

A comparison of the speciation and fate of mercury in two contaminated coastal marine ecosystems: The Venice Lagoon (Italy) and Lavaca Bay (Texas)

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Abstract

We compared the speciation of Hg in two estuaries, Lavaca Bay (Texas) and the Venice Lagoon (Italy). Both are large, shallow embayments that are contaminated by direct discharges from mercury-cell chlor-alkali plants and dominated by rapid tidal flushing. Although contaminated by discharges into Lavaca Bay from 1966 to 1979 and into the Venice Lagoon from 1951 to 1989, Hg concentrations have dwindled to similar moderate levels in sediments (200–2,000 ng g⁻¹) and water (1–3 ng L⁻¹ dissolved) since the advent of pollution abatement. The Venice Lagoon contains lower levels of CH₃Hg than Lavaca Bay, which is surprising, given the much larger degree of wetlands coverage in the lagoon. A narrow temporal peak in methylation was seen in early spring at both sites, although it was much stronger in Lavaca Bay. Data indicated that sediment CH₃Hg is more strongly correlated with variables such as habitat and seasonality than with total Hg. In Lavaca Bay, because of high sedimentation rates and low remixing, the highest levels of Hg are buried 10–30 cm below the surface. Combined with previous observations of strong Hg methylation after dredging activities, this argues for leaving Hg-contaminated sediment in place, to be buried by the deposition of cleaner sediments. In Venice Lagoon, decisions may be complicated by continuous remixing of the upper sediment layers, moving the highest levels of Hg toward the surface and distributing it over a far larger area than has been seen in Lavaca Bay.

Unlike deep lakes and the oceans, the Hg cycle of estuarine systems is dominated by direct coupling between the sediments and the food chain (Locarnini and Presley 1996). This occurs particularly in shallow estuaries, which provide a large ratio of sediment surface to water volume, frequent wind-driven and anthropogenic resuspension events, and more proximity to intertidal wetlands. Here we compare the occurrence and speciation of Hg in two contaminated estuaries, Lavaca Bay (Texas, sampled in 1996–1997) and Venice Lagoon (Italy, sampled in 2001–2003). Both systems were similarly contaminated from the 1950s to 1980s by aqueous discharges of Hg from mercury-cell chlor-alkali plants (Locarnini and Presley 1996; Provincia Venezia 2002). The sites differ in that Venice Lagoon is located in a highly urbanized industrial/agricultural region with substantial discharges of sewage, agricultural runoff, and industrial wastes (Pavoni et al. 1990), whereas Lavaca Bay is located in a sparsely populated rural agricultural area. Of significance, from the standpoint of mercury methylation, ~30% of the area of Venice Lagoon consists of various intertidal wetlands such as salt marshes, mud flats, and diked fish

farms (Pellizzato 1996), whereas we estimate that <5% of Lavaca Bay contains these features.

Mercury biogeochemistry in Lavaca Bay has been extensively studied over the past 30 yr. An initial dramatic decline in the Hg content of fish and shellfish was observed after the institution of wastewater controls at the chlor-alkali plant in 1970, followed by a rebound in concentrations during the 1980s and 1990s (Locarnini and Presley 1996). This stimulated an intensive investigation during the mid-1990s, the results of which showed a dramatic early-spring peak in sediment methylation (Bloom et al. 1999) that was strongly correlated with concentrations in organisms at the bottom of the food chain. Investigators also found that the bulk of the Hg discharged to the bay between 1965 and 1970 was buried in a sharply defined layer ~15–40 cm below the more moderately contaminated surficial sediments (Santchi et al. 1999). This deeper layer of Hg appeared to be completely isolated and did not interact with the methylation and bioaccumulation cycles, which only occurred in the upper several centimeters of the sediments. Decisions were thus made to remediate the site by reducing ongoing small discharges of new Hg(II) to the water column and to dredge only a small quantity of highly contaminated sediments near the historic discharge point (TGLO et al. 2001).

By contrast, although researchers have known for some time, as a result of sediment surveys, that Hg was the major metal contaminant of concern in Venice Lagoon (Critto and Marcomini 2001), to date there has not been a comprehensive study of biogeochemical cycling or strategy to reduce Hg contamination. Until recently, only a few scattered measurements of total Hg that have used methods with sufficiently low limits of detection have been attempted for aque-

Acknowledgments

We thank Italo Ongaro and Paolo Scopece of the Universita Ca' Foscari, Murst Cluster 22, for their invaluable assistance in the collection of field samples in the Venice Lagoon; Beth Kuhn and Steve Cappellino, for the collection of samples in Lavaca Bay; and Sharon Goldblatt and Jennifer Parker, for their expert editorial assistance in rendering the manuscript suitable for publication.

We thank Frontier Geosciences' Internal Research, Universita Ca'Foscari di Venezia, Murst/Miur (Rome), project 28 Cluster 22, and the Aluminum Corporation of America for funding the various projects brought together in this paper.

ous samples from Venice Lagoon (Ugo et al. 2001). The concentrations observed were alarmingly high (70 ng L⁻¹ dissolved Hg to 1,500 ng L⁻¹ unfiltered Hg), although the use of standard water sampling methods could have resulted in contamination at the levels observed (Bloom 1995). Preliminary results obtained using ultraclean sampling and analytical methods (Moretto et al. 2003) verified this suspicion, showing that Venice Lagoon more typically contains Hg concentrations in the range of 0.5 ng L⁻¹ dissolved to 50 ng L⁻¹ unfiltered. Here, we provide the first comprehensive results for Hg speciation collected under ultraclean conditions.

Materials and methods

Site descriptions—Samples were collected from Lavaca Bay as part of the Alcoa sponsored “recon study” between March 1996 and July 1997 (Bloom et al. 1999); samples were collected from Venice Lagoon between November 2001 and June 2003. Sampling locations and historic chlor-alkali outfall positions are as indicated in Fig. 1. Physical parameters comparing the two systems are shown in Table 1. The purposes of the two studies were somewhat different, so that the Lavaca Bay sampling emphasized a synoptic study during spring 1996, whereas the samples from Venice Lagoon were collected more evenly but less frequently throughout the study in five seasonal sampling events. Because the present article focuses on a comparison of seasonal changes in CH₃Hg, which is caused by microbial methylation (Gilmour et al. 1992) and is likely temperature dependent, we have compiled (Institute for Marine Biology 2002; Texas A&M University 2002) annual water temperature profiles at representative locations in each estuary (Fig. 2).

