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Mercury contamination of coastal sediments as the result of long-term cinnabar mining activity (Gulf of Trieste, northern Adriatic sea)☆

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Abstract

The Isonzo river mouth has been the source of Hg in the Gulf of Trieste (northern Adriatic sea) since the sixteenth century, making this shallow basin one of the most contaminated marine areas in the length of time and amount of metal accumulated. The occurrence and behaviour of total Hg (range 0.064–30.38 μg g^{-1}; average 5.04 μg g^{-1}; median 3.10 μg g^{-1}, $n=80$) and related size fractions in sediments of this coastal area were investigated in detail. The relationship between total Hg and the fine silt-clay (< 16 μm) fraction has provided information on the hydrological and mineralogical fractionation process affecting this element, when compared to other heavy metals associated with fluvial inputs. Mercury contents are very high along the littoral zone of the northern (Italian) sector where this metal is present in detrital form (cinnabar) in sandy-silty sediments near the river mouth and the surrounding beaches. Within the sediments belonging to the Gulf area, Hg is bound either to fine particles or adsorbed onto the surface of clay minerals and/or partially complexed by colloids and organic matter. Recent accumulation of Hg in a 70 cm long ^{210}Pb dated core, collected in the central part of the Gulf, was also compared to other heavy metals (Fe, Cr, Cu, Mn, Ni and Zn). A preliminary estimate of Hg enrichment shows that the first 50 cm of sediment in the central sector of the Gulf of Trieste are noticeably contaminated, reaching a maximum of up to 25-fold above the proposed natural regional background of 0.17 μg g^{-1}. The vertical trend is well correlated to historical data of Hg extraction activity at the Idrija mine.

1. Introduction

Among the heavy metals introduced into the environment, Hg is undoubtedly one of the major contaminants, due to its toxicity and to the relatively easy uptake of its chemical compounds, mostly organic, by biota and its consequent accumulation in the aquatic food chain. Human activities have contributed for a long time to increasing the amount of Hg in the natural environment, with different species which are not always immediately available for the biosphere. However, Hg is reactive in the aquatic environment where several types of bacteria play an important role in reduction, methylation and demethylation reactions involving this heavy metal accumulated in sediments (e.g. Compeau and Bartha, 1984; Baldi et al., 1989).

Mercury concentration in off-shore marine sediments of the Mediterranean sea is, on average, 0.1 mg kg^{-1}

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(Baldi et al., 1983), twice as high as the supposed worldwide natural background (Hans Nelson et al., 1975). This enrichment is, firstly, a consequence of the natural composition of the area, characterised by some of the largest cinnabar deposits in the world and, secondly, by surficial and submarine volcanic and geothermal activities. It has been estimated that approximately 65% of the world's Hg resources are located in the Mediterranean area (Bernhard and Buffoni, 1982). In addition to this natural origin, industrial and domestic wastes (Griggs et al., 1978; Baldi and Bargagli, 1984; Krom et al., 1994), through direct and/or river discharges, have contributed to increased Hg fluxes to the Mediterranean sea.

In accordance with the quite large data set for Hg concentrations in the sediments of the Adriatic sea (Selli et al., 1977; Kosta et al., 1978; Donazzolo et al., 1983; Ferrara and Maserti, 1992), it is evident that a substantial "positive gradient" from the southern to the northern sector of the basin exists. The highest levels of Hg on the western (Italian) side were found in the salt marshes near Ravenna's oil refinery (Anconelli et al., 1980; Fabbri et al., 1996), whereas sediments of Kastela Bay near Split, on the eastern (Croatian) coast, have been contaminated due to the uncontrolled effluent of a chlor-alkali plant (Tudor et al., 1990; Odzak et al., 1996). Coastal sediments of the Po river delta area appeared to be enriched in Hg as a direct consequence of anthropogenic inputs from the very extensive industrial activities located in the riverine drainage basin (Guerzoni et al., 1984). Sources of Hg contamination were also identified east of the Po river delta in the Marghera industrial zone, located along the inner shoreline of the Venice Lagoon (Donazzolo et al., 1981; Pavoni et al., 1987) and in the Grado and Marano Lagoons close to an important chemical complex (Daris et al., 1993; Marocco, 1995; Brambati, 1997). High concentrations of Hg (23.6–47 $\mu g\ g^{-1}$) reported by several authors for coastal sediments of the Gulf of Trieste (Majori et al., 1976; Kosta et al., 1978; Bussani and Princi, 1979) are the consequence of long term mining activity in the Idrija district (western Slovenia).

In spite of the previous studies on the spatial distribution of Hg in the Gulf of Trieste, which showed progressive decrease of metal content in relation to the distance of the riverine source, there are some unresolved questions regarding Hg dispersion in this area. First, it should be noted that there is a lack of an extensive data set reporting Hg content in sediments of the whole Gulf area and no detailed mapping, although Donazzolo et al. (1983) and Faganeli et al. (1991) presented a simplified interpretation of the metal distribution in the area. Hence, the aim of this work was to provide comprehensive information on partitioning, distribution and transport patterns of Hg and methylmercury (MeHg) in surficial sediments in the Gulf of Trieste. The present Hg data are integrated into a general illustration with the data of those authors (Bussani and Princi, 1979; Rafvg, 1985; Faganeli et al., 1991; Ferrara and Maserti, 1992; Brambati, 1997) who used standard methods of extraction and analysis, and/or had performed intercalibration exercises. In addition, preliminary results on historical records of Hg contamination in a sediment core are reported.

2. Environmental setting and mercury contamination source

The Gulf of Trieste is a semi-enclosed marine basin located in the north-eastern Adriatic sea (Fig. 1a). Water depth is generally shallow, reaching a maximum of about 25 m only in the central part of the Gulf. The Isonzo and Timavo Rivers are the main freshwater inputs to the coastal area with an approximate average annual rate of flow of 16–20 and 80–110 $m^3\ s^{-1}$, respectively (Olivotti et al., 1986). Whereas the Timavo river suspended load is small due to its karst origin, the Isonzo river terrigenous contribution is relevant, especially during high river flow, when the average flow rate exceeds 2500 $m^3\ s^{-1}$ (Rafvg, 1986a). By contrast, a number of streams entering the Gulf from the eastern coastline (e.g. Rosandra, Rizana, Dragonja) are far less relevant.

Typical marine values of salinity (33.0–38.5 ‰ surface; 36.0–38.5 ‰ bottom) and temperature (7–24°C surface; 8–20°C bottom) are registered in the central sector of the Gulf (Olivotti et al., 1986). The water circulation system in the Gulf is influenced by the action of winds, tide (commonly in the range of 0.5–1 m) and by the main anticlockwise circulation system affecting the whole northern Adriatic. The latter acts on deep water layers flowing permanently at current speed of 2–3 cm s^{-1}, whereas anemometrical conditions play an important role in surficial (up to about 5 m thick) water mass movements: the direction of prevailing circulation is anticlockwise with eastern winds and clockwise with western winds (Malacic, 1991). The time of water renewal has been estimated to range from a few days, when the strong Bora wind blows, to a few weeks.

Carbonate sediments, originating from Mesozoic limestone outcropping in the Isonzo river drainage basin dominate the marine area near the river mouth (Stefanini, 1968, 1970–1971; Macchi, 1968). Only the southeastern sector of the Gulf is marked by a significant amount of quartz-feldspar material deriving from the Eocene flysch in the hinterland (Brambati, 1970). Coarse sediments, mainly medium to fine sands and pelitic sands prevail along beaches of the western littoral zone on both sides of the river delta. The distribution pattern of fine deposits is related to the decrease in riverine influences and it is confirmed by grain-size

