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An Integrated Approach to the Assessment of Pollutant Delivery Chronologies to Impacted Areas: Hg in the Augusta Bay (Italy)

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Ⓢ *Supporting Information*


The industrial settlement of the Augusta Bay at night

photo by G. Marozzi (ISMAR-CNR)

ABSTRACT: Assessing pollution levels and trends in heavily impacted environments is important but hardly achievable due to the difficulty of recovering suitable undisturbed sediment records. An integrated approach is here presented to solve this kind of problem. It was adopted in the Augusta Bay (Italy) for the study of Hg historical inputs and present trends. Archive information on dredging and mud disposal, together with bathymetry and high-resolution seismic profiles, were used to identify suitable sampling sites. Undisturbed sediment cores were collected in the port and bay. Sediments were analyzed for depth distributions of radiotracers (^{210}Pb and ^{137}Cs), Hg, and main sediment parameters (magnetic susceptibility, grain size, dry bulk density, mineralogy, and organic carbon and nitrogen contents). Hexachlorobenzene (HCB) was also analyzed as an additional time tracer, since its production history in the area was well-known. Results show that peak Hg contamination (up to 575 mg·kg^{-1}) was reached in the 1970s. Technological improvements and waste treatment in the following years determined a consistent decrease, but high concentrations still affect surficial sediments (0.25−92 mg·kg^{-1}). Hg−HCB correlation suggests that this situation is likely the effect of resuspension and redistribution of deep sediments by dredging and naval traffic.

■ INTRODUCTION

The Augusta Bay hosts one of the most important ports of the Mediterranean, capable of housing very large ships due to its great depth (>50 m) and characterized by the presence of many industries all along its western part, including petroleum and petrochemical plants (Figure 1). As a consequence, a wide range of contaminants was introduced into this area since the early 1960s, at the beginning of the industrial development in the area, and was partially retained by sediments. The environmental degradation became evident during the early 1970s, when eutrophication crises were quite frequent, worsened by the combined influence of natural geographical features (e.g., the absence of strong winds and the prevalence of high temperatures) and enhanced nutrient inputs.[1] A recovery has been observed since then, but chemical contamination is still a matter of concern, as elevated concentrations of pollutants are detected in surficial sediments.[2,3] Hg contamination from the chlor-alkali plant is by far the most important environmental issue.[3−6] Indeed, this plant discharged without treatments in the bay until the 1970s, when a demercurization plant and the consortial biological depurator for waste treatments became operative, in response to national laws. In spite of that, the high Hg levels in surficial sediments imply the possibility of a recent contribution that needs to be verified.

Sediment cores can provide excellent means for evaluating and reconstructing historical records of industrial contaminant inputs to the environment (e.g., refs 7−9). However, the assessment of event chronology from sediment cores requires undisturbed accumulation. This situation is hard to find in a highly impacted environment such as the Augusta Port and Bay, where bottom sediments are constantly remobilized by dredging and can be affected by ship transit. It is then very important to know which are the areas interested by these processes, and coring sites have to be carefully identified where preservation of the sedimentary record is most likely. Because of this, we developed an integrated approach that can be applied to evaluate the impact of industrial activities in highly impacted locations and for a variety of pollutants. The approach involves the use of different methods, in order to (1) reconstruct the history of industrial productions (with evaluation of discharges, dredging operations, and sediment disposal areas), based on documents found in the archives of local administrations and factories; (2) locate the sites where sediment accumulation is abundant and less disturbed, based on results from bathymetric and high-resolution seismic surveys; (3) obtain suitable sediment cores by sampling with a gravity corer (SW-104, patented by CNR-IGM) specifically designed to minimize disturbance and preserve an optimal sediment−water interface; (4) obtain a careful subsampling by

