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Possible impacts of Hg and PAH contamination on benthic foraminiferal assemblages: An example from the Sicilian coast, central Mediterranean

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Abstract

The Palermo and Augusta urban/industrial areas (Sicily) are examples of contaminated coastal environments with a relatively high influx of unregulated industrial and domestic effluents. Three sediment box-cores were collected offshore of these urban/industrial areas in water depths of 60–150 m during two cruises (summers 2003/2004), dated by ^{210}Pb and ^{137}Cs, and analysed for total mercury concentration and total polycyclic aromatic hydrocarbon (PAH) concentration. Benthic foraminiferal assemblages were also examined (in terms of their distribution and morphology) to assess the potential use of benthic foraminifera as bioindicators of pollutant input and environmental change in these Mediterranean shelf environments. The Hg and PAHs vs depth profiles show a clear increase in concentration with decreasing depth. Most of the sediments are highly enriched in mercury and show concentrations more than 20 times the background mercury value estimated for sediments from the Sicily Strait. The Hg and PAH concentrations appear to be potentially hazardous, grossly exceeding national and international regulatory guidelines. A reduction in abundance of benthic foraminifera, increasing percentages of tests with various morphological deformities, and the dominance of opportunistic species in more recent sediments can be correlated to anthropogenic impact.

Keywords: Mercury; PAHs; ^{210}Pb and ^{137}Cs dating; Benthic foraminifera; Marine sediments; Sicily

1. Introduction

As a consequence of human activities, Hg and polycyclic aromatic hydrocarbons (PAHs) are among the most widespread and dangerous environmental pollutants. Major sources of Hg contamination are industrial chlor-alkali plants, illegal dumping of industrial wastes, waste incineration, and metal smelting. PAHs are known to be mainly products of incomplete combustion of organic materials (wood, coal and oil). PAHs can also enter marine systems through petroleum spillages and various offshore activities. In marine environments, a significant fraction of mercury, and of PAHs, is strongly bound by suspended sediments, which subsequently may settle, removing the contaminants via seafloor burial. Such

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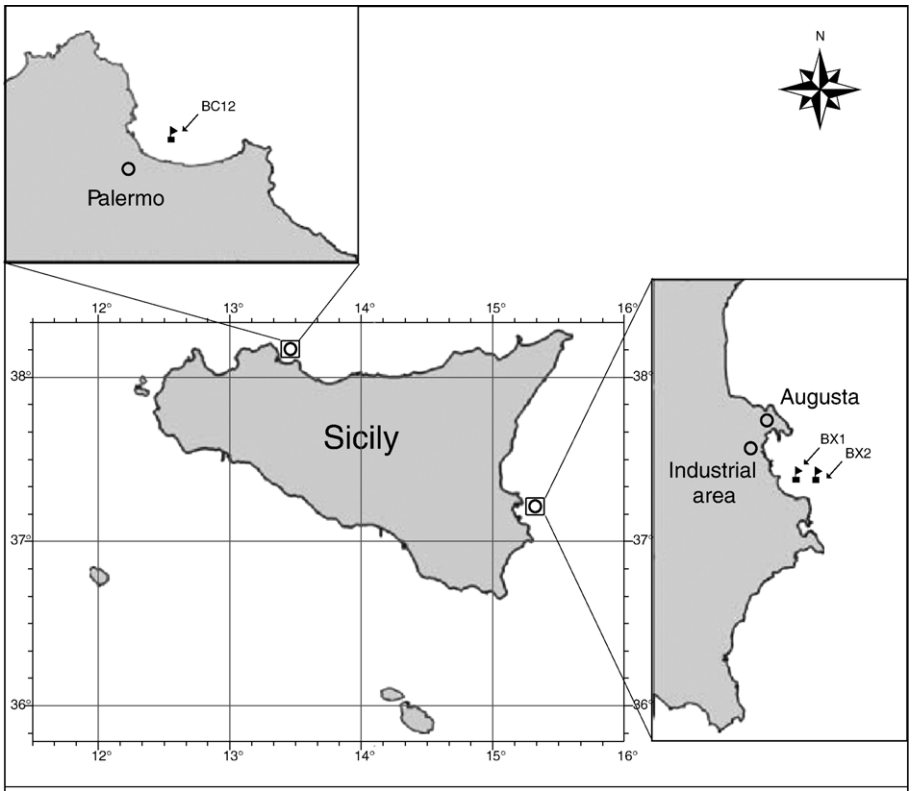
removal, however, may only be temporary, as the sorbed contaminants may be subsequently released by various transformation processes, including chemical transformation and biodegradation (Covelli et al., 2001; Yunker et al., 2002; Fitzgerald and Lamborg, 2005; among others). Increasing concern about the detrimental effects of these contaminants on the health and viability of marine biota has stimulated a number of investigations on the transfer of sedimentary Hg and PAH at the top of the marine benthic food chain (Baumard et al., 1998; Bothner et al., 1998; Charlesworth et al., 2002; De Luca et al., 2004; Berto et al., 2006) and recent studies have addressed the toxic and genotoxic potential of contaminated sediments (Leady and Gottgens, 2001 and Meador et al., 2005 for Hg; Bihari et al., 2006 and references therein for PAH). Relatively few studies have been undertaken on the biotic effects of Hg and PAH contamination in the often highly contaminated coastal environments of Europe (e.g. Debenay et al., 2001; Cearreta et al., 2002; Armynot du Châtelet et al., 2004). In particular, little attention has been paid to Italian lagoonal and coastal environments (Coccioni, 2000; Ferraro et al., 2006), despite their relatively widespread distribution, and ecological and economic importance. Moreover, the impact of contaminants on offshore ecosystems has been poorly investigated, although the environmental quality in deeper water regions is a major concern especially in a semi-enclosed basin such as the Mediterranean Sea.

A low cost method of investigating the environmental impact of polluted marine sediments may be provided by the analysis of benthic foraminifera, which may record the ecological state of the marine environment and its spatial and temporal variability. Early work by Zalesny (1959), Resig (1960), and Watkins (1961) evaluated the impact of pollutants on the morphological variability of benthic foraminiferal tests, and this has been followed by a large volume of work focussed on the use of morphological abnormalities in foraminifera as indicators of heavy metal pollution (Sharifi et al., 1991; Alve, 1991; Yanko et al., 1994, 1998), eutrophication (Caralp, 1989), and industrial and domestic sewage waste input (Watkins, 1961). Common features of foraminiferal assemblages in polluted environments include reduced foraminiferal population diversity and density (Bretsky and Lorenz, 1970; Schafer et al., 1991; Yanko et al., 1998), stunting of the adult tests, frequent presence of deformed tests, and an increase in percentage of individuals belonging to a few opportunistic species (Murray, 1973; Pearson and Rosenberg, 1976; Ellison et al., 1986). Hydrocarbon contamination is suspected to affect foraminiferal distribution (Alve, 1995; Yanko et al., 1998) and, although a direct influence of hydrocarbons on foraminiferal assemblages is not well documented, Vénec-Peyré (1981) and Locklin and Maddocks (1982) suggested a positive correlation between PAH and petroleum contamination and the deformation of foraminiferal tests.

Geochemical data, including total mercury and total polycyclic aromatic hydrocarbon (PAH) concentrations, are presented together with investigations of benthic foraminiferal assemblages from recent sediments collected offshore of the Palermo and Augusta urban/industrial areas, Sicily. The Palermo urban area (NW Sicily) has a high population density (900,000 inhabitants) and hosts a variety of industrial and commercial activities (such as oil and electric power production systems, and engineering, shipbuilding, manufacturing companies). However, the primary source of contaminants to the Palermo Gulf derives from urban and harbour activities. The Augusta coastal area receives significant discharges of heavy metals from the adjacent industrial areas, particularly from a number of chlor-alkali plants established in the 1950s. It is the location of Sicily's major port. Moreover, agricultural and domestic effluents contribute to make it one of the most contaminated areas along the Mediterranean coasts. Owing to the high state of environmental degradation, this area was included in 2002 in the National Remediation Plan by the Italian Environmental Ministry. The choice of Hg and PAH as primary indicators of contamination in the two areas is due to the following reason: among highly contaminant and mutagenic heavy metals and organics that have been preliminarily investigated in sediments of the Augusta artificial Bay, mercury and PAH were found in alarmingly high concentrations (ICRAM, 2005). In this paper, trends in contaminant input in both areas are assessed, and the biological response of benthic foraminifera, in terms of their distribution and morphology, to different sources of pollution is examined. Comparative geochemical and micropaleontologic records, dated by ^{210}Pb and ^{137}Cs, are used to test the potential of benthic foraminifera as bioindicators of pollutant input and environmental change in central Mediterranean coastal/distal areas.

