Journal of Sea Research 85 (2014) 428–442

Contents lists available at ScienceDirect

Journal of Sea Research

journal homepage: www.elsevier.com/locate/seares

Analysis and assessment of trace element contamination in offshore sediments of the Augusta Bay (SE Sicily): A multivariate statistical approach based on canonical correlation analysis and mixture density estimation approach

Rossella Di Leonardo [a,*], Giada Adelfio [b], Adriana Bellanca [a], Marcello Chiodi [b], Salvatore Mazzola [c]

[a] Dipartimento di Scienze della Terra e del Mare (DiSTeM), Università degli Studi di Palermo, via Archirafi 18, 90123 Palermo, Italy
[b] Dipartimento di Scienze Statistiche e Matematiche Silvio Vianelli (DSSM), Università degli Studi di Palermo, viale delle Scienze ed.13, 90128 Palermo, Italy
[c] IAMC-CNR, U.O. di Capo Granitola, Via del Faro 4, 91021 Campobello di Mazara (TP), Italy

ARTICLE INFO

Article history:
Received 20 November 2012
Received in revised form 16 July 2013
Accepted 23 July 2013
Available online 30 July 2013

Keywords:
Trace Elements
Box-core Sediment
Canonical Correlation Analysis
Pre-industrial Level
Offshore
Augusta Bay

ABSTRACT

An application of multivariate statistical methods is provided to identify anthropogenic contaminants and lithogenic elements in offshore sediments collected near the heavily industrialized Augusta Bay, Sicily. An exploratory statistical technique, based on canonical correlation analysis (CCA) and mixture density estimation approach, is used for distinguishing between natural and anthropogenic contributions of trace elements in the investigated sediments.

Following the intensive industrialization of Augusta area, marine sediments reveal the severe impact of local anthropogenic activities for many elements (e.g. As, Cd, Hg, Pb, and Sb), which are considered very dangerous for the environment. In contrast, a prevalent natural/lithogenic origin can be ascribed to Co, Cr, Cu, Mn, Ni, V, and Zn.

The multivariate statistical approach used in this study, which aims to estimate and to classify trace element pre-industrial levels and sources, could be easily applied to other different contaminated areas.

1. Introduction

Coastal environments are globally declining in ecological quality because pollutants/contaminants tend to accumulate in these sensitive ecosystems (Alley, 2000). Among others, nutrients, trace elements, and persistent organic pollutants derived from watersheds where urban, agricultural, and industrial activities are major contributors to that decline. Previous geochemical studies demonstrate the usefulness of box-cores for monitoring marine environmental contamination (Baptista Neto et al., 2000; Hung and Hsu, 2004; Mil-Homens et al., 2006; Pekey et al., 2004; Romano et al., 2009; Zonta et al., 2007). Analysis of these records reveals past changes produced in marine ecosystems and show overall contamination trends (Tuncel et al., 2007). The evaluation of natural trace element concentrations is indispensable to estimate the effective anthropogenic contamination of an investigated area, especially when the trace element backgrounds are naturally high (Qi et al., 2010).

Trace elements emitted by natural processes (such as erosion of ore-bearing rocks, wind-blown dust, volcanic activity, and forest fires) and human activities enter the coastal and estuarine regions by means of rivers in particulate form (Gibbs, 1977; Martin and Meybeck, 1979), through wet and dry atmospheric depositions (Guieu et al., 1997), and through direct discharges or dumping (Clark, 2001). Here, marine sediments act as sink, accumulating many persistent pollutants/contaminants (Szefer et al., 1995). Therefore, geochemical investigations of marine sediments can reveal the weathering trends and the sources of pollution/contamination (e.g., Förstner and Salomons, 1980; Nath et al., 2000; Nesbitt et al., 1996).

The Sicilian coastal areas have been intensely modified and transformed by industrial and urban activities particularly over the last 60 years. Notably, the Augusta area (SE Sicily), located along the Ionian coast of the Hyblean mountain range, has been extensively modified at the beginning of the 1950s, when the natural gulf, dominated by Holocene and Late Pleistocene alluvial and fluvial deposits together with coarse sands, calcarenites and limestone as old as Late Cretaceous (Lentini et al., 1986), has been walled up with breakwaters, forming an important harbor in connection with the open sea through two narrow inlets (Scirocco and Levante).

Since 1955 the Augusta Bay has hosted a variety of different chemical and petrochemical refining plants, a commercial harbor, and part of the bay is a basis of the Italian Navy and NATO activities. Due to the dangerous contamination of air, seawater, and marine biota documented in this area, Augusta coastal area has been included by the Italian Government in the national remediation plan (G.U.R.I., L. 426/1998) and evaluated by the World Health Organization as providing

---

* Corresponding author. Tel.: +39 091 23862874; fax: +39 091 6100278.
E-mail address: rosselladileonardo@gmail.com (R. Di Leonardo).

1385-1101/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.seares.2013.07.015

a high environmental risk (Martuzzi et al., 2002). In fact, since the 1970s very frequent episodes of seawater eutrophication were registered inside the Augusta Bay, causing many fish die-offs (De Domenico, 1972; Genovese and De Domenico, 1975); indeed, elevated concentrations of trace elements and hydrocarbons measured inside the bay appeared to be correlated with industrial emissions (Sciacca and Fallico, 1978). High concentrations of polychlorobiphenyls (PCBs: 2.3 to 6.1 mg kg^{-1}) were recorded in the edible part of some marine organisms (Castelli et al., 1983). According to the contamination degree registered by some biomarkers, Augusta Bay was divided in different zones at increasing pollution (Cantone and Pilato, 1981; Di Geronimo, 1983). Librando and Fazzino (1993) documented high concentrations of polycyclic aromatic hydrocarbons (PAHs) and their nitro derivatives in atmospheric particulate matter of Augusta city; Magazzù et al. (1995) correlated the high state of degradation of seawater quality in the Augusta Bay, due to elevated concentrations of Dissolved/Dispersed Petroleum Hydrocarbons (DDPH), ionic and non-ionic detergents (ABS, BiAS), and inorganic N, with occasional eutrophication caused by urban and industrial run-off. The lowlands facing the sea in the Augusta coastal area are drained by several small rivers and streams, which could carry pollutants/contaminants into the marine environment deriving from urban and industrial activities. In our knowledge, only Cundy et al. (1998) have investigated a short saltmarsh core collected from "Mulinello" estuary in the northern part of the Augusta Bay to evaluate the impact of rapid coastal development in the area. The authors have demonstrated that despite saltmarsh and intertidal areas in the Mulinello estuary has undergone extensive modification, the documented change in trace element flux may be a result of increased input of trace element-rich alluvial deposits, derived from basic igneous and volcanic sequences in the Mulinello catchment, rather than trace element of anthropogenic origin (Cundy et al., 1998). Weekly intake for total Hg and methylmercury in *Merluccius merluccius* and *Mullus barbatus* have been estimated by Storelli et al. (2005). Values of anthropogenic trace element input to the Augusta Bay for the year 2005, including discharges from wastewater treatment facilities and industrial atmospheric emissions, are reported in the European pollutant emission register (http://www.eper.sinanet.apat.it/site/it-IT/Registro_INES/Ricerca_per_complesso_industriale/). Sediments collected inside the Augusta Bay registered extreme Hg and PAHs concentrations, exceeding national and international regulatory guidelines (ICRAM, 2005). Ausili et al. (2008) suggested a still active Hg release mechanism from Augusta polluted sediments to marine biota (*M. barbatus* and *Mytilus galloprovincialis*), which exhibited marked genotoxic damages. Recently, Di Leonardo et al. (2007, 2008) analyzed box-core sediments from the Ionian Sea and proved a significant alteration of the natural fluxes of Hg in the offshore sedimentary environment from the Sicilian coastal zone seawards of the industrial area of Augusta. This finding is probably related to the presence of a chlor-alkali plant that employed Hg as cathode electrolysis, dumping directly into the sea the enriched Hg sewages. Although the combined presence of different chemicals in sediments could theoretically enhance the risk for the marine ecosystem, sedimentary records of trace metals and metalloids in this area are lacking.

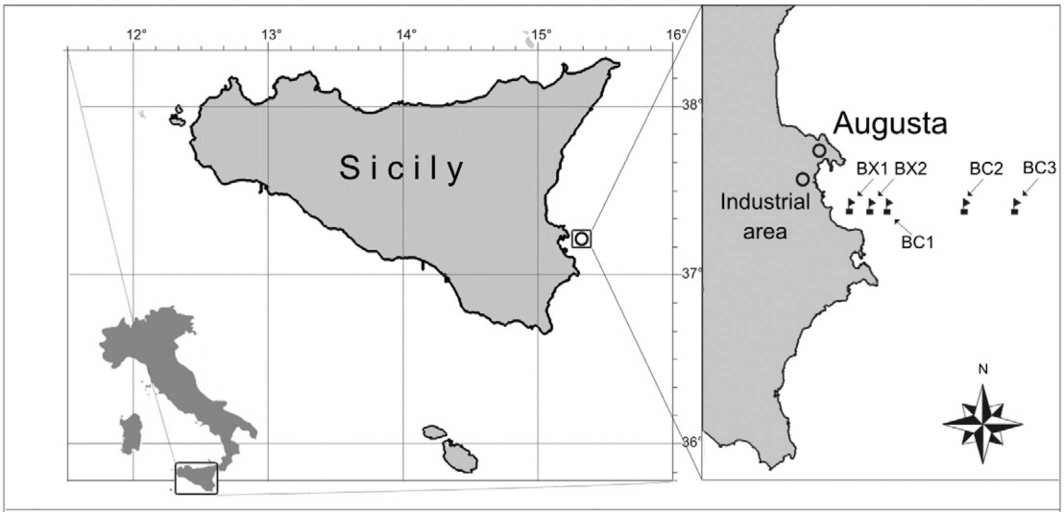
To overcome this difficulty, some statistical analysis procedures (e.g. CCA, principal component analysis—PCA, factor analysis—FA) are useful tools to interpret the environmental data. Both univariate and multivariate statistical methods have been widely applied to detect correlations between variables, to allow a deep interpretation of data, and, specifically, to investigate trace element distribution in sediments (Apitz et al., 2009; Araújo et al., 2002; Emmerson et al., 1997; Liu et al., 2003; Ratha and Sahu, 1993; Reid and Spencer, 2009; Romano et al., 2004; Spencer, 2002). According to these authors trace element distribution in sediments can be studied applying both multivariate analysis techniques (e.g. CCA, PCA, and FA) and frequency distribution analysis. In this study, the geochemical distribution patterns of major (Al, P, Fe, Mg, Ca, K, Si, Ti) and trace elements (As, Cd, Co, Cr, Cu, Ni, Pb, Sb, V, and Zn) of sediments collected offshore of the Augusta urban/industrial area (SE Sicily) are described by the application of multivariate exploratory statistical (CCA and FDA) techniques. Data of major elements, total Hg, and pseudo-total Mn, previously measured for the same sediments by Di Leonardo et al. (2007, 2008), were enclosed to the dataset. The CCA, used to describe symmetric relationships between two sets of variables without assuming causality, allows to evaluate the relationship between trace element concentrations in marine sediment and to identify their mutual concentration dependence to their source/origin. This procedure is applied twice: first on logarithmic normalized data and then on residuals provided by linear regressions accounting for sediment depth and sampling site effects. Usually, some attempts have been made to establish the regional background level of trace elements: by using older deep sediments not perturbed by anthropogenic activities (Rémy et al., 2003), or different statistical approaches, such as the probability plots that partitioned data into component populations thus obtaining background and anomalous values (Tobías et al., 1997). Here, the frequency distribution analysis can give directions to assess the pre-industrial contaminant levels and to easily compare the recent and historical inputs of toxic substances to coastal areas with evaluated natural background, when available (Apitz et al., 2009; Reid and Spencer, 2009). These statistical approaches, which allow to understand the geochemical processes controlling the elemental concentrations, including possible anthropogenic influences, and to identify the effects of those anthropogenic sources of trace elements over the natural geochemical background, can successfully be employed in other polluted/contaminated environment.

