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Mercury contamination in Marano Lagoon (Northern Adriatic sea, Italy): Source identification by analyses of Hg phases

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Abstract

Total Hg concentrations and Hg speciation were determined in bottom sediments of Marano lagoon to investigate the consequences of Hg phases on fish farms and shellfish cultivation areas. Mercury phases were separated into cinnabar (HgS) and non-cinnabar compounds, via a thermo-desorption technique, in surface and core sediments; both of which had been contaminated by industrial wastes and mining activity residues. The former are due to an industrial complex, which has been producing cellulose, chlor-alkali and textile artificial fibres since 1940. Processing and seepage wastewaters, which were historically discharged into the Aussa-Corno river system and therefore into the lagoon, have been significantly reduced since 1984 due to the construction of wastewater treatment facilities. The second source is the Isonzo River, which has been the largest contributor of Hg into the northern Adriatic Sea since the 16th century due to Hg mining at the Idrija mine (western Slovenia). Red cinnabar (HgS) derived from the mining area is mostly stable and insoluble under current environmental conditions. In contrast, organically bound Hg, such as Hg bound to humic acids, has the potential to be transformed into bioavailable Hg compounds (for example, methylmercury). The presence of the two Hg forms permitted each Hg source to be quantified. It also allowed the areas with the highest risk of Hg contamination from Hg-rich sediment to be identified; thus potentially avoiding the transfer of Hg from the sediment into the water column and eventually into living biota. The results show that Hg Enrichment Factors in bottom sediments exceed values of 10 and cinnabar dominates the central sector near the main tidal channel where tidal flux is more effective. Non-cinnabar compounds were found to be enriched in fine grained material and organic matter. In fact, up to 98% of total Hg at the Aussa-Corno river mouth and in the inner margin of the basin occurred in an organic form. This evidence, combined with the high contents of total Hg (4.1–6.6 $\mu g\ g^{-1}$ and EF > 10) measured in surface sediments, suggest that Hg in Marano lagoon is involved in biogeochemical transformations (e.g., methylation).

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1. Introduction

The biogeochemistry of Hg has become one of the most important topics in environmental sciences in the last 4 decades. This is due, in part, to Hg dispersion on a

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global scale, its extreme toxicity at low levels, and its tendency to bioaccumulate within food chains (Mastrine et al., 1999; WHO, 1990; Porcella, 1994; Salomons, 1997). The ecological and human health effects of Hg are generally related to the environmental transformation of inorganic Hg to the more toxic methylmercury and biomagnification in ecological systems (Compeau and Bartha, 1985). Moreover, several studies have demonstrated that wetlands are important areas for Hg methylation (Kierfve, 1994; King et al., 2002; Lacerda and Gonçalves, 2001) and that SO_4-reducing bacteria (SRB) are the major biological mediators of Hg methylation in sediments (Gilmour et al., 1992; King et al., 1999). Also, particulate and dissolved organic C play a significant role in the biogeochemical cycling of Hg in the aquatic environment (Gill and Bruland, 1990; Mason et al., 1993; Stordal et al., 1996). Possible remobilisation of heavy metal compounds, and Hg in particular, from bottom sediments into the water column of coastal lagoon ecosystems may result in variable accumulation by the lagoon biota (Lacerda et al., 1992). The presence of Hg in aquatic systems is due to several inputs, such as atmospheric deposition (Marins et al., 1996), and/or mining and industrial discharges (Baldi and Bargagli, 1984; Hines et al., 2000; Biester et al., 2002). Speciation of Hg in the water column of coastal lagoons may be of great environmental significance, since it will not only control the eventual transfer of Hg to coastal waters but also the capacity of water bodies to accumulate large amounts of Hg in their sediments. As such, it is important to determine the distribution and the forms of this metal in contaminated sediments in order to establish potential risks and appropriate remediation technologies (Kaplan et al., 2002). Sequential extraction techniques have been widely used in order to differentiate between anthropogenic and geogenic Hg sources in soils and sediments and to evaluate the potential for remobilisation of Hg into the aqueous phase (Wallschläger et al., 1995; Bloom et al., 2003). Alternatively, Hg-thermo-desorption techniques have been successfully applied to distinguish metallic Hg from Hg(II)-binding forms; for example, between humic acids and sulphides in fluvial and marine sediments (Biester and Scholz, 1996; Biester et al., 2000, 2002; Sladek et al., 2002).

The Po River and the industrial zone of the Venice Lagoon are the primary sources of Hg contamination in coastal sediments of the Northern Adriatic sea (Fabbri et al., 2001; Donazzolo et al., 1981). Further east, the Isonzo River supplies suspended material enriched in Hg to the Gulf of Trieste from sediments and tailings of the Idrija mining area (western Slovenia). Since late 1970 several investigations on coastal sediments of the Gulf of Trieste have reported high concentrations of total Hg (23.6–47.0 $\mu g\, g^{-1}$), which exponentially decrease with distance from the fluvial source (Faganeli et al., 1991; Covelli et al., 2001). The Isonzo river inputs are dispersing westward and out of the gulf, following the main circulation system, and are also contributing to the Hg load in bottom sediments and, most importantly, to biota of the adjacent Grado and Marano lagoons (Brambati, 2001). Biester et al. (2000) have shown that cinnabar is the predominant form of Hg at the Isonzo River mouth, whereas organically bound Hg forms, which are mainly associated with fine particles, are subject to long range transport. In addition, the influx of this element into the western part of the lagoon system was significantly enhanced by an industrial complex located along a stream flowing into the lagoon. The industrial plant has been producing cellulose, chlor-alkali and textil artificial fibres since the 1940s (RFVG, 1991; Marocco, 1995; Brambati, 1997).

The aim of this study was to determine and quantify the proportion of cinnabar (HgS) and non-cinnabar compounds by a thermo-desorption technique in recent sediments of the Marano lagoon. As the industrial complex is a major source of non-cinnabar Hg compounds, attention was specifically given to locating areas of prevalent organomercury accumulation in comparison to sulphide-bound Hg. The circulation system and the relationships between Hg compounds and sediment particle characteristics were also investigated in order to recognise sites of potentially bioavailable Hg and the transfer of these Hg species from lagoon sediments into the water column and eventually into biota. Bioaccumulation, biotransfer and bioconcentration of Hg in the local environment is of direct health concern, as bivalves (clams and mussels), and a large number of fish farms in the lagoon are of local economic importance.

