

Heavy metal and arsenic distributions in sediments of the Elba-Argentario basin, southern Tuscany, Italy

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Abstract Arsenic, chromium, cobalt, copper, lead, nickel, vanadium and zinc distributions in surficial and core sediments of the Elba-Argentario marine basin (southern Tuscany, central-western Italy) are reported. Analysis of such distributions compared with grain size and mineralogical data allowed the identification of areas showing trace element enrichments with respect to natural background. These enrichments are moderate and essentially restricted to Pb and Zn; only As shows a widespread, though not high, positive anomaly. This general pattern is in good agreement with the minor industrialization affecting the basin's watershed. An unexpected anomaly, concerning Co, Pb, and As, as well as Fe and Ti, has been pointed out close to Montecristo Island. This has been ascribed to illegal local dumping of chemical waste.

Introduction

In recent years, the need for a better understanding of heavy metal concentration and dispersion patterns in populated coastal environments of the Mediterranean Sea has been highlighted following the discovery of high levels of toxic heavy metals (particularly mercury) in both benthonic and pelagic marine organisms (Aston and Fowler 1985; Bacci 1989). These organisms, particularly filter-feeders, can take up metals through their digestive systems, thus increasing the potential for their entry into the human food chain. However, until a few years ago systematic studies involving the assessment of sources of heavy metals, their modes of transport, and distribution pattern in the Tuscany coastal zone were scarce. The problem was compounded by the absence of reliable in-

formation on background values of such metals in soils and sediments and limited knowledge of the source-transport-trap sequences under the prevailing coastal hydrodynamic conditions.

In the late 1980s and the early 1990s studies on the sedimentological and chemical characteristics of the sediments in the Tyrrhenian Sea basin, off the Tuscany coast, were undertaken as part of a series of Regione Toscana-sponsored studies on environmental quality. The study area, that is the continental shelf off Tuscany's coast, was divided into three units, each corresponding to a marine basin with distinct geographical, morphological and sedimentological features. The studies of the northern and the central basins have been completed and the results published in several papers (Leoni and others 1991a, b, 1992, 1995; Leoni and Sartori 1996a).

The present article provides results from a study on heavy metal (and As) concentration patterns in the Tuscany shelf's southernmost basin, which stretches from Elba Island to the Argentario Promontory. The study aims to provide a geochemical framework for assessing the sources and mechanism of heavy metal input, enrichment, and distribution in the coastal sediments. Its main goal is the identification and the assessment of natural (inherited) processes versus anthropogenic processes, which is fundamental in understanding environmental degradation problems and is essential for the establishment of meaningful coastal zone management strategies.

Geographic and oceanographic setting

The investigated zone is an approximately circular basin with a diameter of about 85 km and an area of 5600 km² (Fig. 1). It is a semi-enclosed basin confined in the east and northeast by the mainland of Italy, in the north by Elba Island and the Piombino Channel's sill, and in the west by the Elba Ridge. On the southern side the basin is open toward the southern Tyrrhenian Sea, the study area being confined here by an ideal line linking the Argentario Promontory to Giglio and Montecristo Islands. The basin corresponds to a block-faulted region limited in the west by a long, submerged anticlinal arch (Elba Ridge). The sea bed of the peripheral parts is mostly a relatively

