Toxicology and Industrial Health 2009; **25:** 351–363
http://tih.sagepub.com

Assessment of environmental pollutants in ten southern Italy harbor sediments

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In 2003–2006, the distribution of macronutrients and pollutants of environmental interest was investigated in surficial sediments collected from 10 southern Italy harbors selected in four different regions. About 167 stations were sampled to determine levels of total organic carbon, total nitrogen, total phosphorous, trace elements (Al, Cd, Pb, Ni, Cr, Cu, Zn, Hg, As), short- and long-chain aliphatic hydrocarbons (*Hy* C > 12 and *Hy* C < 12), and concentrations of persistent organic pollutants (polychlorinated biphenyls, polycyclic aromatic hydrocarbons [PAHs], p-p-Dichlorodiphenyldichloroethylene (*4,4′*-DDE), and Hexachlorobenzene (HCB). General relationships between studied variables and harbors systems were explored by multivariate statistical approaches. Results show that wide fluctuations are reported for all variables both among harbors and inside each studied system. Principal components analysis suggests that major significance in explaining total average variability is due to lead, copper, zinc, silts, sands, and PAHs. No significance has been observed when testing nonmetric multidimensional scaling distributions relating with the factor "region," while performing analyses on factor "main human activity," a higher significance is observed. These results suggest a strong relationship between the main human use of marine systems and observed pollution levels in sediments. *Toxicology and Industrial Health* 2009; **25**: 351–363.

Key words: *harbor pollution; Mediterranean Sea; POPs; sediment quality assessment; trace elements*

Introduction

Harbors represent key structures of great economical and social importance in coastal areas (Bortone, *et al*., 2004), and it is expected that in the next decades, they will show a great increase both in number and dimensions because of changes in business practices to world level and related to the development of commerce globalization (UN ESCAP, 2002). Because of the growing presence of impacting human activities, ecosystems of harbors are frequently stressed by high levels of pollution (Ausili, *et al*., 1998). Industry, commerce, tourism, and urbanization represent both direct and indirect sources of macronutrients, trace elements, aliphatic compounds, aromatic hydrocarbons, and xenobiotics (Kralik, *et al*., 2007; Renzi, *et al*., 2009). These pollutants could be directly discharged in harbor water or could be transported by rain-off and leaching phenomena. The toxicological effects of such substances on adults (Corsi, *et al*., 2003; McCarthy, *et al*., 2004), juvenile phases or early life stages

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10.1177/0748233709104868

(Volpi-Ghirardini, *et al.*, 2001; Gopalakrishnan, *et al.*, 2006), and gametes and embryos (Arizzi-Novelli, *et al.*, 2002) are well documented by the scientific literature on marine species. Moreover, the bioconcentration (Ritcher and Nagel, 2007), bioaccumulation (Mackay and Fraser, 2000), and biomagnification (Focardi, *et al.*, 1983, 1996; Corsolini, *et al.*, 1995, 2000) properties of some of these molecules and their related toxicological effects on algae (Meriç, *et al.*, 2005), invertebrates (Gopalakrishnan, *et al.*, 2008; Meriläinen and Oikari, 2008), and vertebrates (Calevro, *et al.*, 1998; Shahidul Islam and Tanaka, 2004) are also well known. Even if part of the discharged molecules can be diluted and dispersed by water exchanges between harbors and the marine system, nevertheless, a great part of them tends to be adsorbed and accumulated to the particulate organic matter and suspended solids, which are present in water column (Sternbeck and Ostlund, 2001). Because of their structure, characterized by scarce circulation of water and large terrestrial and urban inputs, harbors show high sedimentation rates of finer particles (Sprovieri, *et al.*, 2007), which, accumulating on bottoms, determine the increase of macronutrients (Herut and Sandler, 2006), trace elements (El Nemr, *et al.*, 2007; Suntornvongsagul, *et al.*, 2007), and xenobiotics (Sun, *et al.*, 2003; Chefetz, *et al.*, 2004) in sediments.

For these reasons, the characterization of surficial harbor sediments represents a procedure useful to define global pollution levels, to describe and map pollutant distribution inside harbor basins, and to localize unknown pollution sources. Obtained information could be used to plan management strategies or to control polluted sediment's resuspension and related ecotoxicological effects on marine species (Calevro, *et al.*, 1998; Birch and Taylor, 2002; Erftemeijer and Lewis, 2006; Gopalakrishnan, *et al.*, 2008) during dredging procedures.

Even if literatures have been produced to assess distribution in harbor sediments of some pollutants (Ausili, *et al.*, 1998; Fortune, 2006), few papers have analyzed relationships among a great number of molecules spread from different sources. Based on a large number of field data, the aim of this study was to assess surficial sediment pollution in 10 southern Italy harbors and to analyze, on multivariate statistical bases, relationships both among studied variables and among harbors related to different main human pollution sources and activities.

Methods

Study areas

In this study, we selected 10 harbors in four different regions of the southern Italy (Apulia, Lazio, Calabria, and Sicily) characterized by different environmental and economical conditions (Table 1). We selected at least two harbors from each region exception made for Apulia in which four harbors were sampled. In Table 2, some general information about studied harbors is summarized (i.e., region of locations, sea name, year of sampling, main human activities, and basin dimensions). In Apulia region, all selected harbors are sited on the Adriatic coast, while in Calabria region, Crotone and Vibo Marina are located, respectively, on Ionic and Tyrrhenian coasts.