2. Sampling strategy

Three box-cores containing recent sediments were collected from the Sicilian coastal zone seawards of the industrial area of Augusta and the Palermo Gulf (Fig. 1). Sampling was carried out during two oceanographic cruises on board the oceanographic ship "URANIA" in the summers of 2003 and 2004. Sediments were immediately subsampled on board using an acrylic tube,



Core number	Latitude (N)	Longitude (E)	Water depth (m)	Core length (cm)	Nautical miles	Transect
BX1	37° 09' 00	15° 16' 00	61.6	12	2.15	Augusta area
BX2	37° 09' 00	15° 19' 00	145.4	23	4.29	
BC12	38° 07' 98	13° 24' 95	100	21	2.57	Palermo Gulf

Fig. 1. Location of sampling stations, with core length and water depth at each station.

sealed in polyethylene flasks, and stored at −20 °C until analysis.

3. Analytical methods

On return to the laboratory, the cores were sliced at 1 cm intervals with a stainless steel bandsaw, prior to geochemical, radiometric, and microfaunal analyses.

3.1. Geochemical analyses

Samples were oven dried at 50 °C, powdered manually in an agate mortar and analysed for bulk geochemistry, total organic carbon (TOC), calcium carbonate content, total mercury and total PAH concentrations, ^{210}Pb and ^{137}Cs activities.

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). Analytical errors are below 1% for Si, Al, Na, 3% for Ti, K, Fe, Ca, and 10% for Mg and P.

Total organic carbon (TOC) analyses were performed with a Perkin Elmer CHN Elemental Analyser (Mod. 2400), using acetanilide as a standard, at a combustion temperature of 920 °C, after removal of carbonates with HCl vapour (Hedges and Stern, 1984). $CaCO_3$ content was determined by a classic gas-volumetric technique, as reported in Husselmann (1966). Analytical error for both methods is below 5%.

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

single gold 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. Accuracy (<5%) was checked using standard reference material (MESS-3) and duplicate samples. The quality control gave good precision, with a relative uncertainty (at 95% confidence) of <5% for all samples.

Total PAH concentrations were determined following solvent extraction in a sonication bath with a mixture of *n*-hexane/dichloromethane (glass distilled grade), following the method of King et al. (2004). Prior to the extraction a mixture of three deuterated PAHs (acenaphthene-d10, phenanthrene-d10 and perylene-d12) was added to the dry sediment as internal standard in order to quantify compound losses through the extraction procedure. Sample extracts were purified by passage through columns containing 50:50 ashed silica:deactivated alumina, followed by elution with 75:25 *n*-hexane/dichloromethane. The eluants were concentrated by N_2 blow down to ca. 250 μl and analysed for PAHs. Each sample was analysed for 16 PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo-[k]fluoranthene, benzo[a]fluoranthene, dibenzo[a,h]anthracene, indeno [1,2,3-cd]pyrene and benzo[ghi]perylene), which were identified and quantified using a ThermoQuest Trace GC PolarisQ Ion Trap Mass Spectrometer fitted with an AS2000 Liquid Autosampler. Detection limits of approximately 0.003 mg kg^{-1} were obtained for each compound. Accuracy was evaluated by using the standard CRM 104-100 containing naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo-[k]fluoranthene, dibenzo[a,h]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene. Mean recovery (based on extraction of matrix-matched certified reference materials, $n=5$) was in the range 60–112% for the higher molecular weight PAHs, but was typically less than 50% for lower molecular weight compounds (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene). Precision of the procedure, calculated as RSD on the duplicate samples, is less than 5% for the higher molecular weight PAHs and less than 15% for the lower molecular weight compounds.

^{210}Pb specific activities were determined to calculate sediment accumulation rates and to examine temporal trends in contaminant concentration/microfaunal assemblages, following alpha and gamma spectrometric methods. For the box-core BX2, specific activities of ^{210}Pb were indirectly determined through analysis of ^{210}Po, assuming secular equilibrium between the two isotopes. Following Frignani and Langone (1991), ^{210}Po was extracted from the sediment and plated onto silver discs, prior to alpha spectrometric counting. ^{209}Po was used as internal standard. The analytical error was <5% (1σ). For the box-cores BX1 and BC12, subsamples were counted for a minimum of 15,000 s on a Canberra well-type ultra-low background HPGe gamma ray spectrometer to determine the specific activities of both ^{210}Pb and ^{137}Cs, using their 46 keV and 661 keV gamma energies respectively. Detection limits depend on sample size, count time and radionuclide energy, but are typically <15 Bq kg^{-1} at 46 keV and <1 Bq kg^{-1} at 661 keV for a 5 g sample. Energy and efficiency calibrations were carried out using bentonite clay spiked with a mixed gamma-emitting radionuclide standard, QCYK8163, and checked by matrix-matched International Atomic Energy Agency certified reference materials. Drift in the detector was assessed via bimonthly counting of the certified reference material IAEA 135, and was found to be minimal.

3.2. Benthic foraminifera analyses

Samples from the bottom, the middle and the top of each core were investigated for micropaleontological analyses. Specifically, three samples from BX1 and five samples from BX2 (cores from the Augusta area), and three samples from BC12 (core adjacent to the Palermo Gulf) were analysed.

Samples were washed through a 90 μm sieve and dried at 50 °C. Qualitative and quantitative analyses were performed on the size fraction >90 μm. The residues were split to get a subset of more than 300 benthic foraminiferal specimens, which were identified and counted. Benthic foraminifers were identified following the classifications of Sgarrella and Moncharmont-Zei (1993), Cimerman and Langer (1991), Loeblich and Tappan (1988) and AGIP (1982). Results were expressed as number of specimens per gram of dry sediment. Deformed tests, whenever present, were picked from each sample, morphologically examined and scanned via electronic microscopy (SEM).

4. Results and discussion

4.1. Bulk sediment geochemistry

The bulk-sediment major element composition for the three box-cores is summarised by a ternary plot (Fig. 2).

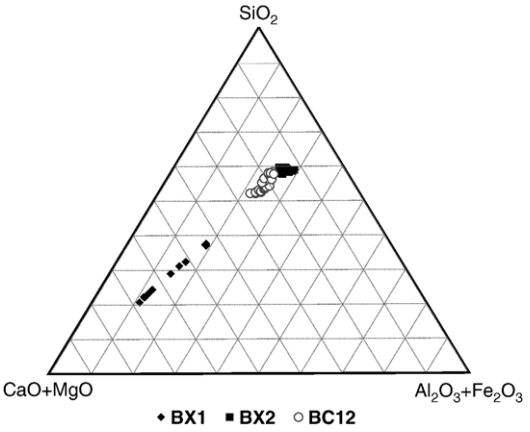


Fig. 2. Ternary plot of major elements determined in bulk sediments from box-cores BX1 and BX2 (Augusta area), and BC12 (Palermo Gulf).

Samples from BX2 and BC12 show very similar geochemical composition, with SiO_2 content generally greater than 50%. Core BX2 from Augusta shows the highest Al_2O_3 concentrations (8%), due to the presence of an abundant clay fraction (based on X-ray diffraction data by Di Leonardo, 2007). The proximal sediments from Augusta (box-core BX1) show higher CaO + MgO values that reflect abundant coarse-grained, biogenic carbonates. $CaCO_3$ concentrations vary between 12 and 32% in cores BX2 and BC12 and from 47 to 67% in core BX1. At all stations, markedly at BX1, carbonate concentrations decrease with depth.