Lavaca Bay is a large (155 km²) secondary embayment off of Matagorda Bay on the Gulf of Mexico. The northern part of the bay is separated by a natural constriction and is significantly less contaminated than the southern portion, which received ~75,000 kg of Hg as direct discharges from the chlor-alkali plant between 1965 and 1970. More diffuse inputs followed until 1979, when the plant was closed (TGLO et al. 2001). The Lavaca River enters the bay at the north and supplies, on average, ~5% of the total water exchange in the system, although between-year variations in rainfall and irrigation usage result in dramatic variability. There was a period of drought during the synoptic Lavaca Bay study (1996–1997), so the freshwater inputs were only 43% of the average flow (State of Texas 2003). The Lavaca River watershed is very sparsely populated, with only ~41,000 inhabitants, most of whom are employed in agriculture or live in the town of Port Lavaca and work at one of several large chemical manufacturers located in the area. Lavaca Bay consists primarily of shallow, open-water habitats (average depth 1.5 m), with small coverage by intertidal marshlands and mudflats that emerge at low tide. Marshlands are concentrated in Cox Cove, just south of the most contaminated areas. A dominant feature of the bay is “Dredge Island,” a large artificial island made of dredge spoils. It is Hg contaminated in some places, because its surface served as the receiving area for discharges from the chlor-alkali plant between 1970 and 1979. At the time of the recon study,

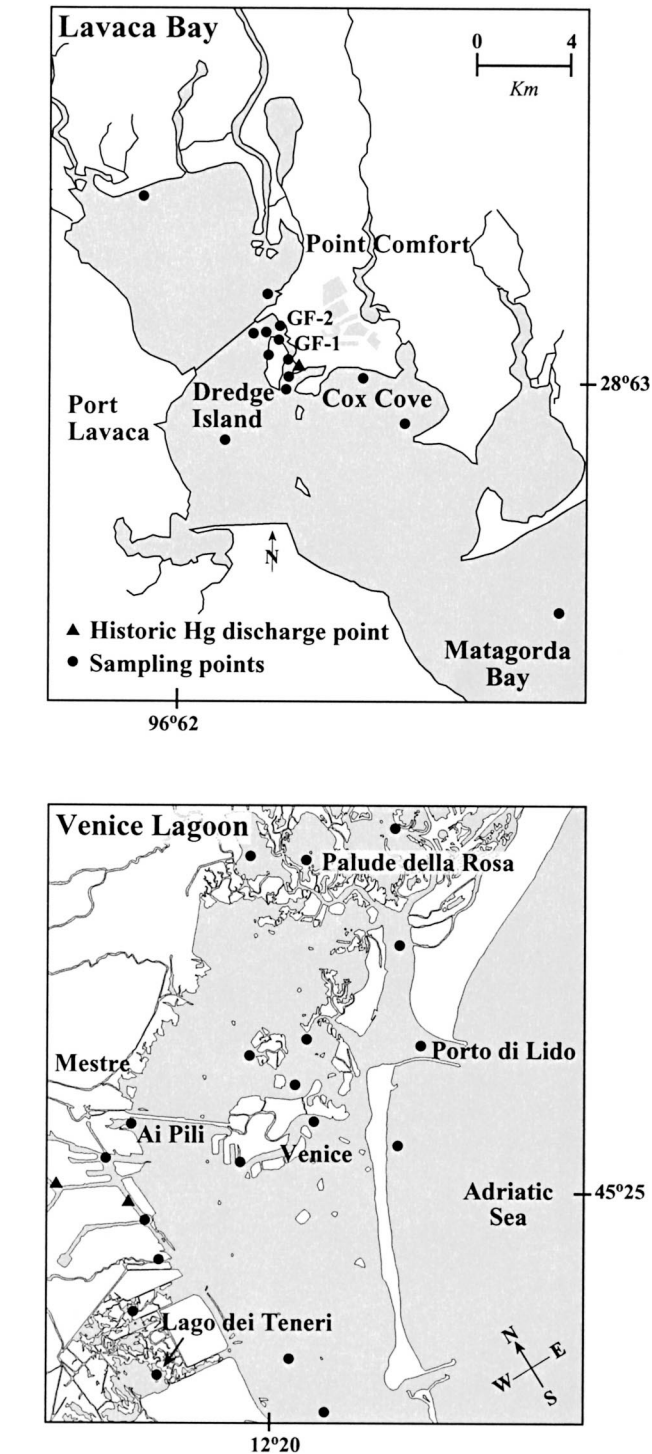


Fig. 1. Sampling locations in Venice Lagoon (Italy) and Lavaca Bay (Texas).

the island was rapidly eroding into the bay, a process that has since been halted by reinforcing the island's shores and capping its surface. Salient to its future prospects for recovery, much of Lavaca Bay experiences high sedimentation rates of 0.5–1 cm yr⁻¹ (Santchi et al. 1999).

Venice lagoon is about three times the size of Lavaca Bay

Table 1. Comparison of Lavaca Bay and the Venice Lagoon. The Hg and TSS averages were determined from a preponderance of sites close to the discharge point (0–10 km), because the studies tended to emphasize the affected areas. Values in italics were based on calculations or estimates.