Samplings

Surficial sediment samples (0–10 cm) were collected between 2003 and 2006 in 167 georeferenced

Table 1. Main characteristics of the four southern Italy regions selected in this study

Region	Surface (km^2)	Coastal extension (km)	Inhabitants ($Inh.km^{-2}$)	Economical resource of coastal areas	Coast characteristics
Apulia	19,358	784	210.6	Tourism, fishery, industry	Cliffed coasts and sandy coastline. Prevalence of carbonate (calcite, dolomite) minerals
Lazio	17,203	≈300	322.7	Tourism, commerce	Sandy coastlines rich in carbonates
Calabria	15,082	802	133.1	Tourism, fishery, commerce	Granite and metamorphic rocks
Sicily	25,710	1013	195.1	Tourism, commerce, fishery	Mixed coastlines with metamorphic and calcareous rocks

Table 2. Main characteristics of selected harbors

Harbor	Region	Sea	Year	Spatial location	Main use of sampling areas	Harbor size	Sampled area size	Number sampling stations
Vieste	Apulia	Adriatic	2004	41°53′, 37 N; 16°10′, 79 E	Fishery, tourism	Small	Small	6
Bari	Apulia	Adriatic	2003	41°07′, 54 N; 16°52′, 80 E	Commerce	High	High	36
Brindisi[a]	Apulia	Adriatic	2003	40°39′, 56 N; 17°59′, 38 E	Industry	High	Small	13
Barletta	Apulia	Adriatic	2004	41°19′, 95 N; 16°17′, 52 E	Commerce	High	High	57
Civitavecchia[b]	Lazio	Tyrrhenian	2004	42°05′, 97 N; 11°46′, 32 E	Industry	Medium	Small	13
Scalo Matteuzzi	Lazio	Tyrrhenian	2004	42°05′, 97 N; 11°46′, 32 E	Tourism	Small	Small	6
Vibo Marina	Calabria	Tyrrhenian	2006	38°43′, 26 N; 16°07′, 80 E	Industry	Medium	Medium	15
Crotone	Calabria	Ionic	2003	39°05′, 74 N; 17°07′, 48 E	Commerce	Medium	Medium	11
Catania[c]	Sicily	Tyrrhenian	2003	37°29′, 16 N; 15°05′, 90 E	Fishery	High	Small	8
Cefalù	Sicily	Tyrrhenian	2004	38°02′, 12 N; 14°02′, 19 E	Tourism	Small	Small	2

[a]The harbor of Brindisi is divided into three parts: internal, medium, and external ones. We considered only external harbor.
[b]The Civitavecchia harbor is divided into two parts: internal and external. We sampled the external one.
[c]Catania “la Plaja”.

stations randomly distributed inside each harbor basin according to a square grid of about 100-m length, crossed with additive sampling stations positioned along transects located in correspondence of presumed pollution sources, sea–harbor channels, and inner areas. Because of their high surfaces, in the cases of Brindisi, Civitavecchia, and Catania harbors, we sampled only a little part with respect to the whole dimension of each basin. Particularly, we chosen to study the industrial areas of Brindisi and Civitavecchia and decided to collect samples only from the bench turned to the berth of the fishing-boats in Catania harbor (“la Plaja”). More details, concerning the extensions of sampled areas and the total number of sampling stations, are reported in Table 2. Samples were collected using an hydraulic *vibrocorer* equipped with a precleaned high-density polyethylene liner tube (Ø 10 cm), homogenized, and stored in darkness in Teflon bottles at +4 °C before analyses.

Physical analyses

Grain size was determined using a set of steel test sieves (DIN EN ISO 9001) of various diameters according to Shepard’s (1954) method. Collected data for each class of size were expressed as percentage dry weight (d.w.). Total amount of sands was calculated by the addition of the Udden-Wenthworth’s classes characterized by particle diameters between 63 μm and 2 mm dimensions, while silts (mud and clay) were reported as sum of particles with diameter <63 μm.

Quantification of macronutrients

Total organic carbon (TOC), total nitrogen (TN), and total phosphorous (TP) were measured in sediments after being air-dried and passed through a 2-mm steel sieve. TOC analyses were performed according to the titration Wilkley–Black method modified by Gaudette, *et al.* (1974), TN was quantified using a carbon, hydrogen, nitrogen, sulphur, oxigen, CHNS-O Elemental Analyser with a thermo-conductivity detector (PerkinElmer, mod. CHN/O 200, Waltham, Massachusetts 02451, USA) by direct total flash combustion (ICRAM, 2001), while TP determination was carried out according to Aspila, *et al.* (1976) by acid digestion and successively quantification using a spectrophotometer UV-vis (PerkinElmer, mod 6505 Uv-vis Spectrophotometer) after colorimetric reaction. Results were expressed as percentage d.w.

Quantification of trace elements

Trace elements were determined after mineralization with a mixture H_2O_2–HNO_3 in a microwave oven (Milestone, Shelton, Connecticut, mod. ETHOS D Microwave Labstation) according to EPA (1996a) Method 3051A. Aluminum (Al), cadmium (Cd), lead (Pb), nickel (Ni), chromium (Cr), and copper (Cu) determinations were performed by atomic absorption spectrometry with electrotermic atomization (GF-AAS) (PerkinElmer, mod. AAnalyst 700), while zinc (Zn) was determined by atomic absorption spectrometry with flame atomization (Flame-AAS) according to the US-EPA (1996d) 6010B and

US-EPA (1996e) 7010 methods. Mercury (Hg) and arsenic (As) were determined, respectively, by atomic absorption via cold vapor generation (CV-AAS) according to US-EPA (1996f) 7473 method and by atomic absorption after the hydride generation following US-EPA 7011 method. Analytical results were reported as milligrams per kilogram d.w.

