of $CH_3{}^{203}HgCl$ also favoured the particulate phase, but equilibrium was established more slowly and the relative amounts present in the dissolved phase (3–5%) and in the HCl extract were higher than with $HgCl_2$. This higher proportion of organic Hg in the aqueous phase presumably contributes to its greater bioavailability in oxic sediments, as determined in sediment-water microcosms[13].

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