



## Impact of human activities on the central Mediterranean offshore: Evidence from Hg distribution in box-core sediments from the Ionian Sea

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### ABSTRACT

Total Hg concentrations have been measured for five box-core sediments collected seawards of the Augusta industrial area (SE Sicily). In more coastal sediments, upcore increasing Hg concentrations, exceeding the Hg background concentration estimated for the Strait of Sicily, indicate Hg contamination over time due to the industrial area development. Strong correlation between total organic C (TOC) and Hg concentrations was found only for core BX2, that displays organic C to total N (C/N) ratios indicative of autochthonous organic matter. For other sediments, high Hg enrichment factors with respect to TOC indicate, in addition to Hg trapping by TOC, other factors as responsible for Hg accumulation. In the presence of some contribution of detrital organic matter, Hg is mainly adsorbed onto the mineral component of the bottom sediments probably because TOC is saturated by Hg excess. Contaminant impact affected also the open sea environment. Main drivers of Hg flux towards the offshore were dredged materials, which repeatedly discharged sediment, resulting in substantial increases in TOC contents and high C/N ratios. Consistent with the geochemistry of recent turbidites, these anomalous sedimentary inputs induced sediment redox environment modifications, constrained by Mn peaks, which affected Hg distribution.

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### 1. Introduction

Marine sediments are a fundamental component of biogeochemical cycles of many organic and inorganic compounds. They tend to act as sinks, frequently containing contaminant concentrations that exceed those in seawater by many orders of magnitude. The distribution and accumulation of trace metals in sediment are controlled by complex physical–geochemical mechanisms depending on sediment texture, mineralogical composition, and reduction/oxidation state (Windom et al., 1989; Murray, 1996; Birch and Taylor, 1999; Lin et al., 2002). A major role is played by processes of adsorption/desorption into/from fine-grained particles and Fe/Mn oxy-hydroxides, by

adsorption/complexation on/with organic matter and by formation of S complexes (Horovitz, 1991; Sanei et al., 2001; El Bilali et al., 2002; Fitzgerald and Lamborg, 2005). Sediments accumulated near point sources such as industrial and urban areas are potentially enriched in contaminants, which can be subsequently released into surrounding aquatic ecosystems through various natural (e.g. biological and physico-chemical) processes and anthropogenic activities (e.g. dredging and fishing) (Covelli et al., 2001; Cundy et al., 2003).

Recently, attention has been paid to controlling environmental Hg contamination because elevated concentrations of this metal have a lethal–sub-lethal potential for the biota (Wagemann et al., 2000; Goodsite et al., 2004; Mirlean et al., 2005). Mercury is not an essential element and, because of its ability to bio-accumulate in the adipose tissues of living organisms, it is a potential problem for

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human health. In fact, Hg is not easily eliminated by humans and animals (Eisler, 1987), has adverse effects on the central nervous system (Fitzgerald and Clarkson, 1991), and causes teratogenic damage during the early stage of development (Clarkson, 1990; USEPA, 1997).

Since the beginning of the industrial age, increasing amounts of Hg have been mobilized and released into the environment (Mason et al., 1994). Industrial production of NaOH and plastic, illegal dumping of industrial rubbish, waste incineration, fossil fuel burning, and metal smelting are the major sources of Hg contamination. Polluted rivers and discharges from industrial facilities can carry Hg along the coasts. Particularly, installation of industrial chlor-alkali plants has been recognized to be responsible for persistent contamination of various ecosystems worldwide (Hissler and Probst, 2006a). This is a broad phenomenon in Europe, where discharges from chlor-alkali plants constitute 14% of the total anthropogenic Hg emissions (Biester et al., 2002).

There is a considerable body of literature documenting distribution of Hg in fluvial, lagoonal, and coastal sediments close to point sources of Hg contamination (Bothner et al., 1998; Marvin et al., 2004; Meador et al., 2005; Berto et al., 2006; Gray et al., 2006; Canário et al., 2007). In contrast, relatively few studies have focused attention on offshore ecosystems even if the open sea quality can be heavily influenced by coastal anthropogenic activities, especially in a semi-enclosed basin such as the Mediterranean Sea. In this work, spatial distribution and historical changes in offshore sediments from the Augusta area (SE Sicily) have been investigated. New total Hg data for three sediment box-cores from the Augusta area (SE Sicily), collected in a water depth of 1220–2416 m, are reported in this study and compared to previous coastal sediment data (Di Leonardo et al., 2007) to provide a baseline for assessing the perturbations of the coastal ecosystem due to local and industrial activities and to highlight the influence of coastal processes on the open sea environment of the central Mediterranean. Furthermore, the scavenging role of organic matter is investigated due to its great potential to control Hg and other contaminant metal distribution in aquatic sediments (Sanei and Goodarzi, 2006; Outridge et al., 2007).

## 2. Study area

The Augusta area shows a high state of environmental degradation due to heavy industrialization, mainly represented by a number of chlor-alkali plants that use metallic Hg for electrolytical production of  $\text{Cl}_2$ . In this region, considerable amounts of Hg have been released since the middle of the 20th century to the atmosphere and marine environments, causing persistent pollution of the Augusta ecosystem. Based on recent reports published by ICRAM (2005), surface sediments of the Augusta Bay contain Hg concentrations in excess of 90% of the standard limit ( $5 \text{ mg kg}^{-1}$ ) reported by the national regulatory guidelines (G.U.R.I., D.M. 471/1999). Moreover, previous investigations carried out in the area have highlighted a significant impact on benthic foraminiferal communities (Di Leonardo et al., 2007), as well as a marked destruction of mollusc and polychaete communities (Di Geronimo et al., 1984; Giacobbe et al., 1989). Eutrophication processes are enhanced by

significant quantities of N and P derived from industrial (fertilizer production) and agricultural activities resulting in discharges into the Augusta Bay (Azzaro, 1993; De Domenico et al., 1994). Finally, the Augusta area has been recognized as a site of high environmental risk by the World Health Organization (Martuzzi et al., 2002) and Italian Government (G.U.R.I., L. 426/1998).