TOC concentrations are in the range reported for open sea sediments from the NW Mediterranean (0.38–1.47%; Bouloubassi et al., 1997), but higher than the average value (0.62%) reported for Mediterranean sediments by Emelyanov and Shimkus (1986). Concentrations vary between 0.63 and 0.99% in the Augusta samples, with values increasing from distal to the proximal box-cores, and with a decreasing core depth. Core BC12, located in the Palermo Gulf, in front of the city and of its harbour, exhibits the highest TOC concentrations (from 0.96 to 1.17%), suggesting inputs probably linked to anthropogenic sources, such as urban sewage run-off, or anthropogenic eutrophication.

The atomic C/N ratio has proven to be a useful proxy in distinguishing between marine and continental sources of sedimentary organic matter. Organic matter of algal origin typically displays atomic C/N ratios of 4 to 10, whereas vascular land plants have C/N ratios greater than 20 (Meyers et al., 1996; Twichell et al., 2002). The C/N ratios measured in the box-cores investigated vary between 6.3 and 11.0, and between 8.0 and 10.2 at the Augusta and Palermo sites, respectively. These relatively low ratios suggest a dominantly marine origin for the organic matter, supporting the idea that eutrophication, rather than direct land run-off, is the source of the elevated TOC concentrations measured in samples from Palermo.

4.2. Radiometric dating

Specific activities of ^{210}Pb and ^{137}Cs were measured in order to date the sediments, and compare sediment accumulation rates in each core. In box-core BC12 from the Palermo Gulf, ^{210}Pb shows a general decline in specific activity with depth (Fig. 3). Based on the simple model of ^{210}Pb dating (see Appleby and Oldfield, 1992, for a review of ^{210}Pb dating models), the average sediment accumulation rate in this core is 2.1 mm a^{-1} (95% confidence interval = 1.7–2.8 mm a^{-1}, calculated over the depth interval 0–21 cm). In the same core, ^{137}Cs shows a broad subsurface maximum in specific activity between 3.5 and 11.5 cm depth. ^{137}Cs is an artificially produced radionuclide, present in the study area due to atmospheric fallout from nuclear weapons testing and reactor accidents. Marked maxima in the deposition of ^{137}Cs occurred in 1958, 1963 (due to nuclear weapons testing), and 1986 (due to the Chernobyl accident), and correlation of these input maxima with subsurface maxima in ^{137}Cs specific activity in sediment cores provides a widely-used method of dating (e.g. Cundy et al., 2003). It is difficult, however, to calculate a precise sediment accumulation rate from the ^{137}Cs data here, because of the broad nature of ^{137}Cs subsurface specific activity maximum, i.e. discrete maxima in specific activity related to ^{137}Cs fallout from nuclear weapons testing (maximum input in 1963) or the Chernobyl accident (1986) cannot be distinguished. Previous work on coastal sediments in eastern Sicily (Cundy et al., 1998; Cundy et al., 2003) has shown little evidence for significant input or retention of Chernobyl-derived ^{137}Cs in dated sediment profiles from this region. Therefore, attributing at least the lower part of the ^{137}Cs maximum to 1963 indicates a sediment accumulation rate of between 1.3 and 2.8 mm a^{-1}, in broad agreement with the ^{210}Pb-derived rate. The broad nature of the ^{137}Cs peak here is likely a consequence of either bioturbation or, more likely (given the lack of evidence of significant bioturbation in the ^{210}Pb profile in this core), of continued input of ^{137}Cs on reworked sediments after the main fallout event in 1963.

As in core BC12, ^{210}Pb shows a general decline in specific activity with depth in box-core BX1 from the Augusta area (Fig. 3). There is, however, a significant inflection in the ^{210}Pb profile between 3.5 and 5.5 cm depth, which may indicate a change in sediment supply,

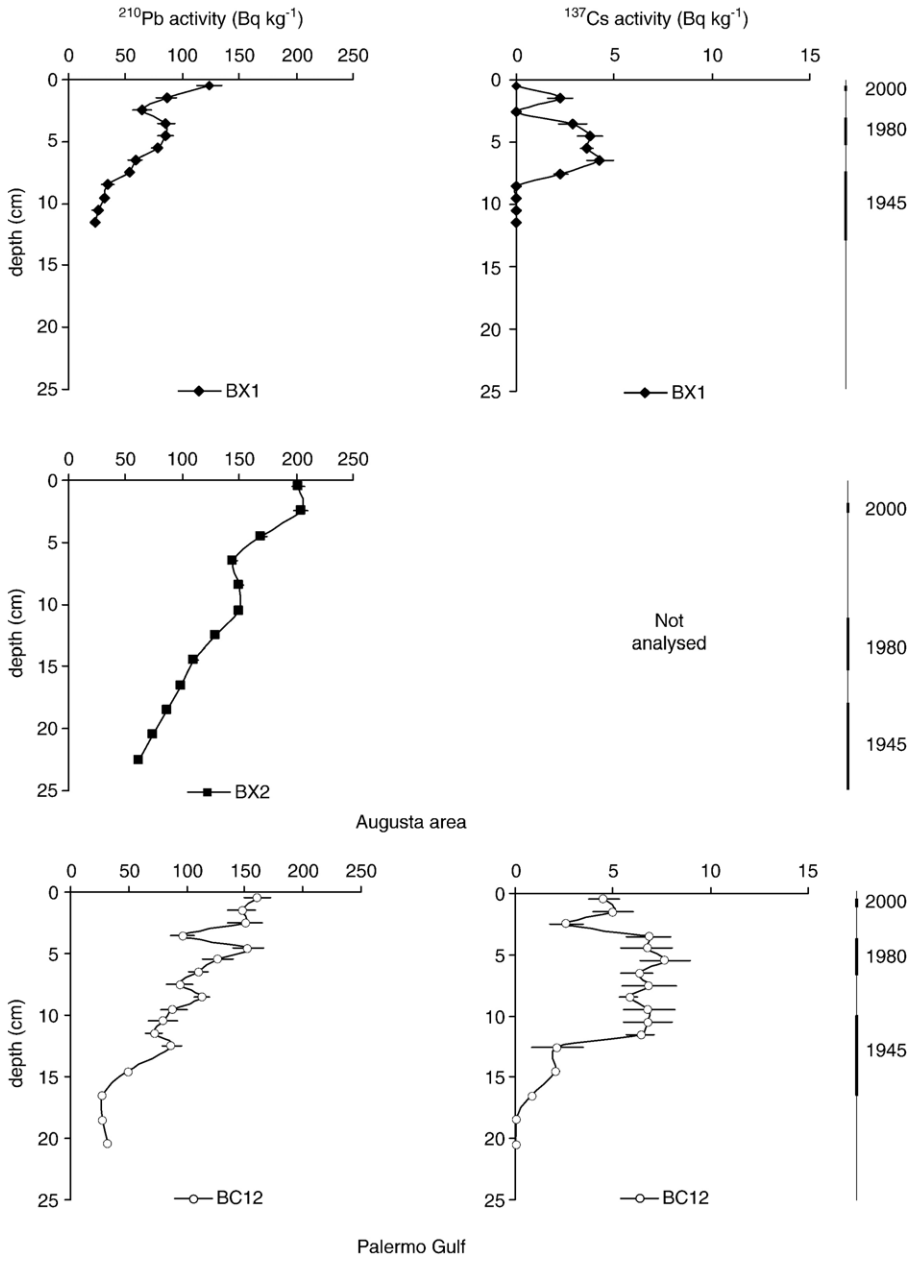


Fig. 3. ^{210}Pb and ^{137}Cs activities vs depth for Augusta and Palermo cores. Vertical scale on the right shows the year of sediment deposition, based on ^{210}Pb dating. The error bars on each date are calculated using the 2 SD error on the ^{210}Pb-derived sediment accumulation rate for each core (see text).

possibly from a depositional event such as a slump or turbidity current (N.B.: this could also be, at least partly, responsible for the relatively broad nature of the ^{137}Cs subsurface specific activity maximum in this core — see below). Over the depth profile as a whole (i.e. between 0 and 12 cm depth), applying the simple model of ^{210}Pb dating indicates an average sediment accumulation rate of 1.6 mm a^{-1} (95% confidence interval = 1.3–2.2 mm a^{-1}). As observed for core BC12, the ^{137}Cs specific activity vs depth profile shows a single broad subsurface maximum. Attributing this subsurface maximum in specific activity to the 1963 peak fallout from nuclear weapons testing indicates a sediment accumulation rate of between 1.1 and 1.6 mm a^{-1}, in reasonably good agreement with the ^{210}Pb-derived rate.