Quantification of persistent organic pollutants

Total amounts of polychlorinated biphenyl (PCBs), HCB, *4,4′*-DDE, and polycyclic aromatic hydrocarbons (PAHs) were also determined in sediments of harbors. Samples were extracted (Accelerated solvent extractor, Dionex, Sunnyvale, USA, mod. ASE 200) according to US-EPA (1996b) 3545A method. Extracts were split into two aliquots; the first one was purified on multilayer silica columns and quantified by gas chromatography with a ^{63}Ni electron capture detector (ECD) detector (PerkinElmer, mod. Clarus 500) following the gas-chromatographic conditions reported in Mariottini, *et al.* (2007). In this study, weights of single PCB congeners were added and reported as total weight in nanograms per gram d.w. The other aliquot was purified on multilayer silica–alumina column, concentrated, and injected in high-performance liquid chromatography system (Waters, Milford Massachusetts, mod. 474 SFD and 996 PDA detectors) following the analytical method reported by Perra, *et al.* (2007) for the quantification of the 16 PAH molecules considered as major environmental pollutants by the US-EPA. Even in this case, results of single molecules were added and expressed as nanograms per gram d.w. of total PAHs.

Quantification of aliphatic hydrocarbons

Total concentration (nanograms per gram d.w.) of long-chain linear aliphatic hydrocarbons (*Hy* C > 12, C_{10}–C_{36}) was also evaluated in sediment samples as single congeners by extraction (Accelerated solvent extractor, Dionex, mod. ASE 200) with a n-hexane solution [US-EPA (1996b) 3545A], purification on multilayer florisil columns, and quantification by gas chromatography (PerkinElmer, mod. Clarus 500, FID detector) according to US-EPA (1996g) 8015B method. We performed analyses using a SPB-5 (Supelco, Bellefonte, Pennsylvania, USA,) chromatographic column (0.25-μm film thickness, Ø 0.2 mm, 30-m length) and the following temperature program: 45 °C (held for 3 min) to 275 °C at 12 °C min^{-1} (held for 12 min). Flame ionization detector (FID) temperature was 280 °C, and carrier gas He was fluxed at 3 mL min^{-1}. Total concentrations (nanograms per gram d.w.) of linear short-chain aliphatic hydrocarbons (*Hy* C < 12, C_5–C_{12}) were also evaluated in sediment samples by Head-Space static extraction (PerkinElmer, mod. Turbomatrix40) performed following the US-EPA (1996c) 5021 method and successively direct injection in a gas chromatograph system (PerkinElmer, mod. AutosystemA) equipped with a FID detector [US-EPA (1996h) 8021B].

Quality assurance and quality control

Chemicals and reagents were analytical grade, and glassware was carefully washed to avoid sample cross-over contamination. Recoveries and reproducibility were checked by analyzing procedural blanks and reference materials purchased from National Institute of Standard and Technologies (NIST – NewJork waterway Sediment *SRM1944*; Estuarine Sediment *SRM1646a*) and Institute of Environmental Chemistry Academy Sinica, Beijing, China (*Tibet soil*). Analytical blanks were prepared prior to test samples using the same analytical procedures. A solvent or matrix blank was analyzed for every 15 samples to check the response of detection instruments. Standard reference materials were analyzed in statistical replicates (n = 10) to calculate averages and standard deviation (SD) of recoveries. Measured average recoveries for macronutrients were the follows: TOC 101.4% (0.33% SD, *SRM1944*), TN 94.4% (0.005% SD, *Tibet soil*), and TP 98.9% (3.30% SD, *SRM1646a*). Recoveries of trace elements (Al, Cd, Pb, Ni, Cr, Cu, Zn, Hg, and As) were checked testing the SRM *harbor sediment* purchased from the Department of Trade Industry as a part of the National Measurement System of the United Kingdom. Average percentages of recoveries for all tested trace elements were within 75.5–103.0% range of variation. Total PCBs, PAHs, *Hy* C > 12, and *Hy* C < 12 recoveries were also measured, and averages recorded were, respectively, of 94.5% (2.4% SD, *SRM1944*), 82.5% (0.12% SD, *SRM1944*), 87.0% (1.5% SD, *CRM560*, Ultra Scientific), and 83.0% (3.4% SD, internal standard addition). Analytical concentrations were not recovery corrected. Limit of quantification (LOQ) was calculated for the adopted procedures and was of 0.01% for TOC, 0.01% for TN, 0.001% for TP. For trace elements, the LOQs were 1000 mg kg^{-1} (Al), 0.05 mg kg^{-1} (Cd), 0.1 mg kg^{-1} (Pb, Zn), 0.01 mg kg^{-1} (Ni, Cu, Hg), 0.5 mg kg^{-1} (Cr, As), while LOQs for PCBs, HCB, *4,4′*-DDE, PAHs, *Hy* C > 12, and *Hy* C < 12 were, respectively, of 0.01, 0.001, 0.001, 0.1, 25, and 1 ng g^{-1}.

Statistical analyses

Univariate basic statistics (averages, SD, maximum, minimum) were performed for all studied variables using Statistica 7.1 (StatSoft Italia srl, Padova, Italy). Pearson's correlation matrix (1894) results ($P < 0.05$, $n = 167$) and 2D scatter plots were also calculated. Multivariate analyses were developed with the Primer-E Software package v6.0 (Plymouth Marine Laboratory, Plymouth, UK) according to Clarke and Warwick (2001). Euclidean distance resemblance matrices were calculated after square root and $\log(x + 1)$ functions transformation and normalization of field data (Clarke and Green, 1988). Principal component analyses (PCAs) were applied to investigate correlations and similarities between variables (Chatfield and Collins, 1980). Because of PCA weakness in its distance-preserving properties, we also performed nonmetric multidimensional scaling (nMDS) ordinations applying the Kruskal stress formula 1 and imposing the minimum stress level of 0.01. This technique shows a great flexibility both in definition and conversion of dissimilarities to distances preserving these relationships in a low-dimensional ordination space (Somerfield and Clarke, 1995). Obtained ordination significance was explored by the one-way ANOSIM test restarting the process 999 times.