## 3. Methodology

### 3.1. Sampling

Five box-cores were collected, using a United States Geological Survey (USGS)-modified Naval Electronics Laboratory (NEL) box-corer sampler, in the Sicilian coastal zone seawards of the industrial area of Augusta (Fig. 1). Sampling was carried out during two oceanographic cruises on board the oceanographic R/V "URANIA", in the summers of 2003 and 2004, along a west–east transect. Sediment was immediately sub-sampled on board using an acrylic tube, sealed in polyethylene flasks, and stored at  $-20^\circ\text{C}$  until analysis.

The coastal area of southeastern Sicily is characterized by the presence of the Hyblean Plateau. This structure, located on the northern margin of the African Plate, 50 km south of Monte Etna, is bound to the NW by the Gela Nappe thrust belt, representing the collision boundary between the African and European plateaus, and to the east by the Malta Escarpment, a zone of large vertical fault movements (Boccaletti et al., 1989; Ben-Avraham and Grasso, 1990). The Malta Escarpment extends over a length of about 300 km from the eastern coast of Sicily southwards, with a steep slope that drops to more than 3000 m below sea level.

### 3.2. Geochemical analyses

On return to the laboratory, the cores were sliced at 1 cm intervals with a stainless steel bandsaw, oven dried at  $40^\circ\text{C}$ , and powdered manually in an agate mortar prior to geochemical and radiometric analyses.

Bulk mineralogy was determined by powder X-ray diffraction (XRD, Philips PW14 1373) using  $\text{Cu K}\alpha$  radiation filtered by a monochromator crystal and a scanning speed of  $2^\circ/2\theta/\text{min}$ . The relative proportions of minerals were established according to methods and data of Schultz (1964).

The concentrations of major elements were determined by X-ray fluorescence spectrometry (XRF, Philips PW1400 apparatus) on bulk-sample pressed, boric acid-backed pellets. Data reduction was achieved by the method described by Franzini et al. (1975). The accuracy of determinations was checked with certified reference materials (BCR-1, G2, AGV-1; United States Geological Survey). Analytical errors were below 1% for Si, Al, Na, 3% for Ti, K, Fe, Ca, and 10% for Mg and P.

Total Organic C (TOC) and N analyses were performed with a Perkin-Elmer CHN Elemental Analyser (Mod. 2400), using acetanilide as a standard, at a combustion temperature of  $980^\circ\text{C}$ , after removal of carbonates with HCl vapour (Hedges and Stern, 1984).

Concentrations of Hg were determined via atomic absorption spectroscopy after thermal combustion of the freeze-dried sample and Hg pre-concentration on a single

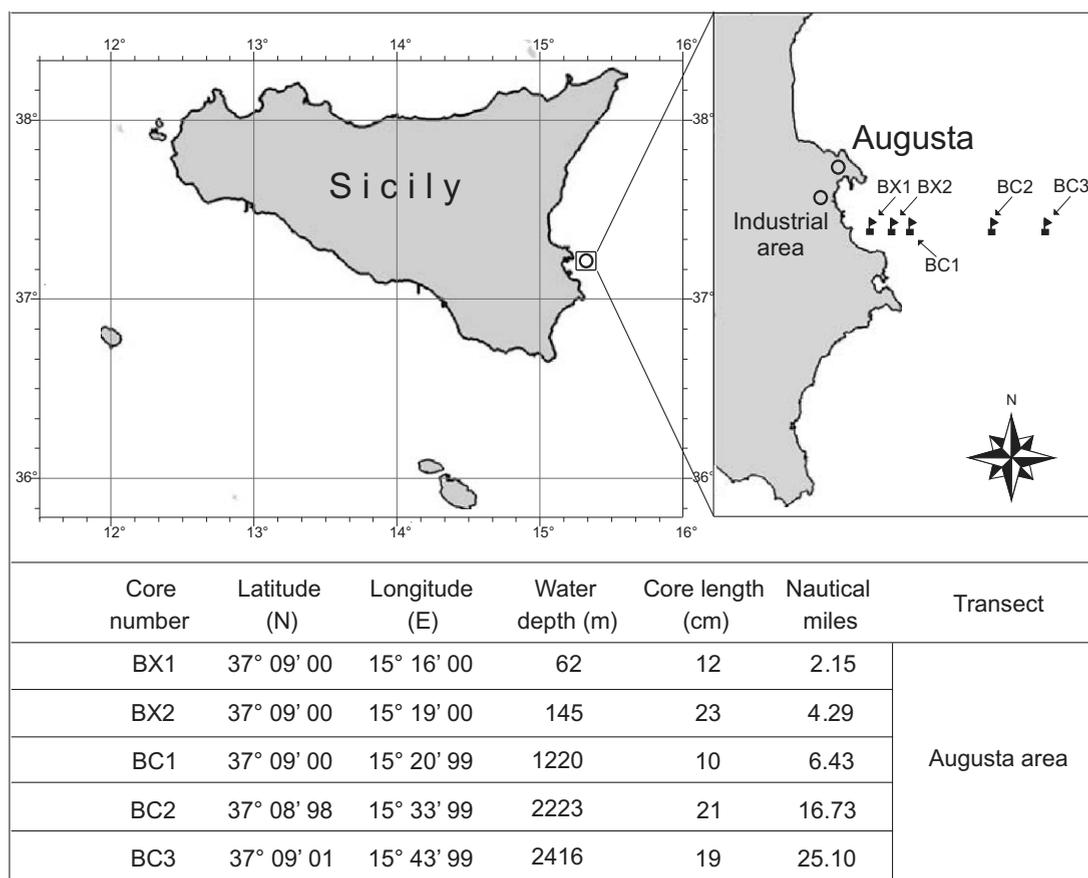


Fig. 1. Location of sampling stations in the Augusta area together with core length, water depth and geographic parameters at each station.