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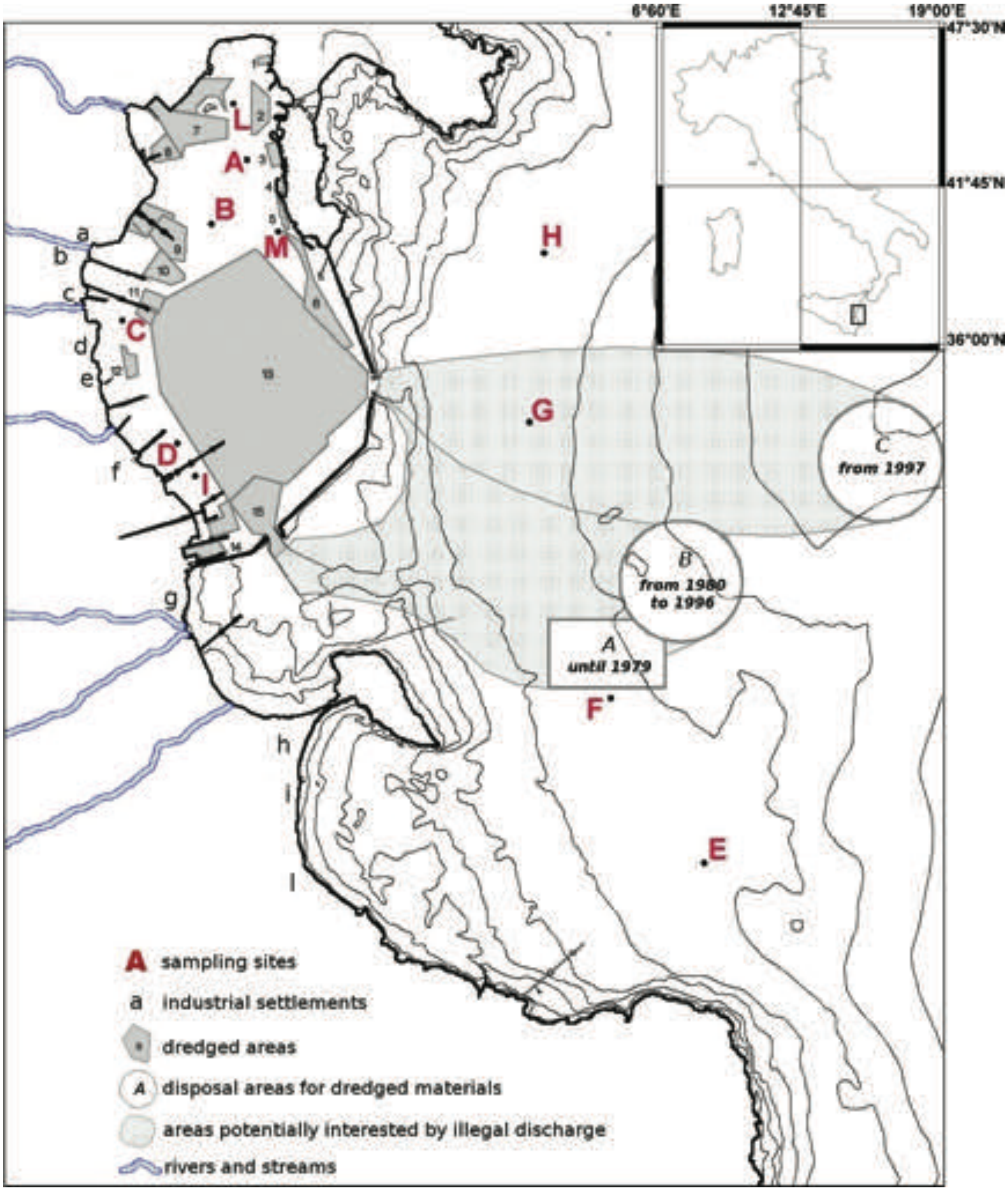

Figure 1. Bay of Augusta with sampling locations, dredged areas, disposal sites and industrial settlements in 1986: (a) Chimica Augusta; (b) Enotria; (c) ENEL thermoelectric power plant of Augusta; (d) Unicem; (e) Icam; (f) Montedipe; (g) Fertimont; (h) ENEL thermoelectric power plant of Priolo; (i) Cogema; (l) Isab.

extrusion and cleaning of the outer part of the section to avoid smearing; (5) determine sediment accumulation rates and dates through the use of ^{210}Pb and ^{137}Cs; (6) obtain independent chronological information (e.g., from magnetic susceptibility profiles), and (7) determine the contaminants' areal distribution and historical concentrations over a significant number of sediment cores. This paper presents the results of such an integrated study, focused at the definition of event chronologies related to the industrial Hg pollution of the Augusta Bay and Port. In this specific case, we could use hexachlorobenzene (HCB) as an additional independent tracer because its production history was well-known.