Results

Basic statistics

In Table 3, basic statistic averages performed on collected data concerning grain-size and macronutrients characteristics are summarized. Grain-size averages show wide SDs (32.07%). Vieste, Cefalù, and Vibo Marina harbors are characterized by a high percentage of sands (over 90%) and low levels of silts (muds and clays). Small SDs calculated among sampling stations are recorded for these harbors (Vieste 1.5% SD, Cefalù 1.4% SD, and Vibo Marina 3.5%). Even if a clear dominance of sands is observed, Catania "la Plaja", Scalo Matteuzzi, and Civitavecchia basins are characterized by a high percentage of silts (higher than 25% d.w.). Brindisi sampled area (external) shows an average high percentage of sands (27.2% SD) with the presence of only one muddy sediment station. On the contrary, Bari and Barletta harbors are mainly characterized by the prevalence of silts. In Barletta and Crotone harbors, a marked spatial gradient from the inner areas (muddy) to the sea channels (sandy) is observed.

SDs of macronutrients are large and of 0.70% for TOC, 0.07% for TN, and 0.29% for TP. Concentrations of macronutrients range within LOQ and maximum values are reported as follows: TOC (0.01–2.51%) in Vieste, Brindisi, Vibo Marina–Bari; TN (0.01–0.45%) in Brindisi, Vieste, Scalo Matteuzzi, Civitavecchia–Barletta; TP (0.009–0.43%) in Cefalù–Barletta.

Pearson's correlation matrix ($P < 0.05$, $n = 167$) calculated for these parameters shows that TOC content was positively correlated to TN ($r = 0.26$, $P < 0.05$) but negatively related to TP ($r = -0.17$, $P < 0.05$). TP is, on the other hand, positively related to TN ($r = 0.44$, $P < 0.05$). All macronutrients were also positively related to silts (silts-TN, $r = 0.46$; silts-TOC, $r = 0.15$; silts-TP, $r = 0.46$) and negatively to sands. Statistical correlation between silts and TOC is shown in Figure 1. Macronutrient average patterns differ significantly in studied basins. A clear dominance of TOC in Crotone, Bari, and Barletta harbors is observed, while in Catania "la Plaja" average TN and TOC values are similar and in Vibo Marina stations TP concentrations are higher than others (Figure 2).

In Table 4, concentrations of trace elements are reported as average values. Al levels range from minimum values of 650 mg kg^{-1} in Brindisi harbor to 22,322 mg kg^{-1} measured in Barletta with a wide SD (15,021 mg kg^{-1}). Vibo Marina shows absolute minimum values for Cd (<0.01 mg kg^{-1}) and Pb (2.3 mg kg^{-1}), while Bari basin shows highest levels for Pb (109.3 mg kg^{-1}), Hg (1.44 mg kg^{-1}), Ni (88.08 mg kg^{-1}), and Zn

Table 3. Grain-size main structure of surficial sediments and macronutrients concentrations

Harbor	TOC	TN	TP	Silts	Sands
Vieste	0.31	0.07	0.024	2.5	97.5
Bari	1.77	0.15	0.068	72.3	27.7
Brindisi	0.22	0.03	0.025	13.5	86.5
Barletta	0.70	0.10	0.066	61.6	38.4
Civitavecchia	0.16	0.05	0.032	34.4	65.6
Scalo Matteuzzi	0.21	0.04	0.040	28.3	71.7
Vibo Marina	0.26	0.01	0.328	8.6	91.4
Crotone	1.21	0.17	0.039	45.2	54.8
Catania	0.21	0.15	0.046	25.8	74.3
Cefalù	0.42	0.04	0.011	1.5	98.5

TOC, total organic carbon; TN, total nitrogen; TP, total phosphorous.
Average data expressed as percentage d.w. TOC, TN, TP, and silts, sediment fraction characterized by a particle diameter <63 μm; sands, sediment fraction characterized by a particle diameter included between 2 mm and 63 μm.

(1131.0 mg kg^{-1}). Barletta shows higher levels for Cd (5.36 mg kg^{-1}), Cu (134.27 mg kg^{-1}), and Cr (89.9 mg kg^{-1}). Arsenic concentrations reached highest values in surficial sediments from Civitavecchia harbor (32.28 mg kg^{-1}). Trace elements show a high-positive correlation between each other and with silts. Higher correlations are reported for silts-Pb ($r = 0.52$), silts-Cu ($r = 0.64$), and silts-Zn ($r = 0.62$) couples.