2. Materials and methods

Five box-cores were collected using a United States Geological Survey (USGS)-modified Naval Electronics Laboratory (NEL) box-corer sampler from the Sicilian coastal zone seawards of the industrial area of Augusta (Fig. 1). Sampling was carried out during two oceanographic cruises on board R/V "*URANIA*" in the summers of 2003 and 2004 along a west-east transect. Sediment was immediately sub-sampled on board using an acrylic tube, sealed in polyethylene flasks, and stored at −20 °C until analysis. In the laboratory, the cores were sliced at 1 cm intervals with a stainless steel bandsaw, and oven dried at 40 °C prior to geochemical analyses. A total of 79 samples were obtained.

Pseudo-total trace element concentrations were obtained by digesting 0.5 g of dried sample with 10 ml of *Aqua Regia* in Teflon vessel using a microwave oven (CEM-MSD 2000 equipment). This digestion method, while not completely destroying silicates, is widely used in environmental geochemical studies to remove non lattice-bound elements, giving an estimation of the potentially mobile fraction that could be mobilized (Chan et al., 1998; Rubio et al., 2001; Salvagio Manta et al., 2002).

Blank ($n = 15$), duplicate sample ($n = 25$) and standard reference material ($n = 15$; MESS-3, Marine Sediment Reference Materials, National Research council of Canada) were prepared with the same amount of acids for quality-control purposes. Working calibration standards were prepared with serial dilution of stock standard solutions containing 10 mg kg^{-1} of each element using the same acid matrix utilized for sample digestion. Caution was used in preparing and analyzing samples to reduce contamination from air, glassware and reagents. Only reagents of Suprapur quality and MilliQ water were used during the laboratory procedures. All glassware and the reaction vessels were previously soaked overnight with 10% nitric acid solution and then rinsed with ultra pure water. Cd, Co, Cr, Cu, Ni, Pb, Sb, and Zn analyses were performed by using an ICP-MS (Perkin-Elmer model ELAN-DRC-e). All determinations were performed with the external standard calibration method, using In and Re as internal standards. As and V were performed by using an ICP-OES. The accuracy and precision of analytical procedures were checked by analyzing replicated measures of an international reference material (MESS-3), reagent blanks and duplicated samples. As the published certified values for MESS-3 referred to



Core number	Latitude (N)	Longitude (E)	Water depth (m)	Core length (cm)	Nautical miles from the coast
BX1	37° 09' 00	15° 16' 00	62	12	2.15
BX2	37° 09' 00	15° 19' 00	145	23	4.29
BC1	37° 09' 00	15° 20' 99	1220	10	6.43
BC2	37° 08' 98	15° 33' 99	2223	21	16.73
BC3	37° 09' 01	15° 43' 99	2416	19	25.10

Fig. 1. Location of sampling stations, with core length, water depth and geographic parameters at each station (modified after Di Leonardo et al., 2008).

completely digested samples (using HF + HCl + HNO_3), measured values were lower than reference values. Recovery was about 90% for Co, Cr, Cu, Ni, Pb, V, and, Zn and about 80% for As, Cd, and Sb. The quality control gave good precision (S.D. $<5\%$) for duplicate samples. In order to assess differences among pseudo-total and total extraction methods, analyses for total trace element concentrations were carried out on 8 representative selected Augusta sediments, via induced coupled mass spectrometry (ICP-MS) at Activation Laboratories Ltd (ActLabs; Ancaster, ON, Canada). For sample preparation, 0.5 g of bulk sample was acid-digested in the following stages: (i) hydrofluoric acid; (ii) a mixture of nitric and perchloric acids; (iii) dried using precise programmer controlled heating in several ramping and holding cycles; and (iv) brought back into solution using hydrochloric acid. The ICP-MS used was a Perkin-Elmer Elan 6000 (Weltech Enterprises, Inc., Capitol Heights, MD, USA). Detection limits were 0.1 mg kg^{-1} for As, Cd, and Co, 0.2 mg kg^{-1} for Cu and Zn, 0.5 mg kg^{-1} for Cr, Ni, and Pb, 1 mg kg^{-1} for Mn and V. Sb was not analyzed. After comparing results from partial and total digestion methods, recovery was averagely $>70\%$ for Ni and Zn, and $>90\%$ for As, Co, Cr, Cu, Pb, and V. Only for Cd, recovery was averagely about 64%: this low value could be attributed to the low pseudo-total Cd concentrations measured in Augusta sediments, lower than the detection limit of Cd in the total extraction method. The good recovery obtained for the majority of trace elements permits to validate the use of Augusta dataset to infer pre-industrial trace element concentrations.

Mineralogical phases, major elements, total Hg, and pseudo-total Mn were previously measured for the same sediments by Di Leonardo et al. (2007, 2008). Briefly, sediment mineralogy was investigated by powder X-ray diffraction (XRD, Philips PW 14 1373 apparatus) using CuKa radiation filtered by Ni. The relative proportions of minerals were established according to methods and data of Schultz (1964). Major element concentrations were determined by X-ray fluorescence using a RIGAKU ZSX PRIMUS spectrometer (Rigaku International Corp., Osaka, Japan) on pressed, boric-acid backed pellets of bulk samples. Data reduction was achieved using the method described by Franzini et al. (1975). Mercury concentrations were determined by using atomic absorption spectroscopy after thermal combustion of the dried sample and Hg pre-concentration on a single gold trap with an AMA 254 Solid/liquid Hg Analyzer (FKV).

3. Data analysis

3.1. Al-normalization

Geochemical normalization of major and trace element data to a variety of conservative elements, such as Al (Din, 1992), Zr (Dellwig et al., 2000), Fe (Schiff and Weisberg, 1999), Li (Loring, 1990), Sc (Loring, 1991), and Ti (Dellwig et al., 2000), is commonly employed, although caution is recommended in the use of these "reference elements" (Reimann and de Caritat, 2005). The application of these normalizers as a normalizing factor implies a strong correlation to the fine-grained sediment fraction and naturally occurring trace elements. If these relationships are established, anthropogenic trace element enrichments can be identified by deviations from the trend defined between the trace element concentrations and the normalizing elements (Liu et al., 2003). In this study, major and trace element concentrations from the investigated sediments are normalized to Al before applying the CCA and estimating the trace element background. Advantages of using Al as "reference element" are that it is the second most abundant element in the earth's crust and, owing to its scarce mobility, is not significantly influenced by diagenetic processes and anthropogenic inputs. As Al concentrations in sediments can be reasonably related to the clay component, which is dominant carrier for adsorbed trace elements, the element/Al ratio is commonly utilized to reduce the impact of grain-size variability (Carral et al., 1995; Daskalakis and O'Connor, 1995). Therefore, changes of element/Al ratios can be indicative of diagenetic, biogenic or anthropogenic inputs of trace elements into the environment.

3.2. Statistical treatment of the data

The data set acquired for the investigated sediments consists of 20 variables and 79 samples. Multivariate analysis of these data is performed by using the R software package (R Development Core Team, 2010, http://www.R-project.org).

In this paper, the comparability of data is achieved by logarithmic normalization of all elements to Al and to highlight the relationships among a large number of interrelated variables a multivariate CCA is applied on the entire Augusta log Al-normalized datasets.

Indeed, the use of CCA could be a useful and fast method to characterize the kind of trace element contamination registered by Augusta offshore sediments and at the same time could be an innovative exploratory method easily applicable to environmental geochemistry studies.

Though CCA has frequently been used in social sciences and bioinformatics researches (Pugh and Hu, 1991; Steinfath et al., 2007), the method has been rarely applied to environmental contamination assessment (Statheropoulos et al., 1998). CCA is here applied in order to identify a lower dimension set of variables with the highest mutual dependence, and therefore to find the main geochemical associations, distinguishing original parent material from other source contributions. The canonical correlation has often been applied to social sciences and bioinformatics (Pugh and Hu, 1991; Steinfath et al., 2007; Stevens, 1986), its use in environmental assessment has recently improved (Liu et al., 2009). The reason of this choice is that, in a natural system influenced by human activities, some variables may be associated together and can be considered as independent variables (predictors) while others (predicted) are dependent on the previous variables. With respect to other statistical approaches for the study of multiple correlation, such as multiple linear regression (Apitz et al., 2009) that computes coefficients for each single trace elements depending on the major ones, CCA has the advantage of providing simultaneous estimates of coefficients of the linear combination of trace elements and linear combination of major elements with the best possible correlation.

More formally, CCA is a way of measuring the linear relationship between two multidimensional variables, say X_{pxn} and Y_{mxn} (Hotelling, 1936). The dimensionality of these new bases is equal to or less than the smallest dimensionality of the two variables. The goal of the canonical correlation is to describe the relationships between the two sets of variables, looking for the canonical weights (coefficients) $a_1, a_2, \ldots, a_p$ to be applied to the p X variables and $b_1, b_2, \ldots, b_m$ to be applied to the m Y variables in such a way that the linear correlation between the new variables U_1 and V_1 is maximized, where:

$$U_1 = a_1X_1 + a_2X_2 + \ldots + a_pX_p, \quad V_1 = b_1Y_1 + b_2Y_2 + \ldots + b_mY_m$$

U_1 and V_1 are the first pair of canonical variables, and ρ_1 is their correlation. If one of the two sets of variables has only one variable, the ordinary multiple regression coefficients would be obtained, and ρ_1^2 equals R^2, i.e. the coefficient of determination, that is the quotient of the variances of the fitted values and observed values of the dependent variable.

CCA proceeds looking for new pairs of vectors with the highest correlation, but uncorrelated with the first pair of canonical variables; this gives the second pair of canonical variables with correlation ρ_2. This continues until the maximum number of pairs (which equals the smaller of m and p) has been found.

An important property of canonical correlations is that they are invariant with respect to affine transformations of the variables: CCA finds the coordinate system that is optimal for correlation analysis, and the eigenvectors defines this coordinate system.

4. Results

4.1. Elemental composition of sediments

Bulk mineralogy and geochemistry of the box-cores from the Augusta area are well-established and are detailed in Di Leonardo et al. (2007, 2008). Briefly, the coastal box-core BX1 contains alumino-silicates and quartz associated with moderate to abundant biogenic carbonate; in the box-cores BX2, BC1, BC2, and BC3 clay fraction and quartz are dominant.

Bulk sediment major element compositions for the Augusta sediments suggest that, with the exception of the more coastal sediments from core BX1, the other distal sediments display a typically terrigenous

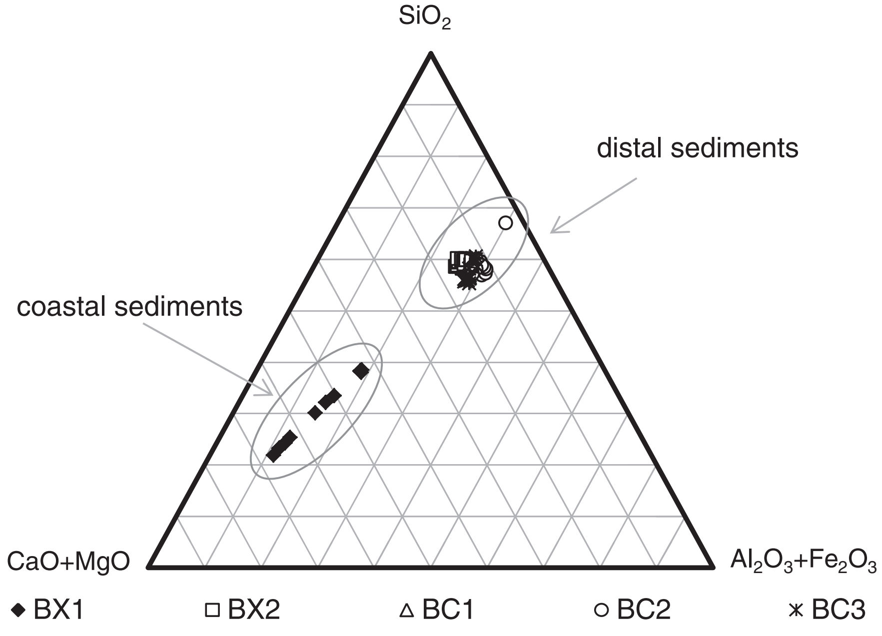


Fig. 2. Ternary plot of major element concentrations in bulk sediments from the studied cores (modified from Di Leonardo et al., 2008).