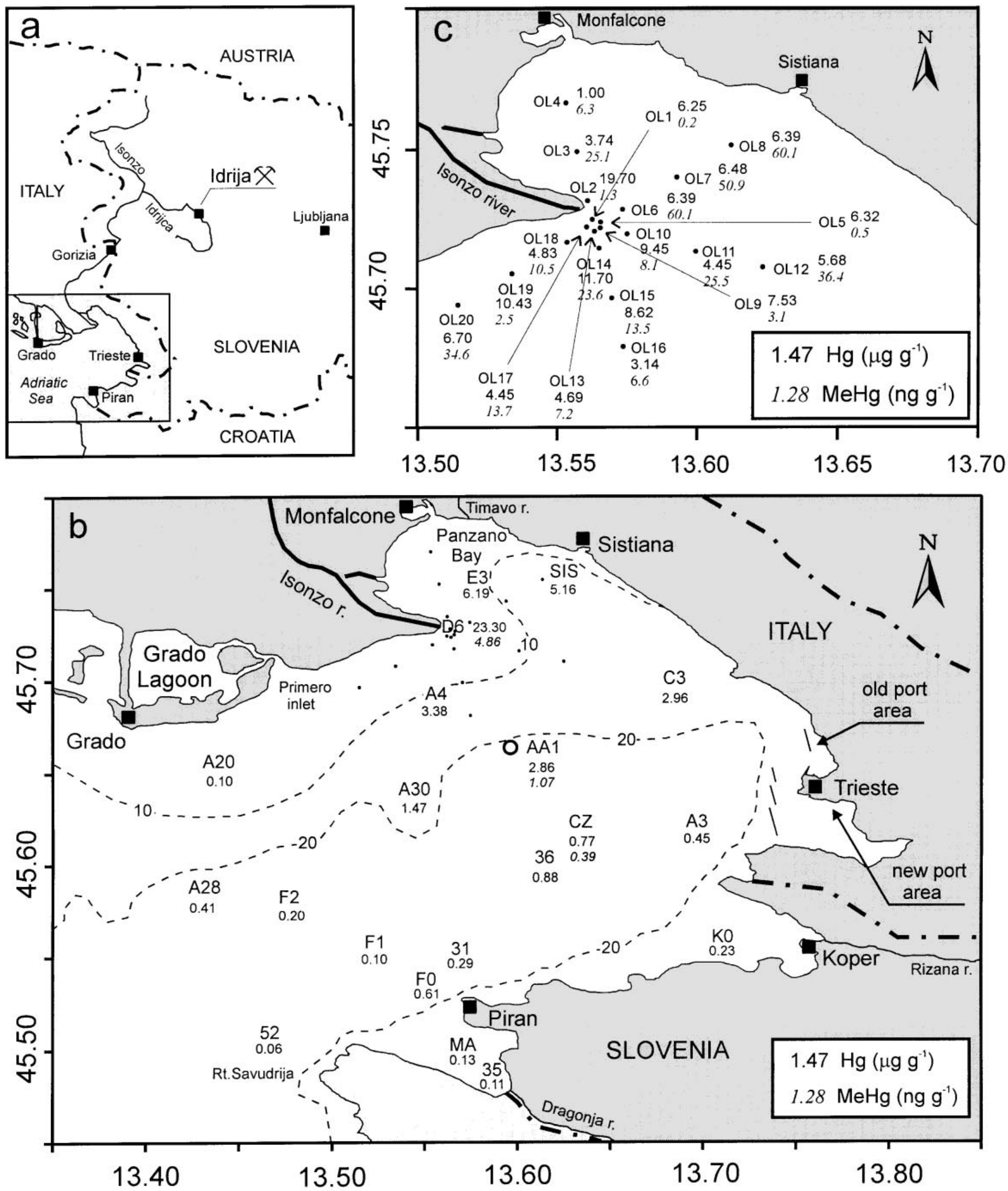

Fig. 1. Index map of (a) study area (Gulf of Trieste, northern Adriatic sea) with sampling stations where Hg and MeHg concentrations are reported (b) and (c). The AA1 core location is indicated by a circle.

decrease, from very sandy pelites not far from the river mouth, to pelites in the mid-Gulf and beyond 6–7 m depth in Panzano bay (Brambati et al., 1983). Sedimentological and mineralogical results reported by Ogorelec et al. (1991) for the south-eastern sector of the Gulf show the progressive increase seawards of mean size along with carbonate components, except for a narrow strip broadening along the coastline where sandy silt and silt are the common sedimentary facies.

The Isonzo river is known as the main source of Hg in the Gulf of Trieste, due to the presence of the Idrija mining district in the Slovenian part of the river drainage basin. Over 5×10^6 metric tons of Hg ore, mostly cinnabar, were excavated during 500 a of intense extraction activity before the main mine closure in 1975 and final closure of the mine in 1995, which was mainly caused by the gradual decline of the Hg price. The amount of Hg obtained (1.05×10^5 metric tons) after smelting has been estimated to be 73% of the total Hg mined, whereas the remaining part was dissipated into the environment. Because of emissions from the roasting plant chimney and ventilation shaft, elemental and particulate Hg have been released into the air (Gosar et al., 1996) and they have subsequently enriched soil through atmospheric fallout (Biester et al., 1998).

Mercury found in stream and recent overbank sediments of the Idrijca and Isonzo rivers is undoubtedly the direct consequence of metal remobilisation through mining and smelting activity. During the plant operation roasted cinnabar residues were dumped along the banks of the Idrijca river and were subsequently swept away by water flooding towards the Isonzo river and carried finally into the Gulf of Trieste. Results reported by Gosar et al. (1997) showed extremely high Hg concentrations (300–1000 mg kg^{-1}) close to the town of Idrija and a progressive decrease downstream, up to 100 mg kg^{-1}, at the confluence with the Isonzo river. Conversely, Hg content measured in upstream sediments, where the influence of mining activity is reduced, was only 2 mg kg^{-1}. Recent Hg measurements performed on freshwater samples by Hines et al. (2000) showed total dissolved Hg in the Idrijca river had increased more than 20-fold downstream of the mine from < 3 to > 60 ng l^{-1} with MeHg accounting for about 0.5%. These authors observed that concentrations were low after the confluence of the Idrijca and the Isonzo rivers, but they increased again at the river mouth with MeHg accounting for nearly 1.5% of the total.

3. Materials and methodology

3.1. Sampling

Surficial (0–2 cm deep layer) sediment samples ($n=39$) in the whole coastal marine area (Fig. 1b) and in the vicinity of the Isonzo river mouth (Fig. 1c) were collected in the years 1995–1996 and 1991, respectively, using a light gravity core sampler (Meischner and Rumohr, 1974). In addition, a 70 cm long core was manually collected at the sampling station AA1 (45°40′.33 N, 13°35′.67 E, depth of 21 m) in the central part of the Gulf by SCUBA divers. Total Hg ($n=39$), MeHg ($n=20$), grain-size, organic C and total N ($n=21$) were analysed in the surficial sediment samples. Total Hg, ^{210}Pb (Frignani, personal communication), Al, Fe, Mn, Zn, Ni, Cu, Cr, both organic and total C, and total N and S were analysed in 16 specimens at different depths from core AA1 after core extrusion, freeze-drying and homogenisation. Physical fractionation of the bulk sediment was performed on samples from stations D6, OL3 and AA1.

3.2. Analyses

The total Hg in freeze-dried sediment samples was determined following the procedure of CV AAS (Ure and Shand, 1974). After overnight decomposition with suprapur HNO_3 in PTFE vessels at 120°C, $SnCl_2$ and hydroxylamine sulphate were added directly to the vessels and Hg vapours were flushed by air into the measuring cell of a Varian AAS (model 1250).

MeHg was detected using aqueous phase ethylation, preconcentration on Tenax, GC separation and CV AFS measurement with 0.05 ng l^{-1} detection limit (Horvat et al., 1993; Liang et al., 1994). Quality control of analysis results for the total Hg and MeHg in samples was performed by analysing certified reference material (CRMs) obtained by the International Atomic Energy Agency (IAEA-356, Polluted Marine Sediment; Horvat et al., 1994) and by regular participation in intercomparison exercises for determination of total Hg and MeHg. The precision expressed as the relative standard deviation of at least 3 replicates varied from 3 to 5% for determination of total Hg and MeHg, respectively. Most of the samples were analysed in duplicate. Each batch of samples was accompanied by at least 3 blank samples and duplicates of appropriate CRMs.

In order to choose the best grain-size proxy to normalise Hg data, major (Al and Fe) and trace elements (Cr, Cu, Mn, Ni, Zn) were also determined in sediment samples from the AA1 core. The total decomposition method using HF + *aqua regia* before AAS analyses, as recommended by Loring and Rantala (1992), was used for the analytical determination. Total C and S contents were analysed with a CHNS elemental analyser Carlo Erba (model EA 1108) at a combustion temperature of 1020°C. The organic C and the total N in the sediments were determined in freeze-dried and homogenised samples, after acidification with 1 M HCl, using a Perkin Elmer C–H–N elemental analyser at a combustion temperature of 920 °C (Hedges and Stern, 1984).

For grain-size analysis, sediments were wet-sieved through a 53 μm sieve after 48 h of H_2O_2 treatment to remove organic matter. The fractions < 53 μm (pelites) were collected, filtered through 50 Whatman filters (R 185 mm) and dried at 40°C. The textural characteristics of pelites were determined on the basis of the suspension of sediments in distilled water, to which a 0.5 g dm^{-3} Na-hexametaphosphate antiflocculant solution was added, using a Micromeritics Sedigraph 5000 ET particle size analyzer. Porosity (Φ) was calculated by measuring the loss of weight of sediments dried overnight at 110°C to constant weight and calculating

$\Phi = (M_w/\rho_w)/(M_s/\rho_s)+(M_w/\rho_w)$. M_W is the weight of water lost on drying, M_s is the weight of dry sediment, $\rho_w = 1.025$ is the water density, whereas ρ_s is the sediment density determined on 5 specimens by a gas Multipicnometer (Quantachrome Corp.). The physical fractionation ($>$ 53 μm, 53–16 μm, 16–2 μm, $<$ 2 μm) of the bulk sediment samples which had been obtained in D6, OL3 and AA1 (Fig. 1b and c) and subsequent Hg and organic C and N analyses of each interval were performed following a procedure based on wet-sieving, centrifugation and settling time according to Stoke's law (Barbanti and Bothner, 1993). In order to avoid flocculation, particles were resuspended in distilled water with Na-hexametaphosphate as a dispersing agent. A qualitative check of the effectiveness of the separation procedure was made using Coulter Counter analysis of the two main silty fractions (53–16 μm, 16–2 μm).

Statistical evaluation of data was performed using the Surfer software program.