In Table 5, basic statistics for persistent organic pollutants are reported. Collected data show a high variability both on spatial bases inside each basin and among studied harbors. PCBs higher values are related to Crotone (10.32 ng g^{-1} SD) and Barletta (9.54 ng g^{-1} SD) harbors, while Brindisi and Catania "la Plaja" show levels near the LOQ. HCB ranges from LOQ for Bari, Brindisi, and Catania "la Plaja" and absolute maximum value measured in Cefalù sediments (56.491 ng g^{-1}), while *4,4′*-DDE range is LOQ 245.920 ng g^{-1} in Brindisi, Civitavecchia, and Vibo Marina–Cefalù sediments. PAHs range from 1.0 ng g^{-1} d.w. (Cefalù) to 296.3 ng g^{-1} measured in Scalo Matteuzzi. Maximum levels of linear aliphatic hydrocarbons are measured in Vibo Marina (*Hy* C > 12: 7934 ng g^{-1}), which reports highest levels also for *Hy* C < 12 (422 ng g^{-1}). On average, PAHs show a significant positive Pearson's correlation matrix with Hg ($r = 0.68$), PCBs ($r = 0.73$), and *Hy* C > 12 ($r = 0.86$). Considering only results obtained for the Apulia harbors, a positive correlation between PAHs-sands ($r = 0.17$) and a significant negative relationship between PAH-As ($r = -0.14$) have been observed. On average, *Hy* C > 12 are negative related with TOC ($r = -0.13$) and As ($r = -0.13$), but positive related with PAHs ($r = 0.86$) and sands ($r = 0.18$). Considering all harbor sites, *Hy* C > 12 are positive related with TP ($r = 0.87$) and *Hy* C < 12 ($r = 0.83$), while *4,4′*-DDE and HCB show a trend that is not related to any other pollutants.

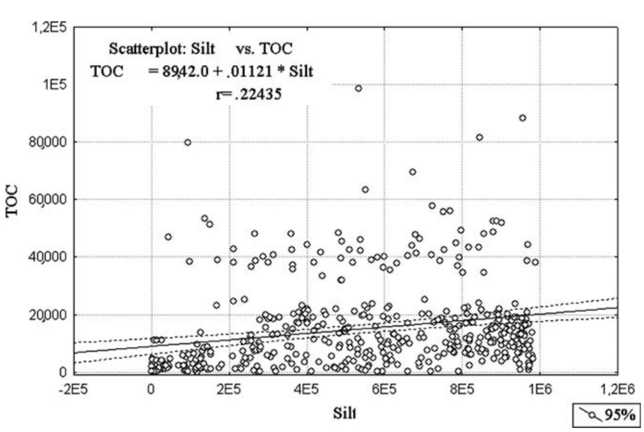

Figure 1 Total organic carbon (TOC)–silts linear regression (values reported as milligrams per kilogram d.w.).

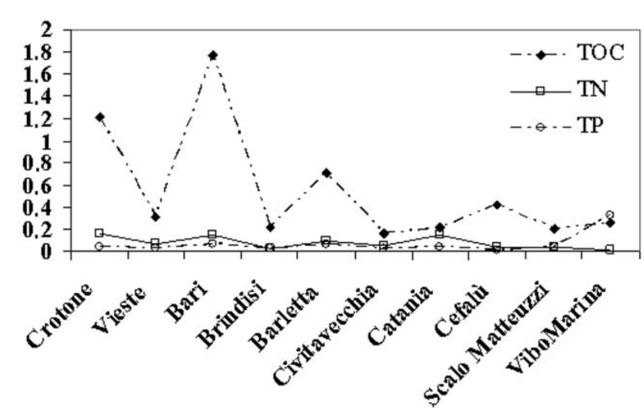

Figure 2 Average trends of macronutrients in surficial sediments. Values reported as percentages d.w. TOC, total organic carbon; TN, total nitrogen; TP, total phosphorous.

Table 4. Concentrations of trace elements in surficial sediments

Harbor	Hg	Cd	Pb	As	Cr	Cu	Ni	Zn	Al
Vieste	0.098	0.14	5.0	4.1	5.9	1.89	6.18	8.0	6,240
Bari	0.168	0.40	94.5	12.4	28.6	61.42	31.40	212.1	6,235
Brindisi	0.019	0.06	14.4	18.3	11.8	4.78	11.72	30.2	1,638
Barletta	0.089	0.29	31.9	10.0	38.1	36.18	30.72	109.2	20,907
Civitavecchia	0.162	0.15	10.1	24.1	31.4	14.07	26.86	47.9	16,936
Scalo Matteuzzi	X	0.09	13.9	20.9	26.4	14.42	20.55	64.7	6,397
Vibo Marina	0.011	<0.05	3.2	5.4	15.3	1.95	2.64	45.5	16,716
Crotone	X	X	X	X	X	X	X	X	X
Catania	0.009	0.07	7.0	9.4	13.9	9.07	31.29	65.2	7,470
Cefalù	0.100	<0.05	5.4	4.2	6.2	1.38	6.83	9.0	5,770

Hg, mercury; Cd, cadmium; Pb, lead; As, arsenic; Cr, chromium; Cu, copper; Ni, nickel; Zn, zinc; Al, aluminum; X, not measured.
Average data expressed as milligrams per kilogram d.w.

Multivariate analyses

Relationships of variables have been also explored by multivariate nMDS and cluster analyses; results are shown in Figure 3.

Results of PCA performed on transformed and normalized environmental data (Clarke and Green, 1988) are reported in Figure 4. The first three components (50.2, 18.9, and 10.7%) accounting for 79.8% of the total variance in surface sediment data. In Table 6, we reported the coefficients in the linear combinations of variables making up principal components (PCs) showing the correlations of first five axes. nMDS and cluster analyses have been also performed to explore harbor similarities (Figure 5). A region factor (RF) and a factor of main human activity (MHAF) were also considered to evaluate both significant differences among regions and/or the effect of tourism (T), commerce (C), industry (I), and fishery (F) on the distribution of environmental pollutants. Observed differences have been statistically verified by the one-way ANOSIM test. Results show for the RF, a Global R of 0.007, with a significance level of sample statistic of 48.1% and a number of permuted statistics greater than or equal to Global R of 202, while for the MHAF a Global R of 0.513, with a significance level of sample statistic of 5.1% and a number of permuted statistics greater than or equal to Global R of 43.