■ STUDY AREA AND HISTORICAL INFORMATION

General Overview. The Augusta Port and Bay are shown in Figure 1. The construction of the outer breakwaters took

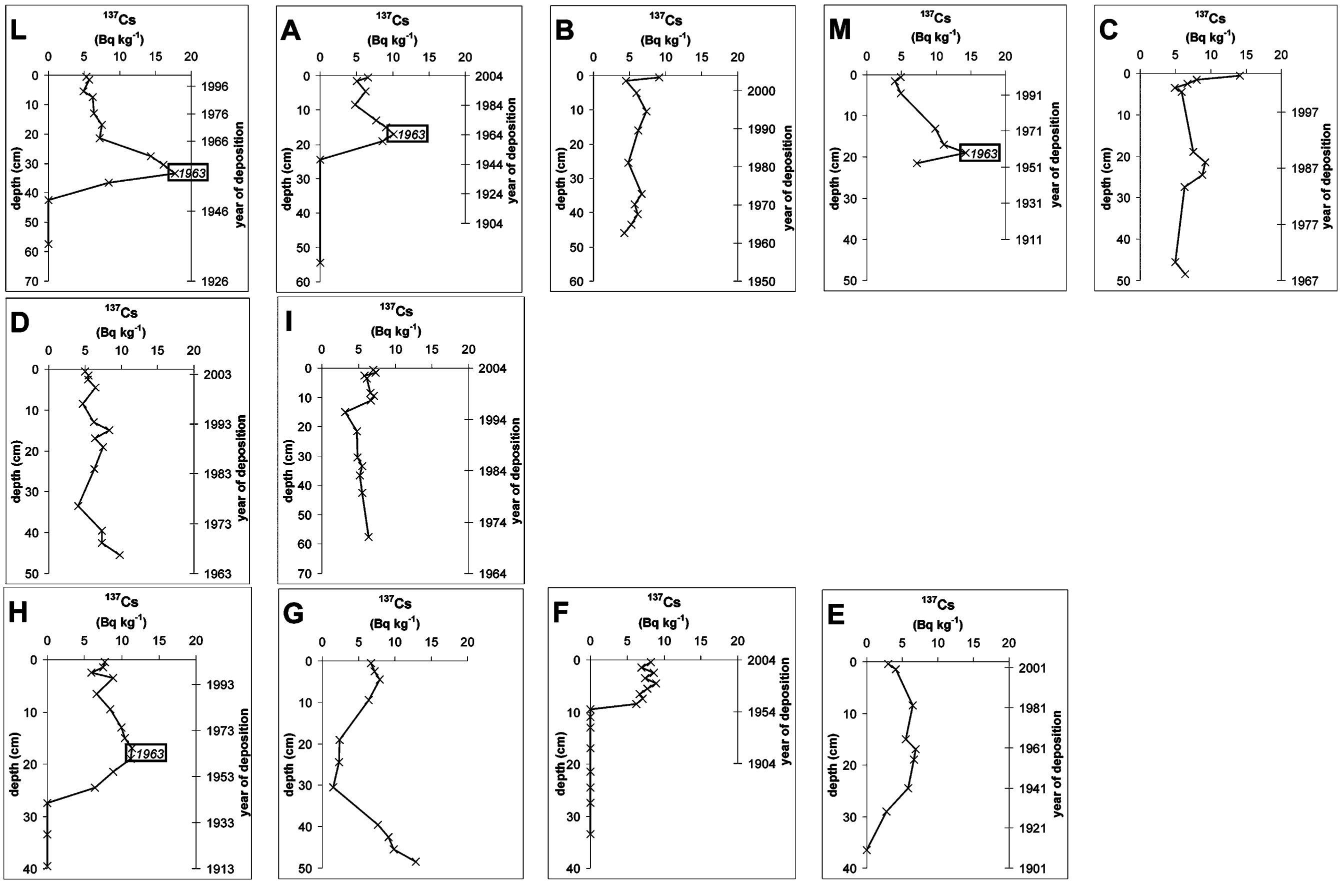

Figure 2. ^{137}Cs activity–depth distributions. Profiles are presented also vs years of deposition, calculated from the *S* values reported in Table 1. The 1963 peak is indicated when detected.

place in the 1960s, contemporary to the settlement along the western coast of a large number of chemical and petrochemical industrial plants, oil refineries, and other productions. The original environment was also modified over time by sediment dredging and partial nourishment of the western coast using materials of unknown origin. Figure 1 shows the dredged areas within the port, and the locations of offshore dumping sites (A, B, and C). The necessary information to draw this map has been retrieved from the Augusta Port Authority archives in 2004. It has been estimated that $^3/_5$ of the port surface has been dredged so far.