^{210}Pb specific activities also show a general decline with depth in the second Augusta core, BX2 (Fig. 3). Applying in this core the simple model of ^{210}Pb dating

indicates a somewhat higher sediment accumulation rate (5.3 mm a^{-1}; 95% confidence interval 4.6–6.3 mm a^{-1}, calculated over the depth interval 0–23 cm). ^{137}Cs specific activities were not measured in this core. Notably, the ^{210}Pb specific activity profile for core BX2 shows a similar inflection to that observed in core BX1, but occurring at 8.5 to 12.5 cm depth rather than 3.5 cm to 5.5 cm depth. Taking into account (i) the uncertainties on the sediment accumulation rates determined in each core and (ii) the higher sediment accumulation rate in core BX2, the event causing this inflection may have occurred simultaneously in both cores, supporting the idea that a turbidity current or similar (regional) depositional process was responsible. Based on the average sediment accumulation rates calculated in each core, this event was relatively recent, occurring in the later part of the 20th century (ca. 1970–1985 AD).

4.3. Distribution of total mercury

Concentrations of total mercury display a wide spatial and temporal variability (Fig. 4). The analysed samples have an average Hg content of 0.57 mg kg^{-1}, which is significantly higher than concentrations previously reported for western Mediterranean sediments (0.10 mg kg^{-1}; Baldi et al., 1983) and for sediments

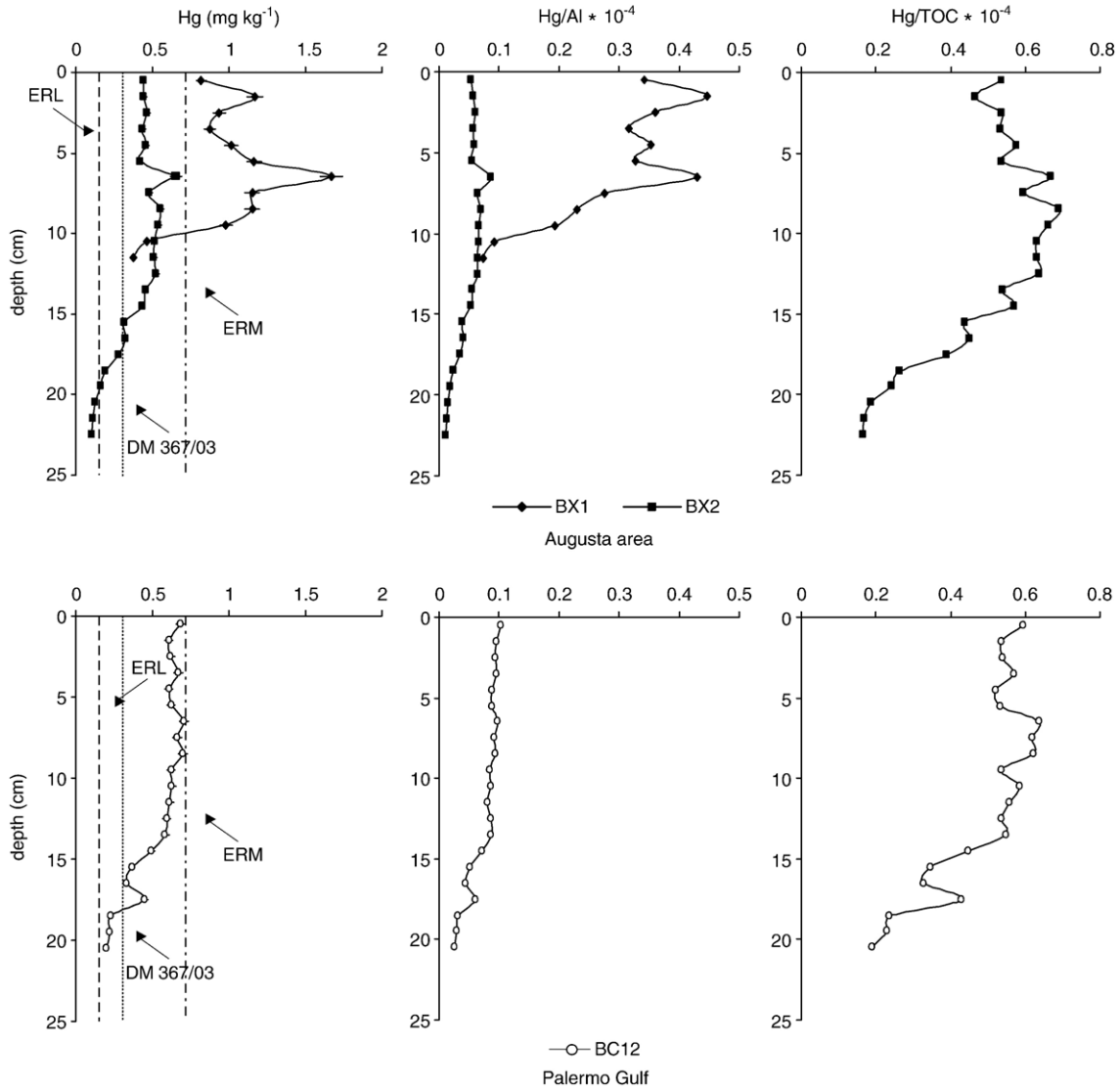


Fig. 4. Total Hg concentration, Hg/Al, and Hg/TOC ratios vs depth in the box-cores studied. ERL and ERM values (Long and Morgan, 1990) and concentration limits specified in Italian regulatory guidelines (G.U.R.I., D.M. 367/03, 2004) are given.

from the Sicily Strait (Di Leonardo et al., 2006: 0.015–0.070 mg kg^{-1}). The highest mercury concentrations observed in this study are 0.70 mg kg^{-1} in the Palermo Gulf and 1.70 mg kg^{-1} in the proximal sediments at Augusta. The Hg vs depth profiles show a clear increase in concentration with decreasing depth. By normalizing to Al concentrations as proxy for detrital (aluminosilicate) sediment content, relative enrichments or depletions of an element can be assessed minimizing the impact of variable carbonate content or varying grain-size (Horovitz, 1991; Sharma et al., 1994; Carral et al., 1995; Daskalakis and O'Connor, 1995). 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 carbonate component at the station BX1, Hg/Al profiles emphasize different compositions at the two stations of Augusta. Normalization of total Hg concentration to TOC content for the box-core BX2 (from Augusta) and BC12 (from Palermo) indicates that the increase in Hg with decreasing core depth is not merely an artefact of changing TOC content, at least up to 5–6 cm depth (Fig. 4), despite the strong correlation between Hg and TOC ($r=0.86$ for BX2; $r=0.81$ for BC12).

The enrichment factor (EF) of mercury in the sediments investigated was calculated as "$[Hg_{(sample)}]/[Hg_{(background)}]$", using the background value (Hg = 0.038 mg kg^{-1}) estimated by Di Leonardo et al. (2006) for sediments from the Strait of Sicily applying the method of maximum likelihood of lognormal distribution parameter to sediments older than 1920. The EF vs age profiles shown in Fig. 5 illustrate the significant enrichment of Hg in these cores. Hg is enriched by more than 30 times (median value = 26) in the Augusta proximal box-core (station BX1), whereas the other box-cores display lower but still strongly elevated EF values, with a median value of 12 and 14 in cores BX2 (Augusta) and BC12 (Palermo), respectively. The mercury EFs begin to increase, taking into account errors on the core dating, from ca. 1940 to 1950 and ca. 1920 to 1930 in the Augusta and the Palermo areas, respectively, and indicate increasing Hg contamination over time due to development of the industrial and port area at Augusta and increased urbanization in Palermo.