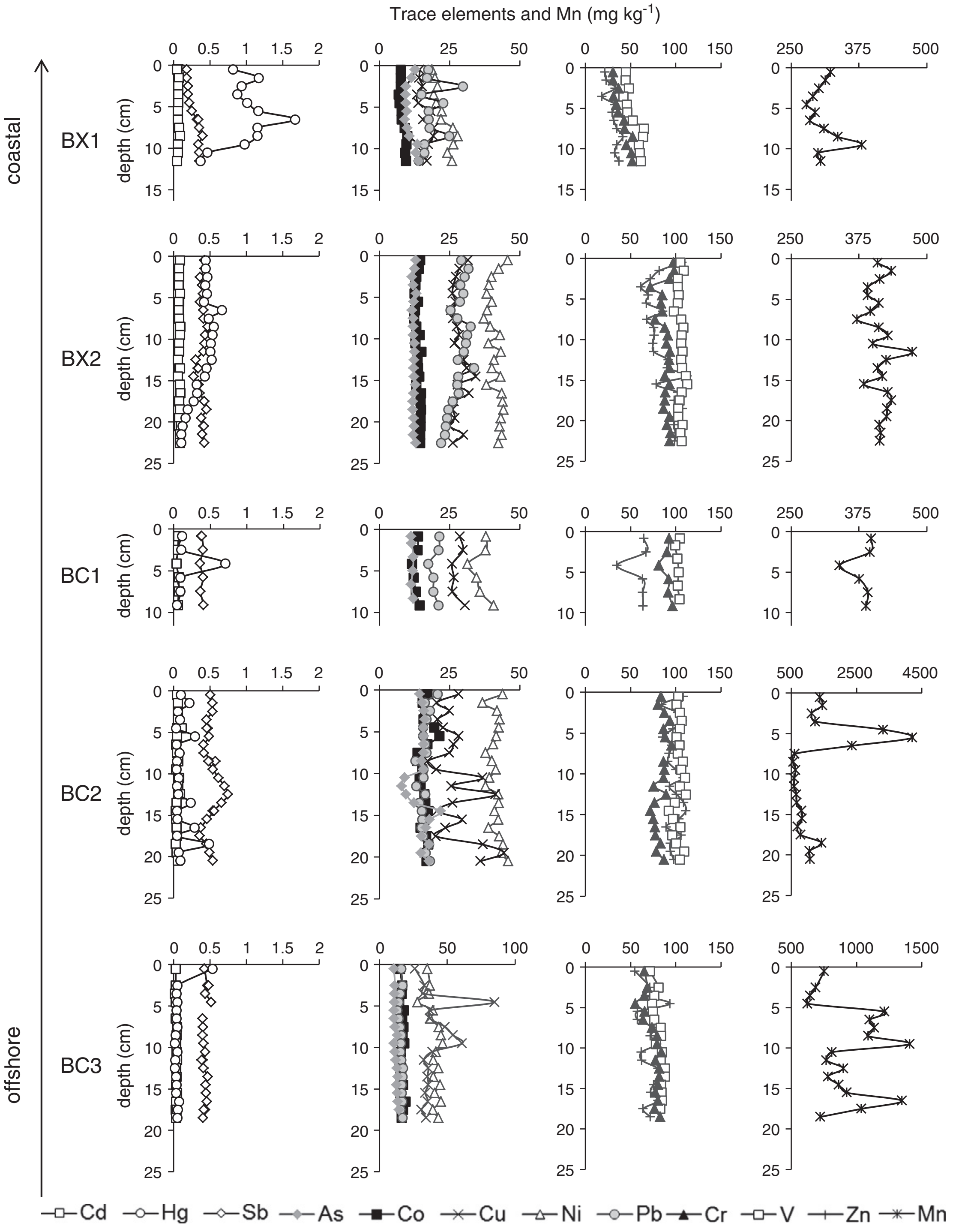


Fig. 3. Trace element and Mn concentrations vs. depth in the studied box-cores; Hg and, Mn concentrations vs. depth reported from Di Leonardo et al. (2008) (note the different scale for As, Co, Cu, Ni, and Pb values of BC3 and for Mn values of BC2 and BC3).

geochemical composition, with SiO_2 and Al_2O_3 concentrations generally greater than 47% and 14%, respectively (Fig. 2). At station BX1, Al_2O_3 concentrations are lower than 10%, whereas CaO + MgO mean concentration is higher than 36%, with a downcore decrease, accounting for a substantial calcareous biogenic component. Trace element depth profiles from the five box-cores are displayed in Fig. 3. The dominant element is Mn, followed by V, Cr, Zn, Ni, Cu, Pb, Co, As, Sb, Hg, and Cd. With the exception of the box-core BX1, many of the investigated trace elements exhibited similar concentrations through the other box-cores (BX2, BC1, BC2, and BC3), although there were some sporadic anomalously high values of Hg and Mn, especially in BC2 and BC3 cores, explained as effect of recent turbidites (see Di Leonardo et al., 2008 for a discussion). Certainly, biogeochemical cycles of trace elements in marine sediments could be impacted by early diagenetic processes (D'Hondt et al., 2004; Mitterer, 2010; Schlesinger, 1997; Schrenk et al., 2010; Vairavamurthy et al., 1995), mainly driven by organic matter fluxes

Fig. 4. Al-normalized trace element and Mn concentrations vs. depth in the studied box-cores; Hg/Al ratios vs. depth reported from Di Leonardo et al. (2007) (note the different scale for Mn values of BX2 and BC1).

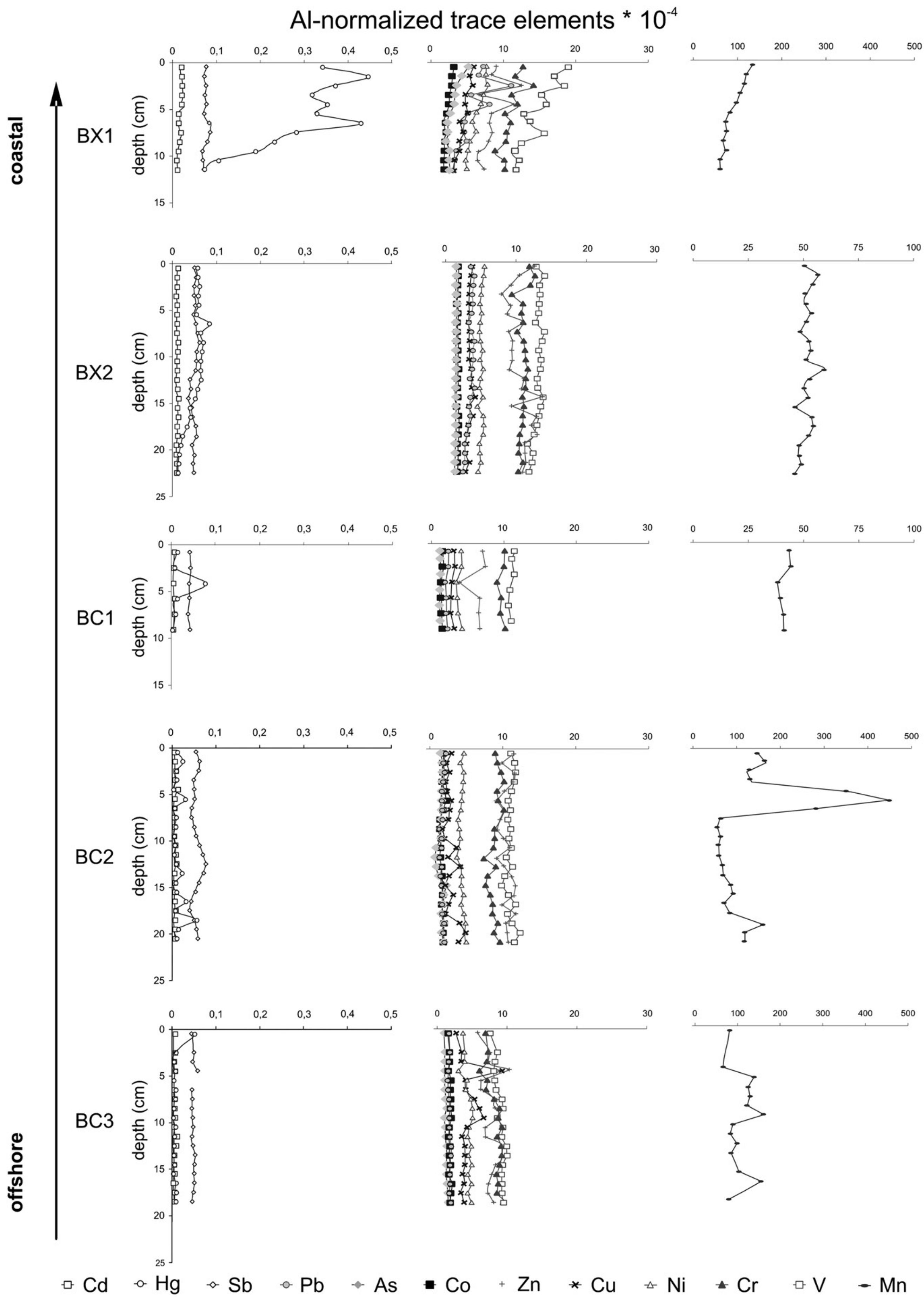

Al-normalized trace elements * 10-4
coastal
offshore
BX1
BX2
BC1
BC2
BC3
depth (cm)
0 0,1 0,2 0,3 0,4 0,5
0 10 20 30
0 100 200 300 400 500
0 25 50 75 100
0 5 10 15 20 25
Cd
Hg
Sb
Pb
As
Co
Zn
Cu
Ni
Cr
V
Mn

Table 1
Estimated coefficients ai, (i = 1,...,7) and bi, (i = 1,...,7) for the sets of log values of Al-normalized major (denoted with U variables) and trace elements (V variables) respectively, and correspondent canonical correlations.