Parameter	Units	Lavaca	Venice	References
Total surface area	km ²	155	540	1, 2
Wetlands area	km ²	<5	71	2
Mean depth	m	1.2	1.1	2, 3
Mean volume	m ³	<i>1.9×10⁸</i>	<i>5.5×10⁸</i>	6
Mean residence time	d	NA	2.0–10	11
Mean rainfall	cm yr ⁻¹	106	83	1, 7
Average river inflow	m ³ yr ⁻¹	<i>4.13×10⁹</i>	<i>1.12×10⁹</i>	8, 12
Drainage basin area	km ²	2,435	1,850	1, 9
Mean wind speed	m s ⁻¹	4–8	1–4	4, 10
Mean sedimentation rate	cm yr ⁻¹	+1.1	-0.2	3, 5
Watershed population	no.	41,000	1,550,000	1
Total suspended solids	mg L ⁻¹	53	15	<i>Present work</i>
0–3 cm sediment [Hg]	ng g ⁻¹	419	1,350	<i>Present work</i>
Unfiltered aqueous [Hg]	mg L ⁻¹	49	22	<i>Present work</i>

1: TLGO et al. 2001, 2: Pellizzato 1996, 3: Day et al. 1995, 4: Texas A&M. 2002, 5: Santchi et al. 1999, 6: Mazzacurati 1995, 7: Zaggia et al. 2001, 8: Zuliani et al. 2001, 9: Zonta 2001, 10: Institute of Marine Biology 2002, 11: Frignani et al. 1997, 12: State of Texas 2003. NA: not available.

and covers an area of ~540 km², of which 62% (335 km²) is open water, 13% (71 km²) is salt marsh, 17% is diked fish farms (92 km²), and 8% is islands (43 km²) (Pellizzato 1996). It is as yet unknown what the effect of such extensive coverage by fish farming may have on the CH₃Hg cycling in the lagoon. Shallow and nutrient rich, fish farms are probably significant areas for methylation, but their limited exchange with lagoon waters may expose their sediments to lower levels of bioavailable Hg(II) and limit the release of produced CH₃Hg to the lagoon as a whole. Because access was restricted, the effect of fish farms was not included in the present study.

Historically almost all river inputs around the lagoon have

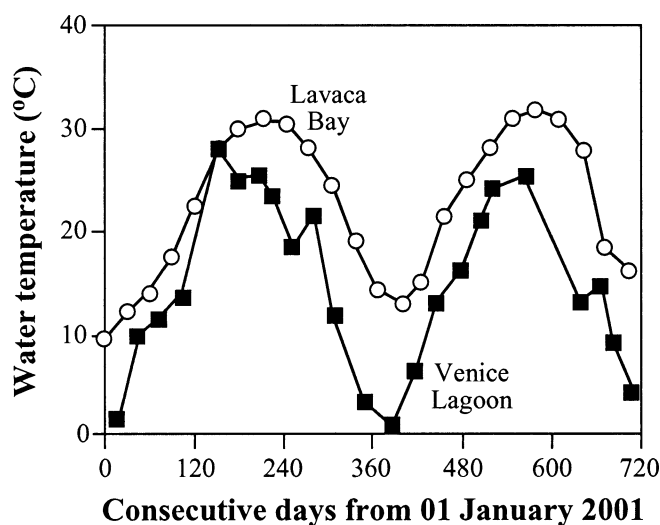


Fig. 2. Monthly water temperatures at Port Lavaca, Lavaca Bay (1996–1997), and Palude della Rosa, Venice Lagoon (2001–2002). For Lavaca Bay, values were averaged from internet-accessible hourly data over a 2-d period at the start of each month. For Venice Lagoon, they were single-point daytime measurements at 30 cm depth.

been diverted at one time or another. Tidal flow has become exaggerated because channels have been deepened for large ship traffic. These factors, combined with anthropogenic re-suspension, mean that Venice Lagoon is now a net exporter of sediments to the Adriatic sea, losing, on average, ~1.1 million m³ or 0.2 cm yr⁻¹ (Day et al. 1995). The circulation patterns introduced by tidal cycling through the three openings in the barrier islands (the Lido, Malamocco, and Chioggia inlets) creates regions in the lagoon that are hydrologically isolated from one another, confining the majority of the pollution to the northern basin, which makes up ~270 km² in surface area (Marcomini et al. 1995).

The watershed of Venice lagoon is heavily populated, supporting ~1.5 million inhabitants who primarily work in agriculture, tourism, or industry. Because there are many chemical and petrochemical companies located in Marghera on the western shore of Venice Lagoon, it is likely that there are multiple contributors to the Hg input to the lagoon. However, the largest single source is almost certainly the mercury cell chlor-alkali complex, which operated largely without pollution control equipment from 1951 until 1988 (Provincia Venezia 2002). Two independent plants were in operation at the complex. The first ran from 1951 to 1994, and the second opened in 1971 and is still in operation. No clear records are available as to the amount of Hg discharged to the lagoon by these plants, but, if scaled to the period of production in Lavaca Bay, it would not be unreasonable to assume that ~200,000 kg was discharged.

Sample collection—Samples were collected using ultra-clean sample handling protocols (Bloom 1995) into acid-cleaned Teflon or borosilicate glass containers. Because the waters at both sites are very shallow and vertically well mixed, samples were collected by grab sampling at a depth of ~25 cm off the bow of a small plastic boat facing into the flow direction of the water or, in some cases, by wading from shore. At each site, three independent samples were collected: one 250-ml Teflon bottle was directly preserved

with 0.2% (vol/vol) 9 M H_2SO_4 or 0.4% (vol/vol) 12 M HCl for the unfiltered fraction, whereas another was vacuum filtered within 6 h through a disposable 0.4- μm nitrocellulose filtration unit and then similarly preserved for the dissolved fraction. A 500-ml polyethylene bottle of unfiltered water was also collected and kept unpreserved (in the dark at 0–4°C) for the determination of total suspended solids (TSS), total dissolved solids, and pH. These ancillary parameters were determined within 1 week of collection.

Sediments were collected by hand from shallow areas using 8–10-cm diameter acrylic corers. For the Lavaca Bay study, cores were taken, intact and with undisturbed overlying water, to a nearby clean room, where they were subsampled in an N_2 -purged glove box for solids and pore-water extraction by centrifugation and 0.4- μm filtration (Bloom et al. 1999). After processing, solids were immediately preserved by freezing, and pore waters were preserved by the addition of 0.4% (vol/vol) 12 M HCl. In the Venice Lagoon study, sediments were similarly collected, but pore water was generally not extracted. Instead, the sediments from each layer were extruded in the field, rapidly homogenized, and a 10-g aliquot was placed into a glass vial. The vials were immediately (within 15 min of collection) placed into a cooler held at -5°C until transport to the lab freezer, where they were kept at -20°C until analysis. In one case, pore water was obtained from the Venice Lagoon sediments using a semipermanently installed diffusion sampler (“peeper”) with in situ pumpable sample chambers having ~ 10 cm depth resolution (Ugo et al. 1999).