Several small rivers and streams flow into the Augusta Port, which communicates with the surrounding bay and the Ionian Sea through two inlets (Figure 1). In spite of this, the hydrodynamics within the port is characterized by a slack cyclonic circulation, not promoting exchange with the external waters. Therefore, nutrients and pollutants are generally confined within the breakwaters, favoring accumulation in sediments and the occurrence of eutrophication episodes.[1]

Previous Studies on Sediment Contamination. When dealing with sediment contamination by Hg in the Augusta Port, no previous studies have ever been published in international journals so far. Just a few reports can be retrieved from national archives, all of them considering only surficial sediments; thus no information has been provided on the chronology of Hg inputs and its historical trends. Indeed, the only high-resolution chronological records are those obtained by Cundy et al.[10] for trace metals (although not for Hg) on salt marsh sediments from the Mulinello river estuary in the northern part of the Augusta Bay (Figure 1). National reports[4,5] define a significant reduction of surficial Hg concentrations over time, from an average value of 101 mg·kg^{-1} in 1975 to 46.3 mg·kg^{-1} in 1980. Sampling sites close to the outfall of the chlor-alkali plant (southern sector of the port, Figure 1) experienced an even greater decrease, being 38–99 mg·kg^{-1} in 1980[5] with respect to 140–213 mg·kg^{-1} in 1975.[4]

Where the Augusta Bay is concerned, recently published papers[2,3,6] focused their attention on box core sediments collected a few miles outside the breakwaters. In general, Hg concentrations in sites closer to the coast exceeded by more than 20 times the estimated background level for the Strait of Sicily (0.038 mg·kg^{-1}).[2] In addition, it is suggested that anthropogenic impacts can be correlated to a reduction in abundance of benthic foraminifera and to an increase of their morphological deformities.[2]

■ MATERIALS AND METHODS

Seismic Survey and Sampling. The seismic survey was carried out from 15 to 18 October 2003 by use of a CHIRP II (Datasonic) subbottom profiler. Routes are shown in Figure S1 (Supporting Information), together with examples of the resulting seismic profiles and relative reflectivities. Sampling activities took place immediately after. The sampling strategy was designed according to seismic data, bottom reflectivities, and historical information relative to dredging and dumping areas. Attention was paid to avoid dredged and dumping areas or zones close to piers and/or influenced by docking and maneuvering of ships. Core G was sampled on purpose in an area of supposed illegal dumping of dredged material from the port, in order to evaluate the effectiveness of this practice.

Analyses. Analytical methods are fully described in Appendix II (Supporting Information). After collection, cores were scanned for magnetic susceptibility and X-radiographed. They were then extruded and carefully sectioned in 1−3 cm intervals with higher resolution at the top.

Samples for radiotracer measurements and the definition of sediment characteristics (bulk dry density, organic matter content, mineral composition, and grain size) were stored at 4 °C before the analysis and then freeze-dried. The principal chronological tracer, ^{210}Pb, was determined via α spectrometry of its granddaughter ^{210}Po, with the assumption of secular equilibrium.[11] Supported ^{210}Pb (in equilibrium with ^{226}Ra, naturally present in sediments) was obtained from the activities of ^{214}Pb measured in sealed vials after a period of storage and showed values ranging from 15 to 25 Bq·kg^{-1}. The excess ^{210}Pb (^{210}Pb$_{ex}$) was calculated by subtracting the supported fraction from the total. ^{137}Cs activities were obtained directly via γ spectrometry on dry sediments.

For Hg and HCB analyses, sediments were stored at −18 °C, dried at 40 °C, and then ground.

Hg was extracted following the procedure outlined in the EPA 3051A REV.1. Concentrations were determined following the method EPA 6010 C, by use of an inductively coupled plasma atomic emission spectrometer (ICP-AES) Spectro Ciros, and by flameless atomic absorption spectroscopy (AAS) to confirm the ICP-AES results.

For HCB analyses, samples were spiked with ^{13}C$_{12}$-HCB, extracted, and cleaned up before measurement via high-resolution (HR) gas chromatography (GC)/mass spectrometry (MS). The quantitative determination was performed by an isotope dilution method using relative response factors obtained from the injection of five standard solutions. Three ^{13}C 12-labeled polychlorinated biphenyls (PCBs) were added to the extracts before injection for recovery calculations.

All concentrations were calculated with respect to dry weight.

RESULTS AND DISCUSSION

Detailed descriptions of sediment compositions and characteristics are reported in Appendices III and IV (Supporting Information), together with the relative figures and tables.