$\rho1$	$\rho2$	$\rho3$	$\rho4$	$\rho5$	$\rho6$	$\rho7$
0.989	0.900	0.737	0.682	0.541	0.493	0.329

	a1	a2	a3	a4	a5	a6	a7
P	−0.001	−0.023	0.063	−0.052	0.083	0.056	0.343
Fe	0.194	0.035	−2.339	1.734	−0.371	2.116	0.456
Mg	0.069	−0.256	0.435	0.059	1.255	−1.965	−0.429
Ca	0.052	0.249	0.045	0.002	−0.797	0.764	0.144
K	−0.301	0.153	2.464	0.07	−2.283	−1.738	0.776
Si	0.13	0.976	0.899	1.738	2.72	2.531	−0.977
Ti	0.065	−1.745	1.476	−1.658	−3.151	−3.455	0.207
	b1	*b2*	*b3*	*b4*	*b5*	*b6*	*b7*
Mn	−0.025	0.096	0.023	0.057	0.186	0.195	−0.234
Co	0.144	−0.45	−0.619	0.656	−0.079	−1.787	0.847
Ni	−0.014	0.489	0.625	−0.224	−1.003	1.063	−0.678
Cu	0.017	0.099	0.084	0.031	−0.154	0.051	−0.171
Zn	−0.051	−0.075	0.051	0.073	0.28	0.072	−0.053
Pb	0.078	−0.088	0.416	0.187	0.351	0.129	0.237
V	0.000	−0.388	−0.086	0.761	−0.099	−0.456	0.481
Cr	−0.073	−0.218	−0.686	−0.378	−0.423	0.359	0.502
Sb	0.003	0.199	0.198	−0.306	0.032	0.002	0.575
Cd	0.063	0.004	−0.255	−0.143	0.05	−0.275	−0.385
Hg	0.008	0.000	0.031	−0.037	0.036	0.041	−0.086
As	0.112	0.223	−0.239	−0.15	0.04	0.361	0.075

and mineralization (Klinkhammer, 1980; Petersen et al., 1995). In many coastal environments, trace elements could be diagenetically remobilized or trapped from the water column initiated by aerobic decomposition of biogenic or sewage-derived organic matter or by sulfate reduction (e.g., Jørgensen et al., 2004; Parkes et al., 2005; Passier et al., 1998; Schippers et al., 2005; Teske and Sørensen, 2008). Both processes are equally important in mineralizing organic matter in marine systems where sedimentation rates are above about 0.1 cm y^{-1} (Matthai et al., 1998) and they could be misleading for the data statistical elaborations. Nevertheless, the low concentrations of total organic carbon (TOC = 0.54%) averagely measured in Augusta sediments (Di Leonardo et al., 2008), in agreement with data reported by Emelyanov and Shimkus (1986) for Mediterranean sediments, together with the absence of evident redox potential discontinuity layers in sediment samples allow to suppose that generally diagenetic processes might not play significant role for the trace element cycling in the investigated sediments; they probably could be limited to some depth layers in cores BC2 and BC3, where Di Leonardo et al. (2008) measured a Mn-TOC covariation patterns.

In the coastal station BX1, trace element concentrations were lower than those registered in the more seaward box-cores and the depth profiles exhibited a downwards increase, excepting Hg. This distribution can be reasonably attributed to carbonate-dominated mineralogy and the coarse grain-size of sediments at the station BX1 against the alumino-silicate nature of the other sediments. Accordingly, after removing the grain size effect by normalization to Al, element/Al depth profiles for the coastal site BX1, with the exception of Sb, showed a clear downcore decrease (Fig. 4). For the other investigated cores, the normalization of trace elements to Al generally confirmed the spatial variability patterns, indicating considerable landward enrichments for Cd, Cr, Hg, Ni, Pb, and V. By using the core dating established in Di Leonardo et al. (2007, 2008) limited to BX1 and BX2 sediments, trace element concentrations, with the exception of As, Cd, and Co for BX2 core, began to increase from ca. 1940 to 1950, probably due to developments of the Augusta industrial area.

4.2. First application of canonical correlation

In this application CCA allowed to identify correlations between groups of elements and recognize those having similar behavior and a common origin (natural or anthropogenic) along the studied area. With respect to an ordinary correlation matrix, which displayed pairs correlation measures, the CCA, described in Section 3.2, allowed to find relationships between the two sets of variables, that in this case corresponded to log values normalized to Al of major (7 variables) and trace elements (12 variables) for this reason the set of variables reduces to 19 elements (excluding Al; Table 1). All the estimated canonical correlations were statistically significant (p-value < 0.05). In Fig. 5a the first six canonical variables for major elements and trace elements are reported; in particular, the first six pairs of canonical variables corresponding to the first three canonical correlations are plotted in the first row, while in the second row the pairs of canonical variables from the fourth to the sixth canonical correlations are reported. Analyzing the plot of the first pairs of vectors of the scores (Fig. 5a) for the first canonical correlation, a good correlation between sets was observed ($\rho_1 = 0.989$); all points are distributed along the bisector between the two axis of the plot, with each investigated box-core perfectly noticeable from the others. From the interpretation of the scores associated with the second canonical correlation variables (Fig. 5a, second plot on the first row), two distinct groups of points can be easily identified, one coinciding with box-cores BX2 and BC1 (open square and open triangle symbols, respectively) and the other with the other three box-cores (BX1, BC2, and BC3, respectively in full rhombus, open circle and cross symbols). The interpretation of remaining scatterplots is not as well interesting, reflecting the value of the associated estimated canonical correlations of Table 1.

4.3. Second application of canonical correlation

Actually part of the canonical correlation can be explained by the clustered nature of data, induced by the belonging of sediments at fixed box-core. To verify if this effect had a significant influence on the results of the CCA, a linear regression model was performed on each of the 19 elements vs. sediment depth and sampling site. The sampling site was a measure of the distance from the coast and was a qualitative variable that assumed levels BX1, BX2, BC1, BC2, and BC3. The results of this fitting (Table 2) suggested that the variable “depth” had not always a significant effect on the response variables, unlike the “sampling site”,

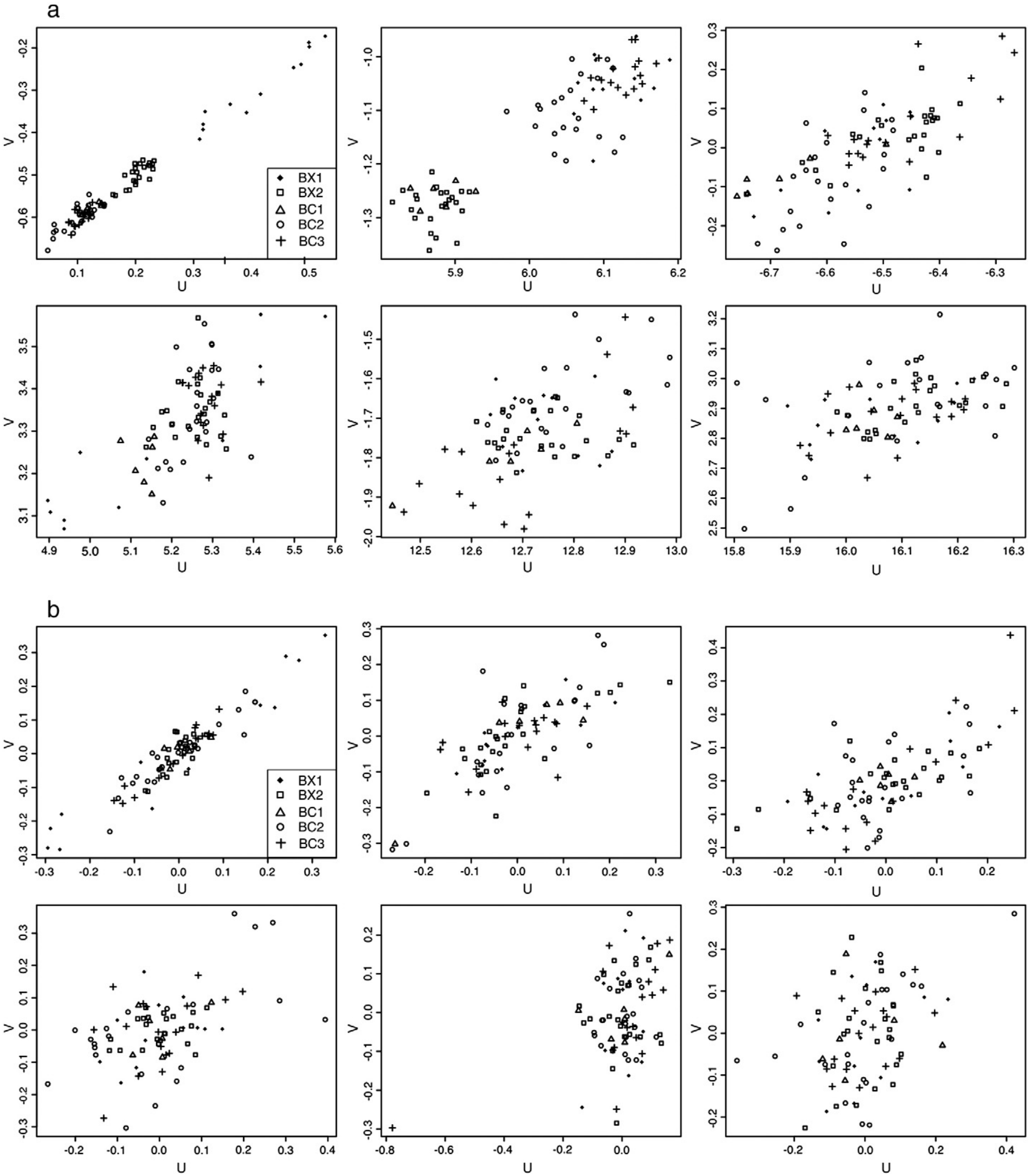


Fig. 5. (a) Canonical variables for the U variables (major elements) and V variables (trace elements); (b) Canonical variables for the U variables (major elements) and V variables (trace elements) once removed the effects of depth and coast distance.

which suggested that the distance from the coast had a significant influence on the responses.

Therefore, to remove the effects of sediment depth and coast distance, residuals defined by the difference between log Al-normalized variables and the predicted values obtained by a regression on sediment depth and sampling site were computed. Then, a new CCA was carried out on the 19 residuals of log-variables normalized to Al (Table 3). A useful adjunct to the analysis of the elements of the predictors and response sets was provided by the plots of the canonical components (Fig. 5b). For instance, the first canonical component identified two new variables: U_1 (that was a linear combination of residual major elements with coefficients given by the vector a_1), and a linear combination

Table 2
P-values of the ANOVA table obtained from the linear regression models estimated for all elements vs depth and sampling site.

	Depth	Sampling site
Mn	0.112	0.000
Co	0.057	0.000
Ni	0.484	0.000
Cu	0.343	0.000
Zn	0.000	0.000
Pb	0.000	0.000
V	0.006	0.000
Cr	0.255	0.000
Sb	0.002	0.000
Cd	0.001	0.000
Hg	0.000	0.000
As	0.008	0.000
P	0.009	0.000
Fe	0.107	0.000
Mg	0.000	0.000
Ca	0.000	0.000
K	0.000	0.000
Si	0.008	0.000
Ti	0.002	0.000

of the residual of trace elements V_1 (with coefficients given by b_1 vector) (Fig. 5b top left), with a correlation $\rho_1 = 0.944$. Now the distinct groups were not observable, since the effect of the box-core variable has been removed by the estimation of the linear models introduced above. Particularly, the residuals of elements that contributed mainly in the identification of the first canonical variable were rNi, rV, and rAs in the set of trace elements and rK, rSI, and rTi in the set of major elements (Table 3). The second canonical correlation ($\rho_2 = 0.738$) identified a couple of new variables (U_2 and V_2) reported in the second plot (first row) of Fig. 5b.

Although after the second application of CCA, a decrement of coefficients of canonical correlation performed on the residual variables appeared clear (p-values < 0.05), among the analyzed trace elements only Hg never manifested significant weight to the found correlation variables, suggesting that Hg had a clear different behavior with respect to the other variables.

4.4. Pre-industrial level estimations

To evaluate the 12 trace element background levels of the Augusta offshore sediments, a mixture density estimation approach of log Al-normalized trace element concentrations was considered. Moreover, looking into the nature of the source of each element distribution components of a mixture normal were estimated based on a maximum likelihood approach. In particular, the best estimates of the parameters (proportions π_i, means μ_i and standard deviations σ_i, $i = 1,2$) are obtained by the numerical maximization of the likelihood, given the observed data, using a combination of a Newton-type method and EM algorithm (Dempster et al., 1977; Mineo, 1964; Ypma, 1995). The fitting results are provided in Fig. 6. The estimated number of components, reported in Table 4, has been determined on the basis of a classical *T* test for the means of two distributions assuming different variances. In particular, the presence of two normal populations that overlapped in the case of Co, Cr, Cu, Ni, and V have been observed, while clear separate density components can be identified for Hg and Pb. On the basis of the statistical test, two components are also estimated for As, Cd, Sb, and Zn, although it does not appear so clear from a graphical point of view.