Except for sediments from the lower parts of the cores, mercury concentrations exceed the limits indicated both by international and national regulatory guidelines (Ligero et al., 2002; G.U.R.I., D.M. 367/03, 2004), and therefore these sediments can be considered as significantly contaminated (Fig. 4). Mercury concentrations in the samples studied also exceed the eco-toxicological

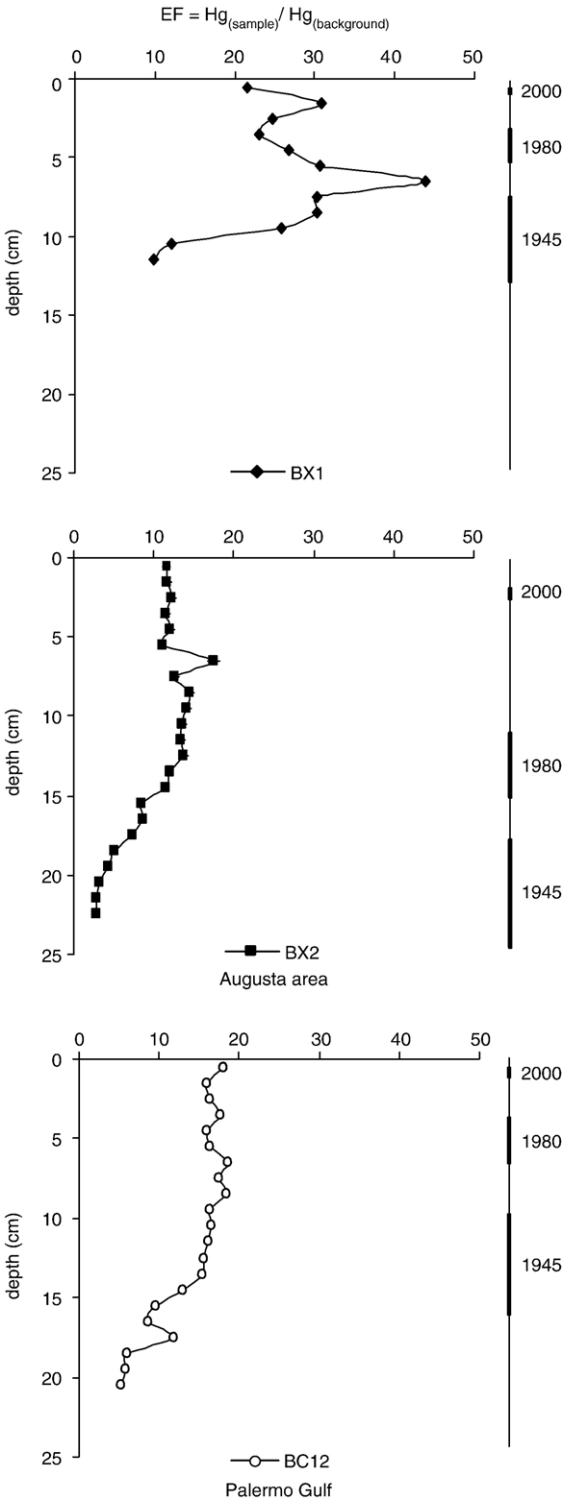


Fig. 5. Hg enrichment factor (EF) vs depth in the box-cores studied. Chronology derived from ^{210}Pb dating as in Fig. 3.

screening values used by the North American Sediment Quality Guidelines to quantify the polluting effect of marine sediments (SQG; Long et al., 1995). These limits, called Effects Range Low (ERL; Long and Morgan, 1990) and Effects Range Medium (ERM), correspond to mercury concentrations of 0.15 and 0.71 mg kg^{-1}, respectively. At both the Palermo and Augusta stations, the nearshore mercury concentrations exceed the ERL value and, in the case of the box-core BX1, the ERM (Fig. 4), thus indicating a degree of Hg contamination that may be detrimental to benthic fauna (and other marine biota).

4.4. Distribution of total PAHs

Total PAH concentrations vary from 0.1 to 1.6 mg kg^{-1}(mean value: 0.7 mg kg^{-1}) in the Augusta sediments and from 2.3 to 29.3 mg kg^{-1} (mean value: 16.6 mg kg^{-1}) at the Palermo station (Fig. 6). After normalization to Al, the PAHs/Al depth profile for the carbonate-rich, sand-sized sediments of core BX1 shifts close to that of core BX2. As expected, the more abundant mud-sized fraction of BX2 tends to accumulate higher amounts of PAHs. The PAHs/TOC depth profile confirms the pattern of spatial and temporal variability of PAHs in the areas studied (Fig. 6). PAHs are significantly associated with TOC in the core BC12 ($r=0.75$) whereas there is no significant correlation between PAHs and TOC in the box-core BX2.

In terms of PAH composition, six PAHs (naphthalene, phenanthrene, fluoranthene, pyrene, benzo(a) anthracene, and chrysene) are present at all sampling sites. The 2-ring average PAH content was 3% of the total PAHs (Fig. 7). The PAHs present are dominated by 3-ring (5–30%), 4-ring (40–62%), and 5-ring (2–33%) aromatic hydrocarbons. 6-ring PAHs were below the detection limit (<0.003 mg kg^{-1}) in sediments from cores BX1 and BX2. PAHs with high molecular masses