2. Environmental setting

The Marano and Grado lagoons (Fig. 1(a)) are part of the extensive system of transitional environments developing along the northern Adriatic coast from the Po river delta to the Isonzo river mouth in the Gulf of Trieste. The Marano and Grado lagoons extend for about 32 km, between the Tagliamento and Isonzo River deltas, reaching up to 5 km for a total area of 160 km^2. The lagoon basin is characterised by semi-diurnal tidal fluxes (65 and 105 cm mean and spring tidal range, respectively). Small rivers flow into the lagoon, which drain waters coming from the spring line and those from irrigation canals, which are conveyed into the water scooping machines. Particulate matter from these streams is of secondary importance, restricted to areas surrounding the spring river mouths. Conversely, the primary source of suspended sediments arrives from the sea, as the contribution of river deltas and from erosion of the barrier islands. Dispersion of sediments into the lagoon is controlled by tidal fluxes through tidal inlets (Brambati, 1970).

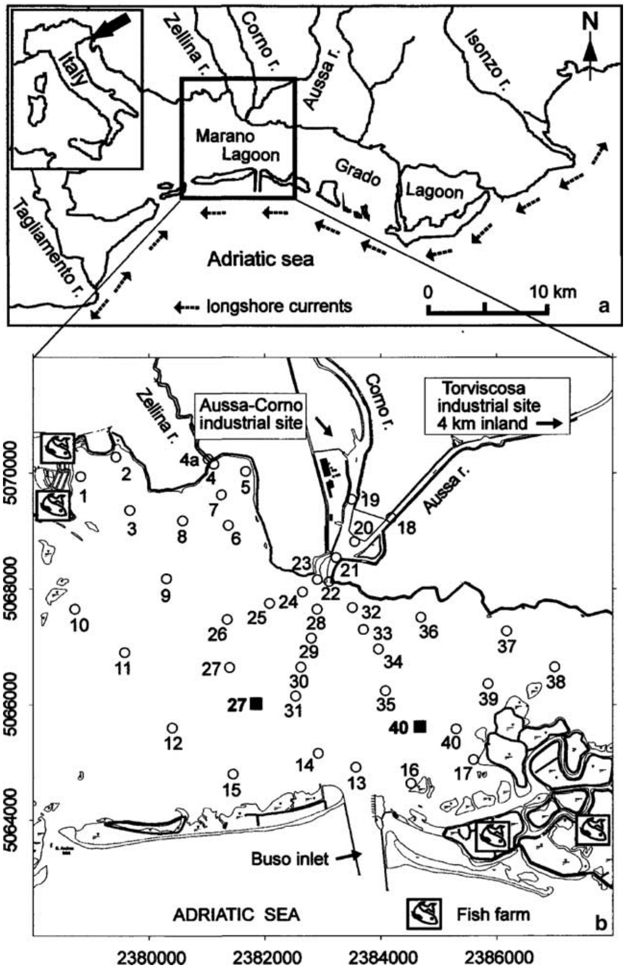

Fig. 1. Central sector (Buso basin) of the Marano and Grado lagoons (a) and location of sampling points (b). Circles indicate bottom samples and black squares show core sites. Fish farm sites are also reported.

The sampling area is located in the Buso basin (Fig. 1(b)), which occupies the central position of the lagoon system and presently has a surface area of 45 km^2. The width of the Buso inlet was modified and reduced to 450 m after the building of jetties from 1964 to 1969. Commercial shipping through the main channel is maintained by periodical dredging, which ensures a channel depth of approximately 8 m along its axis. The most important freshwater stream flowing into the Buso basin is the Aussa-Corno River, which has a steady flow in the order of 25–27 m^3 s^{-1} (RFVG, 1983). The suspended load reaches 8–10 mg L^{-1} during normal run off periods (Piani, 1992 unpublished data). The Zellina River, which is the second and less influential tributary of Buso basin, has a flow rate of just 1–2 m^3 s^{-1} (RFVG, 1983).

The general grain-size distribution observed for the whole lagoon is also found in the Buso basin (Piani and Covelli, 2000). Medium to fine sands are only present in front of the Buso inlet, along the main channel and the two lateral secondary channels and, subordinately, at the lower limit of the tidal flats. The fine pelitic component is widely dispersed in the basin and varies from 52% to 100%. The silty fraction (52–2 μm) normally comprises a higher percentage than the clay fraction (<2 μm) in the pelitic component. In fact, the ratio fine-silt/clay (2–16/<2 μm) identifies areas affected by freshwater inputs into the lagoon: a high ratio indicates an area of fresh water input and vice versa. The highest contents of fine silt occur where the Zellina and Aussa-Corno rivers enter the lagoon. Moreover, areas affected by fresh water inputs and the inner part of the basin show the highest values of organic C (0.2–3.5%) and C/N ratios (up to 14). This suggests that organic matter of prevalently continental origin is partially preserved in those sectors where reducing conditions (Eh $\leqslant -300$ mV) in bottom sediments occur due to limited fluvial influence and interchange of marine waters through tidal cycles (Brambati, 1997).

This area of the lagoon has high vulnerability due to the substantial human impact caused by urban settlements and industrial activities. Porto Nogaro, located 1 km north of the Aussa-Corno mouth is the most important industrial site in the region. In addition, the Torviscosa industrial complex produced cellulose from cane (*Arundo donax* sp.) from the 1940s until 1992. It is estimated that about 20 kg day^{-1} of Hg has discharged into the Aussa River since 1949 (when the chlor-alkali plant became operative). As reported in RFVG (1991), soda production was increased from 4500 tons in 1950 to 20,000 tons during the following 10 a. The decrease of Hg discharged amounted to 6–7 kg day^{-1} in 1970 and it presumably stopped in 1984 when wastewater treatment systems were installed. At the present time, industrial effluents flow through submarine pipes that discharge processing effluent into the open sea; about 6.5 km offshore from the main tidal inlet. According to the report mentioned above, an estimated total amount of 186,000 kg of Hg was released into the river. It is likely that a significant volume of this Hg reached the lagoon environment. This site is currently under intense investigation and some corrective actions (e.g., soil removal and groundwater treatment) are in progress. Although high levels of Hg in bottom sediments of the Gulf of Trieste revealed a very strong supply of suspended material from the Isonzo River due to the long-term mining activity in the Idrija region (Brambati, 2001; Covelli et al., 2001), no estimation of the contributions from this source to the total amount of Hg into the lagoon has been attempted.