Sediment Accumulation Rates and Chronologies. Figure 2 reports ^{137}Cs profiles versus depths and years of deposition, as determined from ^{210}Pb$_{ex}$ derived accumulation rates (*S*, centimeters per year; Table 1) that were calculated with the assumption of constant flux of the radiotracer and constant sedimentation (CF-CS).[12] Details of the dating procedures are reported in Appendix III (Supporting Information).

The CF-CS model was preferred to others (e.g., constant rate of supply) because it provides an average *S* useful for a first approximation dating. Since no evaluation of the effect of bioturbation could be achieved, the most surficial levels were excluded from the calculation of *S*. Thus, values in Table 1 should be considered as apparent, probably overestimated rates.[13] This would explain the presence of anthropogenic Hg in layers with calculated years of deposition before the 1960s. However, the ^{210}Pb$_{ex}$ derived chronologies were further discussed and validated in the light of other independent tracers, such as ^{137}Cs, magnetic susceptibility, and the history of HCB production (see below).

Table 1. Sediment Accumulation Rates within the Augusta Port and Bay[a]

core	depth interval (cm)	*S* (cm·year^{-1})	HCB (μg·kg^{-1})
L	0−13	0.46	23
L	13−bottom	1.12	23
A	whole core	0.43	34
B	whole core	1.02	31
M	whole core	0.42	48
C	whole core	1.34	20
D	whole core	1.24	518
I	whole core	1.78	nd
H	whole core	0.42	16
G	whole core	1.08[b]	23
F	whole core	0.21	30
E	whole core	0.39	8

[a] *S* associated errors range from 0.01 to 0.05 cm·year^{-1}. Surficial (0−1 cm) HCB values are also shown. [b] This value is unreal, as influenced by the illegal dumping of dredged materials from the port.

S values in the bay range from 0.42 cm·year^{-1} at site H to 0.21 cm·year^{-1} at site F, in agreement with accumulation rates determined on box core sediments from the same area (0.16−0.53 cm·year^{-1}).[2] Site G is very peculiar, with a relatively high rate of 1.08 cm·year^{-1}. This value is unreal, as it is very likely influenced by the dumping of dredged material on the way to the disposal areas. Indeed, this practice could reproduce conditions of high sedimentation, with thick layers of sediments deposited in a relatively short time. For this reason, any further discussion relative to the chronology of core G is avoided.

As for the Augusta port, *S* values calculated for cores L (deeper section), B, C, D, and I are rather high, from 1.78 cm·year^{-1} (I) to 1.02 cm·year^{-1} (B). Consequently, the time intervals represented by these cores are short, starting from the mid-1940s (core L) or early 1950s. Despite these limits, the cores cover the period of interest for this work, as they include the industrial setting, its development, and decline (early 1960s to late 1980s). Lower accumulation rates characterize cores M and A (0.42−0.43 cm·year^{-1}), probably due to the greater distance from the principal terrestrial sources.

^{137}Cs results confirmed the ^{210}Pb$_{ex}$ dating in cores L, A, M, and H (Figure 2), where the 1963 peak (corresponding to the year of maximum number of nuclear weapon tests in the atmosphere) was detected. Furthermore, measurable radiocesium values started to be observed from the mid-1950s (when ^{137}Cs was first introduced in the environment). Cores F and E present only this latter feature, and some postdepositional diffusion (or mixing) processes seem to have affected the profile in cores M and E, where ^{137}Cs was detected at depths before 1950 (Figure 2). In cores B, C, D, G, and I, characterized by high sediment accumulation rates, the 1963 level could not be found. Indeed, the rather linear/vertical profile of ^{137}Cs in core B (Figure 2) indicates that *S* might be higher than estimated, as this site is probably influenced by sediment remobilization and delivery from dredging activities and ships' passage. This uncertainty prevents the definition of a reliable chronology also for this core. None of the ^{137}Cs profiles presents the Chernobyl signal (1986), because this latter source did not significantly influence the southern part of Italy.