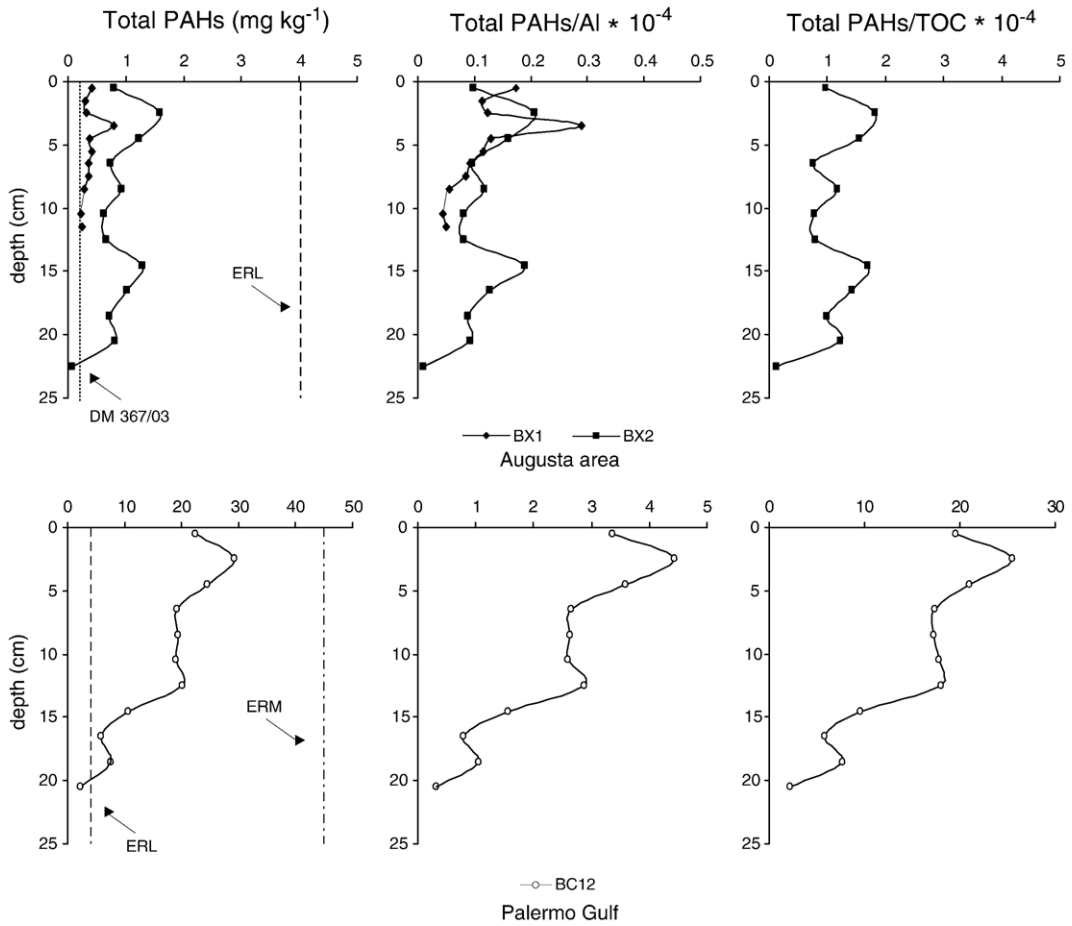


Fig. 6. PAHs concentration, PAHs/Al, and PAHs/TOC ratios vs depth in the box-cores studied. ERL and ERM values (Long and Morgan, 1990) and concentration limits specified in Italian regulatory guidelines (G.U.R.I., D.M. 367/03, 2004) are given.

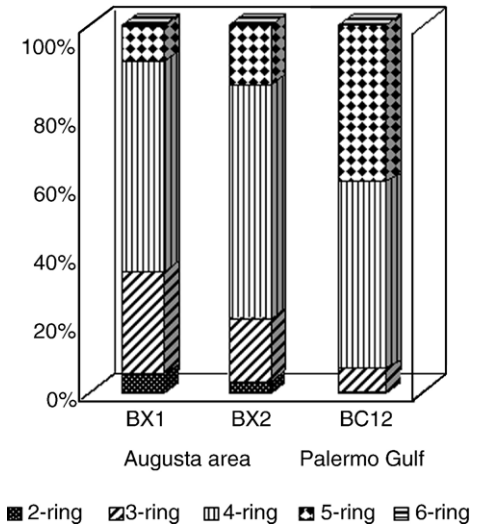


Fig. 7. PAH molecular profiles for the box-cores studied.

(4–6 rings) are generally of pyrogenic origin (Frignani et al., 2003; Bihari et al., 2006). For the areas studied, PAH distribution patterns (2- to 6-ring PAHs) are consistent with a dominantly pyrogenic origin due to the prevalence of 3- and 4-ring PAHs (>67% at all sampling sites) in the Augusta samples and 4- and 5-ring PAHs (>71%) in the Palermo samples. Enrichment of 4-ring PAHs in proximal sediments from Augusta (62% for BX1, and 67% for BX2) indicates significant inputs of PAHs from diesel fuel usage (Prahl and Carpenter, 1983), probably due to the intense harbour traffic in this area.

Similar to studies in the Gulf of Trieste, North Adriatic (Notar et al., 2001), samples from the core BX1 (Augusta area) are considered fairly contaminated (total PAHs in the range 0.250 to 0.500 mg kg^{-1}), whereas sediments from the box-core BX2 (Augusta area) and BC12 (Palermo Gulf) are classified as highly

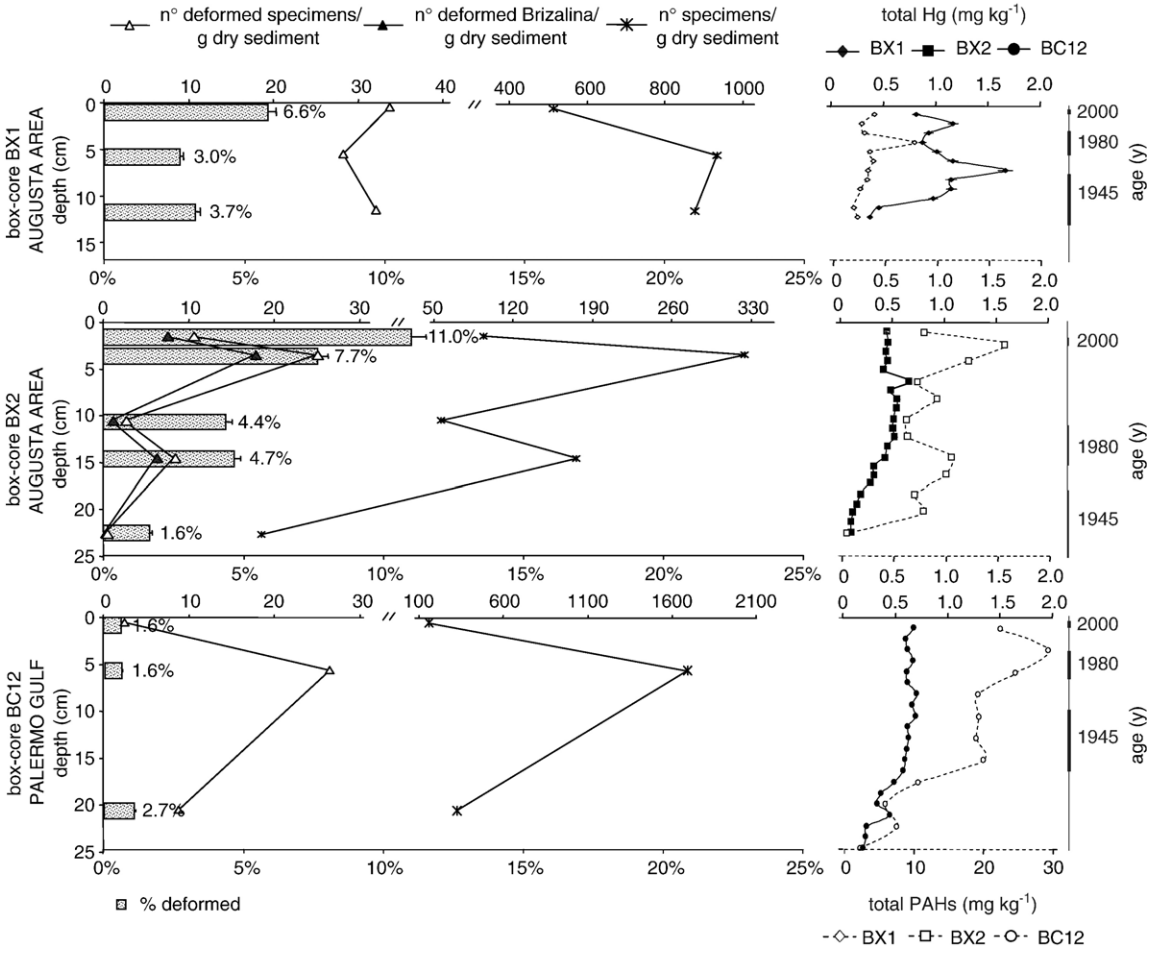
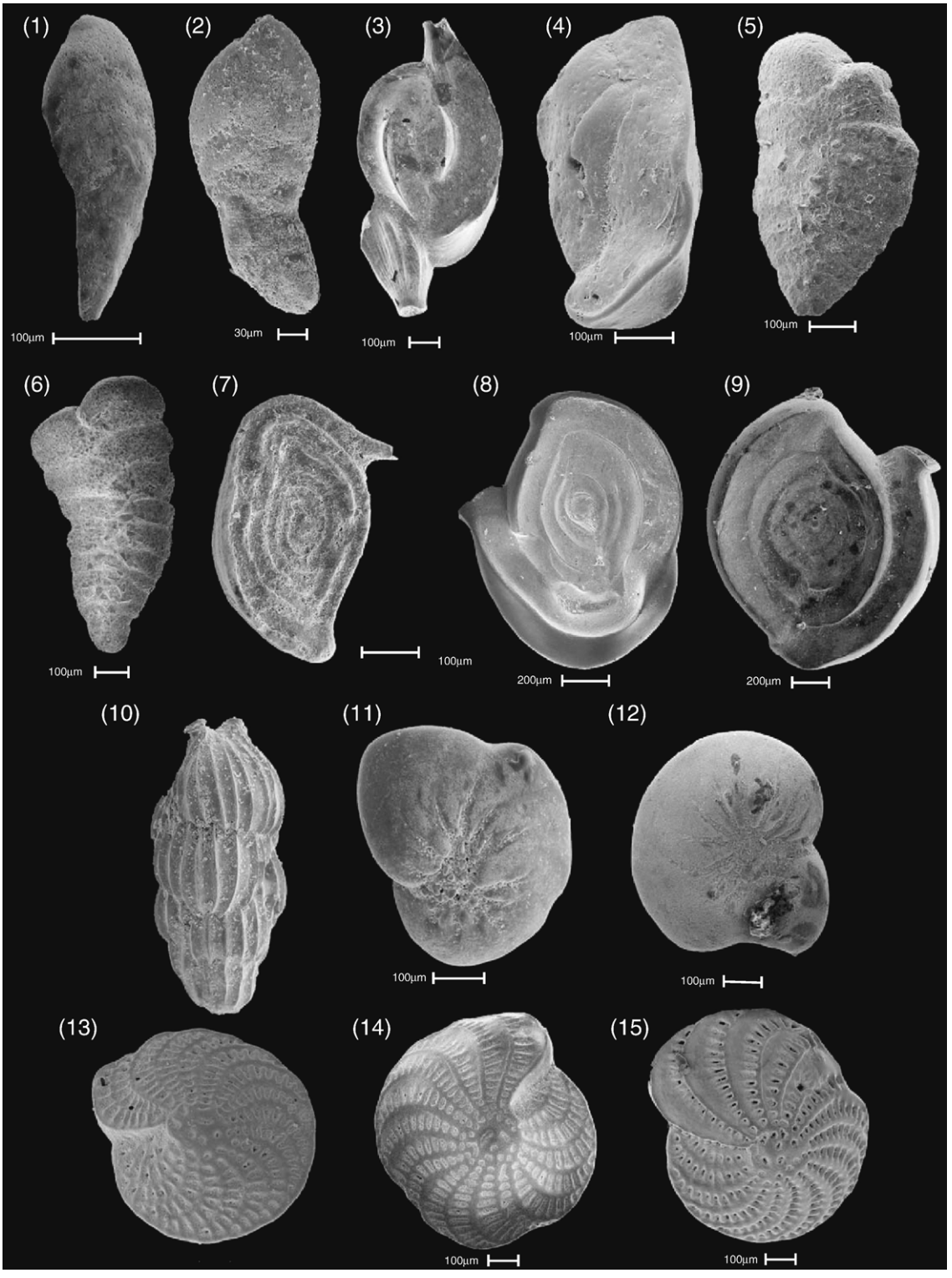