Standard errors for the means of the two populations were computed to verify the graphical results reported in Fig. 6 and to distinguish between anthropogenic and/or natural input of trace elements (Table 4). From the values of the estimated parameters together with their standard errors and the results of the *T* test above, for the variables As, Cd, Hg, Pb, Sb, and Zn, the two normal populations had significantly different means, implying that together with a natural source an anthropogenic input should be also evaluated in Augusta sediments for that trace element. Contrarily, the normal density distributions were overlapped in mean for Co, Cr, Cu, Mn, Ni, and V, and, therefore, a natural source for these elements can be assumed in the studied area. For Mn only one component has been considered, since all the observations were assigned to one population as deduced from the estimated proportion values.

By using the above described approach and selecting Al as a normalization element, the regionally geochemical background of the study area has been established for As Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, V,

Table 3
Estimated coefficients ai, ($i = 1,...,7$) and bi, ($i = 1,...,7$) for the sets of log values of Al-normalized major (U variables) and trace elements (V variables) respectively, once removed the effects of sampling depth and coast distance, and correspondent canonical correlations.

$\rho1$	$\rho2$	$\rho3$	$\rho4$	$\rho5$	$\rho6$	$\rho7$
0.944	0.738	0.643	0.506	0.394	0.379	0.106

U	a1	a2	a3	a4	a5	a6	a7
rP	−0.023	−0.082	0.067	−0.071	0.294	−0.101	−0.165
rFe	−0.123	2.907	0.461	−2.555	2.171	2.872	2.687
rMg	0.422	−0.167	1.125	0.742	−1.734	−0.903	−2.02
rCa	0.32	−0.595	−0.927	0.246	0.517	0.331	0.493
rK	−0.739	−2.377	1.969	2.951	0.847	1.228	1.96
rSi	0.62	−2.63	1.956	−4.141	−1.393	4.036	−0.054
rTi	−0.447	1.245	0.51	4.05	0.145	−7.01	1.76
V	*b1*	*b2*	*b3*	*b4*	*b5*	*b6*	*b7*
rMn	−0.031	−0.058	−0.339	−0.197	−0.292	−0.292	−0.257
rCo	0.087	1.311	2.205	0.262	0.993	1.083	1.457
rNi	0.275	−0.834	−1.841	0.769	−0.816	−1.175	0.422
rCu	0.069	−0.231	−0.023	0.064	−0.111	0.321	0.084
rZn	−0.073	0.223	0.039	−0.179	−0.467	−0.408	−0.295
rPb	0.118	−0.26	0.246	−0.11	0.541	−0.295	−0.556
rV	0.452	−0.408	0.377	0.499	−0.765	−0.423	−0.974
rCr	−0.28	0.548	−0.227	0.159	1.32	1.247	0.487
rSb	−0.088	−0.188	−0.191	−0.143	0.343	−0.756	0.198
rCd	0.092	0.331	0.054	0.015	−0.215	0.215	−0.017
rHg	0.021	−0.037	0.001	−0.031	−0.081	0.034	0.071
rAs	0.255	−0.016	−0.246	−0.594	0.041	0.078	−0.003

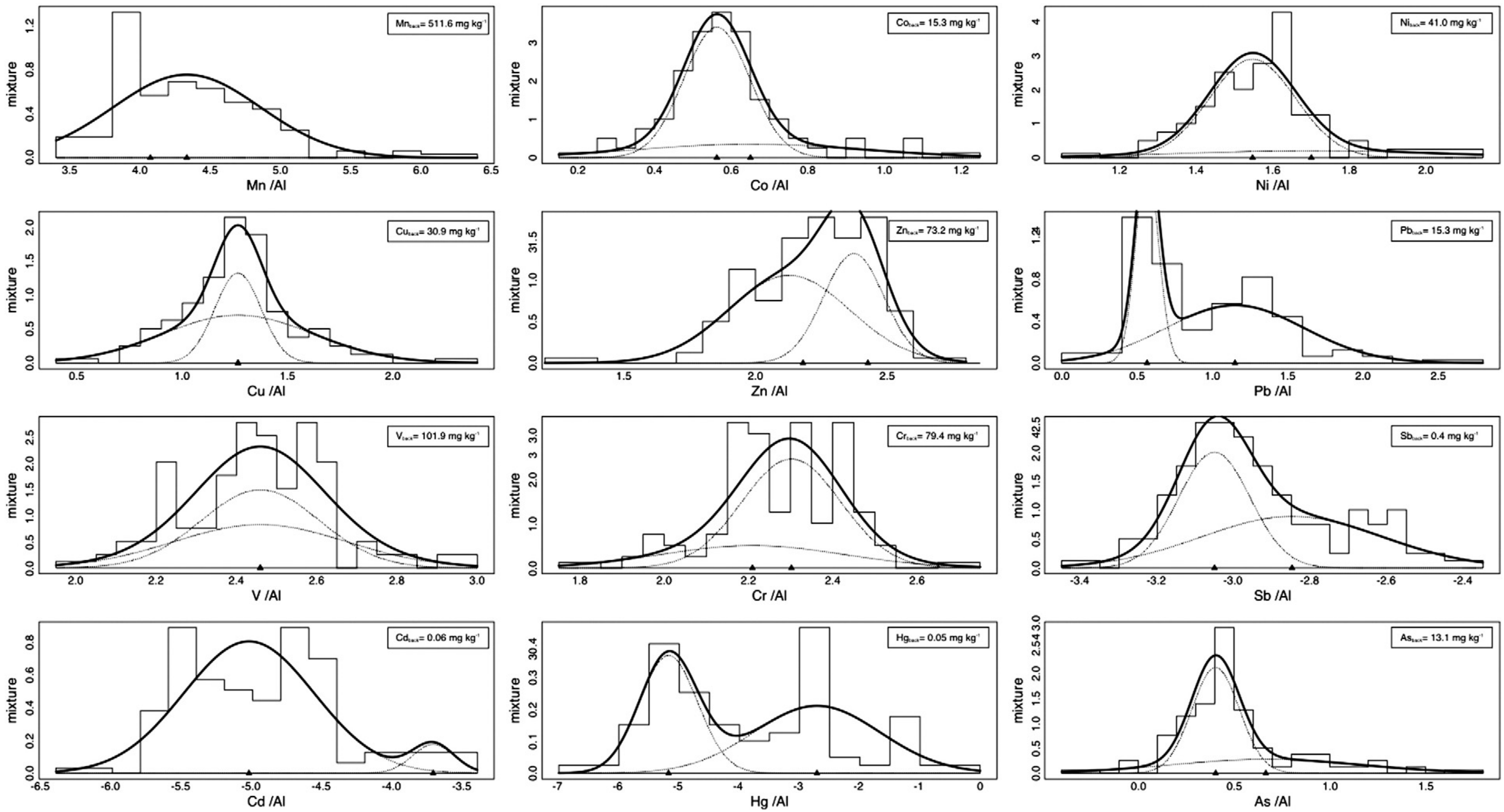


Fig. 6. Mixture probability density function of Al-normalized trace element concentrations (solid line) and single normal component distributions (dotted lines). For each trace element the estimated background concentration has been reported.

Table 4
Estimated values for parameters of component distributions (in order the proportions, means, and standard deviations), a significance level (P-value) for the goodness-of-fit test, and number of estimated components for each log Al-normalized element. Estimated standard errors of means for the variables with two normal components are reported inside brackets.

	π1	π2	μ1	μ2	σ1	σ2	p-value	N. comp.
Mn	0.00	1.00	4.07	4.33	0.03	0.53	0.00	1
Co	0.74	0.26	0.56	0.65	0.09	0.29	0.59	1
Ni	0.82	0.18	1.55	1.70	0.11	0.35	0.27	1
Cu	0.37	0.63	1.26	1.26	0.11	0.36	0.75	1
Zn	0.62	0.39	2.13 (0.08)	2.37 (0.07)	0.23	0.12	0.14	2
Pb	0.37	0.64	0.57 (0.06)	1.15 (0.17)	0.08	0.46	0.13	2
V	0.55	0.45	2.46	2.46	0.15	0.22	0.04	1
Cr	0.27	0.73	2.21	2.30	0.22	0.12	0.01	1
Sb	0.47	0.53	−3.05 (0.02)	−2.85 (0.06)	0.09	0.24	0.91	2
Cd	0.94	0.07	−5.03 (0.06)	−3.71 (0.17)	0.46	0.15	0.00	2
Hg	0.45	0.56	−5.18 (0.12)	−2.71 (0.28)	0.48	1.05	0.00	2
As	0.66	0.34	0.40 (0.02)	0.67 (0.12)	0.12	0.49	0.28	2

and Zn, respectively, using the mean value of the first normal density distribution (μ1 in Table 4).

5. Discussion

5.1. Exploratory statistical techniques for the interpretation of geochemical data

As suggested by the plot of the transformed scores of the first observational factor (Fig. 5a), the similarity of distribution patterns and the significant correlation between log Al-normalized trace and major element concentrations in the Augusta sediments indicate that these variables might have the same origin. The CCA results provide also statistical evidence that trace elements were not homogeneously distributed along the coast. In fact, distinct groups of elements are recognized, and each group could be associated with a specific sampling site (Fig. 5a). A probable link between trace element mobility in the water column and each sampling site and, therefore, with their different capacity of the sediment to entrap trace elements could not be excluded. Probably, a major input of trace elements to the seawater close to the industrialized coastal area has reasonably implied their enrichments in the matching sediments (core BX1).

Among the trace elements, Hg displays low weights in the CCA (Table 3), suggesting an anthropogenic source for the more coastal stations (see discussion below).

5.2. Pre-industrial element assessment and spatial distribution of trace element contamination

It is difficult to quantify the anthropogenic input of trace elements into many contaminated/polluted environments as frequently sediment trace element concentrations from pre-industrial periods are unknown. Therefore, defining appropriate trace element pre-industrial levels for sediments is an essential precursor for discriminating and quantifying anthropogenic input. Usually, if no specific information was available for the investigated area, the average shale is a broadly approved analog for the lithogenic background, being its composition comparable to that of the upper continental crust (Taylor and McLennan, 1985; Turekian and Wedepohl, 1961). However, it is generally accepted that each specific coastal system, depending on local geological properties, can be characterized by regional pre-industrial background concentrations that might be different to globe-scale reference levels. Therefore, the use of the average shale or the upper continental crust as lithogenic background of trace elements could be misleading (Gibbs, 1993), while a clarification of the regional background or pre-industrial trace element concentrations is essential in environmental assessment and legislation (Matschullat et al., 2000; Salminen and Gregorauskienè, 2000).

In this study, the pre-industrial levels for each investigated trace elements can be set up on the basis of the frequency histograms of Al-trace element log-concentrations, and, consequently, natural and other than natural enrichments can be distinguished. Sediment samples are considered to be trace element-enriched when two components for each log-values element normalized to Al have been estimated.

The two normal populations have substantially different means (μ1 and μ2 values in Table 4) for Cd, Hg, Pb, and Sb, and moderately different means for As and Zn, indicating for the first elements an undoubted anthropogenic source, instead of As and Zn an anthropogenic input mixed to a natural source could not be excluded. If the results of canonical correlation clearly indicate that mercury is the most dangerous pollutant/contaminant in the investigated sediments, the frequency histograms allow to better discriminate among trace element sources, suggesting for the Augusta offshore sediments also a possible As, Cd, Pb, and Sb contamination.

The trace element pre-industrial values determined for the Augusta offshore sediments are compared with those estimated for sediments from the Strait of Sicily applying the same method of maximum likelihood of lognormal distribution parameter to sediments older than 1920 AD recovered along three coastal–offshore transects and with concentration values of the average shale and upper crustal materials (Table 5; Di Leonardo et al., 2006; Tranchida et al., 2010). This comparison does not reveal significant differences; in particular, Augusta pre-industrial trace element values are similar with those previously determined in the Strait of Sicily; only the As pre-industrial level is significantly lower than that estimated for the Strait of Sicily (Tranchida et al., 2010), probably because this area is influenced by geothermal and/or magmatic activities.