A further confirmation of the ^{210}Pb$_{ex}$ chronology comes from the dates associated with magnetic susceptibility peaks that have been related to recent activities of Mount Etna (see Appendix IV, Supporting Information). Indeed, magnetic

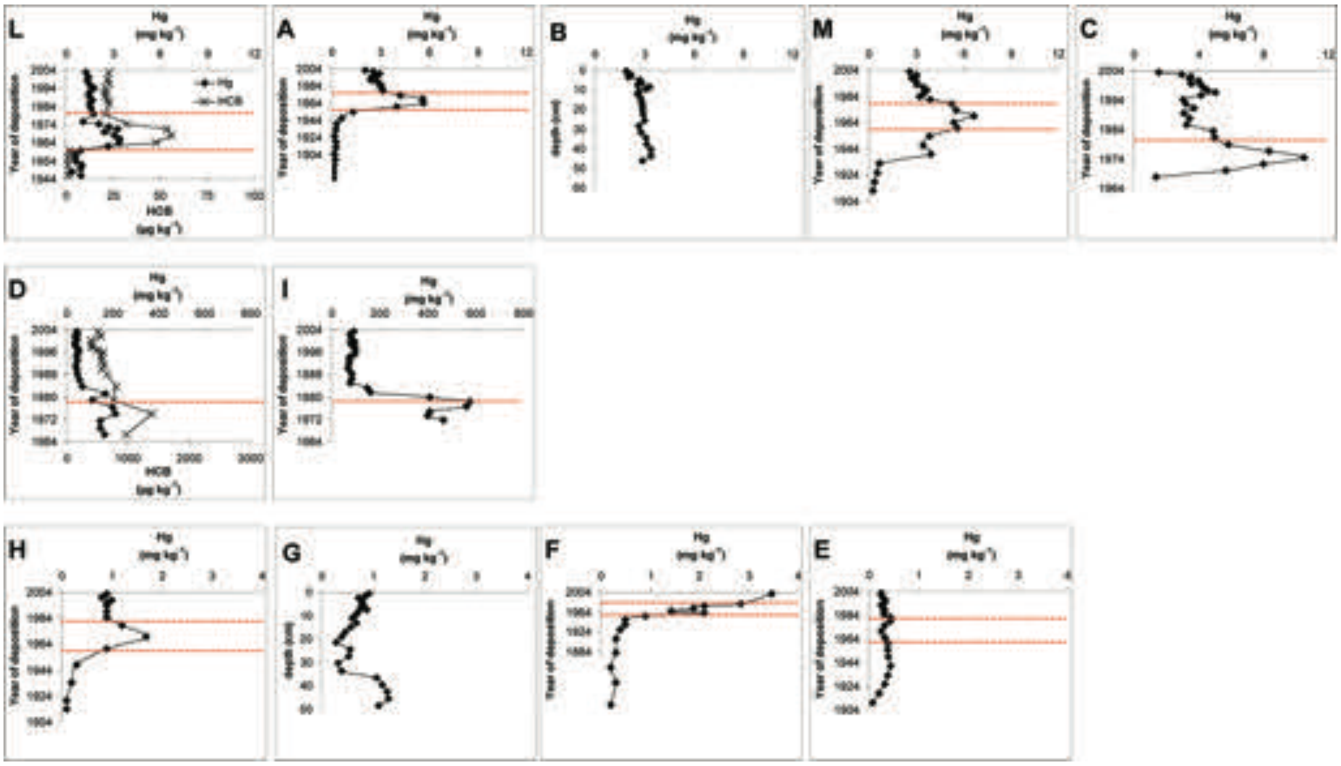

Figure 3. Hg and HCB concentrations vs year of deposition in all cores. The dotted lines encompass the period from the beginning of industrialization in the area (early 1960s) to the promotion of the first remediation measures (late 1970s).

susceptibility measurements, being directly related to the content of magnetic and paramagnetic minerals, are able to detect also limited increases of these components that are linked to the inputs of volcanic ashes. For example, the average *S* value of 0.43 cm·year^{-1} assigned to core A (Table 1) associates the peak at 45 cm depth (Figure S3 and Appendix IV, Supporting Information) to the year 1899, in good agreement with a relevant strombolian eruption that took place from July to December 1892.[14] Moreover, the intense and violent activity relative to the period late 1950s to early 1960s[14] has been recorded both in cores from the northern sector of the bay (e.g., at 24 and 20 cm depth in cores L and A, respectively; Figure S3, Supporting Information) and in core E (peak at 19 cm depth; Figure S3, Supporting Information). Finally, the strombolian eruption that occurred in June–August 2001[14] is evidenced by the progressive increase of magnetic susceptibility values in surficial layers of cores M, C, D, and I (Figure S3, Supporting Information).