Au trap with an AMA 254 Solid/liquid Hg Analyser (FKV). Parameters of the Hg analysis were 70 s for drying and 140 s for decomposition. The main advantage of this procedure is that no acid digestion of the sample is necessary (Franzen et al., 2004). During analysis, reference material and blanks were analysed every six samples. Precision and accuracy were tested using a marine sediment reference certified material (MESS-3; National Research Council of Canada). The mean Hg concentration measured was  $0.084 \text{ mg kg}^{-1}$ . The average concentrations obtained ( $n = 13$ ) had a precision of 3% for total Hg and with an accuracy of 7% of the certified value.

Manganese analyses were performed by inductively coupled plasma-mass spectrometry (Perkin-Elmer model ELAN-DRC-e) after digesting 0.5 g of sediment sample with 10 mL of *Aqua Regia* in bombs using a microwave oven (CEM MSD, 2000). This method is widely used in environmental geochemistry studies because it does not completely destroy silicates (Salvagio Manta et al., 2002). All determinations were performed with the external standard calibration method, using In and Re as internal standards. During digestion and analysis, reference material and blanks were analysed every six samples. Precision and accuracy of analytical procedures have been checked by analysing replicate aliquots of SRM MESS-3 (National Research Council of Canada). The mean Mn concentration

measured was  $289 \text{ mg kg}^{-1}$ . The average concentrations obtained ( $n = 13$ ) had a precision of 4% for pseudo-total Mn and with an accuracy of 10% of the certified value.

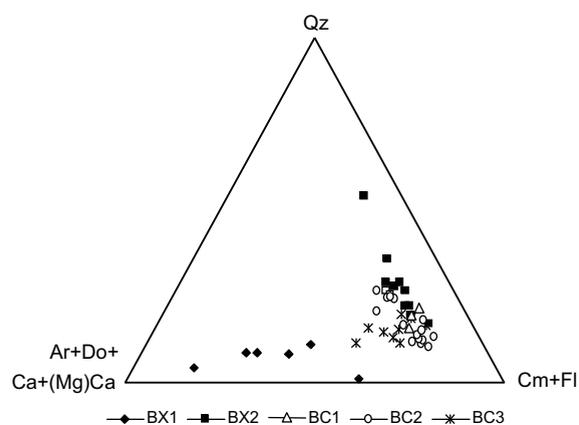
All statistical analyses were carried out using the STATISTICA (v. 6.0) software package.

## 4. Results

### 4.1. Bulk sediment mineralogy and chemistry

Mineralogy of five box-cores from the Augusta area is summarized by a ternary plot (Fig. 2). Major differences in the relative percentages of quartz, carbonates (calcite, Mg-calcite, aragonite, and dolomite), and alumino-silicates (clay minerals and feldspar) are observed between shelf and slope sediments. Carbonate dominates the nearshore site BX1 (on average 56%). At this station, the occurrence of equal proportions of calcite, Mg-calcite and aragonite accounts for a substantial calcareous biogenic component. In the other seaward sites BX2, BC2 and BC3, dominant phases are alumino-silicates (on average 58–63%), quartz percentages (on average 15–28%) decreasing offshore towards the slope. In the more distal cores carbonates are represented only by calcite (on average 14–22%).

Bulk sediment major element compositions for the five box-cores (Fig. 3) indicate that, except for the core BX1, all



**Fig. 2.** Ternary plot of mineralogical phases determined in bulk sediments from the studied cores. Qz = quartz, Cm + Fl = clay minerals + feldspar, Ca + (Mg)Ca + Ar + Do = calcite + (Mg)calcite + aragonite + dolomite.

sediments show similar geochemical composition and could be considered typically terrigenous, with  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  concentrations generally greater than 47% and 14%, respectively. At station BX1, located inside the continental shelf,  $\text{Al}_2\text{O}_3$  concentrations are mostly less than 10% whereas CaO + MgO mean concentration is higher than 36%, with a downcore decrease, accounting for a substantial calcareous biogenic component.

#### 4.2. Total organic carbon (TOC) and C/N ratio

Total organic C concentrations of the Augusta samples vary between 0.15% and 0.99%, with a progressive decrease from coastal to distal box-cores (Fig. 4). The measured concentrations reasonably agree with data reported by Emelyanov and Shimkus (1986) for Mediterranean sediment (on average 0.62%). At site BX2, TOC concentrations exhibit a clear upcore increase. TOC depth profiles for the cores BC2 and BC3 evidence abrupt and repeated TOC enrichments (Fig. 4).

The organic C to total N (C/N) ratio permits discrimination of the sediments according to the origin of sedimentary

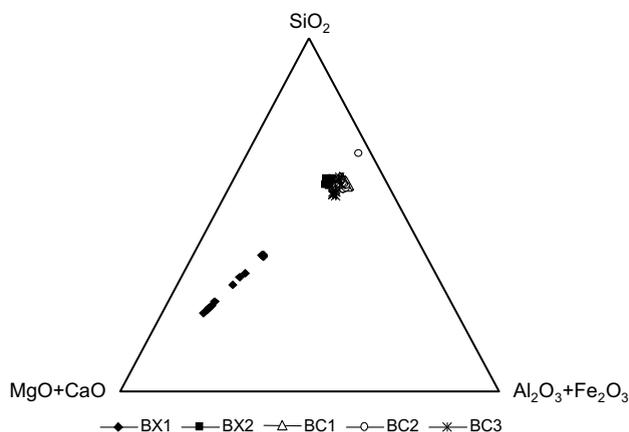
organic matter (e.g. Prahl et al., 1980, 1994; Meyers et al., 1996; Silliman et al., 1996; Ujiie et al., 2001; St-Onge and Hillaire-Marcel, 2001). Usually, C/N ratios between five and eight characterize autochthonous organic matter (from green algae), whereas C/N ratios greater than twenty indicate an allochthonous source, as vascular land plants (Emerson and Hedges, 1988; Meyers, 1994).