3. Materials and methods

A total of 41 bottom sediment samples were recovered by a Van Veen grab and two cores (sampling stations 27 and 40) were hand collected from both sides of the main navigation channel (Fig. 1(b)), which connects the tidal inlet to the Aussa-Corno river mouth. Organic debris and shelly fragments were removed by sieving (<2 mm) each sample prior to grain-size analysis. Subsamples from each core and grab sample were subjected to 24 h of H_2O_2 treatment to remove organic matter, and subsequently wet sieved using a 52-μm sieve to separate sand from the pelitic fraction. Additionally, pelite was treated with H_2O_2 (10 v/v) prior to being analysed by a Micromeritics Sedigraph 5000 ET.

The organic C and total N were determined on 40 °C dried and homogenised samples, after acidification with progressively increasing concentration of HCl (Hedges and Stern, 1984), using a Perkin–Elmer C–H–N Elemental Analyser at a combustion temperature of 920 °C.

Sediments were digested with HNO_3 and H_2SO_4 solution (IRSA-CNR, 1985) and total Hg was measured following a modified form of CV AAS procedure by using a Perkin–Elmer Mercury Hydride System coupled to an AAS Perkin–Elmer mod.380.

Determination of Hg phases by solid-phase-Hg-thermo-desorption is based on the specific thermal decomposition of Hg compounds from sub-samples of dry sediment at different temperatures. A detailed description of the method is found elsewhere (Biester and Zimmer, 1998; Biester et al., 2000). Results are represented by Hg-thermo-desorption curves showing release of Hg(0) versus increasing temperature. Mercury desorbed from matrix-bound Hg, such as Hg associated with humic acids, is in general normally distributed, in contrast to cinnabar which is irregularly released during thermo-desorption. Mercury peaks were then quantified by peak integration. Since non-cinnabar and cinnabar peaks usually partially overlap, non-cinnabar Hg was calculated by doubling the first half of the corresponding peak (150–250 °C). Therefore, Hg bound in cinnabar was obtained as the difference between total Hg and non-cinnabar Hg.

Geochemical data for the overall Buso basin surface area were processed using the Surfer software program (Kriging algorithm).

4. Results and discussion

4.1. Mercury occurrence in the lagoon sediments

The high vulnerability of coastal lagoon ecosystems is related to the shallowness and the limited water exchange of these semi-enclosed basins. Due to these features, the residence time of water, sediments and, consequently, contaminants, in the lagoon is much longer than in river mouths and in open coastal areas. Heavy metals, and in particular, Hg accumulated in sediments may be subjected to burial and/or to biogeochemical processes, which affect their distribution, speciation and bioavailability to the lagoon biota. The high potential risk of Hg remobilisation from sediments into the water column and its subsequent bioaccumulation in the trophic chain is also enhanced by the abundance of animal and plant species in this ecosystem. Human activities such as fishing, collection of clams and mussels and cultivation of edible fish species in fish farms increase chances of Hg uptake by living organisms and, ultimately, by human residents in the surrounding area.

Mercury levels in aquatic plants and organisms from the trophic chains (Brambati, 1997) of the Marano and Grado lagoons suggest that tissue Hg is correlated with bottom sediment Hg concentrations, which show a progressive westward decrease from about 10 mg kg^{-1} (Grado lagoon) to 1 mg kg^{-1} (Marano lagoon). However, different concentrations of Hg found in aquatic

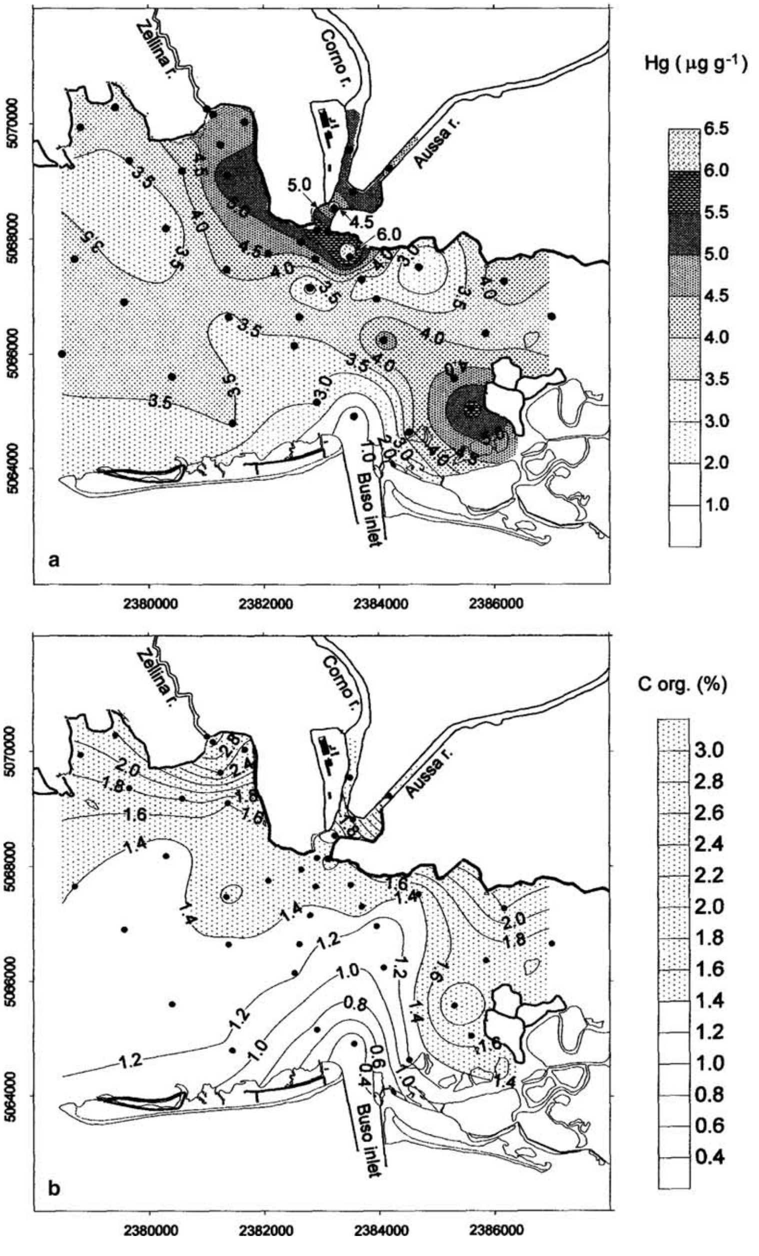

Fig. 2. Distribution of total Hg (a) in µg g^{-1} and organic C (b) in % for the surface sediments of the lagoon basin.