4. Results and discussion

4.1. Extension and dynamics of mercury contamination

Mercury content in surficial sediments from the Gulf of Trieste is very high in comparison with other coastal areas in the Mediterranean region (Table 1), not only in terms of absolute values, but also considering that the contamination source is located about 100 km upstream from the Isonzo river mouth. The range of Hg concentrations in marine sediments is 0.064–30.4 μg g^{-1} (average 5.04 μg g^{-1}, median 3.10 μg g^{-1}, geometric mean 2.12 μg g^{-1}, $n = 80$) taking into account only data available since 1979, which is approximately after the date when production at the Idrija mine was, for the most part, stopped. Results from this work, included in the comprehensive data set, show concentrations of the same magnitude, ranging between 0.10 and 23.30 μg g^{-1} (average 5.24 μg g^{-1}, median 4.45 μg g^{-1}, geometric mean 2.43 μg g^{-1}, $n = 39$).

The large number of data points available for the overall Gulf's surface area (500 km^2) allowed the authors to process them using the Surfer program which requires a great number of samples in order to obtain a reasonable interpretation. The Hg contents in the Gulf sediments fit the exponential spatial distribution function. In interpolating data the Kriging algorithm was used with an exponential variogram model. In order to establish the anisotropy of the model, 3 semi-variograms were constructed, two at right angles to a third one. Since they showed the same trend, the distribution values can be considered substantially isotropic (Davis, 1986). Mercury concentration (Fig. 2) provides information both on metal dispersion and accumulation in the study area, and on the main transport pathways from the riverine source. Fig. 2 shows that mercury contamination is extensive in the nearshore areas of the northern (Italian) sector (Panzano Bay) and, particularly, along the shoreline of two sides of the Isonzo River delta, which are greatly affected by present and ancient terrigenous supplies. The highest Hg values are

Table 1
Comparison of Hg concentrations in surficial sediments in the Gulf of Trieste and other coastal sites in the Mediterranean region

Location	μg g^{-1}	Authors	
Gulf of Trieste	0.10–23.30	This work	
Gulf of Trieste	1.51–24.00	Bussani and Princi, 1979	Italian sector
Gulf of Trieste	0.15–30.38	Rafvg, 1986b	Italian sector
Gulf of Trieste	0.055–0.880	Faganeli et al., 1991	Slovenian sector
Gulf of Trieste	1.00–19.67	Rafvg, 1992	Italian sector
Grado Lagoon	0.83–10.00[a]	Brambati, 1997	
Marano Lagoon	0.27–1.12[a]	Brambati, 1997	
Northern Adriatic sea	$<$0.10–16.88	Donazzolo et al., 1983	
Adriatic sea	0.01–35.1	Kosta et al., 1978	Surface sediments
Po outer delta	0.01–1.05	Guerzoni et al., 1984	
Kastela Bay (Croatia)	0.04–6.90	Odzak et al., 1996	Chlor-alkali plant
Northern Adriatic sea	0.05–8.63	Ferrara and Maserti, 1992	
Central Adriatic sea	0.02–0.13	Ferrara and Maserti, 1992	
Southern Adriatic sea	0.03–0.07	Ferrara and Maserti, 1992	
Tyrrhenian Sea (Tuscany)	0.10–4.06	Baldi and Bargagli, 1984	Chlor-alkali plant
Tyrrhenian Sea (Tuscany)	0.1–5.3	Baldi and Bargagli, 1982	River mouths which drain mining areas
Southern Tyrrhenian sea	$<$0.03–0.11	Giordano et al., 1992	Excluded port areas
Gulf of Athens (Greece)	0.3–10	Griggs et al., 1978	Industrial wastes
Haifa Bay (Israel)	0.035–0.656	Krom et al., 1994	Chlor-alkali plant

[a] Data from measurements performed in 1989. In the following campaign (1992) Hg concentrations for Grado and Marano Lagoons are, respectively, in the range of 2.34–10.63 and 1.62–4.26 μg g^{-1}.

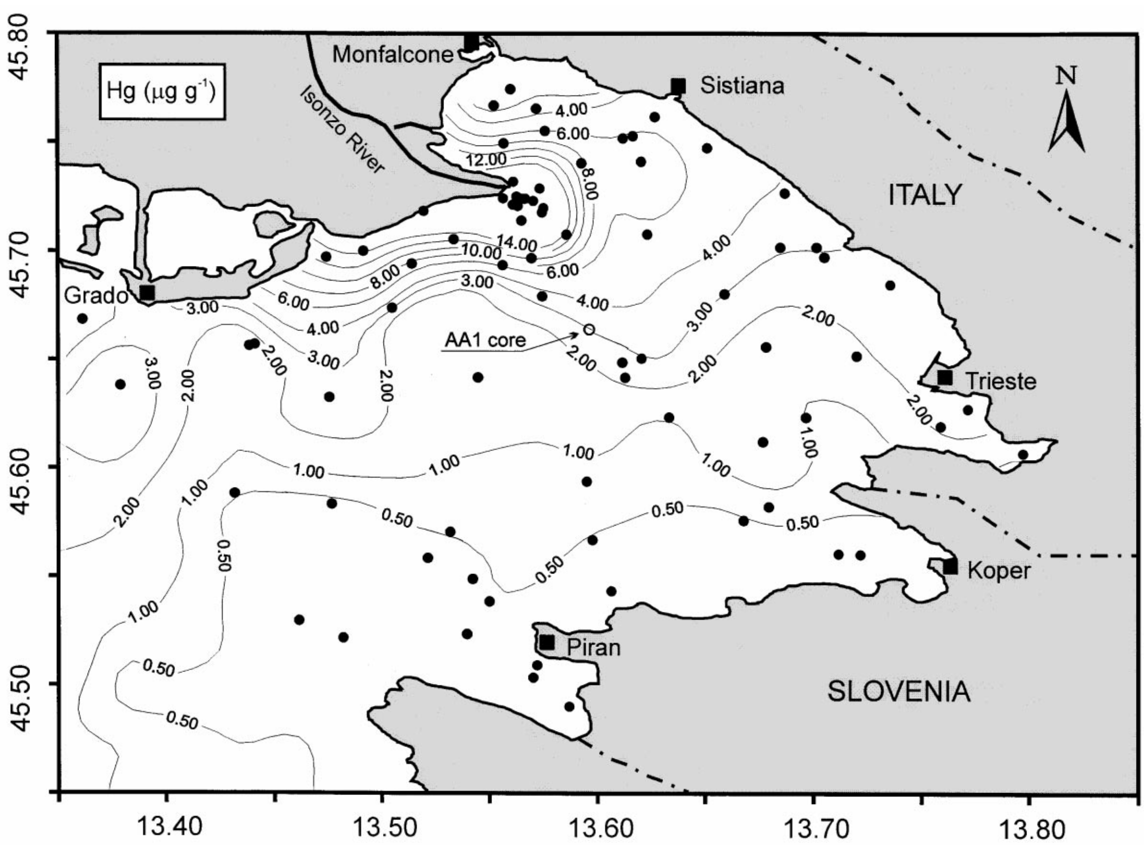

Fig. 2. Distribution of Hg in surface sediments. Contours were calculated by means of Surfer software program using Kriging algorithm. Data are from present work and from Bussani and Princi (1979), Rafvg (1985), Faganeli et al. (1991), Ferrara and Maserti (1992) and Brambati (1997).

located at the river mouth and south-westwards from the source. Due to the sharp metal decrease with distance, 14 μg g^{-1} is used as the maximum contour to avoid clutter, and to best illustrate the areal distribution. This should theoretically show a radial and almost symmetrical diffusion if the river mouth is considered as a single source point of contaminants usually bound to finer particles according to the grain-size distribution of the sea-bottom sediments in the Gulf (Brambati et al., 1983). It is evident from the map that the dynamics of Hg dispersion in the Gulf is affected by several factors and not only by the general decrease of grain-size sediments which has been observed for other heavy metals and organic carbon (Covelli and Fontolan, 1997). Transport and partial accumulation of mercury is evident along the northwestern coast (Isonzo river mouth–Grado direction) due to longshore currents and, even more effective, due to interaction between meteo-marine and riverine hydrological conditions. When a strong Bora wind blows from E-NE in association with river flood events, the fluvial plume cannot expand symmetrically and it is diverted and stretched NE-SW with sediments carried away south-westwards along the coast. Conversely, when winds from the second and third quadrants (Libeccio and Scirocco) are dominant, Hg bound to riverine suspended load is trapped in Panzano Bay, where fine particle settling is completed in a couple of days. Only a small amount of Hg reaches the south-eastern (Slovenian) sector of the Gulf, where metal concentrations in sediments average about 0.5 μg g^{-1}, which is significantly lower but still higher than the estimated natural background of the Mediterranean sediments (0.1 μg g^{-1}) reported by Baldi et al. (1983).