This resemblance suggests the robustness of the reasoning about background interpretation and about the validity of the method chosen in this work. Indeed, the background evaluation approach based on the frequency plots is innovative compared to others (Apitz et al., 2009; Rémy et al., 2003), because it permits the establishment of background concentrations from the raw data set (only after normalization procedure) where anomalous values may be present and when no information about sediment radiometric dating are available.

Once each element pre-industrial values are established, a further way to explore element variability is to look at the spatial variations using Al as normalizing element. The normalized-enrichment factor of

Table 5
Comparison among trace element pre-industrial concentrations estimated for the Augusta sediments, the Strait of Sicily, the average shale, and the continental crust, respectively (data are expressed in mg kg^{-1}).

	Augusta area	Strait of Sicily	Average shale	Continental crust
As	13.1[#]	38.00[*]	13[^]	1.5[+]
Cd	0.06[#]	0.12[*]	0.3[^]	0.098[+]
Co	15.3[#]	11.48[*]	19[^]	17[+]
Cr	79.4[#]	67.61[*]	90[^]	85[+]
Cu	30.9[#]	17.38[*]	45[^]	25[+]
Hg	0.05[#]	0.038[**]	0.40[^]	–
Mn	511.6[#]	478.63[*]	850[^]	542[+]
Ni	41[#]	38.90[*]	68[^]	44[+]
Pb	15.3[#]	20.89[*]	20[^]	20[+]
Sb	0.4[#]	0.52[*]	1.5[^]	0.2[+]
V	101.9[#]	107.15[*]	130[^]	107[+]
Zn	73.2[#]	–	95[^]	71[+]

[#] This study.
[*] Tranchida (2005).
[**] Di Leonardo et al. (2006).
[^] Turekian and Wedepohl (1961).
[+] Taylor and McLennan (1985).

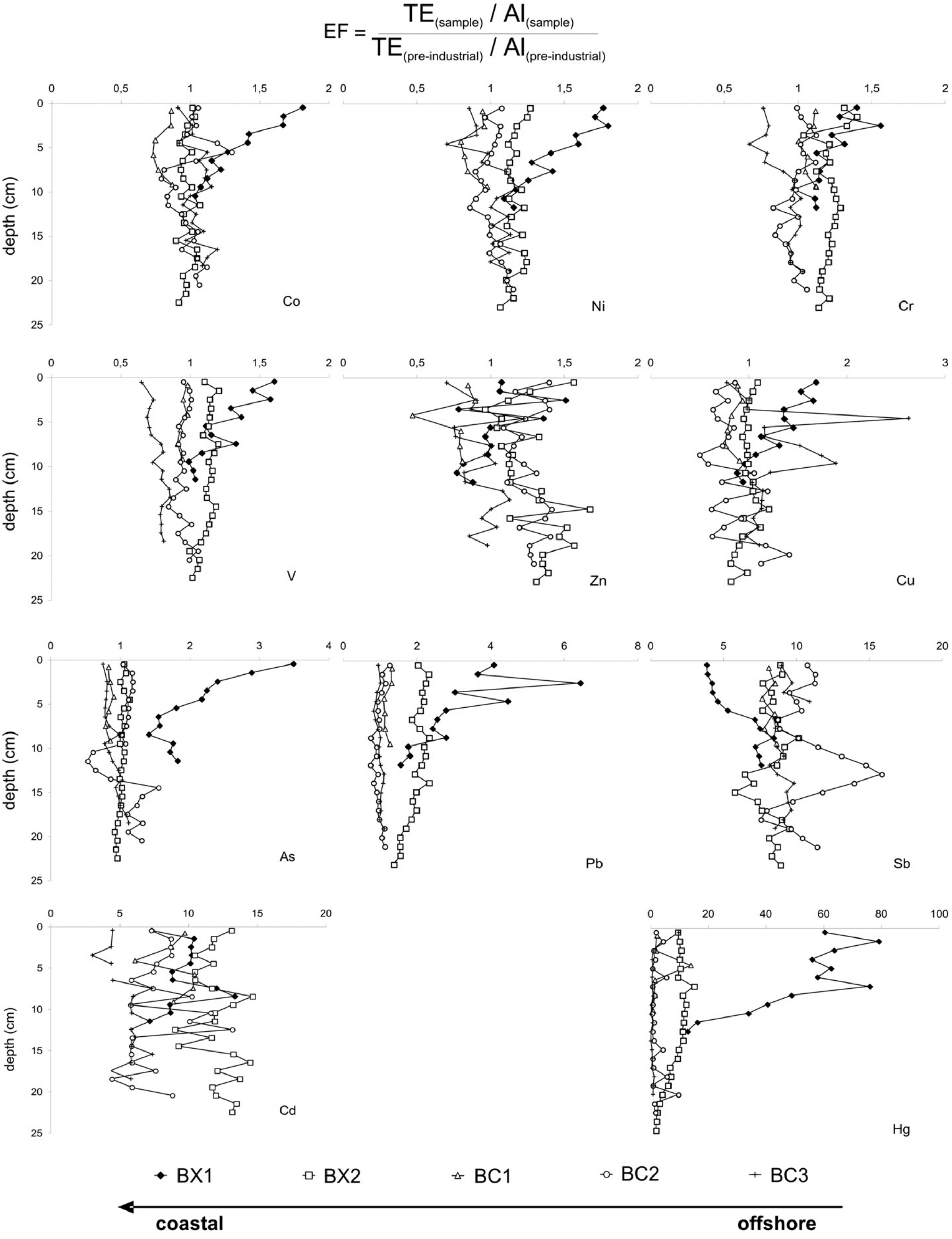


Fig. 7. Trace element enrichment factors normalized to Al (EF) *vs* depth for sediments from the Augusta area.

chemical species with respect to a pre-industrial value is often used and calculated as "$[TE_{(sample)}/Al_{(sample)}]/[TE_{(pre\text{-}industrial)}/Al_{(pre\text{-}industrial)}]$", with TE = trace element. The enrichment factors of the investigated trace elements highlight a meaningful relationship between trace element enrichments and the distance from the coast (Fig. 7). For some elements (Hg, Pb, and As), the more coastal sediments from site BX1 display the greatest upcore relative enrichment values (EF mean values of 50.8, 3.1, and 2.1 for Hg, Pb, and As, respectively). Considering the proximity of industrial and urban activities, these values presumably reflect significant anthropogenic inputs in the coastal studied area. Sb and Cd display elevated EFs in all the box-cores studied, with means values of 8.8 and 8.9, respectively. Co, Ni, Cu, Zn, and V EFs are close to the geochemical background. Despite the low EF values, at core BX1 these trace elements display upcore EF increases, similar to the other trace elements (As, Hg, Pb) derived from anthropogenic sources, suggesting a recent anthropogenic inputs.

Inside the Augusta Bay, mercury was found in alarmingly high concentrations in sediments and marine organisms sampled close to the chlor-alkali plant (Ausili et al., 2008; ICRAM, 2008). Indeed, ICRAM (2008) indicated that inside the bay the first meter of sediment was seriously polluted also by hydrocarbons and hexachlorobenzene. In many portions of the bay, and, especially, in the surface sediments, exceedances of the national regulatory guidelines (G.U.R.I., D.M. 56/2009) for As, Cd, Cu, Pb, V, Zn, PAHs, and PCBs have been extensively registered. Enrichments of As, Cd, Hg, Pb, and Sb registered in this study for sediment box-cores collected offshore of the Augusta show that, unfortunately, the strong contamination of the Augusta Bay, though extremely severe and dangerous, is not confined and localized to the enclosed area. This result is consistent with the findings of Sprovieri et al. (2011) who, based on mass-balance of total mercury (HgT) in the Augusta basin, demonstrated an essential role played by this area as mercury point source for the whole Mediterranean Sea, as well as other Hg sources to the Mediterranean Sea represented by the Idrija region in the Gulf of Trieste (Foucher et al., 2009) and by the The Pierre Blanche Lagoon in the southwestern French Mediterranean coast (Elbaz-Poulichet et al., 2011). The bay has been subjected to numerous dredgings over time and harbor dredged materials have been for a long time discharged without any cleaned treatments in marine zones outside and also very close to the bay. Already, Molinier and Picard (1953) stated that in the Augusta Bay many anthropogenic activities, such as the digging to expand the harbor area, the construction of access channels to large ships and the excavation of land along the coast, were frequently carried out and, at the most, without to follow any specific legislative regulation. These practices caused the deconstruction of the original benthic communities inside the bay, such as seagrass population of *Posidonia oceanica* (L.) Delile. Furthermore, during the 1980s, Augusta Bay was repeatedly dredged and the resulting material was transported and discharged about two nautical miles from the coast (ESTRAMED s.p.a., 1982), close to BX1 and BX2 sampling stations. Recently, Bellucci et al. (2012) suggested that the original environment of the bay was modified over time by sediment dredging and partial nourishment using materials of unknown origin. Moreover, Budillon et al. (2008) recognized different possible sediment dumping sites at several places on the shelf offshore the Augusta Bay (see also Di Leonardo et al., 2008, 2009) and also large seabed areas deeply scratched by trawls and anchorages. Like Hg, the other anthropogenic trace elements also registered enrichments especially in the more coastal sediments (site BX1) of the Augusta offshore. Since the role of the Augusta basin as a critical point source of Hg for the Mediterranean Sea cannot be excluded, it is reasonable that together with Hg a net output of As, Cd, Pb, and Sb from the Augusta basin can be suggested.

6. Conclusions

The distributions of major and trace element concentrations in the Augusta sediments provide a solid database to examine the influence and the extent of anthropogenic contamination on the Augusta offshore sediments.

Despite the restrictive environmental legislation, Augusta Bay is probably still the main source of contamination for the offshore marine zone, reflecting the legacy of past anthropogenic emissions that will be maintained for a long time in the environment. The results of this study suggest as source of contamination the industrialized zones bordering the Augusta Bay, and are consistent with the previous studies on the same area about Hg (Di Leonardo et al., 2008) and the response of benthic foraminifera to environmental stress (Di Leonardo et al., 2007).

The CCA discriminates among major and trace elements on the basis of the anthropogenic activity influence, and evidences the unambiguous anthropogenic origin of mercury. The geochemical background for trace elements in the Augusta offshore is provided by mixture density estimation approach. Its definition provides an appropriate basis for comparison in other independent environmental investigations and helps to identify database deviations, reliability, metal-rich contributions from source sediment, and impact from human activities; indeed, the geochemical background is valuable for documenting differences between geographic areas as well as environmental change over time.

The multivariate exploratory statistical techniques (CCA and Frequency Distribution Analysis) used in this study constitute a powerful and economic tool in distinguishing between anthropogenic and natural origin for trace elements and can be adequately applied to other similar environments.

Acknowledgments

The authors would like to express sincere thanks to Prof. A. Aiuppa (Università di Palermo) and Dr. G. Valastro (ARPA DAP-Siracusa) for their support during the trace element analyses. Thanks are also due to the Urania Team for the assistance in sampling during oceanographic cruises. Dr. G. Scarcella kindly helped us in sample preparation. This research is part of the PhD Thesis of Rossella Di Leonardo supported by the European Social Fund. Other financial support comes from MIUR grants to Adriana Bellanca.

References

Alley, E.R., 2000. Water Quality Control Handbook. McGraw-Hill Inc., New York 12.

Apitz, S.E., Degetto, S., Cantaluppi, C., 2009. The use of statistical methods to separate natural background and anthropogenic concentrations of trace elements in radio-chronologically selected surface sediments of the Venice Lagoon. Marine Pollution Bulletin 58, 402–414.