Discussion

Collected multivariate database shows a great variability both inside each single harbor basin and among harbors related with different pollution sources, water currents, and grain-size characteristics of different areas, which act as cofactors in

Table 5. Concentrations of persistent organic pollutants in surficial sediments

Harbor	PCBs	HCB	*4,4′*-DDE	PAHs	*Hy* C > 12	*Hy* C < 12
Vieste	0.31	0.045	0.015	7.8	154	X
Bari	2.56	<0.001	1.810	80.0	3870	X
Brindisi	0.07	<0.001	<0.001	28.0	1170	63
Barletta	24.45	0.530	8.408	71.8	84	X
Civitavecchia	X	X	<0.001	69.4	X	X
Scalo Matteuzzi	X	X	X	272.6	2800	X
Vibo Marina	0.24	0.040	0.053	1.9	7642	396
Crotone	58.20	X	X	55.0	X	X
Catania	0.15	<0.001	19.012	5.0	X	X
Cefalù	0.75	47.032	220.033	1.0	1	X

PCB, polychlorinated biphenyl; PAH, polycyclic aromatic hydrocarbons; X, not measured.
Average data expressed as nanograms per gram d.w. PCBs, total amount of Arochlor 1260; PAHs, total amount of the 16 PAHs molecules suggested by the US-EPA as priority.

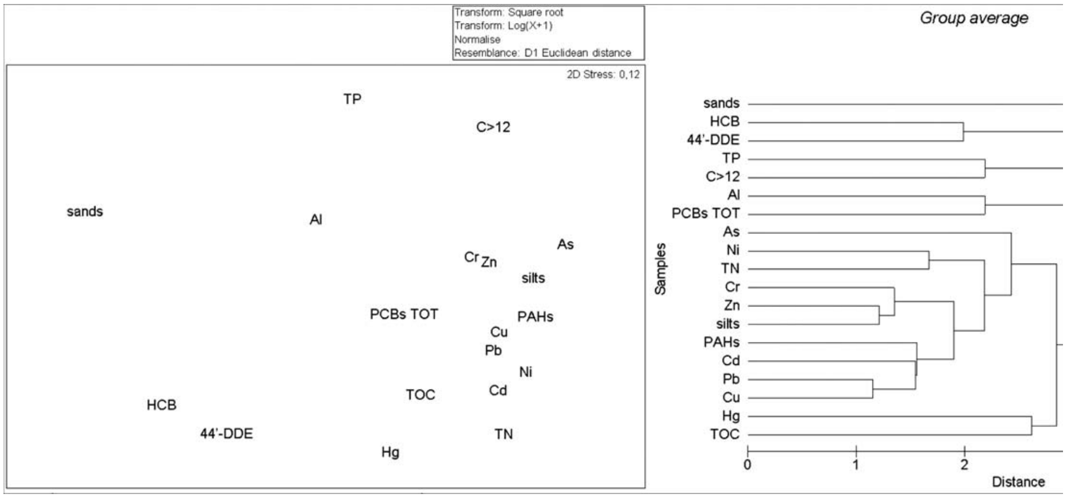

Figure 3 nMDS and cluster analyses performed on variables.

pollutant distribution. Few harbors (Barletta and Crotone) showed a strong gradient from inner to sea-channel stations.

Grain-size characteristics

The grain-size characteristics show little variability and a homogeneous distribution in Vieste, Brindisi (external area), Vibo Marina, and Cefalù, with a clear dominance of sandy bottoms in comparison to the silts. This is probably due to both the reduced presence of terrestrial and human sources of particulate in sampled areas (i.e., rivers, effluents of municipal waste water treatment plants) and a local hydrodynamics that reduce the sedimentation

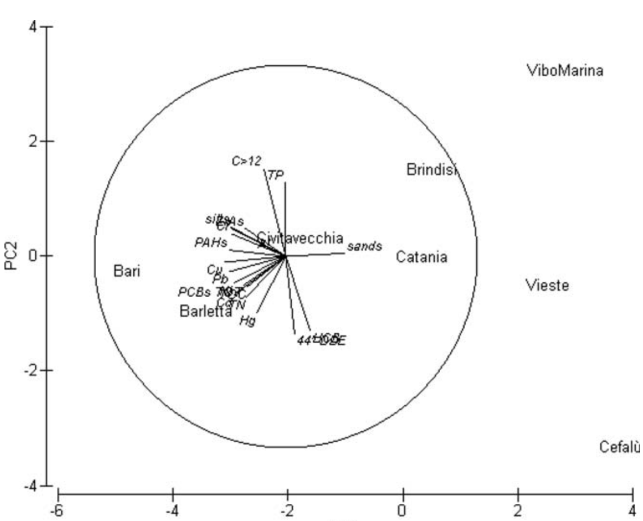

Figure 4 PCA results. Analysis performed on field data.

rates (Jensen and Mogensen, 2000). High percentages of small-size muddy-clay particles are observed in Bari and Barletta harbors due to high terrestrial and urban inputs observed in these basins, which represent a good trap for silt sedimentation.