It is worth noting that the SW direction seems to be the most important Hg dispersion path from the Isonzo river mouth. This observation is also supported by the high metal concentrations (up to 14 μg g^{-1}) recently found in the bottom sediments of the eastern sector of the Grado Lagoon (Daris et al., 1993; Marocco, 1995; Brambati, 1997). Through the Primero inlet, riverborne Hg bound to fine suspended particles flows into the lagoon carried by tidal currents and due to wave energy action, only gradually accumulating at the bottom after several tidal cycles. When rivers or direct effluent out-falls were claimed as the single Hg contamination source, a good negative correlation between the metal content in sediment and the distance from the input was often shown (Rae and Aston, 1981; Lacerda et al., 1993; Benoit et al., 1994; Barghigiani et al., 1996). The decrease of concentrations related to the distance from the point source are described by a negative exponential relationship:

$$C = C_0 e^{-kx}$$

where C is the Hg concentration at any distance x from the river mouth, C_0 is the concentration at the source and k is the rate constant for contaminant dispersion. The Gulf is, however, affected by physical factors which control water mass circulation, thus partially interfering with the single exponential model of uniform sediment dispersion from the river mouth. Therefore, it should be assumed that the dispersion rate is not unique but depends on the considered direction. Five sets of sediment samples were chosen, corresponding to related transects radially developing from the Isonzo river mouth, and separated from each other by a 60° circular areal sector. Regression analysis, independently conducted on each data set, indicates that an exponential model describes Hg dispersion along, at least, 4 directions (Fig. 3). The southward Isonzo river mouth–Piran transect shows the best correlation ($r = 0.962$) but a good response is also provided by statistical data evaluation along the transects towards the Monfalcone port area ($r = 0.943$), Grado city ($r = 0.937$) and Sistiana Bay ($r = 0.928$). The low correlation coefficient ($r = 0.653$) obtained from data points located along the W–E direction (Trieste port area) is due to the homogeneity of Hg values after a remarkable initial decrease. Shoreline currents from Panzano Bay are responsible for suspended matter transport towards Trieste, thus, Hg occurrence is higher further east than fluvial energy can account for alone. The highest values of the rate constant k, indicative of metal dispersion degree related to the distance from source, suggest that along both directions, Grado city and the Monfalcone port area, this process is more effective. Real Hg concentrations measured at the sampling points located within about 8 km from the river mouth towards Trieste and Piran are lower than those reported by the theoretical regression line. Partial removal of sediment from the sea-bottom due to physical resuspension at shallow depths and/or from the water column, while the settling process is still active, cannot be excluded.

Trace metals are in general positively correlated to fine sediment fractions, even though the grain-size range of the "fine fraction" is not universally defined in the literature. The pelitic fraction, which includes silt and

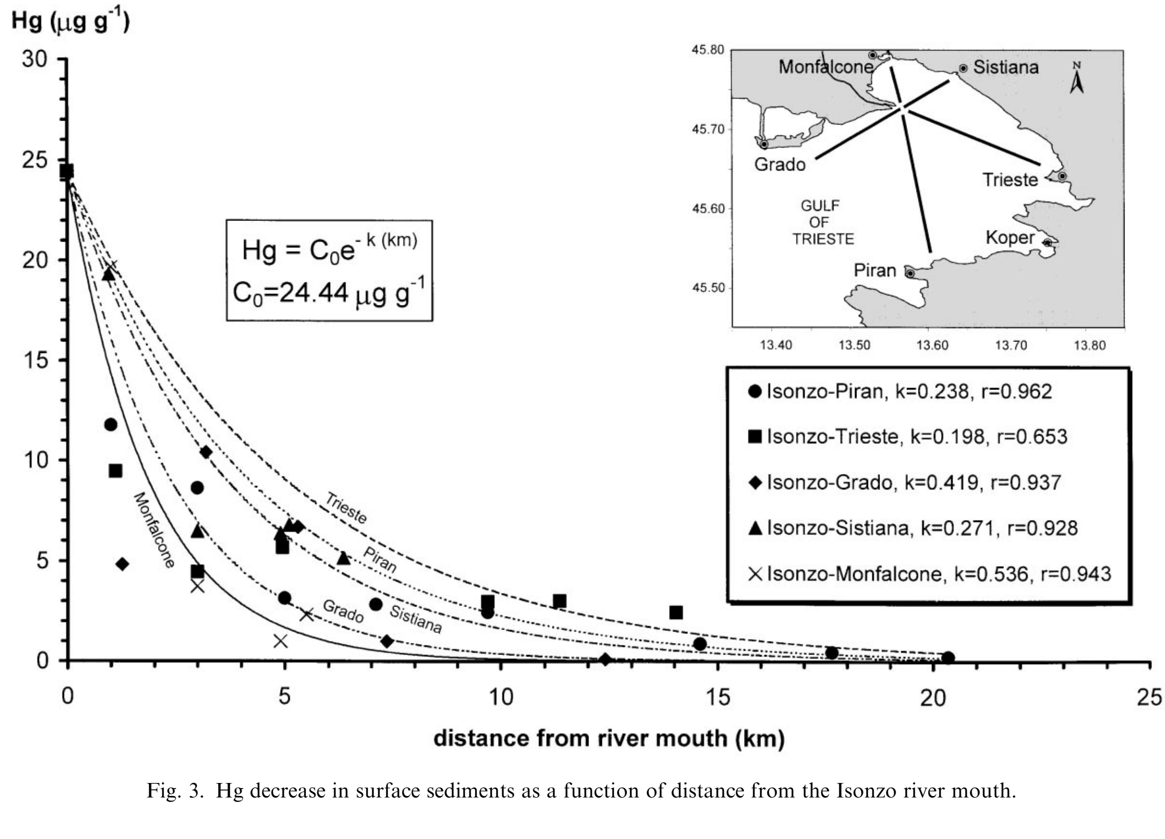

Fig. 3. Hg decrease in surface sediments as a function of distance from the Isonzo river mouth.

clay, and is formed by particles with smaller diameter than 53 μm (Loring, 1990) or 63 μm (Donazzolo et al., 1981; Rae and Aston, 1981; Lapp and Balzer, 1993), usually contains the greatest amount of trace metals and organic C in sediments. Some studies suggest the great effectiveness of < 20 μm (Ackermann et al., 1983; Barghigiani et al., 1996), < 16 μm (de Groot et al., 1976; Zwolsman et al., 1996) and < 2 μm fractions (Covelli and Fontolan, 1997; Furlan et al., 1999) in discriminating the anthropogenic from lithogenic provenance of trace metals bound to sediment particles. The clayey fraction, well known for its important adsorbing capacity due to its high surface area (Rabitti et al., 1983), normally accounts, along with organic matter, for the great majority of anthropogenic trace elements in sediments. Mercury only partially follows this general rule because its behaviour strictly depends on the chemical form of the element introduced into the aquatic environment. Mercury associated with industrial effluents was found to be positively correlated with finer grain-sizes such as < 63 μm (Rae and Aston, 1981) or < 20 μm (Barghigiani et al., 1996) and was also reported to have a good affinity with organic matter (Lindberg and Harriss, 1974; Crecelius et al., 1975; Smith and Loring, 1981; Baldi and Bargagli, 1982). Where chlor-alkali plants are responsible for Hg inputs into the aquatic environment, up to 70–90% of the total metal in sediments can be associated with easily oxidizable organic matter which is then potentially releasable as a consequence of its degradation (Crecelius et al., 1975; Smith and Loring, 1981).

In spite of the good correlation between < 2 μm particles and major and minor elements found in the sediments of the Gulf influenced by riverine inputs (Covelli and Fontolan, 1997), no information on the relationship between Hg and grain-size was available to evaluate the principal metal carriers. Hence, the relationship between Hg and percentage of < 2, < 16, < 53, 2–8, 8–16, 16–53 μm grain-size fractions was examined. The results for the surficial sediments of the Trieste Gulf presented in Fig. 4a and b show that the unique linear function describing the increase of Hg with the percentage of < 16 μm fraction cannot be considered. Two main linear trends are recognisable: the first one is related to samples collected from the whole Gulf area; the second one is representative of bottom sediments found at the Isonzo river mouth and along the surrounding beaches. The correlation coefficients in both groups are improved if the 2–16 μm range is considered. Sediments located close to the main terrigenous source are affected by higher Hg content than the offshore zone as indicated by the angular coefficient value. An explanation for this observation may be the presence of detrital Hg, i.e. cinnabar particles, settling in areas where the sandy fraction is predominant. In the central sector of the Gulf, Hg would be preferentially linked to the finest particles in the form of Hg^{2+}, Hg^{+} and Hg^{0} which are weakly bound to sediments adsorbed by the prevailing silty-clay fraction with its higher specific surface area (Baldi and Bargagli, 1982), although the presence of microcristalline cinnabar cannot be excluded.

In addition to the above set of samples, a limited number of Hg data recently obtained for the port area of Trieste (Furlan et al.,1999) were introduced in the same scatterplots (Fig. 4a and b). It is evident that sediment from the old port area is highly contaminated but, due to the rather long distance involved, any connection with the freshwater inputs of the Isonzo river can be excluded. Mercury could reach this area through urban sewage and local stream inputs flowing between docks after crossing the city center. Possible Hg losses during the enbankment operation should also be taken into account, since Trieste was the main port for exporting metal over maritime routes especially in the period before the First World War. On the other hand, sediment samples collected in the new southern industrial port area show lower Hg contents with respect to the linear function obtained for the whole Gulf. A factor limiting suspended loads from the Isonzo mouth entering the port area could be the existence of a breakwater system, extending approximately N–S, which protects this area. If data from subsurficial sedimentary samples of the core AA1 (Fig. 8) are reported in the same graph, only the 3 deepest levels fall outside the specific function, showing Hg contents close to the average background values proposed for Hg (Table. 2) in the northern Adriatic sediments. These 3 samples represent riverborne sediments which were not affected at deposition time by Hg residues related to mining activity and the cinnabar roasting process at Idrija.