Hg Trends and Timing in Sediments. Figure 3 shows the historical trends of Hg in sediments. Values range from a minimum of 0.07 mg·kg^{-1} to a maximum of 575 mg·kg^{-1}, and great variability is observed among the different sectors of the port and bay. These consistent lateral differences account for the presence of a point source that strongly influenced nearby locations (i.e., cores I and D), and the level of contamination seems to be inversely proportional to the distance from the inputs. Natural sources of mercury in the region (i.e., those connected to the volcanic activity of Mount Etna) have been estimated to account for approximately half the total budget released in the atmosphere,[15] but Hg concentrations in volcanic matrices are too low to explain the levels measured in the studied area.[16]

In the northern sector of the Augusta Port, Hg values are between 0.13 and 10.5 mg·kg^{-1} (Figure 3). The profiles of core A and M cover the entire period of industrial development and can therefore better describe the impact of industrial settlements from the beginning. There, sediments recorded a significant increase of Hg concentrations, passing from near background values in the preindustrial period to ca. 6–8 mg·kg^{-1} in the 1950s. From the early 1970s, concentrations gradually and constantly decreased, truthfully as the result of both technological improvements and remediation measures that came into use in that period, in response to new legislative regulations. Present-day values, even if still higher than natural background, confirm the recent improvement in environmental conditions. Cores L and C can be considered as magnified versions of cores A and M, in that they represent recent events (i.e., the last 50–60 years) with more detail. The post-1970s decrease is well recognizable also at these sites (Figure 3). Core B shows a nearly vertical Hg profile, completely consistent with the higher-than-estimated *S* evidenced by ^{137}Cs profile for this core.

In the southern sector of the port, cores D and I present concentrations that are much higher than anywhere else, with values spanning from a minimum of 38 to a maximum of 575 mg·kg^{-1} (Figure 3). This evidence confirms the predominant role of industrial inputs in the contamination of these sediments, since both sites are located in the proximity of chlor-alkali plants that are considered among the main sources of Hg to the aquatic system.[15,17] Core I seems to be affected to a higher extent, since concentrations there are 2–3 times higher than in core D. However, the chronological pattern is better defined for this latter core, due to the good correlation between radiochemical dating and HCB information (see below). At both sites Hg shows a significant decrease starting from the late

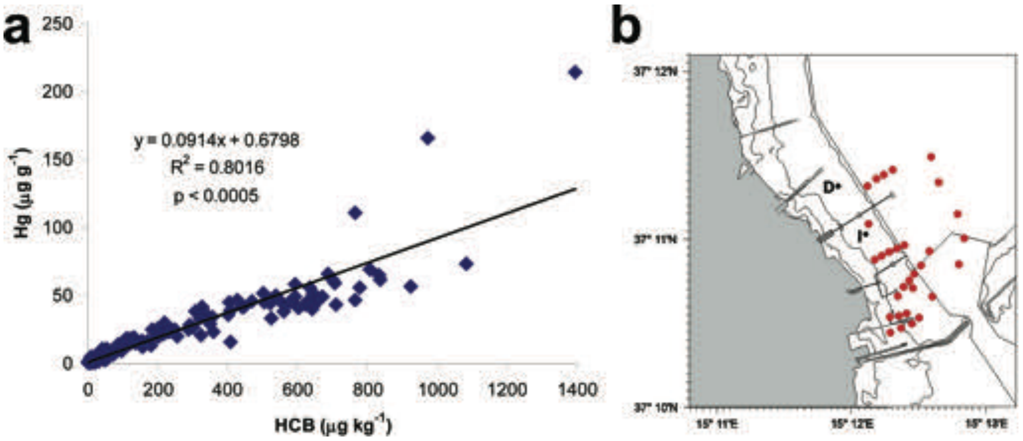

Figure 4. (a) Hg and HCB correlation in surficial samples and in cores D and L. Additional values are presented from surficial and subsurficial (up to 26 cm depth) samples collected in 2005. (b) Map of the 2005 sampling campaign. Location of cores D and I is also reported.

1970s, in perfect timing with the implementation of both a demercurization plant within the factory and a consortial biological depurator for the treatment of wastes. Therefore, the situation has improved considerably ever since, even if surficial values are still high (45 and 92 mg·kg^{-1} in cores D and I, respectively; Figure 3).