Analysis and quality assurance—Samples were extracted or digested as described below in a Hg-clean laboratory and analyzed using cold-vapor atomic fluorescence spectrometric (CVAFS) detection (Bloom and Fitzgerald 1988). The absolute detection limit for this instrument is ~ 0.1 pg Hg, but all reported detection limits are determined by the variability of the measured blanks, which vary according to the different extraction procedures. All reported data were corrected for the mean method blank of a given extraction batch and for changes in instrumental drift on each analytical day. Aqueous CH_3Hg concentrations were also corrected for the empirically derived distillation efficiency (Bloom and von der Geest 1995). Solids were analyzed on a wet basis, to avoid artifacts and losses associated with drying. A separate aliquot was also analyzed for the percentage of moisture, and this value was used to correct the wet-basis measurements to a dry basis. Every analytical batch was accompanied by at least three identically processed method blanks, a sample extracted in duplicate or triplicate, a matrix spike and matrix spike duplicate, and certified reference material in as similar a matrix as possible.

Before the determination of CH_3Hg , acidified waters were distilled to separate CH_3HgCl into a pure deionized water matrix. Distillates were analyzed by aqueous-phase ethylation, purging onto Carbotrap, and isothermal gas chromatograph separation followed by CVAFS detection (Bloom and Von der Geest 1995). Sediment aliquots of 1 g were extracted into CH_2Cl_2 from a mixture of H_2SO_4 , KBr, and CuSO_4 and then back-extracted into deionized water before the ethylation step, to avoid positive artifacts associated with the

distillation of sediments (Bloom et al. 1997). Detection limits for CH_3Hg were ~ 0.01 ng L^{-1} for waters, 0.1 ng L^{-1} for pore waters, and 0.004 ng g^{-1} for sediments. For samples with concentrations > 10 times the detection limits, the relative difference of duplicate analyses was typically 5–15%, whereas matrix spike and certified reference material (CRM) recoveries ranged 85–120%.

Aqueous samples to be analyzed for total Hg were first oxidized by the addition of 1% (vol/vol) of 0.2 M BrCl in 12 M HCl directly to the original sample bottle and allowed to digest overnight at room temperature (Bloom and Crecelius 1983). Sediment aliquots of 1 g were digested overnight at room temperature with aqua regia (1:3 HNO_3 + HCl) and then diluted to 40 ml with deionized water before analysis. Aliquots of water and sediment digests ranging 0.005–100 ml, depending on concentration, were analyzed using SnCl_2 reduction, purge and trap on gold-coated sand, and CVAFS quantification. Detection limits for Hg were ~ 0.2 ng L^{-1} for waters and 0.4 ng g^{-1} for sediments. For samples with concentrations > 10 times the detection limits, the relative difference of duplicate analyses was typically 4–8%, and matrix spike and CRM recoveries ranged 90–110%.

TSS were measured for each water sample by filtering 100–500 ml of water through a preweighed 0.4- μm pore size, 47-mm diameter polycarbonate membrane filter, rinsing out the salts with deionized water, and drying at 65°C for several hours before reweighing. The limit of detection for TSS in a 500-ml sample was typically ~ 0.5 mg L^{-1} . Suspended matter Hg and CH_3Hg concentrations (ng g^{-1}) were calculated as the unfiltered minus the dissolved concentrations (ng L^{-1}), divided by the TSS (g L^{-1}).

Results and discussion

Water-column Hg speciation—The examination of the unfiltered water concentrations in areas affected by industrial discharges showed that for both Hg and CH_3Hg Venice Lagoon and Lavaca Bay appear to be similarly and highly contaminated in comparison to other shallow estuarine systems (Table 2). Although the urban canal system of Venice is likely to be a small source on a mass basis, owing to limited flushing into the lagoon, higher mean Hg concentrations were found here than at the discharges of the Marghera industrial zone. This is likely caused by the direct discharge of primary sewage effluent to the canals via urban septic tanks. Both study systems are quite contaminated with Hg, but comparison of unfiltered waters exaggerates this because of the unusually high levels of total suspended solids. Surface sediments, which are continually resuspended by both human activities and wind driven mixing contribute 80–95% of the observed Hg and 30–80% of the CH_3Hg in the water column at any given time. By contrast, although Lavaca Bay and Elliott Bay (Table 2) have similar average surface sediment Hg concentrations (~ 400 ng g^{-1}), TSS in the water column of Lavaca Bay average ~ 50 mg L^{-1} and so contribute upward of 30 ng L^{-1} of the total Hg burden. In Elliott Bay, on the other hand, with a mean depth of > 20 m, there is virtually no sediment resuspension. This is reflected in both the typical TSS values in the range of 1 mg L^{-1} , and

Table 2. Comparison of average unfiltered aqueous Hg concentrations in the Venice Lagoon and Lavaca Bay with other estuarine systems (\pm SE [=SD/ \sqrt{n}]).