species are related to their trophic characteristics. For example, mussel (*Mytilus*) and common cockle (*Cardium edule*) which are filter feeders show low concentrations; higher concentrations were found in prawn (*Palaemon*) a coarse detritus feeder; whereas very high levels (average 0.5–0.7 mg kg^{-1}, maximum 2–3 mg kg^{-1}) were detected in the carnivorous goby (*Zosterissessor ophiocephalus*) and silverside (*Atherina boyeri*). The same high Hg anomalies were observed in the fish farms where edible fish (e.g., gilt-head bream, *Sparus auratus* and bass, *Dicentrarchus labrax*), which are at the top of the food chain, showed levels far higher (up to about 5 mg kg^{-1}) than the same species collected in the natural environment. Unfortunately, Hg biomagnification increases the total Hg levels in marine species of commercial value (Brambati, 2001), and the magnification process seems to be more effective in the fish farms. Brambati (2001) also found high Hg concentrations in the hair of people having a fish-based

Table 1
Relative abundances of main textural and geochemical parameters in surface sediment samples

Sample	Sand (%)	Silt (%)	Clay (%)	2–16 μm (%)	C org. (%)	Hg ($\mu g\ g^{-1}$)
RP1	0.7	71.3	28.0	42.0	1.92	3.61
RP2	2.5	70.5	27.0	51.0	2.18	3.52
RP3	16.4	62.6	21.0	45.5	1.81	3.51
RP4	0.4	70.1	29.5	51.5	3.06	4.70
RP5	1.5	80.5	18.0	49.5	2.51	4.77
RP6	3.3	75.7	21.0	31.5	1.61	5.48
RP7	1.0	72.0	27.0	46.0	2.62	4.62
RP8	3.0	72.0	25.0	33.0	1.81	3.98
RP9	19.2	55.8	25.0	36.5	1.29	3.03
RP10	13.4	64.1	22.5	35.5	1.40	3.66
RP11	11.2	71.8	17.0	24.0	1.28	3.69
RP12	5.6	74.4	20.0	28.0	1.33	3.57
RP13	98.3	1.7	0	0	0.21	0.13
RP14	47.8	33.7	18.5	23.5	0.75	3.07
RP15	30.5	36.0	33.5	39.5	1.17	3.53
RP16	29.3	36.2	34.5	42.0	1.22	3.89
RP17	8.7	67.3	24.0	36.0	1.68	5.73
RP18	0.9	62.1	37.0	48.5	3.48	4.89
RP19	0.4	61.6	38.0	39.5	2.06	5.24
RP20	0.5	65.5	34.0	40.0	2.08	5.62
RP21	5.0	71.5	23.5	28.5	1.29	4.14
RP22	30.8	42.2	27.0	32.0	1.66	5.63
RP23	4.4	70.6	25.0	36.5	1.53	6.19
RP24	6.1	67.9	26.0	32.5	1.41	4.95
RP25	5.6	71.4	23.0	32.0	1.59	4.56
RP26	7.4	74.1	18.5	43.5	1.64	4.09
RP27	9.6	65.4	25.0	30.0	1.36	3.45
RP28	18.0	57.0	25.0	32.0	1.60	4.57
RP29	16.9	59.1	24.0	31.0	1.30	2.74
RP30	12.0	66.0	22.0	27.5	1.27	4.11
RP31	16.2	62.8	21.0	27.0	1.23	3.20
RP32	3.1	74.9	22.0	31.0	1.42	6.58
RP33	2.1	79.4	18.5	33.5	1.60	3.21
RP34	8.7	73.8	17.5	22.5	1.04	3.55
RP35	21.1	60.9	18.0	24.0	1.07	4.81
RP36	18.6	56.4	25.0	33.0	1.41	2.14
RP37	5.0	63.0	32.0	41.0	2.21	4.50
RP38	7.2	76.8	16.0	36.0	1.64	3.57
RP39	13.6	57.4	29.0	38.0	1.63	3.57
RP40	5.3	71.2	23.5	44.5	2.03	4.69
RP4A	0.2	66.8	33.0	58.5	3.20	5.50

diet (up to 20 $mg\ kg^{-1}$) and Hg levels showed a direct positive correlation with age. Furthermore, high levels of Hg were also found in birds, demonstrating that the top consumers in the area may bioaccumulate Hg.

Results of textural and geochemical parameters of the study area reported by Piani and Covelli (2000) revealed that major and trace elements (Al, Fe, K and Zn, Cr and Ni) as well as organic C, are significantly correlated with fine particles (<16 μm) and they reflect the distribution pattern of this textural component in the lagoon basin.

The anomalously high concentrations of Hg occur near the Zellina and Aussa-Corno river mouths and on tidal flats in the eastern part of the basin (Fig. 2(a) and Table 1). Due to the double source of contamination mentioned above, Hg concentrations in sediments, ranging between 0.1 and 6.6 $\mu g\ g^{-1}$, are on average ($4 \pm 1.2\ \mu g\ g^{-1}$) far higher than natural background values proposed in previous studies for the northern Adriatic sea (0.1 $\mu g\ g^{-1}$, Faganeli et al., 1991; 0.2 $\mu g\ g^{-1}$, Covelli et al., 2001). Higher concentrations of organic C are found in the inner and western parts of the basin where bottom sediments are mostly pelites rich with fine silt (Fig. 2(b)).