Received: 12 January 1996 / Accepted: 9 September 1996

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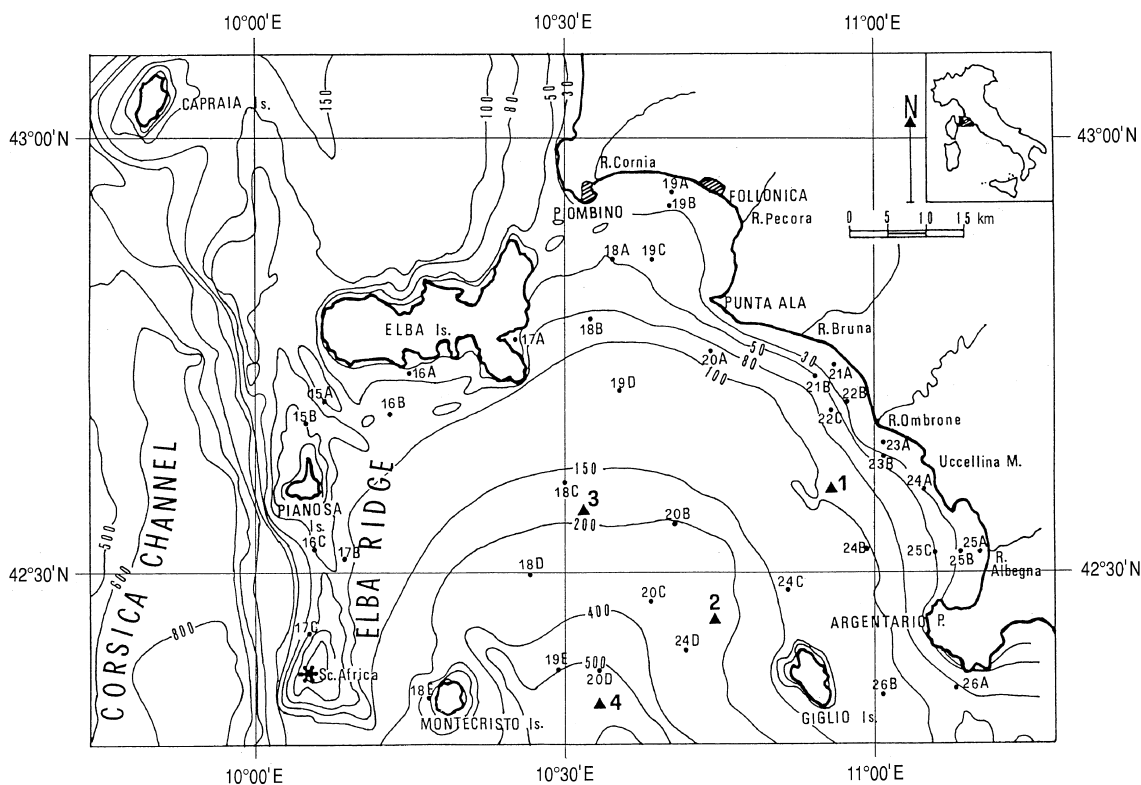


Fig. 1 Geographic setting and location of sampling sites. Surface sediment and core sampling sites are marked by dots and triangles, respectively

shallow plain (depth < 200 m). The basin's center is occupied by a wide, sub-rounded depression progressively deepening southward. This trough represents a graben structure, which reaches its maximum depth just south of Montecristo and Giglio Islands (500–600 m; Wezel and others 1981). Italy's mainland has a morphologically variable coast. Rocky cliffed headlands (Piombino, Punta Ala, Uccellina Mountains, and Argentario) alternate with low-lying sandy shores. There are high cliffs around most of the isles.

The sediments are derived from a watershed characterized by a great variety of mainly sedimentary rocks, ranging from carbonate to marly clay to arenaceous. Magmatic rocks are not uncommon; they mostly consist of intrusive, sub-intrusive or volcanic acidic rocks from the Tertiary and Quaternary post-orogenic magmatism of Tuscany. Less abundant outcrops are the ophiolitic rocks belonging to the Ligurian nappes. Within the studied area there are some of the most important mineral deposits of Tuscany, including the eastern Elba iron ores, the Campiglia Marittima and Boccheggiano (Cu-Pb-Zn) sulfide deposits, the Gavorrano and Niccioleta pyrite mineral deposits, and the Sb and Hg ores of Manciano and Monte Amiata.

The Ombrone River is by far the most important stream delivering sediments to the surveyed marine basin; its

drainage basin covers an area of about 3500 km². The Cornia, Bruna and Albegna rivers are small streams of essentially seasonal flow; their sediment contribution to the marine basin is negligible.