Fig. 8. Number of benthic foraminiferal specimens (asterisks), deformed specimens (open triangles) and deformed *Brizalina* specimens per gram of dry sediment (full triangles), % deformed taxa (dotted bars), total Hg (full symbols, solid lines), total PAHs (open symbols, dashed lines) vs depth for Augusta and Palermo cores. Chronology derived from ^{210}Pb dating as in Fig. 3.

contaminated (total PAH concentrations exceeding 0.500 mg kg^{-1}). The PAH concentrations found in the box-core BC12 (Palermo Gulf) and in the box-core BX2 (Augusta area) are significantly higher than those reported for other Mediterranean areas (0.0002–0.797 mg kg^{-1}; UNEP, 1996; 0.7 mg kg^{-1}; Romano



et al., 1998). Only the proximal sediments from the Augusta area (BX1) show PAH values comparable to those previously measured in other studies. All PAH values in this core exceed the national guideline limit (G.U.R.I., D.M. 367/03, 2004: 0.200 mg kg^{-1}) but are slightly less than the ERL (4.022 mg kg^{-1}; Long et al., 1995). Core BC12 also displays a clear trend of increasing PAH concentration towards the top of the core, with values ranging between the ERL and the ERM (Total PAHs: 44.792 mg kg^{-1}; Long et al., 1995) (Fig. 6). Pyrene and benzo[a]anthracene concentrations exceed their respective ERM values in the upper layers of the core BC12, possibly as a consequence of dumping of contaminated material, urban and sewage runoff, or oil terminal discharges.

4.5. Benthic foraminiferal assemblage and distribution

The foraminiferal assemblages of the investigated box-cores are composed almost entirely of benthic species. Foraminiferal tests are, in general, abundant and well preserved with no signs of carbonate dissolution or pyritization. The principal families present are Anomalinidae, Bolivinitidae, Buliminidae, Elphidiidae, Haueriniidae, Miliolidae, and Nonionidae. Planktonic foraminifera are rare due to the shallow water (depth < 145 m) of the investigated sites. Foraminiferal data expressed as number of benthic foraminiferal tests and benthic abnormal tests per gram of dry sediment and as percentages of benthic abnormal tests in each station are presented in Fig. 8.

Morphological deformities such as abnormal growth, twisted or distorted chamber arrangement, compressed tests, protruding chambers, aberrant chamber shape and size, wrong direction of coiling, additional chambers, and overdeveloped chambers have been observed on different specimens, sometimes accumulating more than one abnormality (Fig. 9). Although deformed tests have been found in areas subjected to natural environmental stresses, such as changes in salinity (Braiser, 1975; Scott and Medioli, 1980) and in trophic levels (Murray, 1963), foraminiferal deformities similar to those observed in our dataset have been described by Samir and El-Din (2001) for sediments of the Alexandria coast (Egypt) and interpreted as expression of sensitivity benthic foraminifera to high levels of heavy metals in the area.

The benthic foraminiferal assemblages at the station BX1 (from Augusta) are abundant and relatively similar throughout the box-core. The microfauna is composed by *Textularia* sp., *Eponides* sp., *Rectouvigerina* sp., *Elphidium* sp., *Bigenerina nodosaria*, *Lobatula lobatula*, *Lagena* sp. and characterized by the presence of large miliolid taxa (e.g. *Quinqueloculina* spp., *Quinqueloculina seminulum*, *Triloculina tricarinata*) (>300 μm).

The number of individuals per gram of dry sediment exhibits low values at the top of the core, ranging from 514 at 0–1 cm depth to 932 at 5–6 cm depth, with an average of 774. In total ~110,000 foraminiferal tests were counted in the 3 analysed samples. In all samples there are deformed foraminifera, at a frequency of ca. 30 specimens/g dry sediment, with a slightly higher value in the upper sediment layer (33 specimens/g dry sediment at 0–1 cm depth). The percentage of deformed benthic tests ranges between 3 and 6.6%, with the highest value in the upper sediment layer (0–1 cm depth). The most common deformed specimens are constituted by large Miliolids (>300 μm), with a distorted chamber arrangement, abnormal growth of the final chamber and double apertures (Fig. 9: 3–4, 7–9). Miliolids have been shown to be related to abundant supply of organic matter from the water column to the sediment and highly sensitive to pollution (Samir and El-Din, 2001; Rao and Rao, 1979). In particular, *Triloculina* sp. is thought to be very adaptable to ecological changes and opportunistic in coastal regions affected by stressed environment conditions caused by anthropogenic pollution (Yanko et al., 1994, 1999).