The two short cores do not show noticeable grain-size variations, although a slight increase in the coarse sandy fraction was detected at the top of core 27. This core was collected in the western part of the basin where salt marshes are absent and tidal fluxes are more efficient

Table 2
Relative abundances of main textural and geochemical parameters in core samples

	Depth (cm)	Sand (%)	Silt (%)	Clay (%)	2–16 μm (%)	C org. (%)	Hg (μg g^{-1})
Core 40							
1	0–3	1.1	74.5	24.4	45.2	2.07	5.80
2	3–5	0.8	68.8	30.4	40.6	1.98	7.19
3	5–7	0.5	73.4	26.1	44.5	1.91	7.43
4	7–9	0.4	65.8	33.8	44.8	1.75	8.41
5	9–12	1.0	67.2	31.8	42.4	1.66	6.55
6	12–14	0.0	60.2	39.8	41.1	2.03	9.84
7	14–16	0.1	62.8	37.1	44.4	1.88	5.99
8	16–18	0.5	63.4	36.1	44.5	1.84	4.23
9	18–20	0.5	64.4	35.1	43.5	1.96	4.13
10	20–22	0.4	63.0	36.6	42.5	1.80	3.58
11	24–26	0.4	65.3	34.3	43.4	1.62	3.55
12	28–30	1.2	70.0	28.8	41.3	1.63	5.13
13	33–35	0.2	67.3	32.5	48.9	1.45	3.40
14	37–39	1.1	76.9	22.0	42.2	1.76	3.42
15	41–43	0.3	75.9	23.8	45.3	1.53	2.09
16	44–46	0.3	71.6	28.1	47.0	2.12	2.14
17	48–50	0.3	68.7	31.0	51.2	2.87	1.10
18	54–55	1.2	75.2	23.6	39.1	1.41	0.52
19	58–60	0.8	73.0	26.2	42.1	–	0.63
20	62–64	0.6	73.2	26.2	42.7	–	0.41
Core 27							
1	0–3	0.7	70.3	29.0	41.9	1.38	2.15
2	5–7	1.8	73.4	24.8	37.0	1.27	2.74
3	9–11	2.3	76.7	21.0	34.3	1.06	2.24
4	13–15	1.9	74.7	23.4	35.9	1.27	2.66
5	17–19	0.1	69.7	30.2	45.1	1.22	2.46
6	21–23	0.4	70.6	29.0	44.7	1.24	0.85
7	25–27	0.6	72.3	27.1	44.4	1.28	0.39
8	29–31	0.9	71.2	27.9	45.1	1.28	0.42
9	33–35	0.4	72.0	27.6	45.0	1.19	0.41
10	37–39	0.1	68.1	31.8	46.3	1.38	0.63
12	41–43	1.3	71.1	27.6	44.9	1.41	0.32
13	45–47	0.4	64.9	34.7	46.9	1.57	0.30

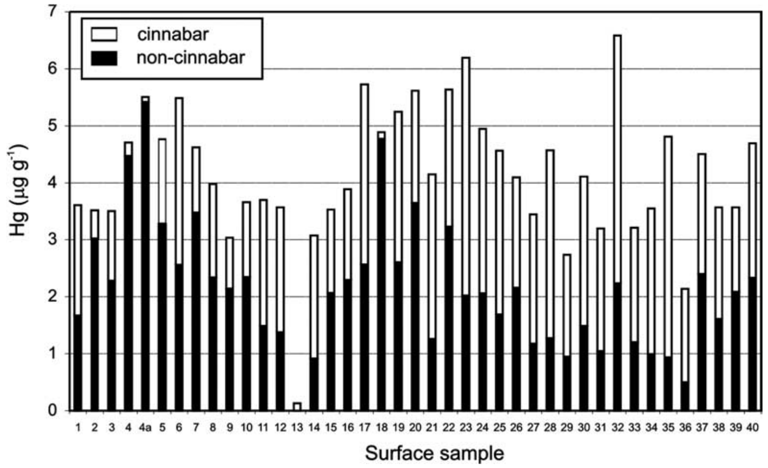

Fig. 3. Calculated contribution of cinnabar and non-cinnabar Hg compounds in surface sediment samples as estimated by peak integration. The cumulative bar charts provide the amount of both fractions related to total Hg content.

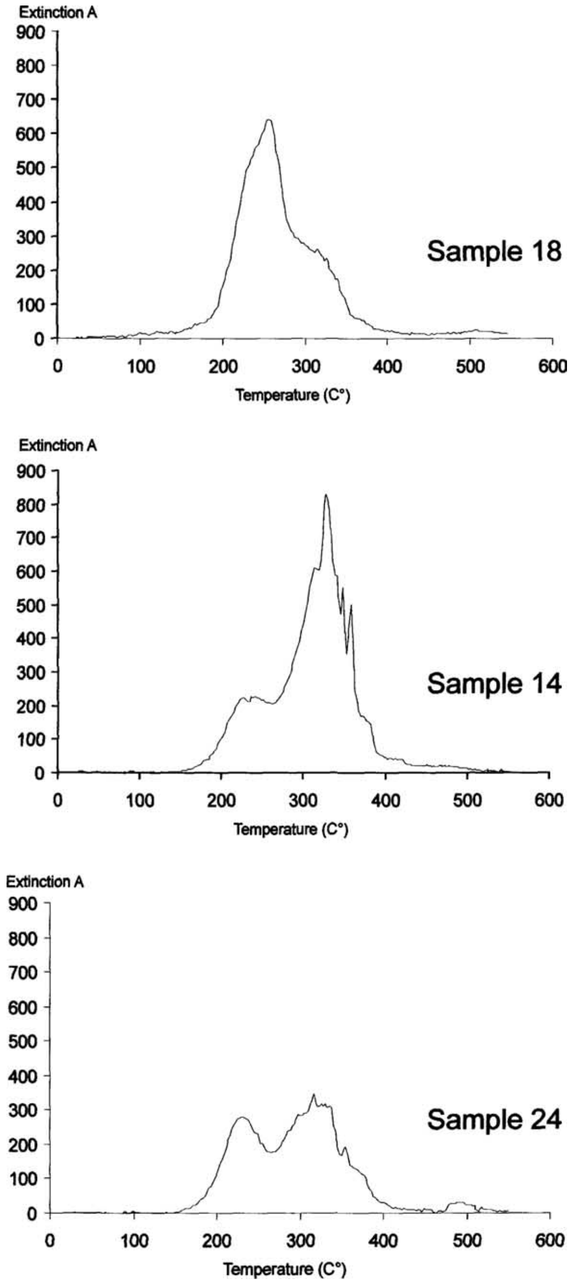

Fig. 4. Typical Hg-thermo-desorption curves show surface sediment samples where Hg is predominantly present as non-cinnabar (sample 18) and cinnabar (sample 14) compounds, and where cinnabar and non-cinnabar compounds are almost equally mixed (sample 24).