Araújo, M.F., Jouanneau, J.M., Valério, P., Barbosa, T., Gouveia, A., Weber, O., Oliveira, A., Rodrigues, A., Dias, J.M.A., 2002. Geochemical tracers of northern Portuguese estuarine sediments on the shelf. Progress in Oceanography 52, 277–297.

Ausili, A., Gabellini, M., Cammarata, G., Fattorini, D., Benedetti, M., Pisanelli, B., Gorbi, S., Regoli, F., 2008. Ecotoxicological and human health risk in a petrochemical district of southern Italy. Marine Environmental Research 66, 215–217.

Baptista Neto, J.A., Smith, B.J., McAllister, J.J., 2000. Heavy metal concentrations in surface sediments in a nearshore environment, Jurujuba Sound, Southeast Brazil. Environmental Pollution 109, 1–9.

Bellucci, L.G., Giuliani, S., Romano, S., Albertazzi, S., Mugnai, C., Frignani, M., 2012. An integrated approach to the assessment of pollutant delivery chronologies to impacted areas: Hg in the Augusta Bay (Italy). Environmental Science and Technology 46, 2040–2046.

Budillon, F., Ferraro, L., Hopkins, T.S., Iorio, M., Lubritto, C., Sprovieri, M., Bellonia, A., Marzaioli, F., Tonielli, R., 2008. Effects of intense anthropogenic settlement of coastal areas on seabed and sedimentary systems: a case study from the Augusta Bay (Southern Italy). Rendiconti Online della Società Geologica Italiana 3, 142–143.

Cantone, G., Pilato, G., 1981. Effects of pollution on the Polychaetous populations in the roadstead of Augusta (Sicily). Journées d'Etudes sur la Pollutions Ciesm 5.

Carral, E., Villares, R., Puente, X., Carballeira, A., 1995. Influence of watershed lithology on heavy metal levels in estuarine sediments and organisms in Galicia (North-West Spain). Marine Pollution Bulletin 30, 604–608.

Castelli, M.G., Martelli, G.P., Spagone, C., Cappellini, L., Fanelli, R., 1983. Quantitative determination of polychlorinated biphenyls (PCBs) in marine organisms analysed by high resolution gas chromatography selected ion monitoring. Chemosphere 12, 291–298.

Chan, L.S., Yeung, C.H., Yim, W.W.S., Or, O.L., 1998. Correlation between magnetic susceptibility and distribution of heavy metals in contaminated sea-floor sediments of Hong Kong Harbour. Environmental Geology 36, 77–86.

Clark, R.B., 2001. Marine Pollution. Oxford University Press, Oxford.

Cundy, A.B., Collins, P.E., Turner, S., Croudace, I.W., Horne, D., 1998. 100 years of environmental change in a coastal wetland, Augusta Bay, southeast Sicily: evidence from geochemical and palaeoecological studies. In: Black, K.S., Paterson, D.M., Cramp, A. (Eds.), Sedimentary Processes in the Intertidal Zone. Geological Society of London Special Publication, 139, pp. 243–254.

D'Hondt, S., Jørgensen, B.B., Miller, D.J., Batzke, A., Blake, R., Cragg, B.A., Cypionka, H., Dickens, G.R., Ferdelman, T., Hinrichs, K.U., Holm, N.G., Mitterer, R., Spivack, A., Wang, G.Z., Bekins, B., Engelen, B., Ford, K., Gettemy, G., Rutherford, S.D., Sass, H., Skilbeck, C.G., Aiello, I.W., Guerin, G., House, C.H., Inagaki, F., Meister, P., Naehr, T., Niitsuma, S., Parkes, R.J., Schippers, A., Smith, D.C., Teske, A., Wiegel, J., Padilla, C.N., Acosta, J.L.S., 2004. Distributions of microbial activities in deep subseafloor sediments. Science 306 (5705), 2216–2221.

Daskalakis, K.D., O'Connor, T.P., 1995. Normalization and elemental sediment contamination in the coastal US. Environmental Science and Technology 29, 470–477.

De Domenico, E., 1972. Sulle condizioni fisico-chimiche e sulla produzione primaria delle acque esterne alla rada di Augusta. Atti della Società Peloritana di Scienze Fisiche Matemàtiche e Naturali 18, 177.

Dellwig, O., Hinrichs, J., Hild, A., Brumsack, H.-J., 2000. Changing sedimentation in tidal flat sediments of the southern North Sea from the Holocene to the present: a geochemical approach. Journal of Sea Research 44, 195–208.

Dempster, A.P., Laird, N.M., Rubin, D.B., 1977. Maximum likelihood from incomplete data via the EM algorithm. Journal of the Royal Statistical Society 39, 1–38.

Di Geronimo, I., 1983. Influence de la pollution sur le peuplements à mollusques de la baie d'Augusta (Sicile). Journées d'Etudes sur la Pollutions Ciesm 6, 715.

Di Leonardo, R., Tranchida, G., Bellanca, A., Neri, R., Angelone, M., Mazzola, S., 2006. Mercury levels in sediments of central Mediterranean Sea: a 150+ year record from box-cores recovered in the Strait of Sicily. Chemosphere 65, 2366–2376.

Di Leonardo, R., Bellanca, A., Capotondi, L., Cundy, A., Neri, R., 2007. Possible impacts of Hg and PAH contamination on benthic foraminiferal assemblages: an example from the Sicilian coast, Central Mediterranean. Science of the Total Environment 388, 168–183.

Di Leonardo, R., Bellanca, A., Angelone, M., Leonardi, M., Neri, R., 2008. Impact of human activities on the central Mediterranean offshore: evidence from Hg distribution in box-core sediments from the Ionian Sea. Applied Geochemistry 23, 3756–3766.

Di Leonardo, R., Bellanca, A., Neri, R., Tranchida, G., Mazzola, S., 2009. Distribution of REEs in box-core sediments offshore an industrial area in SE Sicily, Ionian Sea: evidence of anomalous sedimentary inputs. Chemosphere 77, 778–784.

Din, Z.B., 1992. Use of aluminium to normalize heavy-metal data from estuarine and coastal sediments of Straits of Melaka. Marine Pollution Bulletin 24, 484–491.

Elbaz-Poulichet, F., Dezileau, L., Freydier, R., Cossa, D., Sabatier, P., 2011. A 3500-year record of Hg and Pb contamination in a Mediterranean Sedimentary Archive (The Pierre Blanche Lagoon, France). Environmental Science and Technology 45 (20), 8642–8647.

Emelyanov, E.M., Shimkus, K.M., 1986. Geochemistry and sedimentology of the Mediterranean sea. In: Evans, G., Bush, P.R. (Eds.), Sedimentology and Petroleum Geology. Imperial College, D. Reidel Publishing Company, London.

Emmerson, R.H.C., O'Reilly-Wiese, S.B., Macleod, C.L., Lester, J.N., 1997. A multivariate assessment of metal distribution in inter-tidal sediments of the Blackwater Estuary, UK. Marine Pollution Bulletin 34, 960–968.

ESTRAMED s.p.a., 1982. Lavori di costruzione del 1° lotto funzionale sub-lotto A1 del porto commerciale di Augusta. Relazione tecnica annessa alla domanda di autorizzazione allo scarico dei materiali provenienti dal dragaggio dei fondali marini, ai sensi della delibera del 26 novembre 1980 emanata dal comitato interministeriale di cui all'art. 3 della legge 10.5.1976 n_319. Allegato n_1. 15 (Marzo 1982, Pomezia (RM)).

Förstner, U., Salomons, W., 1980. Trace metal analysis on polluted sediments: I. Assessment of sources and intensities. Environmental Technology Letters 1, 494–505.

Foucher, D., Ogrinc, Hintelmann, H., 2009. Tracing mercury contamination from the Idrija Mining Region (Slovenia) to the Gulf of Trieste using Hg isotope ratio measurements. Environmental Science and Technology 43 (1), 33–39.

Franzini, M., Leoni, L., Saitta, M., 1975. Revisione di una metodologia analitica per la fluorescenza X basata sulla correzione completa degli effetti di matrice. Rendiconti della Societa Italiana di Mineralogia e Petrologia 21, 99–108.

Gazzetta Ufficiale Della Repubblica Italiana (G.U.R.I.), 1998. Legge 9 dicembre 1998, n°426. Nuovi interventi in campo ambientale. Serie Generale n°291 Roma (14 Dicembre).

Gazzetta Ufficiale Della Repubblica Italiana (G.U.R.I.), 2009. Decreto Ministero dell'ambiente e della tutela del territorio 14 aprile 2009, n. 56. Regolamento recante "Criteri tecnici per il monitoraggio dei corpi idrici e l'identificazione delle condizioni di riferimento per la modifica delle norme tecniche del decreto legislativo 3 aprile 2006, n. 152, recante Norme in materia ambientale, predisposto ai sensi dell'articolo 75, comma 3, del decreto legislativo medesimo". Supplemento n. 83 alla Gazzetta Ufficiale 30 maggio 2009 n. 124. In Ministero dell'Ambiente e della Tutela del Territorio, Roma, pp. 1–67.

Genovese, S., De Domenico, E., 1975. Sulle condizioni microbiologiche delle acque esterne alla Rada di Augusta. Atti della Società Peloritana di Scienze Fisiche Matemàtiche e Naturali 21, 123.

Gibbs, R.J., 1977. Transport phases of transition metals in the Amazon and Yukon Rivers. Geological Society of America Bulletin 88, 829–843.

Gibbs, R.J., 1993. Metals of the bottom muds in Townsville Harbor, Australia. Environmental Pollution 81, 297–300.

Guieu, C., Chester, R., Nimmo, M., Martin, J.-M., Guerzoni, S., Nicolas, E., Mateu, J., Keyse, S., 1997. Atmospheric input of dissolved and particulate metals to the north-western Mediterranean. Deep-Sea Research Part II 44, 655–674.

Hotelling, H., 1936. Relations between two sets of variables. Biometrika 28, 321–327.

Hung, J.J., Hsu, C.L., 2004. Present state and historical changes of trace metal pollution in Kaoping coastal sediments, southwestern Taiwan. Marine Pollution Bulletin 49, 986–998.

Istituto Centrale Per La Ricerca Scientifica E Tecnologica Applicata Al Mare (ICRAM), 2005. Valutazione preliminare dei dati della caratterizzazione ambientale della Rada di Augusta e aree prioritarie ai fini della messa in sicurezza di emergenza. Sito di bonifica di interesse nazionale di Priolo, Roma, 33 (BoIPr-SI-GP-Rada di Augusta-01.02).

Istituto Centrale Per La Ricerca Scientifica E Tecnologica Applicata Al Mare (ICRAM), 2008. Progetto preliminare di bonifica dei fondali della rada di Augusta nel sito di interesse nazionale di Priolo—Elaborazione definitiva (BoI-Pr-SI-PR-Rada di Augusta-03.22, 182 pp.).

Jørgensen, B.B., Böttcher, M.E., Lüschen, H., Neretin, L.N., Volkov, I.I., 2004. Anaerobic methane oxidation and a deep H2S sink generate isotopically heavy sulfides in Black Sea sediments. Geochimica et Cosmochimica Acta 68, 2095–2118.

Klinkhammer, G.P., 1980. Early diagenesis in sediments from the eastern equatorial pacific, II. Pore water metal results. Earth and Planetary Science Letters 49, 81–101.

Lentini, F., Carbone, S., Cugno, G., Grasso, M., Scamarda, G., Sciuto, F., Montanari, L., Romeo, M., Ferrara, V., 1986. Geological map of the north-eastern Hyblean sector. Ed. S.E.L.C.A. Map scale 1:50.000, Firenze.

Librando, V., Fazzino, S.D., 1993. Quantification of polycyclic aromatic hydrocarbons and their nitro derivatives in atmospheric particulate matter of Augusta city. Chemosphere 27, 1649–1656.