Three surficial sediment samples representative of distinct areas (Panzano bay, Isonzo river mouth and mid-Gulf) were fractionated and grain-size fractions analysed for total Hg, organic C and N in order to assess the associations of this metal with single particles and organic matter. The results reported in Fig. 5a and b show that Hg is present in every fraction, but the association is important where sandy and coarse silty particles are more abundant. A basic mechanism for particle natural selection is related to the particle's density, which tends to separate heavy minerals from those fractions where light minerals are dominant. This process would trap Hg bound to these minerals increasing metal content in the areas closer to the coastline, and, in contrast, would dilute concentrations in offshore sediments (Hans Nelson et al., 1975). At the Isonzo river mouth and in the areas with higher wave energy, Hg would be present mostly as cinnabar. This phenomenon has already been observed along the Tyrrhenian coast affected by terrigenous inputs of streams draining cinnabar areas (Baldi and Bargagli, 1982). Recent measurements of Hg in the stream sediments from the

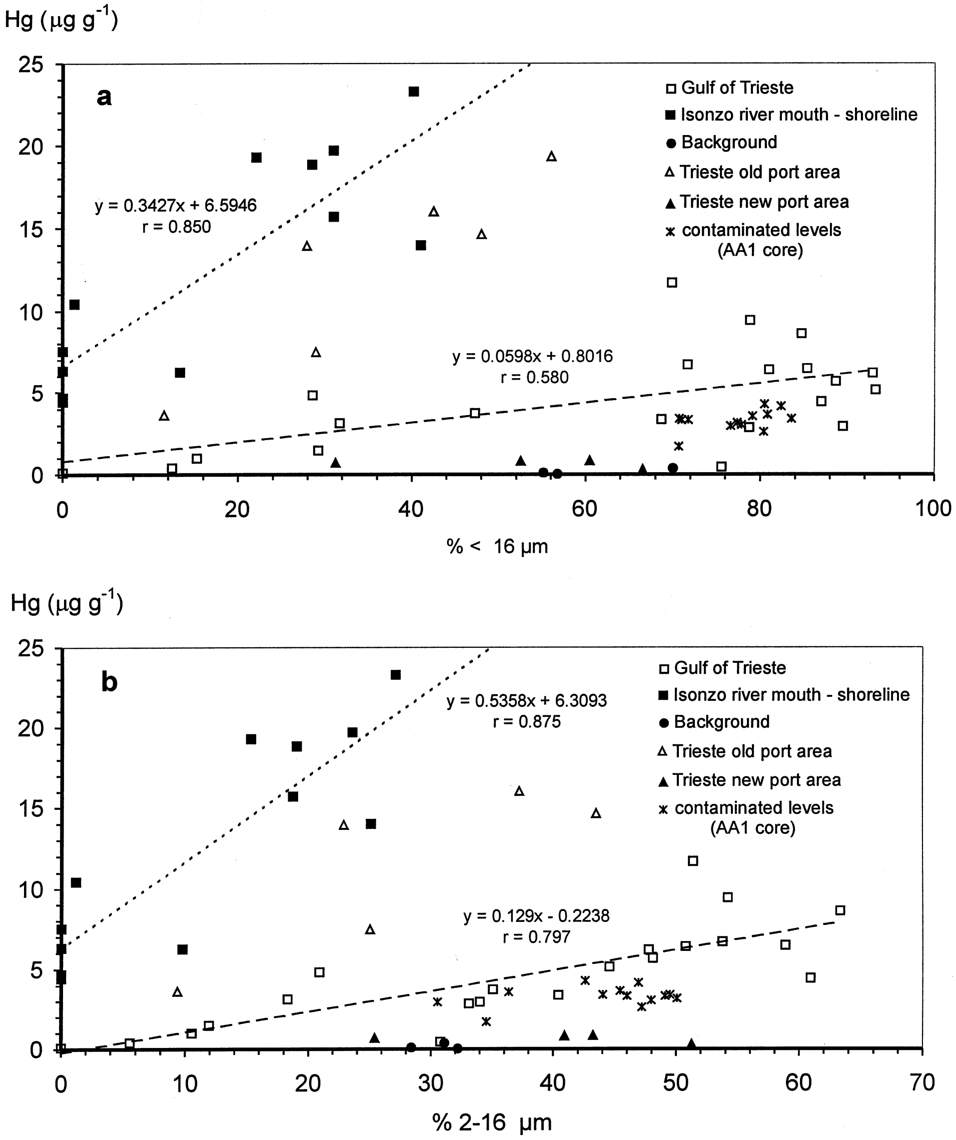

Fig. 4. The relationships between Hg concentration in surface sediments and < 16 μm (a) and 2–16 μm (b) grain-size fractions.

Table 2
Natural background values of Hg in the sediments of the Northern Adriatic sea

Location	Hg ($\mu g\ g^{-1}$)	Authors
Gulf of Trieste, core AA1	0.17	This work
Piran Bay, borehole V-6, 2.2 m deep layer	0.04	Ogorelec et al., 1981
Koper Bay, borehole MK-6, 1.3 m deep layer	0.10	Faganeli et al., 1991
Gulf of Venice	0.13	Donazzolo et al., 1981
Venice Lagoon	0.10	Pavoni et al., 1987
Northern Adriatic	0.12	Guerzoni et al., 1984

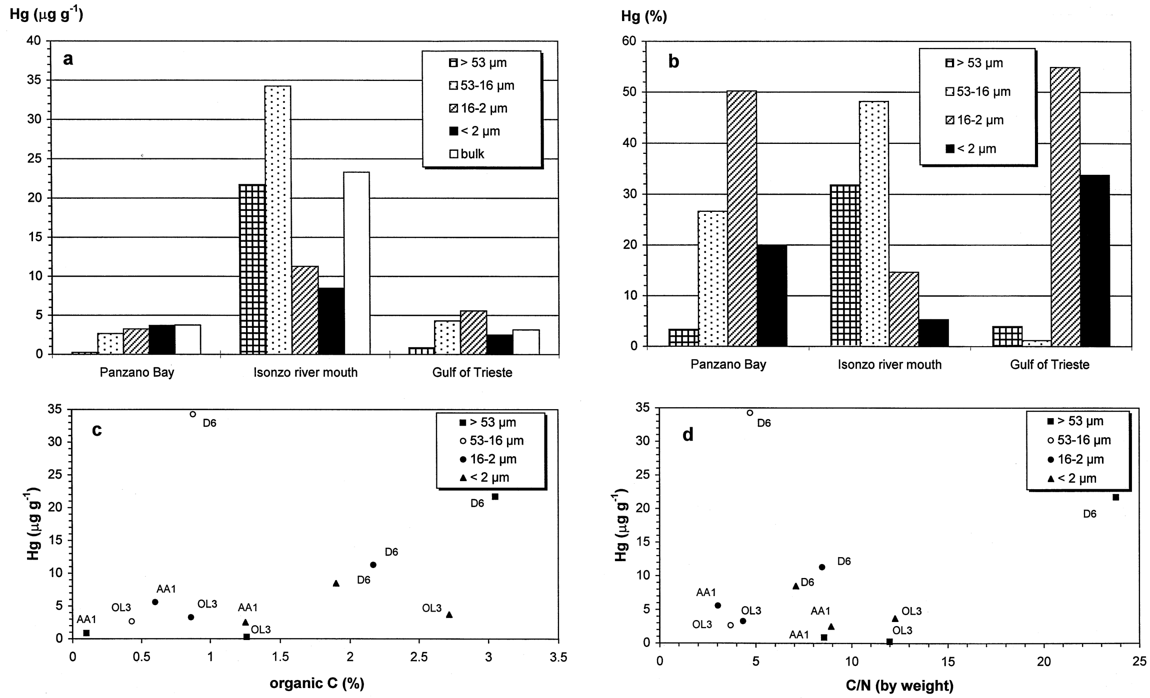

Fig. 5. Hg concentration in the > 53, 53–16, 16–2 and < 2 µm grain-size fractions of sediment; 3 distinct sampling points in the Gulf have been considered (a). Results are normalised to the percentage of the single fraction (b). Relationship between Hg and organic C (c) and C/N ratio by weight (d) in the above mentioned grain-size fractions.

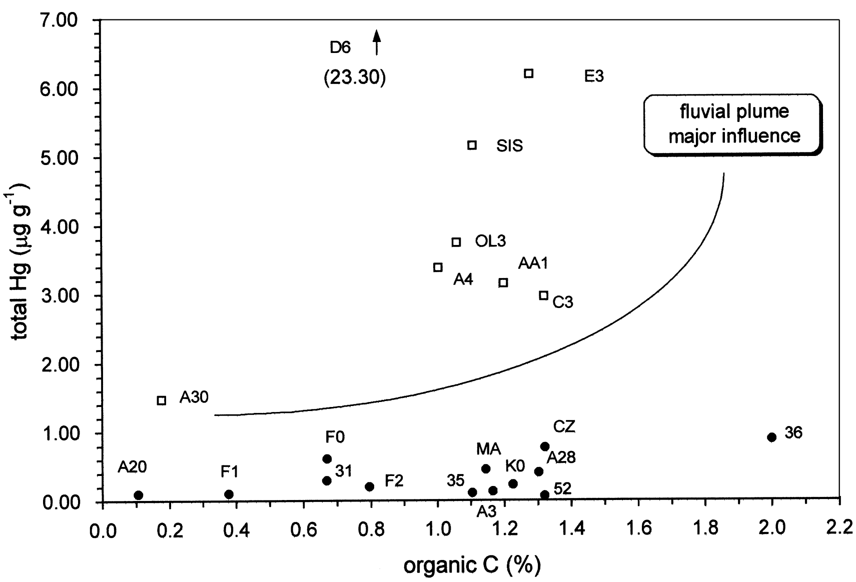

Fig. 6. The relationship between Hg concentration in surface sediments and the associated organic C content.