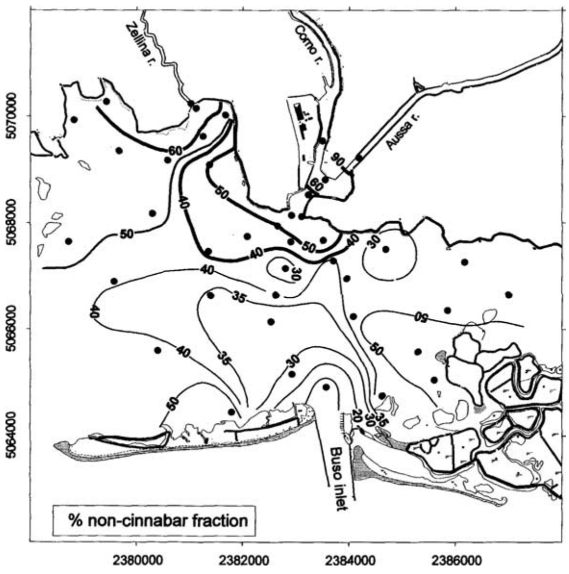

Fig. 5. Areal distribution of the amount of non-cinnabar compounds, expressed as percentage of the total Hg content in the surface sediments of the lagoon.

on the mudflats. In contrast, core 40 was sampled on a tidal flat near a salt marsh area, which is typically a low energy environment. Major and trace elements do not show a significant vertical trend along the core profiles (Piani and Covelli, 2000). The only exception is Hg that is detected at a constant value of about 2 $\mu g\,g^{-1}$ in the first 20 cm of core 27. Higher concentrations are found in core 40 where subsurface maximum is reached at 13 cm depth (9.9 $\mu g\,g^{-1}$) and Hg decreases downcore approaching background values at 50 cm depth (Table 2).

Many trace elements are known to be preferentially associated with fine particles in aquatic systems. Therefore, a common approach is to normalise metal concentrations to account for grain-size variability prior to assessing the degree of contamination (Loring and Rantala, 1992). The degree of enrichment of a metal is then calculated by dividing its ratio to the normalising element by the same ratio found in the baseline (e.g., Middleton and Grant, 1990). A non-dimensional enrichment factor $EF = (Me/N)_{sample}/(Me/N)_{baseline}$ is obtained, where Me is the concentration of the potentially enriched metal and N is the concentration of the normalising element. A value of unity denotes no enrichment or depletion relative to the pre-industrial datum. Iron was chosen as the normalising element due to its significant correlation with the <16 μm fraction ($r = 0.87$; $p < 0.001$) and the local baseline was assumed to be the average concentration of the two elements in the basal levels of the two cores ($Fe_{baseline} = 2.11\%$, from Piani and Covelli, 2000).

Mercury enrichment factors indicate that the central-southern sector of the basin along with the inner coastline extending from the Aussa-Corno river mouth westwards are preferential accumulation areas (EF > 10). In the latter, the higher Hg enrichment (maximum 18) can be explained by freshwater input, whereas in the first

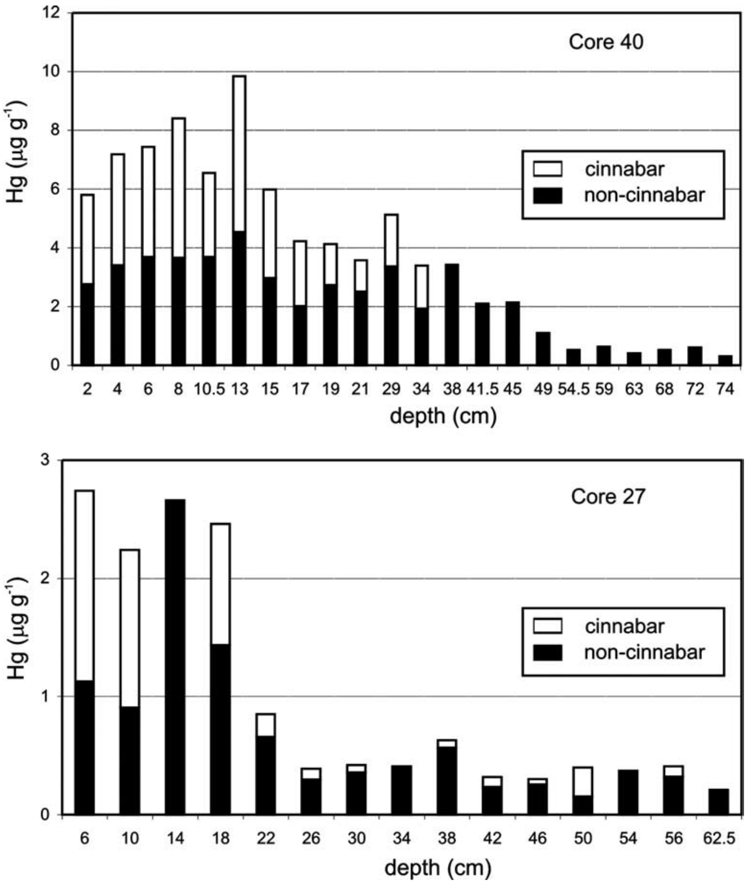

Fig. 6. Calculated contribution of cinnabar and non-cinnabar Hg compounds in core 27 and 40 sediment samples as estimated by peak integration. The cumulative bar charts provide the amount of both fractions related to the total Hg content downcore.

area periodic dredging operations in the main channel could be considered as a factor that contributed to increase metal concentration in sediments. Also, dumping of excavated material in the mudflats, immediately adjacent to tidal channels, was a common procedure followed in the past. These operations were recently ceased due to introduction of severe national legislation rules. Therefore, subsequent reworking and dispersion of dredged sediments through tidal fluxes cannot be excluded and EF areal distributions may reflect this complex situation.

The constant Hg concentrations in the upper part of core 27 (Table 2) appear to be related to mixing effects due to bioturbation in the first 20 cm, which would have homogenised recent metal supplies. This evidence was confirmed by X-ray radiography of the core, which shows concentrations of small tube-like burrows at the core top. Conversely, contamination in the upper section of core 40, extending downcore to about 50 cm, shows two apparent maxima (Table 2). The relevant difference between the two cores, in terms of thickness of contaminated sediment suggests two hypotheses.

The core 40 profile could be explained as the original sedimentary sequence, which was altered by anthropogenic activities, although dumping of excavated muds seems to be improbable due to the distance of the coring site from the main navigation channels. A second hypothesis, supported by ^{137}Cs profiles in the same cores (Piani and Covelli, 2000), suggests that the two sampling sites are characterised by different local sedimentation rates. This has also been reported for example by Pavoni et al. (1987) and Donazzolo et al. (1981) for the Venice lagoon and depends on variable energy hydrodynamic conditions from the lower to the upper mudflats.