The C/N ratios measured in the studied cores are mostly less than 10 (Fig. 4), suggesting a dominantly marine origin for the organic matter of the Augusta sediment. C/N depth profiles generally correlate with the TOC profiles and, notably in cores BC2 and BC3, display abrupt increases with concentrations up to 16. These higher C/N ratios presumably mark horizons containing major contributions of land-derived organic matter.

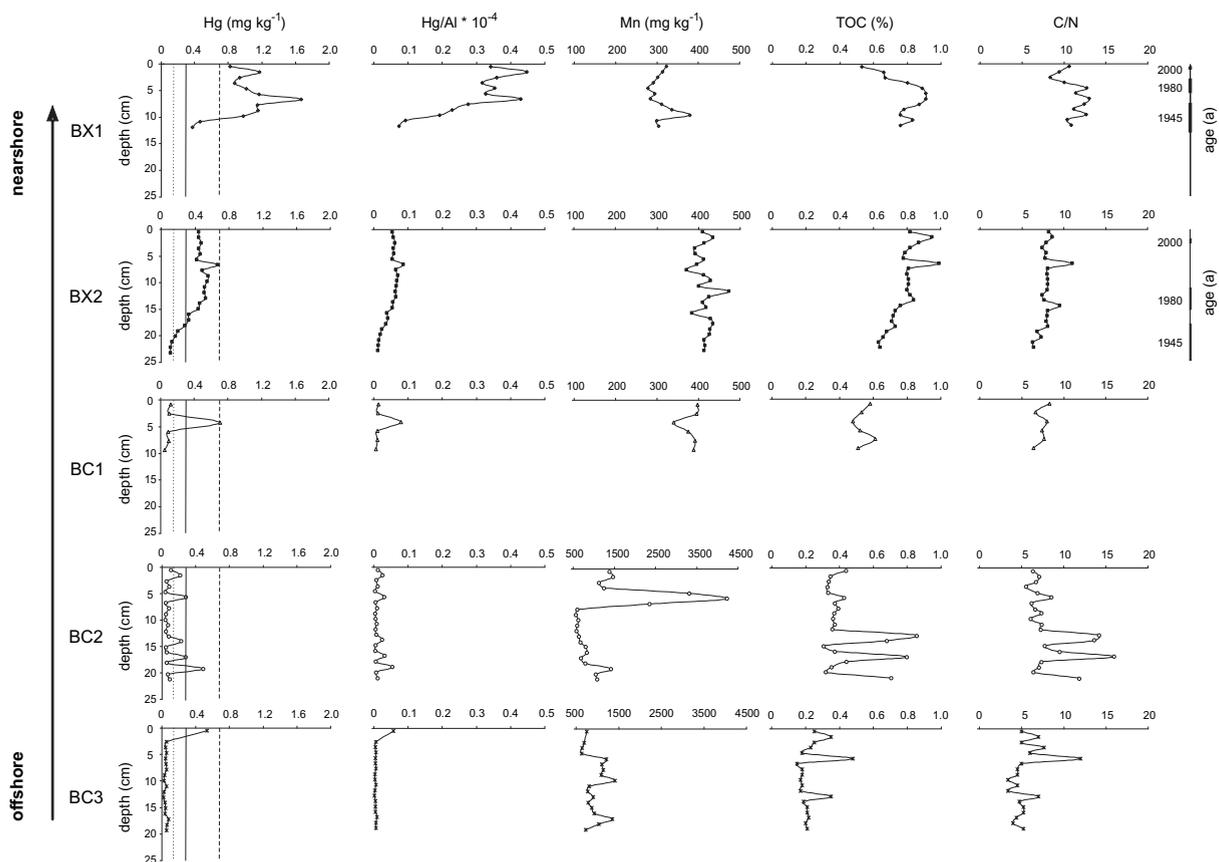
#### 4.3. Dating of sediment cores

Cores BX1 and BX2 have been previously dated using  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  specific activities (Di Leonardo et al., 2007). Based on the simple model of  $^{210}\text{Pb}$  dating (Appleby and Oldfield, 1994), the average sediment accumulation rate is  $1.6 \text{ mm a}^{-1}$  (95% confidence interval =  $1.3\text{--}2.2 \text{ mm a}^{-1}$ ) in core BX1 and  $5.3 \text{ mm a}^{-1}$  (95% confidence interval =  $4.6\text{--}6.3 \text{ mm a}^{-1}$ ) in core BX2. Significant inflections in the  $^{210}\text{Pb}$  specific activity profiles of both cores (Fig. 5) suggest a change in sediment supply that can be attributed to a depositional event such as a slump or turbidity current (Di Leonardo et al., 2007). This event, probably simultaneous in both cores, was relatively recent, occurring in the latter part of the 20th century (ca 1970–1985 AD).

For this paper, cores BC1, BC2, and BC3 have been analysed by the same methodology adopted and described in detail by Di Leonardo et al. (2007) for dating cores BX1 and BX2. Unfortunately,  $^{210}\text{Pb}$  activities measured for these three cores did not permit the estimation of a net sediment accumulation rate.  $^{210}\text{Pb}$  activities are quite constant throughout these cores, exhibiting values close to supported activities, with no clear decline in activity with depth (Fig. 5). Such a pattern suggests a rapid accumulation rate due to variations in sediment source/composition,