Location	Mean [Hg], ng L ⁻¹		Reference
	Total	Methyl	
Venice urban canals ($n = 12$)	60 \pm 14	0.22 \pm 0.04	Present study
Lavaca contaminated areas ($n = 15$)	47 \pm 14	0.30 \pm 0.07	Bloom unpubl. data 1997
Venice north shallow ($n = 19$)	40 \pm 10	0.21 \pm 0.04	Present study
Venice north deep ($n = 20$)	13 \pm 2	0.07 \pm 0.02	Present study
Tropical Brazil lagoons ($n = 8$)	12 \pm 6	0.10 \pm 0.04	Bloom unpubl. data 1996
Gulf of Trieste	5.9	0.04	Horvat et al. 2001
Hong Kong harbor ($n = 6$)	1.6 \pm 0.3	<0.02	Bloom unpubl. data 2002
Venice south deep ($n = 4$)	2.4 \pm 0.4	0.03 \pm 0.01	Present study
Elliott Bay, Seattle ($n = 2$)	0.6 \pm 0.1	0.03 \pm 0.01	Bloom unpubl. data 2001
Puget Sound rural background	0.2 \pm 0.2	NA	Bloom and Creelius 1983
Adriatic Sea	0.2	0.03	Horvat et al. 2001

NA: not applicable.

in the observed total Hg concentration of only 0.6 ng L⁻¹ in this sense, the northern half of Venice Lagoon can be considered to be about three times as contaminated as Lavaca Bay, because resuspension of the surface sediment concentrations averaging 1,400 ng g⁻¹ results in similar unfiltered water column concentrations, despite a mean TSS of only \sim 15 mg L⁻¹. Although not studied in detail, the southern portion of Venice Lagoon, which is hydrostatically isolated and independently flushed with cleaner water from the Adriatic Sea (Marcomini et al. 1995), appears to be about fivefold less affected by Hg than the northern portion.

Figure 3 details some of the mercury chemistry in Lavaca Bay and Venice Lagoon. The comparison is made only for the mean of spring and early summer values in the shallow-water areas (tide flats and salt marshes), because these are the only time periods and regions for which we have substantial data for Lavaca Bay. These productive habitats were emphasized, because they represent the regions of highest expected methylation and the greatest risk for the entry of Hg to the base of the estuarine food chain. Taken as a whole, both systems are remarkably similar in concentrations for both Hg and CH₃Hg, with the higher suspended Hg concentrations of Venice Lagoon being offset by lower TSS levels, resulting in similar unfiltered and dissolved Hg levels in the water column. For CH₃Hg, Lavaca Bay has a higher water column concentration, which is a result of its similar suspended CH₃Hg concentrations, but higher TSS. Both systems showed a similar degree of methylation (1.2% of total Hg). Significant with respect to bioaccumulation, the dissolved CH₃Hg levels in Lavaca Bay averaged about three times those seen in Venice Lagoon, despite higher TSS levels in Lavaca Bay. As will be emphasized later, this may be a result of different profiles for CH₃Hg in sediment pore water between the two sites.

Because CH₃Hg production in sediments is a microbial process that is likely to be strongly dependent on temperature, and given the strong seasonal gradients in water temperature at both sites (Fig. 2), we expected, and in fact observed, a summertime maximum in the percentage of Hg in the methylated form at both sites (Table 3). This was illustrated using the suspended Hg concentrations rather than wa-

ter concentrations, because this normalizes the much larger effects of day-to-day variability in TSS loadings. The overall trends in the two systems were the same, both temporally and in magnitude, with a summertime maximum in suspended CH₃Hg approximately three times as high as the wintertime minimum. Of significance, these trends were observed most strongly in the shallow (near wetlands) contaminated areas of each site. Although the concentrations were similar, Venice Lagoon contains a much higher percentage of contaminated wetland habitat than does Lavaca Bay, which can thus generate a proportionally greater total flux to the food chain. Despite the very close linkage between the surface sediment and the shallow water column, the absolute concentrations and percentage of CH₃Hg in the suspended matter is generally 3–10 times higher than in the surface sediments. We speculate that this is caused by the readsorption of dissolved CH₃Hg diffusing from surface sediments and wetlands, although no direct evidence was collected to verify this.

Hg speciation in sediments—Although most of the data collection in these systems focused on the water column, given the proximity of the shallow waters to the sediments it is critical to understand the dynamics of methylation and transport at the sediment-water interface. The distribution of Hg in the surficial sediments of Lavaca Bay and Venice Lagoon provide a striking contrast (Fig. 4). As expected, in Lavaca Bay, concentrations were highest near the historic chlor-alkali discharge point and then tended to diminish exponentially with distance. Within 10 km of the discharge area, surface sediments in Lavaca Bay dropped 30–50 times, to near-background levels (<20 ng g⁻¹ Hg). By contrast, in the northern part of Venice Lagoon, which, at 225 km² is considerably larger than the entirety of Lavaca Bay, Hg concentrations show an approximately twofold decrease with distance. If the southern lagoon (10–40 km from the discharge point) is also considered, Hg concentrations in the surficial sediments do eventually drop by four–five times, to <250 ng g⁻¹. This, however, is still well above the expected regional background of <100 ng g⁻¹ (Pavoni et al. 1987; Critto and Marcomini 2000).