Liu, W.X., Li, X.D., Shen, Z.G., Wang, D.C., Wai, O.W.H., Li, Y.S., 2003. Multivariate statistical study of heavy metal enrichment in sediments of the Pearl River Estuary. Environmental Pollution 121, 377–388.

Liu, J., Drane, W., Liu, X., Wu, T., 2009. Examination of the relationships between environmental exposures to volatile organic compounds and biochemical liver tests: application of canonical correlation analysis. Environmental Research 109, 193–199.

Loring, D.H., 1990. Lithium — a new approach for the granulometric normalization of trace metal data. Marine Chemistry 29, 155–168.

Loring, D.H., 1991. Normalization of heavy-metal data from estuarine and coastal sediments. ICES Journal of Marine Science 48, 101–115.

Magazzù, G., Romeo, G., Azzaro, F., Decembrini, F., Oliva, F., Piperno, A., 1995. Chemical pollution from urban and industrial seawages in Augusta Bay (Sicily). Water Science and Technology 32, 221–229.

Martin, J.M., Meybeck, M., 1979. Elemental mass-balance of material carried by major world rivers. Marine Chemistry 7, 173–206.

Martuzzi, M., Mitis, F., Buggeri, A., Terracini, B., Bertollini, R., 2002. Gruppo Ambiente e Salute Italia. Ambiente e stato di salute nella popolazione delle aree ad alto rischio di crisi ambientale in Italia. Epidemiologia e Prevenzione 26, 1–53.

Matschullat, J., Ottenstein, R., Reimann, C., 2000. Geochemical background — can we calculate it? Environmental Geology 39, 990–1000.

Matthai, C., Birch, G.F., Szymczak, R., 1998. Suboxic, early diagenetic processes in surficial sediments near a deepwater ocean outfall, Sydney, Australia. Journal of Geochemical Exploration 64, 1–17.

Mil-Homens, M., Stevens, R.L., Abrantes, F., Cato, I., 2006. Heavy metal assessment for surface sediments from three areas of the Portuguese continental shelf. Continental Shelf Research 26, 1184–1205.

Mineo, A., 1964. Sulla scomposizione dei miscugli di distribuzioni di frequenza. Annali della Facoltà di Economia e Commercio dell'Università di Palermo - anno XVIII, 2, pp. 121–145.

Mitterer, R.M., 2010. Methanogenesis and sulfate reduction in marine sediments: a new model. Earth and Planetary Science Letters 295, 358–366.

Molinier, R., Picard, J., 1953. Notes biologiques a propos d'un voyage d'etude sur les cotes de Sicile. Annales de l'Institut Océanographique 28 (4), 163–188.

Nath, B.N., Kunzendorf, H., Pluger, W.L., 2000. Influence of provenancer weathering, and sedimentary processes on the elemental ratios of the fine-grained fraction of the bedload sediments from the Vembanad Lake and the adjoining continental shelf, southwest coast of India. Journal of Sedimentary Petrology 70, 1081–1094.

Nesbitt, H.W., Young, G.M., Mclennan, S.M., Keays, R.R., 1996. Effects of chemical weathering and sorting on the petrogenesis of siliciclastic sediments, with implications for provenance studies. Journal of Geology 104, 525–546.

Parkes, R.J., Webster, G., Cragg, B.A., Weightman, A.J., Newberry, C.J., Ferdelman, T.G., Kallmeyer, J., Jørgensen, B.B., Aiello, I.W., Fry, J.C., 2005. Deep sub-seafloor prokaryotes stimulated at interfaces over geological time. Nature 436, 390–394.

Passier, H.F., Dekkers, M.J., De Lange, G.J., 1998. Sediment chemistry and magnetic properties in an anomalously reducing core from the eastern Mediterranean Sea. Chemical Geology 152, 287–306.

Pekey, H., Karakaş, D., Ayberk, S., Tolun, L., Bakoğlu, M., 2004. Ecological risk assessment using trace elements from surface sediments of İzmit Bay (Northeastern Marmara Sea) Turkey. Marine Pollution Bulletin 48, 946–953.

Petersen, W., Wallmann, K., Pinglin, L., Schroeder, F., Knauth, H.-D., 1995. Exchange of trace elements at the sediment–water interface during early diagenesis processes. Marine and Freshwater Research 46, 19–26.

Pugh, R.C., Hu, Y., 1991. Use and interpretation of canonical correlation analyses in Journal of Educational Research articles: 1978–1989. The Journal of Educational Research 84 (3), 147–152.

Qi, S., Leipe, T., Rueckert, P., Di, Z., Harff, J., 2010. Geochemical sources, deposition and enrichment of heavy metals in short sediment cores from the Pearl River Estuary, Southern China. Journal of Marine Systems 82, S28–S42.

R Development Core Team. R, 2010. A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria (http://www.R-project.org).

Ratha, D.S., Sahu, B.K., 1993. Multivariate canonical correlation techniques: an economic approach for evaluation of pollutants in soil and sediments of Bombay region, India. Environmental Geology 21, 201–207.

Reid, M.K., Spencer, K.L., 2009. Use of principal components analysis (PCA) on estuarine sediment datasets: the effect of data pre-treatment. Environmental Pollution 157, 2275–2281.

Reimann, C., De Caritat, P., 2005. Distinguishing between natural and anthropogenic sources for elements in the environment: regional geochemical surveys versus enrichment factors. Science of the Total Environment 337, 91–107.

Rémy, S., Prudent, P., Hissler, C., Probst, J.L., Krempp, G., 2003. Total mercury concentrations in an industrialized catchment, the Thur River basin (north-eastern France): geochemical background level and contamination factors. Chemosphere 52, 635–644.

Romano, E., Ausili, A., Zharova, N., Magno, M.C., Pavoni, B., Gabellini, M., 2004. Marine sediment contamination of an industrial site at Port of Bagnoli, Gulf of Naples, Southern Italy. Marine Pollution Bulletin 49, 487–495.

Romano, E., Bergamin, L., Finoia, M.G., Celia Magno, M., Ausili, A., Gabellini, M., 2009. The effects of human impact on benthic foraminifera in the Augusta harbour (Sicily, Italy). In: Dahl, E., Moksness, E., Støttrup, J. (Eds.), Integrated Coastal Zone Management. Blackwell Publishing Ltd., Chichester, UK, pp. 97–115.

Rubio, B., Pye, K., Rae, J.E., Rey, D., 2001. Sedimentological characteristics, heavy metal distribution and magnetic properties in subtidal sediments, Ria de Pontevedra, NW Spain. Sedimentology 48, 1277–1296.

Salminen, R., Gregorauskienè, V., 2000. Considerations regarding the definition of a geochemical baseline of elements in the surficial materials in areas differing in basic geology. Applied Geochemistry 15, 647–653.

Salvagio Manta, D., Angelone, M., Bellanca, A., Neri, R., Sprovieri, M., 2002. Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy. Science of the Total Environment 300, 229–243.

Schiff, K.C., Weisberg, S.B., 1999. Iron as a reference element for determining trace metal enrichment in Southern California coastal shelf sediments. Marine Environmental Research 48, 161–176.

Schippers, A., Neretin, L., Kallmeyer, J., Ferdelman, T.G., Cragg, B.A., Parkes, R.J., Jørgensen, B.B., 2005. Prokaryotic cells of the deep sub-seafloor biosphere identified as living bacteria. Nature 433, 861–864.

Schlesinger, W.H., 1997. Biogeochemistry: An Analysis of Global Change. Academic press (588 pp.).

Schrenk, M.O., Huber, J.A., Edwards, K.J., 2010. Microbial provinces in the sub-seafloor. Annual Review of Marine Science 2, 279–304.

Schultz, L.G., 1964. Quantitative interpretation of mineralogical composition from X-ray and chemical data for the Pierre Shale. United States Geological Survey Professional Paper 391.

Sciacca, S., Fallico, R., 1978. Presenza e concentrazione di inquinanti di origine industriale nei fanghi della Rada di Augusta. Inquinamento 20 (6), 1.

Spencer, K.L., 2002. Spatial variability of metals in the inter-tidal sediments of the Medway Estuary, Kent, UK. Marine Pollution Bulletin 44, 933–944.

Sprovieri, M., Oliveri, E., Di Leonardo, R., Romano, E., Ausili, A., Gabellini, M., Saggiomo, V., Barra, M., Tranchida, G., Bellanca, A., Neri, R., Budillon, F., Mazzola, S., 2011. The key role of the Augusta basin (southern Italy) in the mercury contamination of the Mediterranean Sea. Journal of Environmental Monitoring 13, 1753–1760.

Statheropoulos, M., Vassiliadis, N., Pappa, A., 1998. Principal component and canonical correlation analysis for examining air pollution and meteorological data. Atmospheric Environment 32, 1087–1095.

Steinfath, M., Repsilber, D., Scholz, M., Walther, D., Selbig, J., 2007. Integrated data analysis for genome-wide research. EXS 97, 309–329.

Stevens, J., 1986. Applied Multivariate Statistics for the Social Sciences. Lawrence Erlbaum Associates Inc., New Jersey 373–397.

Storelli, M.M., Storelli, A., Giacominelli-Stuffler, R., Marcotrigiano, G.O., 2005. Mercury speciation in the muscle of two commercially important fish, hake (*Merluccius merluccius*) and striped mullet (*Mullus barbatus*) from the Mediterranean sea: estimated weekly intake. Food Chemistry 89, 295–300.

Szefer, P., Glasby, G.P., Pempkowiak, J., Kaliszan, R., 1995. Extraction studies of heavy-metal pollutants in surficial sediments from the southern Baltic Sea off Poland. Chemical Geology 120, 111–126.

Taylor, S.R., Mclennan, S.M., 1985. The continental crust: Its composition and evolution. Blackwell Malden, Mass (328 pp.).

Teske, A., Sørensen, K.B., 2008. Uncultured archaea in deep marine subsurface sediments: have we caught them all? ISME Journal 2, 3–18.

Tobías, F.J., Bech, J., Sánchez Algarra, P., 1997. Statistical approach to discriminate background and anthropogenic input of trace elements in soils of Catalonia, Spain. Water, Air, and Soil Pollution 100, 63–78.

Tranchida, G., 2005. Ecosystem variability in the Sicily Strait: evidence from major and trace elements in sediment box-cores. Ph.D. thesis University of Palermo.

Tranchida, G., Bellanca, A., Angelone, M., Bonanno, A., Langone, L., Mazzola, S., Neri, R., Patti, B., 2010. Chronological records of metal deposition in sediments from the Strait of Sicily, central Mediterranean: assessing natural fluxes and anthropogenic alteration. Journal of Marine Systems 79, 157–172.

Tuncel, S.G., Tugrul, S., Topal, T., 2007. A case study on trace metals in surface sediments and dissolved inorganic nutrients in surface water of Ölüdeniz Lagoon-Mediterranean, Turkey. Water Research 41, 365–372.

Turekian, K., Wedepohl, K.H., 1961. Distribution of the elements in some major units of the earth's crust. Geological Society of America Bulletin 72, 175–192.

Vairavamurthy, M.A., Orr, W.L., Manowitz, B., 1995. Geochemical transformation of sedimentary sulfur: an introduction. In: Vairavamurthy, M.A., Schoonen, M.A.A. (Eds.), Geochemical tranformation of sedimentary sulphur. ACS Symposium, vol. 612. American Chemical Society, Washington, DC, pp. 1–17.

Ypma, T.J., 1995. Historical development of the Newton–Raphson method. SIAM Review 37, 531–551.

Zonta, R., Botter, M., Cassin, D., Pini, R., Scattolin, M., Zaggia, R., 2007. Sediment chemical contamination of a shallow water area close to the industrial zone of Porto Marghera (Venice Lagoon, Italy). Marine Pollution Bulletin 55, 529–542.