**Fig. 3.** Ternary plot of major element concentrations in bulk sediments from the studied cores.



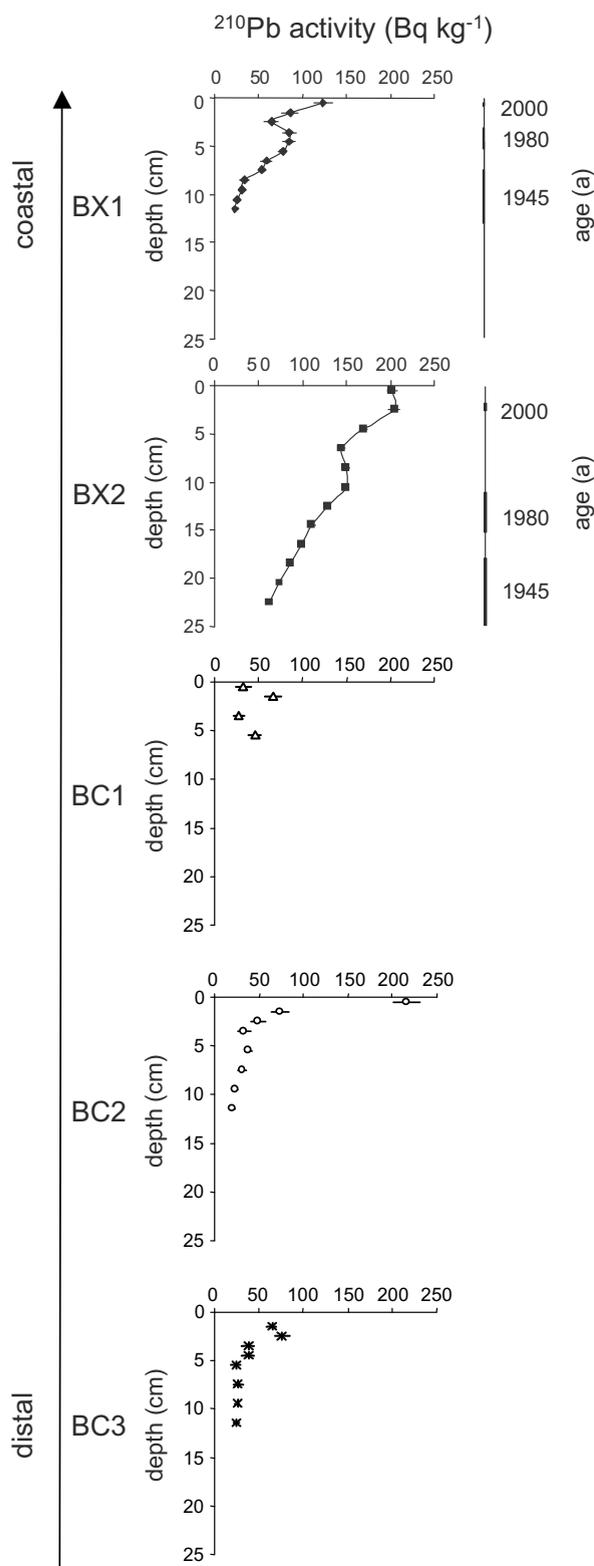
**Fig. 4.** Hg, Mn and TOC concentrations, Hg/Al  $\times 10^{-4}$  and C/N ratios vs depth in the box-cores from the Augusta area (note the different scale for Mn values of BC2 and BC3). ERL ( $0.15 \text{ mg kg}^{-1}$ ) and ERM ( $0.71 \text{ mg kg}^{-1}$ ) concentrations (Long and Morgan, 1990) (dotted and broken-dotted lines, respectively) together with Hg concentration limit ( $0.3 \text{ mg kg}^{-1}$ , G.U.R.I., D.M. 367/2003) (solid line) specified in national regulatory guidelines are given. Based on  $^{210}\text{Pb}$  dating, vertical scale on the right shows the year of sediment deposition. The error bars on each date are calculated by using the 2 sd error on the  $^{210}\text{Pb}$ -derived sediment accumulation rate for each core (Di Leonardo et al., 2007).

consistent with turbidite emplacement, slumping, and/or recent (contaminated) inputs.

#### 4.4. Distribution of total mercury

In the Augusta area the concentrations of total Hg exhibit a wide spatial and temporal variability (see Fig. 4), varying in the range  $0.02\text{--}1.67 \text{ mg kg}^{-1}$ . Significant differences in Hg concentrations between coastal cores (BX1 and BX2) and distal cores (BC1, BC2, and BC3) were tested by the analysis of Welch test for unequal means in a one-way ANOVA (test  $F = 53.78$   $p < 0.0001$ ; 95% confidence). Mean Hg concentrations of the more coastal sites BX1 and BX2 differ significantly from those of the distal stations. Indeed, except for a few samples from the bottom cores, Hg concentrations are higher than those previously reported for western Mediterranean sediments ( $0.10 \text{ mg kg}^{-1}$ ; Baldi et al., 1983) and for sediments from the Sicily Strait (Di Leonardo et al., 2006:  $0.015\text{--}0.070 \text{ mg kg}^{-1}$ ). At sites BC1, BC2 and BC3, most Hg concentrations are less than  $0.20 \text{ mg kg}^{-1}$ . However, the Hg depth profiles are characterized by positive peaks sometimes concurrent with spikes in both TOC and C/N profiles (Fig. 4).

Marine sediments may have variable proportions of mineral phases, which influence their trace element abundances. Calcium carbonate and opal are the most common biogenic diluents, whereas the fine-grained portion of sediments (clay minerals and organic matter) displays ability to scavenge large portions of trace elements from seawater. Therefore, to be sure that Hg concentration patterns for the sediment investigated are not an artefact due to mineralogical and/or sedimentological inhomogeneity, measured Hg concentrations have been normalized to Al. Major reasons for using Al are: (i) this element is generally assumed to represent a reliable measure of the aluminosilicate fraction of the sediments; (ii) Al displays high natural abundance as opposed to low abundances of contaminants; (iii) this element is typically not diagenetically labile (Horovitz, 1991; Sharma et al., 1994; Carral et al., 1995; Daskalakis and O'Connor, 1995; Sanei et al., 2001). Except for core BX1, normalization of Hg concentration to Al generally confirms the pattern of spatial and temporal variability of Hg in the investigated box-cores (Fig. 4). Owing to the presence of an abundant coarse-grained carbonate component at station BX1, Hg/Al profiles emphasize the different composition of this site with respect to other stations from the Augusta area.



**Fig. 5.**  $^{210}\text{Pb}$  activity vs depth for Augusta cores. Data of cores BX1 and BX2 are from Di Leonardo et al. (2007). Vertical scale on the right shows the year of sediment deposition, based on  $^{210}\text{Pb}$  dating. The error bars on each date are calculated using the 2 sd error on the  $^{210}\text{Pb}$ -derived sediment accumulation rate for each core.