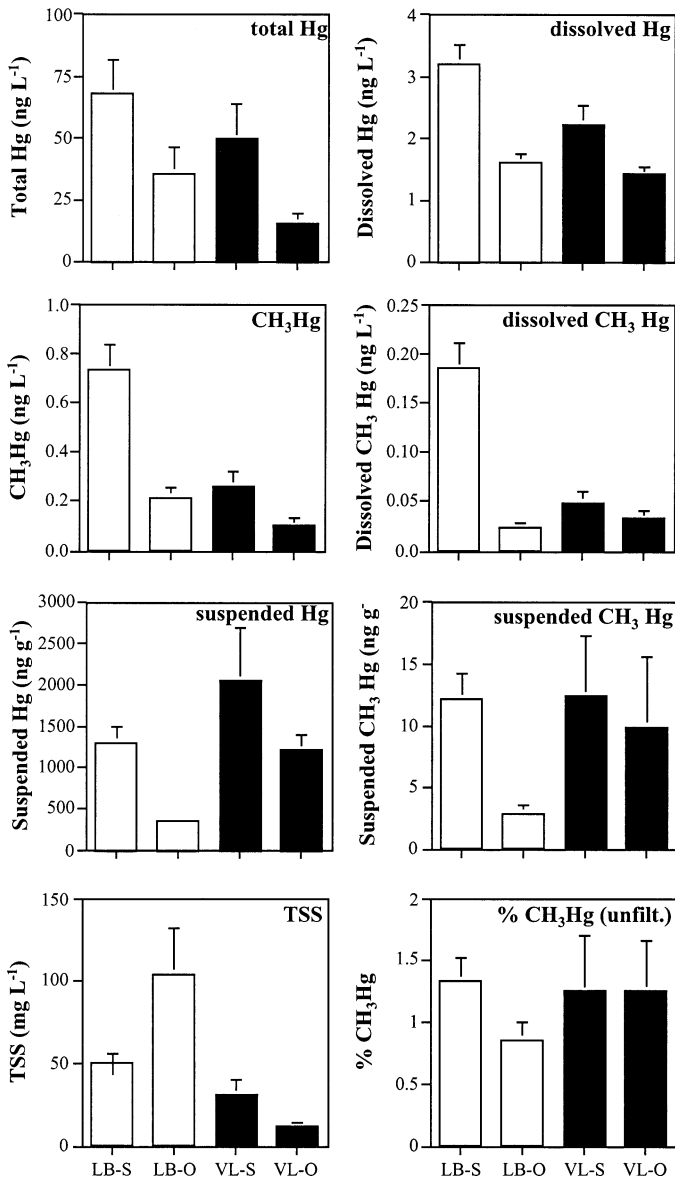


Fig. 3. Mean spring/summer aqueous Hg speciation within 10 km of the Hg discharge point in Lavaca Bay (LB) and Venice Lagoon (VL). Shallow areas (S) are tidally inundated mudflats and salt marshes, and open areas (O) are deeper (1–3 m) that are always under water, even during low tide.

The surface sediments of Venice Lagoon were higher in Hg, and that Hg was more widely distributed than in Lavaca Bay. The most likely reason for this is found in the much more dynamic sediment mixing and resuspension in Venice Lagoon. The northern part of the lagoon is characterized by extreme and near-continuous anthropogenic disturbances to the sediments that result from the combination of dredging, rebuilding salt marshes, and a characteristically regional type of clam harvesting (“*la rasca soffiante*”), in which high-powered boats are driven with their propellers submersed in the sediment layer, kicking out the clams into a net towed behind the fast-moving boat. This type of clamming, although illegal, is very lucrative and is widely practiced at

Table 3. Seasonal changes in the speciation of Hg of the suspended matter in the shallow intertidal zones (<0.5 m). Because of high levels of suspended solids (4–90 mg L⁻¹), ~96% of the Hg and 72% of the CH₃Hg at these sites was found in the suspended matter.

Location and season	n	[Hg] (ng g ⁻¹) (dry basis)		
		Total	Methyl	% Methyl
Lavaca Bay				
Winter	2	550±164	3.0±0.5	0.63±0.28
Spring	17	1,301±150	11.5±3.1	1.03±0.21
Summer	6	1,116±347	14.9±3.8	1.58±0.25
Venice Lagoon				
Winter	2	967±6	4.7±2.3	0.49±0.23
Spring	7	1,741±886	6.0±1.4	0.61±0.14
Summer	6	1,145±472	29.1±14.4	1.77±0.15
Autumn	6	1,332±1,120	6.4±7.6	0.62±0.72

night in the less-monitored areas of the lagoon (Atti Parlamentari 2002). These disturbances, in combination with sediment scouring caused by reduction of fresh suspended matter (because of the historic diversion of most rivers) and increased tidal flow from the deepening of the ship channels, result in both an overall net loss of sediment from the lagoon and a dramatic degree of resuspension and relocation of sediments throughout the lagoon (Mazzacurati 1995).

The overall effect is one of homogenization, such that, instead of the Hg maximum from the past being buried by 20–30 cm of quiescent sediments as in Lavaca Bay, the entire upper 20–50 cm of sediments in the lagoon is contaminated (Fig. 5; Lavaca Bay data plotted from a table in

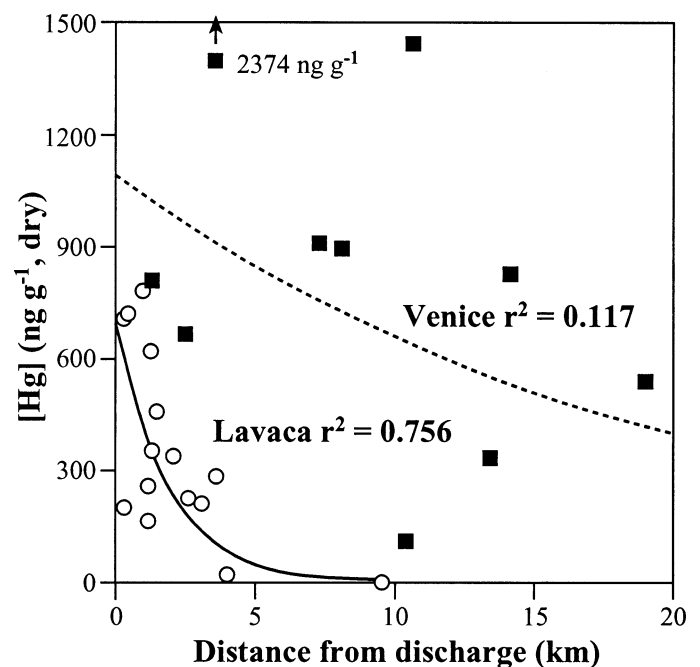


Fig. 4. Hg in surface sediments of Lavaca Bay and Venice Lagoon, as a function of distance from the chlor-alkali plant discharge points.