The benthic foraminiferal microfauna found in the box-core BX2 (from Augusta) is principally represented by *Brizalina* spp. (from 22 to 38% of benthic assemblages) and by *Cassidulina neocarinata* (around 30% of benthic assemblages) with the presence of *Valvulineria bradyana*, *Nonionella turgida*, *Bulimina marginata*, *Florilus* sp., and Miliolids. The number of benthic foraminifera vary irregularly in this core, exhibiting generally low values ranging from 14 to 325 individuals/g dry sediment (average 133 individuals/g). At the top of the core the number of benthic foraminifera/g is slightly more elevated than at the bottom portion, probably due to a co-occurrence of individuals belonging to *Brizalina* spp. and *C. neocarinata*,

Fig. 9. Examples of test deformities in benthic Foraminifera from Augusta and Palermo box-core sediments, central Mediterranean. 1) *Brizalina spathulata*, and 2) *Brizalina* sp. (core BX2) specimens with twisted chamber arrangement and abnormal growth; 3)–4) Deformed test of Miliolids (core BX1) with double aperture and aberrant chamber shape; 5) *Textularia* sp.1 and 6) *Textularia* sp.2 (core BX1) specimens with irregular growth of test; 7) *Spiroloculina depressa* (d'Orbigny), and 8)–9) *Spiroloculina excavata* (d'Orbigny) (core BX1) specimens with abnormal growth of the final chamber; 10) *Uvigerina peregrina* (core BX2), specimen with double aperture; 11)–12) *Nonion fabum* deformed specimen with anomalous protuberances; 13)–14)–15)-*Elphidium crispum* specimens with aberrant shape of the chambers and aperture.

both opportunistic species that together represented 52–68% of the assemblage. In total ~9964 foraminiferal tests were counted in the five samples examined. An increasing occurrence of abnormal tests from the bottom to the top of the core is evident, with values ranging from about 0.2 to 10.3 specimens/g dry sediment and percentages between 1.6 and 11.0%.

The dominant aberrant taxon found in the box-core BX2 is *Brizalina* spp. (Fig. 9: 1–2). *Brizalina* spp., taxa with an infaunal microhabitat, has great tolerance of pollution induced stress and is particularly resistant to oxygen-depleted environments (Murray, 1991; Cearreta et al., 2000; Schmiedl et al., 2003). Specimens from this group show various types of deformity, mainly represented by the distorted axial elongation. The percentages of abnormal *Brizalina* spp. tests increase at the top of the core.

The box-core BC12 (from Palermo) shows a more diversified foraminiferal microfauna compared to those found in the box-cores from Augusta. An interesting feature of this core is the dominance of juvenile and dwarf forms, which is a typical feature of environmental stress (Samir and El-Din, 2001). The foraminiferal assemblage is composed by *Brizalina alata*, *Bolivina punctata*, *B. marginata*, *C. neocarinata*, *C. crassa*, *C. globosa*, *Epistominella vitrea*, *Hanzawaia boueana*, *Hyalinea balthica*, *Melonis* sp., *Uvigerina mediterranea*, *U. peregrina*, and *V. bradyana*. This assemblage is closely associated with middle-outer shelf and has been documented in environments subjected to periodic anoxia and with high organic matter concentration (Murray, 1991; van der Zwaan et al., 1999; Donnici and Serandrei Barbero, 2002: Mendes et al., 2004). In general, the box-core BC12 displays a high concentration of tests (average 721 individuals/g), although concentration values are extremely variable (ranging from 154 at 0–1 cm to 1690 individuals/g at 5–6 cm) (Fig. 8). In total ~40,000 benthic foraminiferal tests were found in the three samples analysed. In the Palermo Gulf, percentages of deformed foraminiferal tests are low, ranging between 1.6 and 2.7%.

4.6. Geochemical and eco-toxicological comparative evaluations

A comparison of the Hg and PAHs profiles for the Augusta stations with the percentages of observed foraminiferal test deformations and population density (Fig. 8) highlights some broad similarities between a "chemical/pollutant" trend and a "biological" trend. Upwards in the cores, there are increasing concentrations of total Hg and total PAHs, an increase in morphological deformities and, at least for the core BX1, a lowering of population density. Moreover, in the absence of an upward decrease of population density, core BX2 exhibits an upward increase of Brizalina that is inferred to be an opportunistic pollution-tolerant taxa. The comparison of chemical and biological patterns seems to indicate that environmental pollution acts as a limiting factor on population density and microfauna composition, this in agreement with Schafer (1973) and Samir and El-Din (2001). This relationship is less evident if the patterns obtained for the Palermo area are compared (Fig. 8).

The Augusta coastal area receives significant discharges of heavy metals from the adjacent industrial areas (particularly, from a number of chlor-alkali plants established in the 1950s). In contrast, the Palermo Gulf seems to be less affected by industrial pollution, but receives significantly more harbour and urban wastes.

The composite results obtained from geochemical and microfaunal proxies clearly show that environmental conditions have been degrading over time in both areas. The presence of a large number of complex environmental variables at each site, however, means that it is difficult to establish an unequivocal cause for the distribution trend found in benthic foraminiferal assemblages (in terms of diversity and density) and for the occurrence of morphological abnormalities. In particular, it is difficult to separate the detrimental effects caused by anthropogenic (pollutant) inputs from those caused by natural environmental changes. However, as far it is known, extreme variations in salinity (hyposalinity or hypersalinity) or in oxygen content or strong hydrodynamics (Geslin et al., 2002) did not affect the studied areas over recent time. Moreover, the geochemical approach used for assessing marine pollution in the Augusta and Palermo areas permitted to well discriminate the pre-industrial environment from the recent settings, and to evaluate the historical contaminant impacts on marine ecosystem. Bearing in mind this reasoning, it is still instructive to compare the foraminiferal depth distribution with the history of pollution in these sediments recorded in terms of total Hg and total PAH contamination.

Despite the consistent anthropogenic chemical input into the Gulf of Palermo, fewer morphological test deformations are found in the foraminiferal assemblage of box-core BC12, and it is not possible to discriminate anthropogenic effects from natural variability. Vondraček et al. (2001) found sediments containing concentrations of PAH <10 mg kg^{-1} to be mutagenic. On this basis, sediments of the Palermo station, which contain PAH concentrations more than double this value, should have a high toxic/genotoxic potential. Notably, the foraminiferal community is dominated, principally in the

sample at 5–6 cm depth, by juvenile and dwarf forms, which are commonly bioindicators of environmental stress (Samir and El-Din, 2001). The elevated TOC content measured in this core, together with the good correlation of TOC with total Hg and PAH concentrations, could explain a moderate impact of pollution on foraminiferal population. Owing to the strong affiliation of most of organic and inorganic contaminants to organic particles, enhanced preservation of organic matter might have reduced contaminant bioavailability in these sediments.

In general, while Hg and PAH concentrations, which frequently exceed regulatory and eco-toxicological screening guidelines, could be responsible for the observed foraminiferal test abnormalities, other contaminants present (e.g. other trace metals or persistent organic pollutants) could have an additive or indeed greater effect, and so the individual and additive effects of different contaminants need to be examined. In addition, many pollutants are strongly associated with the fine particulate and organic fraction of marine sediments; the proximal sediments from the Augusta area, being mainly composed of coarse-grained material, could have scavenged only a limited portion of the total mercury and the total PAHs really available in the marine environment, indicating that the main contaminant sink areas may lie elsewhere.

5. Conclusion

Geochemical and micropaleontological analyses performed on three sedimentary sequences deposited after 1940 in the Augusta area and after 1920 in the Palermo area show clear evidence of increasing environmental stress over recent decades. In the Augusta area, high Hg concentrations and moderate, and still potentially toxic, PAH concentrations appear to correlate with a decrease of density, an increase of opportunistic or tolerant species and a significant incidence of various morphological abnormalities in the foraminifera tests. Miliolids and Brizalina compose the most common deformed taxa, showing to be very sensitive to pollution.

Notably, the response of benthic fauna to environmental stress (as expressed by a modification in the benthic foraminiferal assemblage) is evident even at offshore sites, some considerable distance away from effluent sources.

In the Palermo area, PAH concentrations are sufficiently high to classify sediments as having a high toxic/genotoxic potential but, notably, no significant impact on the foraminiferal population was observed, except for the presence of juvenile and dwarf forms, possibly due to locally reduced contaminant bioavailability.

Although this paper concerns a limited set of contaminants over the possible range of known pollutants, the results confirm that benthic foraminifera in this region may be sensitive and relatively low cost bioindicators of human-induced environmental changes and form the basis for future investigations directed at understanding the different foraminiferal adaptations to anthropogenic stress in natural Mediterranean ecosystems.

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