## 5. Discussion

### 5.1. Spatial and temporal distribution of mercury contamination

It is difficult to quantify the anthropogenic input of metals into polluted environments because the metal content of sediment of pre-industrial periods is often unknown.

In relation to the regional geological setting, coastal areas can be characterized by different metal backgrounds. Therefore, the use of the world average shale as reference background could be misleading (Gibbs, 1993). Alternatively, the average metal concentrations measured in mineralogically similar sediments from a known pristine region can be used as the reference background (Rubio et al., 2000).

In this work, in order to evaluate the amount by which an individual sample is enriched in Hg, the enrichment factor ( $\text{EF}_{\text{Hg}}^{\text{Al}}$ ), a useful indicator reflecting the status and the degree of environmental contamination, was calculated as

$$\text{EF}_{\text{Hg}}^{\text{Al}} = (\text{Hg}/\text{Al})_{\text{sample}} / (\text{Hg}/\text{Al})_{\text{background}}$$

where  $(\text{Hg}/\text{Al})_{\text{background}}$  is the ratio (equal to  $5.0 \times 10^{-2}$ ) estimated by Di Leonardo et al. (2006) for sediment from the Strait of Sicily applying the method of maximum likelihood of lognormal distribution parameter to sediments older than 1920. An  $\text{EF}_{\text{Hg}}^{\text{Al}}$  value of 1 indicates a predominantly natural origin for the element in the sediment, while values greater than 1.5 indicate enrichment by either natural processes (e.g. biota contributions) or anthropogenic influences (Zhang and Liu, 2002) relative to background.

The box-plots in Fig. 6 show very high  $\text{EF}_{\text{Hg}}^{\text{Al}}$  values for the cores BX1 and BX2. In particular, Hg is enriched on average by 57 times in the more coastal sediments (BX1) with values as high as 89, confirming the important role of the anthropogenic sources. Core BX2 displays a moderate enrichment, the  $\text{EF}_{\text{Hg}}^{\text{Al}}$  average value being 10. The  $\text{EF}_{\text{Hg}}^{\text{Al}}$  values are low for cores BC1, BC2, and BC3 (4, 3 and 1.5, respectively) that, however, display extremes ( $\text{EF}_{\text{Hg}}^{\text{Al}}$  up to 16) corresponding to significant spikes in Hg concentration profiles.

In the coastal stations BX1 and BX2, Hg concentrations exceed the limit indicated by national regulatory guidelines ( $0.3 \text{ mg kg}^{-1}$ , G.U.R.I., D.M. 367/2003; see Fig. 4). To assess the environmental hazard of Augusta sediment, Hg concentrations have been also compared to Hg toxicity guidelines for sediment-dwelling species, developed by the North American Sediment Quality Guidelines (SQG; Long et al., 1995). The eco-toxicological screening concentrations called Effects Range Low (ERL) and Effects Range Medium (ERM) for Hg are  $0.15 \text{ mg kg}^{-1}$  and  $0.71 \text{ mg kg}^{-1}$ , respectively. Concentrations of Hg in the cores BX1 and BX2 exceed the ERL value (Fig. 4), indicating an actual probability that these sediments are detrimental to marine biota. In the more distal sediments of the Augusta area, Hg concentrations are generally lower than the ERL value. However, for some samples from cores BC2 and BC3 the ERL value for Hg is exceeded. This is a surprising and alarming finding because these cores have been collected from an area with a water depth of up to 2200 m, located at least 16 nautical miles from the coast.

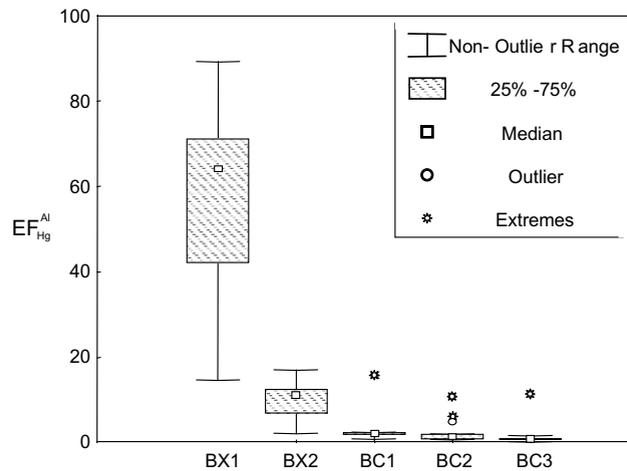


Fig. 6. Box plots of the Hg enrichment factors ( $EF_{Hg}^{Al}$ ) in the studied box-cores.

The Hg profiles for both cores BX1 and BX2 illustrate that Hg concentrations begin to increase in 1940–1950 (Fig. 4), possibly due to recent industrial developments at Augusta.

### 5.2. The role of TOC in mercury preservation

Organic matter content has been shown to correlate with Hg and trace metals in aquatic sediments (Gibbs, 1973; Orem et al., 1986; Chin and Gschwend, 1991; Kainz et al., 2003; Mirlean et al., 2003). Organic matter is a controlling factor because its high surface area increases the number of specific sites able to complex the trace elements (Horovitz, 1991; Sanei et al., 2001; El Bilali et al., 2002; Mirlean et al., 2003).

In the analysed Augusta sediments, Hg does not significantly correlate with TOC (Fig. 7), except for core BX2 ( $r^2 = 0.74$ ; significant at 95% confidence limit,  $p < 0.001$  at 0.65,  $n = 23$ ). The thermally labile fraction of organic matter in sediment is thought to provide a substrate with a large surface area by concentrating on the finer sediment

size fractions and scavenging Hg and other organic-associated elements (Sanei and Goodarzi, 2006). A high sediment accumulation rate at site BX2 (see Section 4.3) could have promoted rapid accumulation of labile organic matter in the surface sediment, which could reasonably explain the good relationship between Hg and TOC throughout this core (Fig. 7).