Macronutrients

Concerning macronutrients, wide fluctuations are reported for all variables both among sampling stations and among harbors, partially because of the differences in sediment grain-size characteristics and the presence of local pollution sources. The effluents both of municipal waste water treatment plants and productive activities contribute, in facts, to increase concentrations of macronutrients in water and sediments (Lenzi, *et al.*, 1998; Renzi, *et al.*, 2009). Higher levels are generally observed for sediments richer in muddy and clay fractions because of silts affinity with macronutrients (Sprovieri, *et al.*, 2007), but also sandy stations characterized by high nutrient concentrations are recorded (TOC > 1.22%). Bari, Crotone, and Barletta levels are very close to values reported for meso-eutrophic Italian lagoon systems (Lenzi, *et al.*, 2003; Focardi, 2005; Renzi, *et al.*, 2006). It is interesting to observe that nutrients show different patterns of distribution in surficial sediments of studied harbors (Figure 2); furthermore, Pearson's correlation matrix results suggest the presence of significant positive correlations between TOC–TN and TN–TP couples but no significant relationships

Table 6. Eigenvectors (coefficients in the linear combinations of variables making up PCs)

Variable	PC1	PC2	PC3	PC4	PC5
Hg	−0.149	**−0.293**	0.088	0.249	−0.498
Cd	−0.273	−0.203	−0.130	0.034	−0.168
Pb	**−0.293**	−0.080	−0.093	−0.195	−0.181
As	−0.212	0.147	−0.241	0.382	0.188
Cr	**−0.283**	0.117	0.243	0.147	0.137
Cu	**−0.321**	−0.030	0.037	−0.071	0.060
Ni	−0.271	−0.140	−0.130	0.072	0.364
Zn	**−0.281**	0.144	0.131	−0.220	0.182
Al	−0.073	0.030	0.624	0.177	0.111
TOC	−0.200	−0.158	0.104	−0.447	−0.371
TN	−0.208	−0.213	−0.125	−0.266	0.213
TP	−0.003	**0.384**	0.423	−0.256	−0.022
Silts	**−0.292**	0.156	−0.082	0.011	0.218
Sands	**0.309**	0.016	0.009	0.172	0.084
PCBs	−0.221	−0.151	0.346	0.336	−0.030
HCB	0.128	**−0.388**	0.228	0.134	−0.025
44′-DDE	0.047	**−0.404**	0.164	−0.284	0.353
PAHs	**−0.295**	0.033	−0.119	0.245	−0.137
Hy C > 12	−0.114	**0.457**	−0.011	−0.062	−0.267

In black most significant relations are highlighted.

between TOC–TP. TP, on the other hand, is strongly related to *Hy* C > 12 (Figure 3). These data support the presence of local enrichments in TP that are not associated with sources of organic matter, suggesting the presence of a common relation between TP and *Hy* C > 12.

Trace elements

The deposition of complexes formed by organics, pollutants, and muddy-clay particles commonly occurs in areas of reduced hydrodynamic energy, which leads to a significant enrichment that is particularly evident in inner harbor areas. The occurrence of this phenomenon can explain the positive correlations among silt, TOC, and some trace elements (Cr, Zn, Pb, Cu, Ni, Cd) observed in this study. In fact, probably related with this phenomenon, trace elements show a clear increase of concentrations in inner stations of Bari, Barletta, and Crotone harbors.

In Table 7, some bibliographical reference values for Mediterranean harbor sediments concerning trace elements are reported. Bari, Barletta, and Civitavecchia sediments show higher trace element concentrations. As reported by the literature, the Hg background levels in Tuscany are generally higher

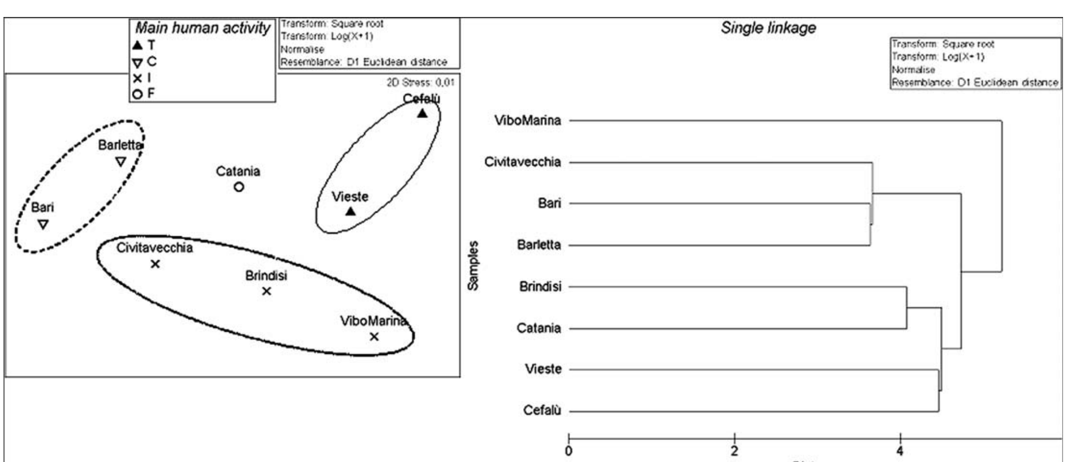

Figure 5 nMDS and cluster analyses performed on multivariate average data collected from sampling stations. A factor main human activity has been selected to evaluate station segregation. T, tourism; C, commerce; I, industry; F, fishery.

Table 7. Average concentrations and ranges of trace elements in surficial sediments of the Mediterranean Sea (milligrams per kilogram p.s.)