As expected, the cores collected in the bay show lower concentrations (0.07–3.5 mg·kg^{-1}, up to 2 orders of magnitude lower when compared to cores D and I; Figure 3), due to the increasing distance from industrial sources, but still slightly higher than those measured on box core sediments from the same area (0.03–1.70 mg·kg^{-1}).[2] The Hg profile in core H reproduces quite faithfully the pattern already observed in the sites within the port, with low concentrations in the preindustrial period, gradually increasing from the 1950s, peaking in the early 1970s and then decreasing to almost stable values in the most recent layers, as observed also by Di Leonardo et al.[2] This similarity suggests that industrial originating contamination was not entirely confined in the port but also reached this site. Core E appears to be less contaminated (0.07–0.43 mg·kg^{-1}), being far from industrial sources and disposal areas. The recent (early 1980s) increase detected in core F might be due to the influence of the nearby area, where dredged polluted sediments are suspected to be illegally discharged before arriving to their final destination. Indeed, the influence of dredged materials has already been hypothesized to explain anomalous sedimentary inputs in box core sediments retrieved in the Augusta Bay near the location of core F,[6] but bottom sediment remobilization by deep currents or bioturbation may also have played a role, as evidenced also by $^{210}Pb_{ex}$ profiles (see Figure S2, Supporting Information). Hg values for core G span from 0.28 to 1.30 mg·kg^{-1} with higher concentrations at depth, but no chronological discussion is possible due to dating uncertainties.

Origin of Hg in Surficial Sediments: HCB as an Independent Tracer. In spite of the significant decrease from the late 1970s–early 1980s, Hg surficial values are still higher than international sediment quality guidelines, defining the concentration at which adverse effects on fauna can be expected (e.g., ERL = 0.15 mg·kg^{-1}).[18] In addition, surficial values within the port and at site F exceed the threshold above which these effects are highly probable (e.g., ERM = 1.3 mg·kg^{-1}).[18] The seriousness of the situation is well-known to the authorities that have forbidden any fishing activity in the port; still it is important to understand if the surficial contamination is determined by either the presence of active industrial sources or the resuspension of old sediment layers. An independent tracer of industrial pollution was then selected (HCB, which is characterized by a well time-constrained history) in order to discriminate between the two hypotheses.

HCB is an artificial compound, extensively used from 1933 to the 1970s as a pesticide and fungicide. Nowadays it can be found, at very low concentrations, only as a byproduct in the manufacture of other chlorinated compounds, especially tetrachloroethylene (TCE).[19] The possible sources of HCB to the Augusta Port and Bay were two: (i) the chlor-alkali plant itself (due to the reaction of chlorine with graphite anode materials such as carbon and oils)[20] and (ii) the production of TCE from dicloroethane and chlorine, having chlorinated pitches (that may contain up to 10% HCB) as a byproduct.[21] The amount of HCB derived from chlor-alkali plants, as reported in literature,[22] cannot justify the high levels observed in sediments of the Augusta Bay. Therefore, TCE production in the industrial area of the Augusta Port seems to be the only significant source and its production history there is very well time constrained: the plant started its activity in 1959 and continued for 20 years, ceasing definitively in 1979. Nine years later the plant was completely decommissioned. During most of this period, no precautions were taken to prevent environmental damages. Actually the chlorinated pitches were mainly solid, but this does not exclude that some HCB contaminated wastes were directly discharged at sea. Only from 1976 were they diluted with dichloropropane and sent to the industrial settlement of Porto Marghera (northern Italy) to be disposed of.[21]

The plot in Figure 4 and the profiles in Figure 3 show that the correlation between Hg and HCB in our samples is highly significant (R = 0.90, p < 0.0005). As observed in Figure 3, HCB temporal records for cores L and D are consistent with the timing of TCE production, with low, close to detection limit values in the preindustrial period (measured just in core L; Figure 3), an increase from the early 1960s, a maximum around the beginning of the 1970s, and a following decrease. Since the inputs of HCB ceased definitively in the 1980s, the persistence of a strong correlation between Hg and HCB in surficial levels (where HCB should be absent) means that the origin of both contaminants here is old, probably due to the mobilization (caused by dredging and ship traffic) of polluted sediment deposited in the period 1958−1980. Presently, no direct source seems to affect these sites.

In conclusion, the multifaceted approach adopted for this research, joining together information from field work (seismic, sampling of selected sites), laboratory analyses (sediment features and contaminants), and archive documents, has proved to be a suitable tool for obtaining a clear view of what happened, and why, in a very complex study area such as the Augusta Port and Bay.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Four appendixes, containing additional text, three figures, and two tables, with brief descriptions of the seismic survey's outputs, analytical methods, radiodating procedure, and results of the analysis regarding sediment composition and characteristics (magnetic susceptibility, dry density, grain size, mineralogy, and organic matter composition). This material is available free of charge via the Internet at http://pubs.acs.org/ .

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