Using the approach of Hissler and Probst (2006a,b) for investigating contamination of sediments and soils, the Hg enrichment ( $EF_{Hg}^{TOC}$ ) with regard to the organic C fraction was estimated for the analysed sediments using the following equation:

$$EF_{Hg}^{TOC} = (Hg/TOC)_{sample} / (Hg/TOC)_{background}$$

In this paper,  $(Hg/TOC)_{background}$  (equal to  $1.8 \times 10^{-2}$ ) is the average ratio measured in deeper layers of the more distal core BC3. Anomalous samples (with TOC percentages  $\gg 2\sigma$  value) marking abrupt TOC enrichments in this core were discarded in calculating the background ratio.

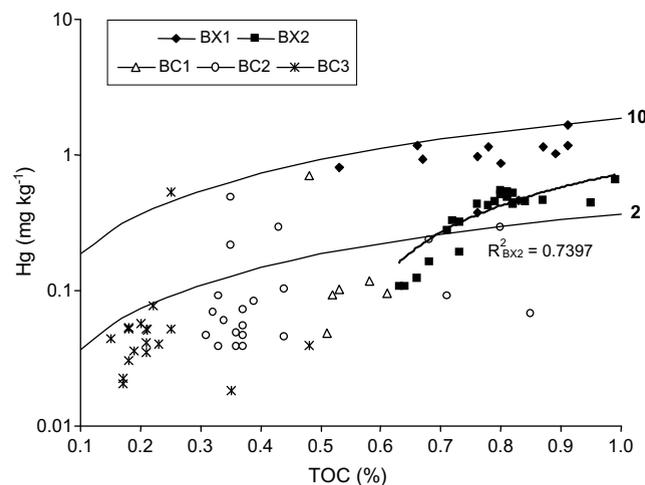


Fig. 7. Cross-plot of Hg vs TOC for sediments from the studied transect. The lines correspond to Hg enrichment factors from 2 to 10 ( $EF_{Hg}^{TOC}$ ) normalized to TOC concentration. A regression line is also shown for core BX2.

For most Augusta sediments  $EF_{Hg}^{TOC}$  is below or close to the value of 2 (plotted as a curve in Fig. 7), indicating generally no Hg enrichment with respect to organic C concentration. However, for the sediments of core BX1 and a few samples of distal cores BC1, BC2, and BC3, the  $EF_{Hg}^{TOC}$  largely exceed 2 (see Fig. 7), suggesting other factors as responsible for Hg enrichment in addition to Hg trapping by organic matter. High C/N ratios measured for these samples indicate input of detrital organic matter that is inferred to play a role as a diluent of Hg as opposed to labile algal biomass acting as scavenger for Hg.

These results are confirmed by the plot of the Hg enrichment factor calculated previously by normalizing to Al ( $EF_{Hg}^{Al}$ ) vs the TOC content (Fig. 8): for the sediments of core BX2 the relationship is strong, whereas for other cores there was no relationship, confirming that Hg enrichment is not mainly proportional to the organic C concentration. Attention is focused on cores BX1 and BX2 displaying relatively high TOC values. At site BX1, C/N ratios are close to eight (Fig. 4), which is a proxy for autochthonous organic matter. Consequently, for these sediments algal biomass could have a major role in accumulating Hg. For the more contaminated coastal core BX1, the lack of correlation between  $EF_{Hg}^{Al}$  and TOC suggests that Hg is mainly adsorbed onto the mineral fraction of the bottom sediments, probably because the organic matter is rapidly saturated by excess Hg.

### 5.3. Interpreting redox conditions from Mn–TOC covariation patterns

Scattered data points (Fig. 7), mainly related to the distal cores BC2 and BC3, correspond to the repeated, roughly concurrent positive spikes observed in Hg, TOC, and C/N ratio profiles (see Fig. 4). These brief excursions mark episodes of abrupt deposition of sedimentary materials that yielded elevated concentrations of organic matter with substantial proportions of land-derived material (see Section 5.2). During the 1980s, Augusta Bay was repeatedly dredged and the resulting material was transported and discharged about two nautical miles from the coast, in an approximately circular area with a radius of 0.5 nautical miles (ESTRAMED s.p.a., 1982). This material was primarily enriched in Hg deriving presumably from the nearby chlor-

alkali plant. Owing to the abrupt morphology of the seafloor and to the semi-permanent meander associated with the Atlantic Ionian Stream (AIS) (Lermusiaux and Robinson, 2001; Astraldi et al., 2002), the discharged material could have been remobilized and transported by the marine currents towards the Hyblean–Maltese escarpment. Repeated inputs of dredged material could have modified the natural sedimentation conditions in the Augusta offshore. Consistently,  $^{210}Pb$  data from cores BC2 and BC3 indicate erratic accumulation rates at these sites. Therefore, it is reasonable to explain the roughly concurrent fluctuations of Hg concentrations and TOC percentages, at different depths in cores BC2 and BC3, as a result of variations in sediment source/composition caused by the repeated inputs of contaminated dredged materials.

An interesting question is: “was the redox environment of the sediments in the area modified as a consequence of these anomalous sedimentary inputs and/or was Hg distribution affected by changes in redox conditions?” Manganese, a redox-sensitive element, can indicate the history of redox changes associated with surface sediments. In fact, Mn tends to be remobilized under reducing conditions at the sediment–water interface and diffused in pore waters precipitating as oxy-hydroxides as soon as pore water  $O_2$  is encountered. The process of distribution of many trace elements can be markedly linked to the Mn redox cycling (e.g. Morford et al., 2005; Tribouillard et al., 2006).