Idrijca river, together with analysis of the mineralogical composition, showed that in the heavy mineral fraction cinnabar grains account for about 1% (10% of the whole sample). Cinnabar coatings were also observed in some opaque minerals, thus suggesting that mercury sulphide is the most common species from the natural source (Gosar et al., 1997). However, Hg in offshore sediments could be mainly found in the form of Hg^{2+}

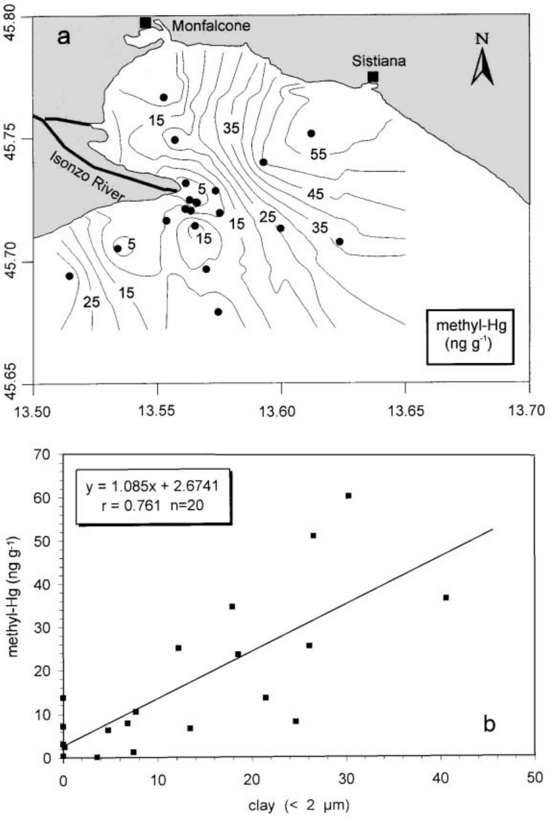

Fig. 7. Methylmercury distribution in surface sediments (a) and its relationship with clay content (b). Contours were calculated by means of the Surfer software program using Kriging algorithm.

through ion exchange, complexing or chelation with organic ligands and/or sorption onto colloids or subparticles of Fe-Mn oxides and/or incorporation into the crystal lattice of mineral grains (Ramamoorthy and Massalki, 1979). Mercury speciation recently performed on Gulf sediment samples using a solid-phase-Hg-thermo-desorption technique complemented by selective extraction (Biester et al., 2000) confirm the results.

Faganeli et al. (1991) described an areal distribution of trace metals, with the exception of Hg and Pb, similar to that observed for organic C and N, thus, suggesting that metals are, to some degree, bonded to organic matter. The higher organic C and N contents (> 1% and > 0.1% respectively) in the Gulf of Trieste, are restricted to the northernmost sector (Stefanini, 1969) and in the smaller bays of Muggia, Koper and Piran (Faganeli et al., 1991) where bottom sediments are characterised almost entirely by the silty-clayey component. On the basis of the limited number of samples ($n=21$), Hg shows a rather weak positive linear relationship with organic C (average 0.998%, geometric mean 0.846%, median 1.109%, $r=0.544$; $P<0.05$) only for those areas characterised by minor metal contents (Fig. 6). This seems to be confirmed by comparing Hg concentrations and organic C (Fig. 5c) and C/N ratio (Fig. 5d), as a proxy of the quality of sedimentary organic matter associated with single grain-size fractions from the 3 selected samples OL3, D6 and AA1. In the area more influenced by the maximum extension of the Isonzo River plume where Hg is mostly associated with coarser fractions (> 16 μm) of bottom sediments, the role of organic matter seems to be less important. In most external areas, organic matter, mostly of autochthonous origin as indicated by lower C/N ratio and associated with silt and clay, would act as a scavenger, since Hg would be partially present in chemical forms directly interacting with it.

Methyl-Hg concentration in surface sediments ranges between 0.2 and 60.1 ng g^{-1} (average 16.9 ng g^{-1}, median 9.3 ng g^{-1}, geometric mean 8.3 ng g^{-1}, $n=20$) corresponding to between 0.3 and 1.0% of total Hg, which falls within the normal values reported in the literature for coastal marine environments (Kudo et al., 1977). After processing methyl-Hg data with the Surfer program (Fig. 7a), it is worth pointing out the inverse behaviour of total Hg with respect to methyl-Hg (Fig. 2), which increases with distance from the Isonzo river mouth and the higher clay content in the bottom sediments (Fig. 7b). The limited number of data does not give a comprehensive view of the Gulf. However, this first evidence is extremely important in terms of the bioavailability of Hg species to the aquatic food chain. The coastal areas where methylation occurs and methyl-Hg accumulates in bottom sediments seem to be not necessarily those with the highest concentrations of total Hg, but rather those characterised by very fine grain-size. These kinds of sediments in front of the Isonzo river mouth are also richer in organic matter, showing a positive relationship between clay and organic C (Covelli and Fontolan, 1997). The organic matter provides the necessary energy for the recycling and transformation of Hg into methylmercury by SO_4-reducing bacterial activity (Mason et al., 1993). Dissolved methyl-Hg in pore waters can be available by diffusion at the water-sediment interface (Covelli et al., 1999) and may eventually become concentrated in aquatic organisms.

4.2. Historical record of environmental contamination

The Hg concentration profile in sediment core AA1 (Fig. 8) is the first information of Hg depositional history in the Gulf of Trieste from the beginning of the intensive extraction activity in the Idrija region to its apparent more recent decline. The vertical variability of Hg contents (0.03–4.30 μg g^{-1}) in core AA1 (Fig. 8) shows a characteristic trend which is undoubtedly related to a progressive increase of metal input into the Gulf as a consequence of mining activity. Textural variability

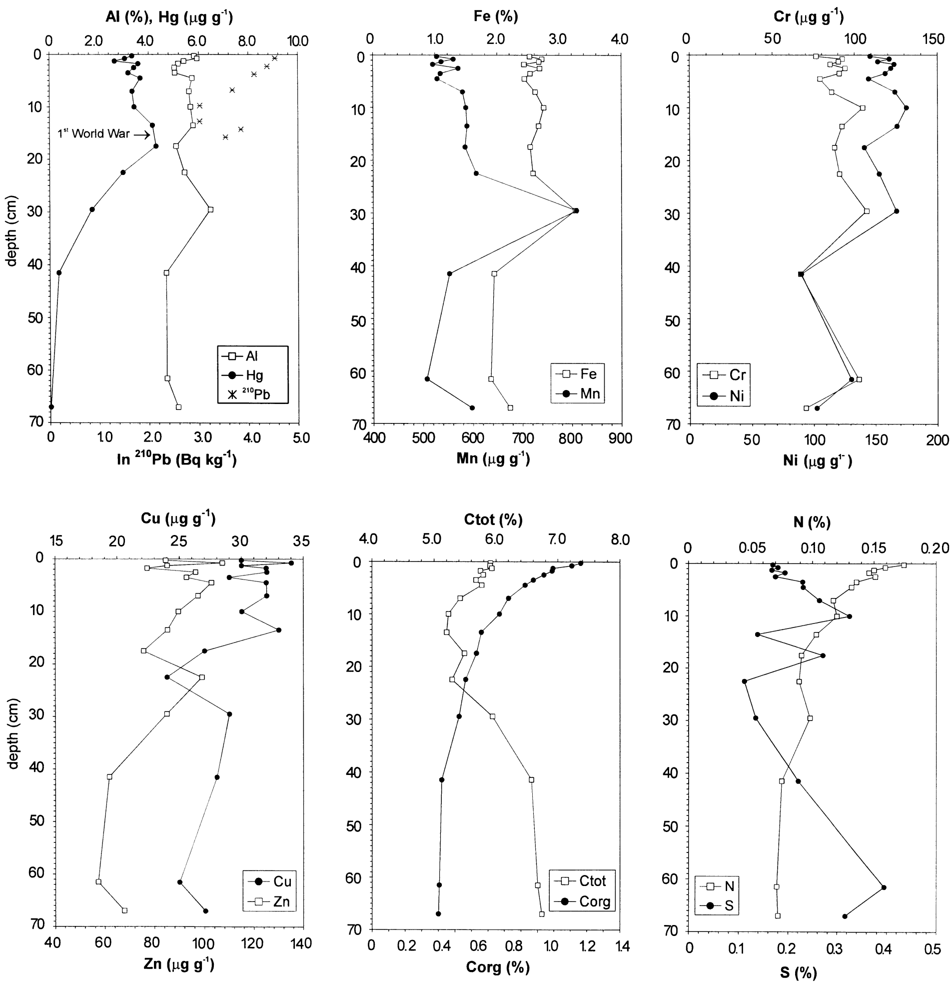

Fig. 8. Vertical distribution of Hg, ^{210}Pb, Al, Fe, Mn, Ni, Zn, Cu, Cr, total and org.C, and total N and S in the AA1 sediment core.