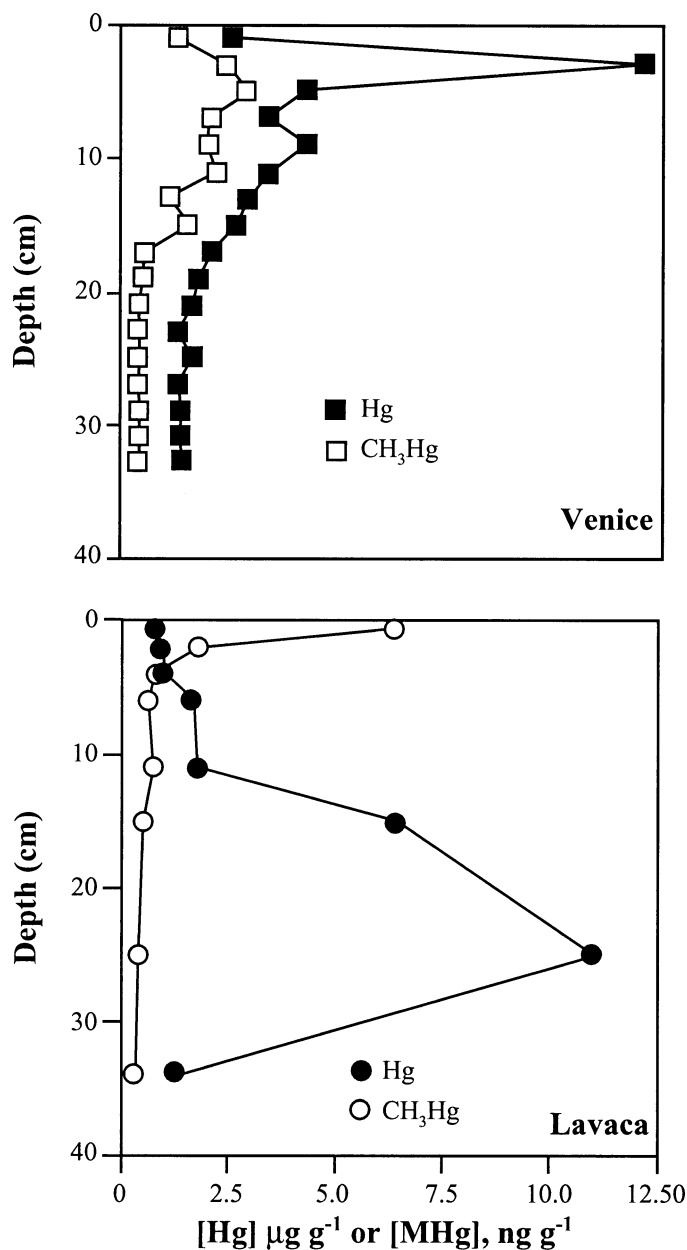


Fig. 5. Sediment core profiles of Hg and CH₃Hg at stations close to the discharge points in the two estuaries: Ai Pili in Venice Lagoon and GF-1 in Lavaca Bay.

Bloom et al. 1999). The sharp peak near the surface of this core from Ai Pili is not typical of other cores collected from Venice Lagoon (Donazzolo et al. 1984; Pavoni et al. 1987). It probably represents a recent, short-term Hg discharge to this enclosed and shallow arm of the lagoon adjacent to the Marghera industrial zone. The minimal degree of sediment reworking in Lavaca Bay is even more evident in cores collected later (Santchi et al. 1999), where the deeper sediments were sectioned at 1-cm intervals, compared with the 10-cm sections in the lower part of the core (Fig. 5). In these high-resolution profiles, the highly contaminated Hg layer was confined to a very sharp band, only 5–10 cm thick, that

decreased exponentially to the current surface concentrations.

Of greater significance for the bioavailability of Hg in these systems, the CH₃Hg depth profile was dramatically different between Lavaca Bay and Venice Lagoon. In Lavaca Bay (Fig. 5, as well as all other cores in Bloom et al. 1999), CH₃Hg concentrations were very high within the upper few cm of the core and then diminished rapidly to near zero concentrations by 10 cm depth. In these cores, the redoxcline was located within a few millimeters of the surface, perhaps even reaching the sediment/water interface during the microbial net respiration period at night (Bloom et al. 1999). These two factors resulted in the highest concentrations of pore-water CH₃Hg residing virtually in contact with the sediment-water interface, where they could easily diffuse to overlying water and affect surface sediment-dwelling organisms near the bottom of the food chain (such as polychaetes, amphipods, and clams). By contrast, cores from Venice Lagoon, although containing perhaps a greater vertical inventory of CH₃Hg, did not show a very high peak at the surface. Instead, the peak appeared to be ~5–10 cm below the sediment-water interface, and, rather than being sharp, had a low, broad peak, with the CH₃Hg inventory spread over 10–30 cm of depth. Although we did not make redox or dissolved oxygen measurements in the sediments of the Venice Lagoon, it was apparent from visual inspection that the redoxcline in these cores was ~3–5 cm below the surface, providing a wide barrier against the transport of dissolved CH₃Hg to the surface. It is, as yet, unclear why the sediments at the two sites differed so much in redox characteristics, although it may have been due to a greater degree of exposure to the air at low tide in Venice Lagoon. Venice lagoon sediments are often left 10–50 cm above the water level at low tide, which allows more-thorough water drainage and air inclusion in the upper sediment layers. In addition, the lagoon sediments experience significant oxygen injection as a result of anthropogenically induced mixing and bioturbation by burrowing organisms such as polychaetes and clams (Frignani et al. 1997).

Another characteristic difference between the sites may be seen on the pore-water Hg speciation: in Lavaca Bay, pore-water Hg concentrations typically peaked at 0–4 cm depth, with concentrations of 10–200 ng L⁻¹, (8–200 ng L⁻¹ as CH₃Hg). Methylated Hg in these cores decreased rapidly, to <1 ng L⁻¹ by the time 10 cm depth was reached, whereas inorganic Hg was seen to increase to 30 ng L⁻¹ over the same interval (Bloom et al. 1999). By contrast, in Venice Lagoon (only one core profile so far examined), the Hg in pore water was typically in the same range (10–123 ng L⁻¹, excluding one anomalous point at 65 cm depth of 155,000 ng L⁻¹), whereas CH₃Hg concentrations were much lower, increasing gradually from 6 ng L⁻¹ at the surface to ~15 ng L⁻¹ at 80 cm depth.