In the Augusta area, Mn concentrations are generally constant and relatively low in the more coastal stations, being  $\sim 300 \text{ mg kg}^{-1}$  at station BX1 and  $\sim 400 \text{ mg kg}^{-1}$  at sites BX2 and BC1 (Fig. 4). Higher and more variable Mn concentrations ( $>600$  and up to  $4200 \text{ mg kg}^{-1}$ ) were measured in the offshore cores BC2 and BC3. This distribution pattern is consistent with the well known process of Mn export from suboxic porewaters of the oxic shelf to the deeper basin due to reoxidation of mobile  $Mn^{2+}$  in oxygenated waters and to its transport in particulate form [ $Mn^{4+}$ -(hydr)oxides] towards the offshore area, where Mn is scavenged in oxic sediments (Morford and Emerson, 1999; Schnetger et al., 2000; Lyons and Severmann, 2006).

In the offshore stations BC2 and BC3 the Mn profiles show significant enrichments at different depths (Fig. 4). Increases in Mn concentration in the depth profiles are situated sometimes in coincidence with and more frequently

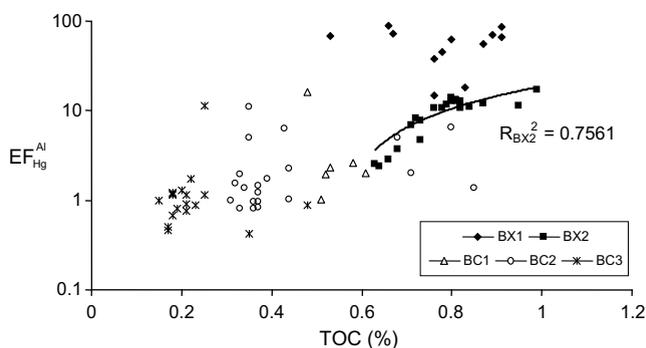


Fig. 8. Relationship between the Hg enrichment factor normalized to Al ( $EF_{Hg}^{Al}$ ) and the total organic C (TOC) for sediments from the Augusta area. A regression line is shown for samples in core BX2.

immediately above abrupt enrichments of Hg and TOC, which suggests that Mn peaks can be a result of diagenetic remobilization. The degree of enrichment of Mn in surface sediment is controlled by the penetration depth of dissolved O<sub>2</sub> from the overlying water, which in turn depends on the flux of organic matter to the sediments (Froelich et al., 1979). Under reducing conditions, pore water Mn increases due to reduction of Mn oxide in the sediment (Stumm and Morgan, 1981).

Deflandre et al. (2002) and Mucci et al. (2003) demonstrated that diagenetic readjustments of Mn are a result of changes in sediment accumulation, such as changes induced by the deposition of recent turbidites. When surface sediment is buried by a turbidite, Mn is reduced to Mn<sup>2+</sup>, which is free to diffuse upwards through the turbidite body. At the sediment/water interface Mn<sup>2+</sup> is oxidized by downwards diffusing O<sub>2</sub>, forming MnO<sub>x</sub> at the turbidite top. Hypothesizing an analogy between repeated, rapid accumulation in the Augusta offshore of dredged Hg- and TOC-enriched materials (see Sections 5.2 and 5.3) and turbidite deposition, the repeated Mn peaks in the cores BC2 and BC3 seem to indicate repeated changes of redox conditions at the turbidite–sediment interface. In deep-sea sediment, in which the sediment accumulation rate is low, oxidation acts on the upper turbidite surface after emplacement for a continued period, causing the change of TOC concentration below the top of the originally homogenous unit. A variety of redox-sensitive metals form diagenetic peak concentrations above and below this boundary (Thomson et al., 1993). Mercione et al. (1999) demonstrated that an efficient natural immobilisation mechanism for Hg exists close to the oxic/post oxic boundary in certain deep-sea sediments such as turbidites.

The reasoning is focused on core BC2, because Hg, Mn and TOC profiles for core BC3, although similar to those of core BC2, display lower concentrations and changes of lesser extent, consistent with greater depth at site BC3 that minimizes effects of massive inputs of discharged materials. In core BC2, Hg and TOC are well correlated to a first approximation whereas, at least in the deeper portion, Mn forms moderate peaks immediately above the C-rich horizons. An explanation for this pattern may be that Hg and organic C were immobilized under reducing conditions, whereas reduced Mn diffused upwards to form Mn oxy-hydroxide close to the oxic boundary. Poorly pronounced Mn peaks might indicate that subsequent burial of sediments, inducing O<sub>2</sub> level decrease, caused inconsistent Mn accumulation. During Hg cycling in a seawater environment, inorganic complexation with S is a primary reaction in reducing conditions. Sulphide affects the chemistry of inorganic Hg in sediments by precipitating it as mercuric sulphide and forming dissolved HgS complexes (Fitzgerald and Lamborg, 2005). Indeed, S–Hg interactions in the analysed system need further investigation by additional geochemical analyses. Upwards in the same core, at about 5 cm depth, there are well developed peaks of Hg and, notably, of Mn that correspond to a slight enrichment of organic C. This result is interpreted to be related to the passage of an oxidation front through the discharged material body, implying partial decay of organic matter and diagenetic enrichment of Hg and Mn.

## 6. Conclusions

This study has revealed a significant alteration of the natural fluxes of elements in the nearshore–offshore sedimentary environment due to industrialization of the SE Sicilian coastal areas since the middle of the 20th century. The spatial and temporal distribution of total Hg displays a pronounced increasing trend that started about 1950 at more coastal core sites. The timing of the change correlates with the advent of the activity of a number of chlor-alkali plants in the Augusta area. At offshore core sites, repeated abrupt Hg enrichments are roughly concurrent with significant increases of TOC with substantial proportions of land-derived organic material, indicating that the region has experienced changes in natural sediment source/composition induced by repeated discharge of contaminated dredged materials.

Although results confirm the affinity of organic particles for adsorption and retention of Hg, the mineral fraction was found to be an important factor in trapping Hg resulting from pollution. By using the patterns of Mn across the offshore cores as a proxy for redox conditions, it has been shown that emplacement of dredged contaminated materials can induce O<sub>2</sub> concentration decrease favouring Hg immobilisation within the sediment under reducing conditions.

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