(Fig. 9) does not affect Hg relative abundance in the core AA1. Mercury concentration in the core increases with increasing sediment depth to a maximum at 16–19 cm before decreasing exponentially to uniform low levels, which are close to the background values reported for the northern Adriatic sediments (Table 2), at a depth of about 40 cm. A recent overbank sediment profile from the Idrijca River (about 40 km downstream from the Idrija mine) shows a similar trend of Hg content from the surface to a depth of about 2 m (Gosar et al., 1997), although the profile was not deep enough to reach sediments accumulated before the beginning of mining. Mercury concentrations (120–240 mg kg^{-1}) are two orders of magnitude higher than those in the mid-Gulf sediment but the similar response of fluvial and marine sediments in recording the history of Hg environmental contamination is clearly evident.

Due to the well known affinity of trace elements for fine-grained sediments, a normalisation procedure against grain-size or a grain-size proxy is usually applied before comparing geochemical data with natural backgrounds (Loring, 1990). In order to quantify the degree of enrichment of an element, its ratio to the normalising element is divided by the same ratio found in the selected baseline obtaining a non-dimensional enrichment factor (E.F.):

$$\text{E.F.} = (\text{M/N})\text{sample}/(\text{M/N})\text{baseline}$$

where M is the potentially enriched element and N is the concentration of the normalising element. The E.F. is highly affected by the baseline choice, which should have geochemical characteristics very similar to those of the investigated samples. The best solution is to calculate

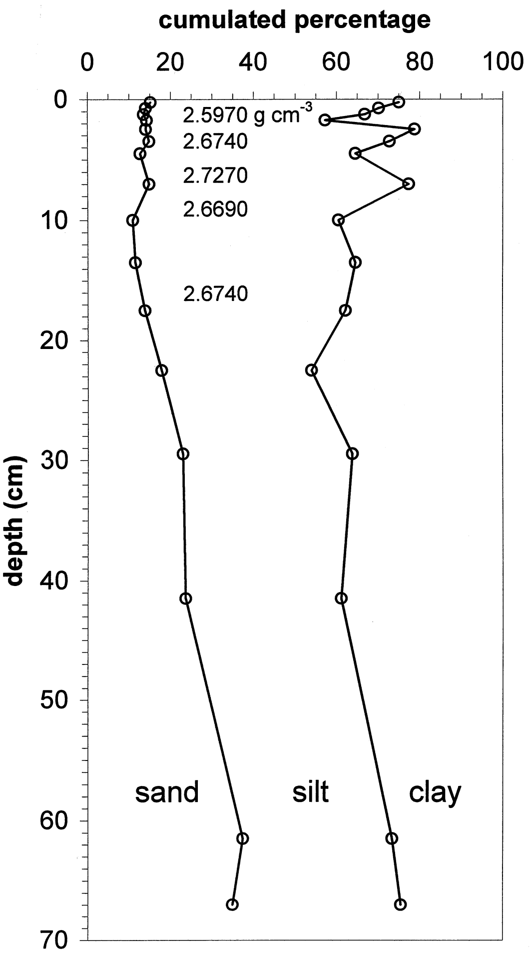

Fig. 9. Textural variability in the AA1 sediment core. Density values (g cm^{-3}) are reported.

enrichment on the basis of a theoretical value obtained from mathematical linear functions between the metal and the normalising element on a local scale (Skowronek et al., 1994; Covelli and Fontolan, 1996). On the basis of the previously described relationship between Hg and grain-size in the Gulf of Trieste, calculation of a background regional function for the metal is not an applicable procedure due to Hg mining residues affecting the whole area. However, the very good relationship between Al and the fine sediment fraction for this marine area (vs silt $r=0.674$; $n=79$; $P<0.001$; vs clay $r=0.944$; $n=79$; $P<0.001$) suggests the use of Al as the normalising element (Covelli and Fontolan, 1997).

Previous studies on the sedimentary geochemistry of the Gulf show Hg average background values around 0.04 ppm (Ogorelec et al., 1981) and 0.10 ppm (Faganeli et al., 1991), respectively. This latter value refers to a 1.3 m deep subsurface layer ^{210}Pb dated to 1760 AD from borehole MK-6 drilled to a depth of about 40 m in Koper Bay. Both values are probably slightly underestimated for a geologically Hg-enriched basin since they were obtained from the southern area of the Gulf, which is not affected by a high amount of sedimentary load from the Isonzo River. A representative background estimation would require more than a single core, hence, the proposed natural background level should be viewed as a preliminary evaluation. Considering the location of core AA1 it would be more reasonable to assume the average Hg concentration below 40 cm depth of 0.17 μg g^{-1} as a natural background. Due to Hg mining residues, recent sediments at AA1 are about 16 times more enriched in Hg than the calculated baseline value (Fig. 10a), but the difference is even more evident in the subsurficial layers (16–19 cm). Contamination processes would have affected the upper 50 cm of sediment with an alteration of the natural or geogenic Hg content of up to 24 times over the background in the more recent past.

A clear distinction between Hg and other heavy metals can be recognised in these sediments (Figs 10b and c). Enrichment values for other heavy metals have a lower magnitude and fall in a very narrow range (0.8–1.5). Zinc E.F. increases progressively from 40 cm depth to the core top showing two peaks at 22.5 cm (E.F. = 1.4) and at 2.5 cm (E.F. = 1.5). Similarly, Ni E.F. increases in the upper 30 cm with a maximum E.F. of 1.4 at 2.5 cm. Copper and Cr are less variable whereas Mn appears slightly depleted in the 15 cm below the water–sediment interface. In coastal environments, where redox conditions in surficial sediments are the consequence of bottom O_2 concentration variations, Mn is released from pore waters in reducing conditions and it remains associated with the solid phase in oxidising conditions (Lapp and Balzer, 1993; Skowronek et al., 1994). Because the AA1 core was collected at the end of a hypoxic period regularly occurring in late summer, it is possible that Mn decrease is due to a more reducing environment (Hines et al., 1997). Iron, although as dependent on redox conditions as Mn (Sundby et al., 1986), seems to behave more conservatively, according to the positive relationship with Al ($r=0.831$; $n=16$), and remains bound in the crystalline structure of minerals, mainly in goethite (Arcon et al., 1999), present in the natural sedimentary matrix. Considering that Ni and Zn enrichments occur in the upper 30–40 cm, it cannot be excluded that a source similar to Hg exists for these heavy metals, since Zn especially is common in mineralogical association with Pb and Hg as sulphides (Loring, 1991).

The mining activity at Idrija reached its maximum between the end of the 18th century and the second half of the 20th century. The greatest annual amount of Hg produced occurred in 1913 (820 tons), following the exponential increase of cinnabar ore extraction (Mlakar 1974). Previously, at the end of the 18th century, the Hg

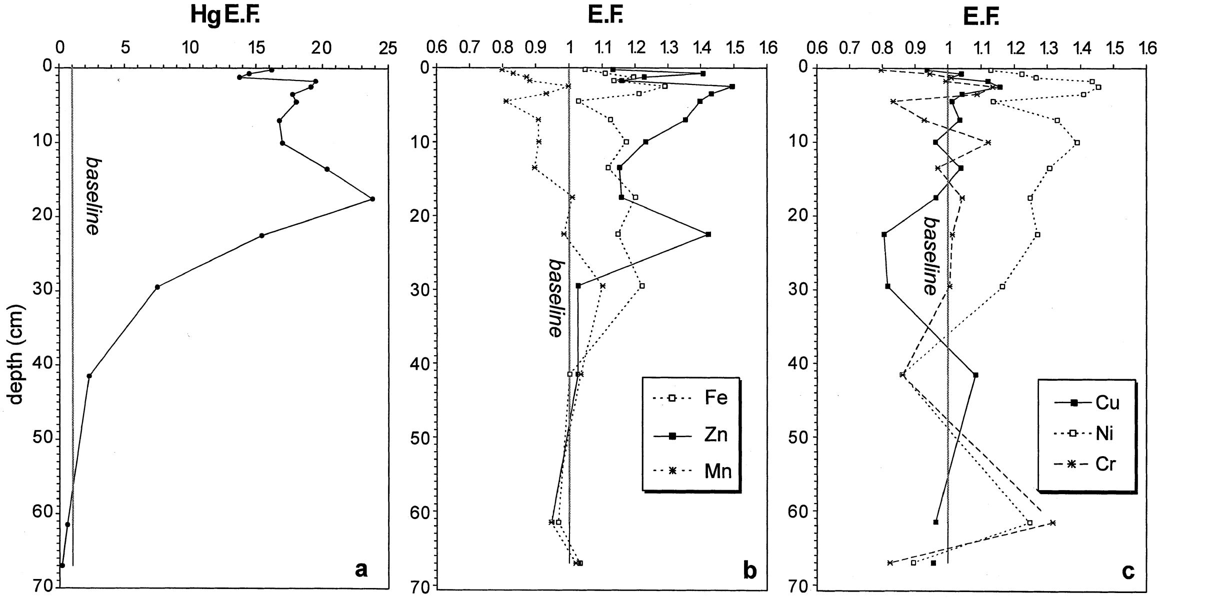

Fig. 10. Vertical enrichment profiles (E.F.) of Hg content (a) and related heavy metals (b) and (c) in recent sediment at sampling station AA1. E.F. = (M/N)sample/(M/N)baseline, where M is the potentially enriched element and N is the concentration of Al as normalising element to compensate for the grain-size variability.