Study area	References	Cd	Cr	Cu	Hg	Pb	Zn
Argentario	Borghini (1998)	0.17 (0.06–0.46)	51.9 (8.4–368.1)	8.00 (4.1–15.8)	—	17.6 (9.9–29.8)	38.4 (24.1–62.1)
Nice Monte Carlo	Bernhard (1978)	1.7 (0.1–2.3)	18.8 (12–30)	—	—	57.9 (35–95)	70.6 (45–114)
Southern Tuscany	Niccolai, *et al.* (1993)	0.14 (0.08–0.28)	95.6 (8.8–162)	30.5 (4.2–85.1)	0.27 (0.05–1.18)	48.9 (6.9–92)	123.7 (22–218)
Follonica	Bargagli, *et al.* (1985)	—	—	36.6	—	48.5	136.1
Northern Tyrrhenian Sea	Leoni, *et al.* (1991)	—	192 (17–1445)	29.6 (11–50)	—	48 (13–97)	94.4 (26–171)
Naples Gulf	Romano, *et al.* (2004)	0.27	32	79	0.18	168	213
Aegean Sea	Dal man, *et al.* (2005)	0.53	—	20		19	100
Southern Adriatic	Storelli, *et al.* (2001)	0.20	—	16.09	0.28	4.43	95.8

than southern Italy reference values; levels measured in Civitavecchia harbor (Table 4) are low if compared with the averages of the Tuscany-Lazio area; nevertheless, Bari shows Hg levels that are similar to average values reported for Naples harbor. Cd levels measured for Bari and Barletta harbors are higher than bibliographical values reported for Naples and South Adriatic Sea. Pb in Bari sediments shows levels lower than Naples but notable higher than reference values for the sediments from the Adriatic Sea. This trend is also observed for Cr, Cu, and Zn while As shows very high concentrations in Lazio region, Bari and Brindisi harbors.

Both phyllosilicates and the organic matter are concentrated in clay (<2 μm) and fine silt (2–20 μm) fractions, and because of their chemical affinity for trace elements, they tend to accumulate pollutants at high concentrations. Nevertheless, phyllosilicates are also rich in feldspars and natural metals (Heruit and Sandler, 2006) because of the enrichment caused by human activities and the natural local geomorphologic structures. To distinguish the contributions of human impact from natural interferences, several authors suggest to perform normalization techniques to reduce the natural interferences in the level of trace elements. Al is considered by the literature to be a good reference element because it represents aluminosilicates, the main group of minerals found in finer sediment fractions, and it is supposed to have negligible origin from human input (Hanson, *et al.*, 1993; Covelli and Fantolan, 1997). Considering average data collected from all the studied harbors, Al is not positive related with any other element, while, considering only Apulia harbors, it shows a significant positive correlation with As (0.19), Ni (0.12), and Cr (0.16) suggesting a general relationship between these elements and natural contents in aluminosilicates. For this reason, As, Ni, and Cr observed high concentrations in Apulia harbors seem to be due principally to natural origin rather than to pollution occurrence. For other elements, no correlations are observed probably related to the presence of real specific pollution sources for Cd, Zn, Pb, and Cu in Apulia harbors.

Persistent organic pollutants

Levels and patterns of persistent organic pollutants are quite different in studied harbors. Concerning PAHs, Scalo Matteuzzi harbor shows the highest PAHs levels similar to values measured in Olbia (De Luca, *et al.*, 2005) and Ancona harbors (Magi, *et al.*, 2002). High PAH levels are also observed in Bari and Barletta surficial sediments compared with lower values measured in Porto Torres (De Luca, *et al.*, 2004), while Brindisi and Vieste show quite low values referable to Naples harbor lower polluted areas (Sprovieri, *et al.*, 2007). The little Scalo Matteuzzi harbor is located very close (within 1500 m) to Civitavecchia industrial area in which a coal thermoelectric central is active; the observed concentrations of PAHs in Scalo Matteuzzi sediments could be probably related to the fall-out occurrence. The absence of relationships with silts and TOC observed in Apulia harbors suggests that PAHs levels are principally due to the presence of local pollution sources rather than to global pollution phenomena. Bari and Brindisi harbors also show high concentrations of *Hy* C > 12 but very low levels concerning PCBs, and pesticides are measured. PCB values observed in Barletta harbor are the highest after Crotone.

Multivariate analyses

PCA results suggest that variables correlated with the first axe that have a great significance in explaining average system variability in sediment descriptors are represented by Pb (−0.293), Cu (−0.321), Zn (−0.281), silts (−0.292), sands (0.309), and PAHs (−0.295). It is interesting to note that Al acquires major significance in explaining system variability when PCA is performed considering only Apulia harbors. nMDS performed on harbors showed no significance in segregation according to RF, while a major significance is observed related with MHAF. In this case, in fact, one-way ANOSIM test shows that H_o hypothesis can be rejected with the confidence of 5.1%.

Conclusions

Levels of pollution of sediments sampled in 10 southern Italy harbors from four different regions are wide variable both among harbors and among stations inside the same basin. PCA results suggest that major significance in explaining average system variability is due to Pb, Cu, Zn, silts, sands, and PAHs. Performing analyses on Apulia harbor results, Al acquired significant positive correlations with As, Ni, and Cr suggesting in this region a general relationship between these elements and natural contents in aluminosilicates. No significance has been observed when we tested nMDS distribution according to the "region" factors, while the factor "main human activity" in harbor basin showed higher significance suggesting a relationship among pollutant distribution and this factor.

Acknowledgements

We thank the whole research team of the Department of Environmental Science of the University of Siena, particularly we thank Angela Giglio Cobuzo, Daniela Calvellini, Marcella Ruta, and Alessio Moroni for their in field activity for Barletta, Bari, and Vibo Marina samplings. We are grateful to Teresa Benincasa and Francesca Cossu for their laboratory activities. We thank also the Polo Universitario Grossetano, which allows us to perform our study. We are grateful to Società Cooperativa *Nautilus*, Società Cooperativa *Poliservizi*, *Naval service*, and Società *Geomare* for logistic operations in field activity. We turn a special thanks to Prof. Silvano Focardi that with his efforts, suggestions, and constant enthusiasm has made our research possible.

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