Because of differences in both the timescale of sampling and in the depth of the methylation maxima, it is difficult to directly compare the seasonality of sediment Hg methylation at the two sites. However, some intuition can be gained from Fig. 6, which shows the mean percent Hg methylated in the upper 2–3 cm of cores taken in similar environments, adjacent to shallow salt marshes within several kilometers of the

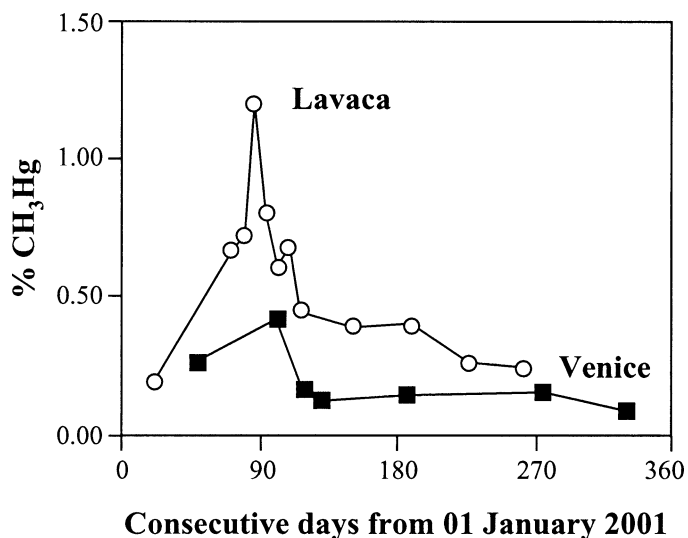


Fig. 6. Seasonal change in the percentage of CH₃Hg in the upper 0–3 cm interval of sediments from site GF-2 in Lavaca Bay and the Lago dei Teneri salt marsh in Venice Lagoon.

historic discharge point in both systems (“GF-1” in Lavaca Bay and “Lago dei Teneri” in Venice Lagoon).

The major difference in the sampling timescale is readily apparent, where, in the case of Lavaca Bay, samples were collected weekly throughout the spring, which resulted in the capture of a big peak in methylation as the water temperatures began to increase rapidly (Bloom et al. 1999). In the case of Venice Lagoon, initial quarterly sampling prevented witnessing such an event. However, in the following spring (2003), an additional three biweekly samplings were made of the Lago dei Teneri sediments (the three points just after day 90 in Fig. 6), which resulted in what appeared to be a similar early-spring peak in methylation rates of Venice Lagoon. It remains apparent that, during all equivalent sampling periods, surface CH₃Hg concentrations were considerably lower in Venice Lagoon than in Lavaca Bay. From the limited data we currently have available (Figs. 4, 5), we believe that this is not because less methylation is occurring but because it is occurring deeper and more diffusely than in Lavaca Bay.

It is curious that the maximum in sediment Hg methylation was found in both systems during early spring—not when the temperatures are warmest but just as they are starting to warm up. Even more perplexing, given the very close interplay between sediments and water in these two systems, was that the CH₃Hg maximum in the water column occurred not during spring, as might be expected, but several months after the peak in the sediments had already diminished. Unfortunately, not all of the data were collected at appropriate time scales to answer this question. A reasonable hypothesis is that there is in fact greater methylation during the summertime but that it occurs at the sediment-water interface, which allows the rapid diffusion of the produced CH₃Hg to the overlying water, where it is quickly adsorbed by the high suspended loads. This could be resolved by collecting detailed sediment and pore-water cores, as well flux chamber

measurements from both systems during the summer rather than in the spring (Lavaca) and autumn (Venice).

Venice Lagoon and Lavaca Bay are significantly more contaminated by Hg than other urban and industrially contaminated sites. Because of heavy nutrient inputs, shallow, seasonally warm water, and extensive wetlands, Venice Lagoon in particular can be viewed as a “methyl Hg incubator,” where even small inputs of inorganic Hg could result in high levels of CH₃Hg production. Given this, we were surprised to find that the contaminated areas of Lavaca Bay appeared to receive considerably more CH₃Hg per unit area than Venice Lagoon. Although supporting data were sparse, this appeared to be because the locus of Hg methylation in Venice Lagoon sediments is much deeper and more diffuse (5–20 cm) than that in Lavaca Bay, which occurs within 0–2 cm of the sediment/water interface. Although the per unit area methylation at the sediment surface in Lavaca Bay appears to be higher, Venice Lagoon contains about an order of magnitude larger surface area of highly contaminated sediments, thus potentially releasing much more CH₃Hg to the food chain. Both humans and sea birds consume fish and shellfish from Venice Lagoon in large quantities, raising the prospect of unacceptable exposure levels.

Water concentrations in the vicinity of the Marghera industrial zone, although elevated, were surprisingly low in Hg, whereas those in the canals of the city of Venice were found to have the highest average levels of any of the areas studied. These findings suggest that recent pollution-control efforts on direct industrial discharges in Venice Lagoon have been successful at reducing new Hg to the lagoon. With the advent of reduced direct discharges, however, future reductions in Hg to the food chain will have to rely more on diffuse sources such as urban sewage releases and sediment and wetland management issues. In Lavaca Bay, high sedimentation rates are rapidly burying the historic Hg peak, leading to the conclusion that the best remedial option, after stopping all residual new Hg inputs, is to allow natural attenuation to take place.

Quite the opposite may be the case in Venice Lagoon, where continual sediment reworking and a net negative sedimentation rate result in ongoing high Hg levels at the sediment/water interface and transport of high Hg sediments to biologically active wetland areas. The results of a recent investigation on the effect of dredging and sediment mobilization on methylation rates (Bloom and Lasorsa 1999) suggested that overall CH₃Hg production in Venice Lagoon may be dramatically increased by such activities. Given the large and diffusely affected area in Venice Lagoon, it is likely that a direct remedial effort would never be a cost-effective option. However, a better understanding of the seasonal effects of sediment remobilization, dredge spoiling, wetlands reconstruction, and alterations to circulation patterns may enable subtle changes in lagoon management that could have major effects on overall methylation rates. Examples include conducting dredging and wetland construction activities only during winter, enforcing a ban on the practice of “la rasca soffiante,” reducing sediment loss from the lagoon by increasing riverine inputs and/or reducing the size and depth of shipping channels, diverting all Venice urban sewage to a wastewater treatment plant, and reconsidering the effect of

the proposed MOSE flood control gates (Bernstein and Cecconi 1995) on flushing rates (and so on CH₃Hg concentrations). All of these factors could have significant effects in reducing Hg methylation without requiring the costly removal of large quantities of contaminated sediments.

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Received: 13 July 2003

Accepted: 2 November 2003

Amended: 27 November 2003