production increased up to 600 tons due to the discovery of an extremely rich vein of cinnabar. About 6×10^6 tons of cinnabar ore were mined in the period 1786–1945 and 1.8×10^6 tons from the end of the 2nd World War until 1960. Mercury production reached 6700 tons in the same period and 7000 t were obtained from 1960 to 1973 when production began to decrease due to the main mine closure (in 1975). The temporal representation of cinnabar ore extraction and Hg production at Idrija (Fig. 11) exhibits a very good correlation with the Hg E.F. profile in core AA1. This evidence allowed the authors to attempt a preliminary assessment of annual average sedimentation rate in the mid-Gulf for the last 80–100 a using Hg as an additional geochemical tracer in addition to the ^{210}Pb dating method. Since Hg production as well as cinnabar ore extraction reached their maximum in 1913, it is reasonable to consider that the contamination process due to metal dissipation into the environment followed a parallel development. If it is assumed that the Hg concentration peak at the depth of 16–19 cm (Fig. 8) corresponds to sediment deposition in 1913–1914, then the estimated average sedimentation rate in the mid-Gulf during the last 80 a would amount to 2.16±0.18 mm a^{-1}. The result is slightly higher than 1.84 mm a^{-1}, obtained by ^{210}Pb determination (Frignani, personal communication), and it is lower than the 2.5 mm a^{-1} suggested by Ogorelec et al. (1991) for the coastal area in front of the Isonzo river mouth.

On the basis of data on cinnabar ore extraction and Hg production at Idrija, the sedimentary level at 16–19 cm depth was considered as a reference point along with the associated date of deposition. Depositional metal flux in sediment (mg m^{-2} a^{-1}) is due to Hg concentration (μg g^{-1}) in sediment $(\mathrm{Hg})_s$ and the accumulation rate of particles (ω):

$$F_{Hg} = \omega(\mathrm{Hg})_s$$

$$\text{with}\ \omega = (1-\phi)v\rho$$

where ϕ is porosity, v is sedimentation rate (mm a^{-1}) and ρ is sediment density (g cm^{-3}). The temporal variability of Hg excess due to mining activity, can be assessed from the difference between total and natural, i.e. pre-extraction activity, mercury fluxes (Fig. 12):

$$F_{Hg}\ \text{total} - F_{Hg}\ \text{mining residues} = F_{Hg}\ \text{natural}$$
(or pre-extraction activity).

Applying the average sedimentation rate, calculated on the basis of Hg as a geochemical marker of mining activity history, to the deepest levels of AA1 core, and if accumulation flux is determined taking into account the vertical variability of porosity and density, a profile with estimated age is obtained (Fig. 12). According to the

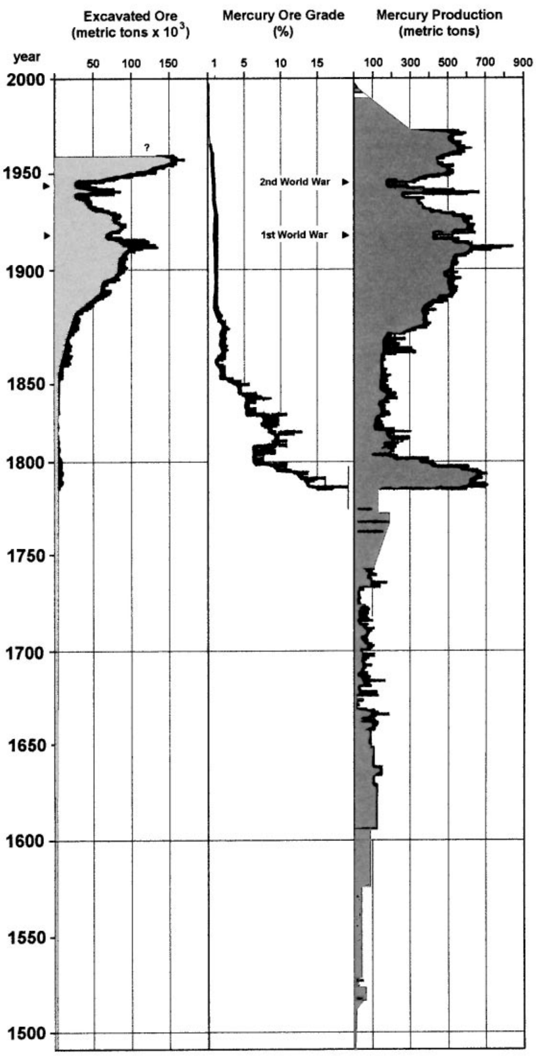

Fig. 11. Cinnabar ore extracted and Hg production at Idrija during 500 a of mining activity (redrawn and modified from Mlakar, 1974).

results, the flux of Hg in the Gulf of Trieste induced by exploitation of cinnabar ore would have started at the end of the 18th century when Hg production increased dramatically, whereas the most surficial peak would correspond to the last important extraction period which occurred around 1970. The present Hg flux to sediments in the central sector of the Gulf is about 2.96 mg m^{-2} a^{-1} which is 4 times the net accumulation rate (0.75 mg m^{-2} a^{-1}) assessed by Coquery et al. (1996) for the Po delta, the most important riverine source in the Adriatic Sea. This result confirms the Isonzo River as the main Hg source in the whole basin if the sedimentation rate in the outer Po delta is considered about 4 times higher than at sampling station AA1.

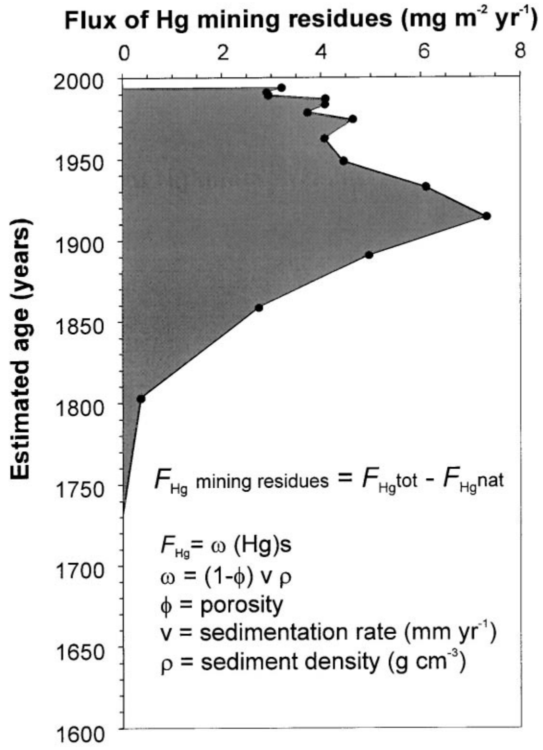

Fig. 12. Tentative estimation of Hg flux from mining activity vs. estimated date of deposition for the central sector of the Gulf (AA1 core).

5. Conclusions

1. Total Hg concentrations in sediments of the Gulf of Trieste do not show an areal distribution strictly correlated to grain-size decrease as previously reported for other heavy metals. Zones of high Hg content are restricted mainly to sandy sediments of shallow waters in the vicinity of the Isonzo River mouth, and secondly to more pelitic textural types at great depths in the northern part of the basin.

2. Dispersion of Hg associated with sediment particles over distance from the river mouth can be sufficiently described by a simple exponential model only if different directions are considered. This observation suggests its dependence on local hydrological and meteo-marine conditions.

3. Methyl-Hg distribution in the Gulf sediments, found in normal percentages for coastal marine environments, shows an increase with distance from the Isonzo river mouth and higher clay content in the bottom sediments. This suggests that coastal areas where methylation potentially occurs in bottom sediments seem not to be necessarily those with the highest concentrations of total Hg in the littoral zone.

4. The relationship between total Hg and the < 16 μm fraction distinguishes two main groups of samples suggesting that at least two types of Hg species are present in coastal sediments. Along the littoral zone of the northern (Italian) sector, this metal is mostly present in detrital form (cinnabar) in sandy-silty sediments near the river mouth. In the more distant areas, Hg as Hg^{2+} is probably bonded to finer particles, adsorbed onto clay minerals and/or partially associated with organic matter.

5. The vertical profile of Hg in core AA1 shows an enrichment trend which is undoubtedly related to the historical mining activity at Idrija. The preliminary estimation of the natural background concentration of Hg in sediments of the Gulf of Trieste (0.17 μg g^{-1}) seems to be more appropriate than the values reported in previous works. However, the interpretation needs to be extended to more cores to be better validated.

6. Hg has been used as an additional geomarker to estimate an average sedimentation rate of 2.16 mm a^{-1} in the mid-Gulf. The flux of Hg mining residues in sea-bottom sediments has decreased in the last 80 a (especially after the main mine closure in 1975) and after the mining operation completely stopped in 1995. However, at present there is no reason to believe that this marine environment can be naturally decontaminated in the near future, since the Isonzo freshwater inputs still have a very high Hg content.

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