4.2. Mercury phases in bottom sediments

Results of Hg thermo-desorption measurements performed on bottom samples demonstrate that both cinnabar and non-cinnabar compounds are present in lagoon sediments (Fig. 3) and that the relative contribution to total Hg contents can be assessed. The specific Hg phase in the sediments is the most important factor in terms of potential bioavailability of Hg to the aquatic food chain

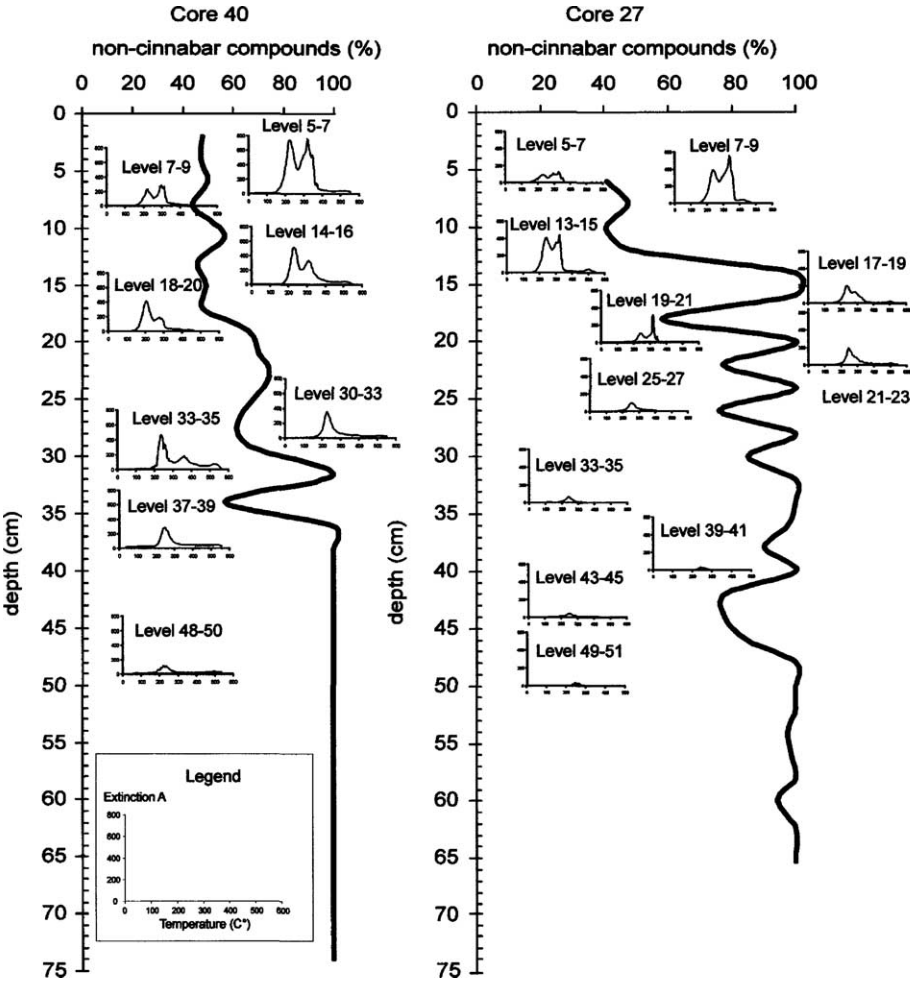

Fig. 7. Distribution of non-cinnabar compounds, expressed as percentage of the total Hg content, in the sedimentary sequence of core 40 and 27. Hg-thermo-desorption curves for each core level are also reported.

rather than the total Hg concentration. Presence and abundance of the non-cinnabar component in bottom sediments of some sampling sites may identify those areas in the lagoon where Hg is present in chemical forms that may be more mobile and/or involved in methylation processes.

Almost all samples show curves with two peaks. A first maximum was detected between 230 and 260 °C, which represents Hg released from non-cinnabar compounds such as humic acids, according to the curves of standard Hg compounds reported by Biester et al. (2000). Similarly, the second peak (300–350°C) is related to red cinnabar. As noted by the same authors, several high narrow Hg peaks usually appear in the curves due to slight differences in the crystallinity and grain-size of cinnabar, which influences Hg release temperatures.

Three types of Hg-thermo-desorption curves were obtained for surface sediments (Fig. 4). Just one sample taken upstream in the Aussa-Corno River is almost entirely characterised by the non-cinnabar peak. Due to the low temperature of this first peak, Hg could be associated with organosulphides or occurs as metacinnabar as a result of absorption of Hg(II) or Hg(0), by the prevailing silty-clay fraction with higher specific surface area, and subsequent transformation. In contrast, thermo-desorption curves of samples (e.g., 14 and 36) collected near the lagoon inlet and in the eastern part of the basin show Hg release temperatures mostly related to red crystalline cinnabar. All other samples from the lagoon show curves with two peaks, thus representing an evident mixing of both Hg compounds in surface sediments as a result of tidal dynamics. The spatial distribution of non-cinnabar compounds (Fig. 5 and also Fig. 3) is clearly influenced by the freshwater inputs (Aussa-Corno and Zellina rivers). Non-cinnabar Hg is relatively more abundant, especially in the lower course of the tributary streams and in the lagoon just in front of the river mouths. This evidence confirms that most of the Hg

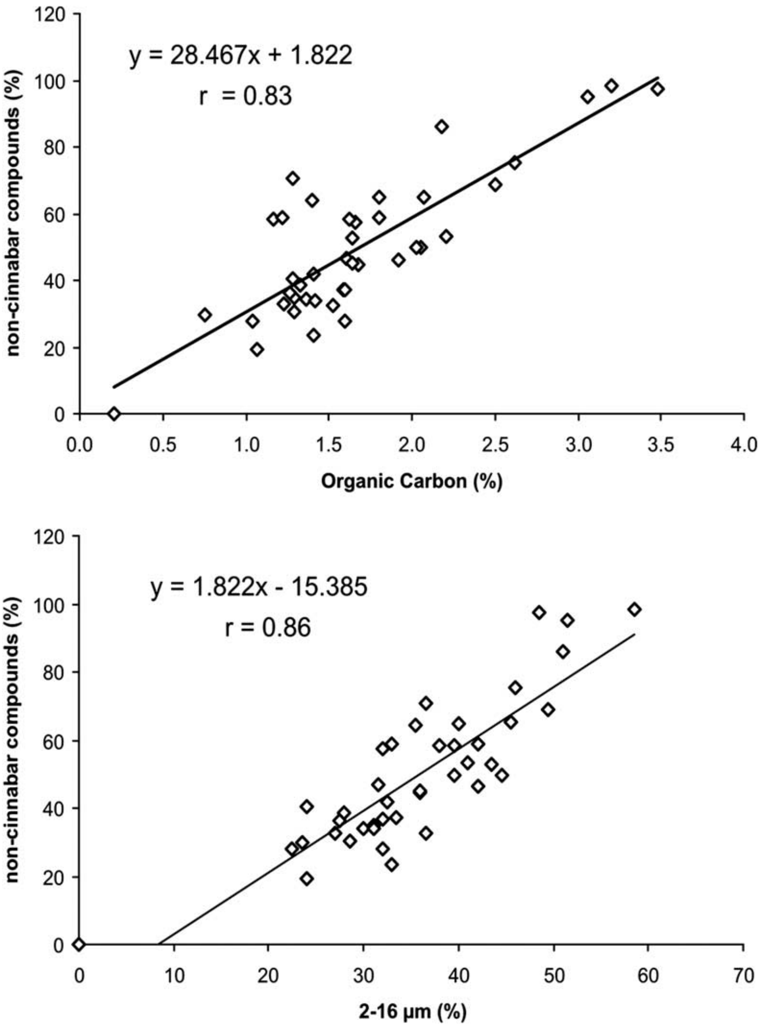

Fig. 8. Relations between non-cinnabar Hg and organic carbon, and the 2–16 μm fraction.

discharged into the Aussa River from the industrial complex preferentially accumulates in the river itself and in the inner part of the lagoon.

In contrast, cinnabar, although present at all locations, is mostly concentrated near the southern and eastern sectors of the basin. This fact testifies to the role of tidal fluxes in controlling dispersion and accumulation of cinnabar bound to suspended matter from Isonzo River and entering the lagoon through at least 3 of the 4 inlets.

4.3. Mercury phases in core sediments

Occurrence of Hg phases in core 27 and 40 (Fig. 6) shows an almost equal distribution of cinnabar and non-cinnabar compounds in the upper section of the sedimentary sequence. In contrast, Hg sulphides decrease downcore. Only non-cinnabar compounds are present in the basal part of the cores where Hg concentrations become very low (Fig. 7). The sediment core from the Gulf of Trieste (Covelli et al., 2001) was mostly composed of fine grained sediments, which have recorded the historical evolution of Hg production at Idrija mine through an exponential increase of metal concentrations since 1800 (although mining activity began in 1496). Between 1850 and 1970 the amount of excavated ore increased as much as the Hg production although the ore grade decreased from several tens to less than 1%. This activity produced an increasing amount of mining residues along with an improved efficiency of the roasting processes, including intensive crushing of the ore, which would have significantly increased the amount of fine grained material in the mining residues (Biester et al., 2000). The large amount of Hg enriched fine particles (silt-clay) transported by freshwaters of the Isonzo river into the Gulf of Trieste would have also entered the lagoons following the anticlockwise circulation system characteristic of this part of the northern Adriatic sea and flood tidal fluxes.

Comparing Hg compounds with other textural and geochemical parameters (Fig. 8), the best correlations were found between Hg and organic C ($r = 0.83$) and the 2–16 μm fraction ($r = 0.86$), suggesting that both the fine particles and organic matter play an important role in transferring and accumulating the metal in the lagoon sediments. Although Hg behaviour in this system depends on its chemical form introduced into the aquatic environment, Hg associated with industrial effluents has been shown to be positively correlated with fine grain sizes such as <63 μm (Rae and Aston, 1981) or <20 μm (Barghigiani et al., 1996); Hg also has a strong affinity for organic matter (Smith and Loring, 1981; Baldi and Bargagli, 1984; Gagnon et al., 1997). In areas where chlor-alkali plants are responsible for Hg contamination of sediments, up to 70–90% of the total metal in sediments can be associated with easily oxidizable organic matter, which is easily degraded and may then be released from the substrate (Smith and Loring, 1981; Gagnon et al., 1997; Biester et al., 2002).

Distinction between detrital Hg, i.e. cinnabar particles, settling in deltaic sandy sediments in front of the Isonzo river mouth and non-cinnabar compounds accumulated in the central sector of the Gulf of Trieste was made on the basis of correlation with the <16 μm grain size fraction (Covelli et al., 2001). According to these authors, Hg is preferentially adsorbed to the finest particles in the form of Hg(II), Hg(I) and Hg(0), due the higher specific surface area of each particle; although the presence of micro-crystalline cinnabar cannot be excluded.

5. Conclusions

Marano and Grado lagoons have experienced significant historic Hg inputs from mining and industrial point sources. The Buso basin, located in the central sector of this lagoon, has been severely affected both by long-term Hg contamination through Isonzo river suspended load and by untreated effluents discharged into the Aussa-Corno river from a chlor-alkali plant since 1950. This study has shown that the Hg-thermo-desorption technique is a useful method to discriminate between organically bound Hg and sulphide (principally cinnabar) bound Hg. Using this method, the relative contribution of each river system to the influx of Hg into the lagoon can be determined. Cinnabar from Isonzo River dominates the central sector of the lagoon, near the main tidal channel where tidal flux is more effective. Non-cinnabar compounds (avg. 49 ± 22%) were found to be enriched in fine grained material and organic matter in the inner margin of the basin, particularly at the Aussa-Corno River mouth where up to 98% of total Hg is bound in non-cinnbar forms as a consequence of recent industrial inputs. The distinction between the two Hg forms allows the areas at most risk from Hg remobilisation from bottom sediments to the water column and, possible interaction with lagoon biota to be identified. The main risk areas occur near some fish farms, which are protected from high energy regimes. For example, the areas of most concern are in front of the Zellina river mouth and the eastern part of the basin, as well as the whole Aussa-Corno River mouth. The relevant, although extremely variable, thickness of sediments contaminated by Hg, the high percentage of non-cinnabar compounds, and the extension of the basin make it difficult to devise an appropriate, in situ, remediation strategy. Due to the importance of local fish farm production, the most suitable choice would be to concentrate the efforts on the bottom sediments and remediation of restricted pools. For example, excavation and removal of the contaminated layer and a reduction of new Hg supplies bound to suspended matter through tidal fluxes flowing periodically into the fish farms could be the most fitting procedures.

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