Information on the basin water circulation pattern is detailed for littoral drifts (Aiello and others 1975; D'Alessandro and others 1979), while for offshore currents there are only fragmentary data restricted to particular areas or time periods, or general investigations concerning the whole Tyrrhenian-Ligurian Sea (Elliott 1979). However, for such currents there is general agreement on a dominant surface water system flowing northward (Elliott 1979). The main branch moves approximately parallel to the coast of mainland Italy, while a minor branch flows toward the Ligurian Sea (north of the studied area) through the Corsica Channel (westernmost part of the mapped area of Fig. 1).

Materials and methods

Sampling was carried out with the Bannock oceanographic ship on 12 traverses roughly perpendicular to the coastline so as to cover most of the basin area uniformly. In nearshore zones, particularly near the mouth of the Ombrone and Albegna rivers, a more closely spaced sampling was performed. Thirty-seven surficial sediment samples, collected with a Shipeck grab (which scrapes about 2–4 cm of sediment from the sea floor), and four short cores (30–40 cm long), collected with a Reineck corer, were selected for this study. Locations of the grab

samples (solid dots) and the cores (solid triangles) are shown in Fig. 1.

The bulk samples (no preliminary removal of bioclastics) were analyzed for grain size, and mineralogical and chemical composition (major elements; Leoni and Sartori 1996b). The trace elements (Table 1) were determined by X-ray fluorescence using a Philips PW 1450 spectrometer following the analytical procedure proposed by Franzini and others (1972, 1975) and Leoni and Saitta (1976). This procedure, which utilizes powder pellets, is based on a full matrix correction method. The results were calibrated with respect to about 40 international standards of rocks and minerals covering a wide range of element concentrations. The pellets are obtained by pressing the powder

Table 1

Trace element contents in surficial and core sediments of the Elba – Argentario basin. Ni, Cr, V, Co, Cu, Zn, Pb, and As concentrations (in ppm) in the bulk samples. The numbers following the core identifier give sub-sample depth from the top of the core (in cm)

Sample	Ni	Cr	V	Co	Cu	Zn	Pb	As
Surficial sediments								
15A	60	60	50	6	48	36	23	17
15B	32	22	25	2	57	25	14	13
16A	73	122	97	16	32	76	35	34
16B	76	136	110	17	31	71	36	34
16C	32	20	29	4	58	24	14	20
17A	99	178	159	29	50	198	87	120
17B	49	60	81	10	36	48	21	17
17C	26	14	17	1	51	16	9	4
18A	54	146	107	14	23	94	36	37
18B	82	159	160	22	31	162	57	48
18C	76	135	176	24	25	130	57	41
18D	82	128	161	24	27	121	56	37
18E	43	68	112	17	33	52	32	80
19A	20	96	22	2	14	22	14	6
19B	80	145	138	18	38	179	67	27
19C	72	147	154	21	26	153	51	30
19D	72	143	181	24	26	141	62	34
19E	91	128	130	20	35	110	40	34
20A	77	149	138	19	27	143	47	33
20B	75	129	170	24	28	123	60	44
20C	81	122	155	22	28	116	56	30
20D	89	127	134	20	29	107	47	25
21A	58	124	83	14	20	68	20	14
21B	74	144	128	19	26	118	32	17
22B	71	139	120	18	26	104	27	15
22C	73	147	152	21	26	130	40	20
23A	60	115	94	13	30	71	22	16
23B	66	130	109	17	25	97	29	17
24A	68	133	113	18	24	100	25	20
24B	56	115	158	22	25	123	62	32
24C	78	133	147	21	26	126	64	38
24D	88	128	135	20	29	118	56	34
25A	77	144	128	19	27	105	25	16
25B	71	138	127	18	26	105	29	18
25C	72	145	143	19	26	121	42	23
26A	48	94	110	15	25	88	47	26
26B	75	131	144	20	26	120	64	36

Table 1
Continued

Sample	Ni	Cr	V	Co	Cu	Zn	Pb	As
Core sediments								
1-01	62	126	165	19	31	136	56	28
1-02	66	132	172	20	31	135	55	25
1-04	61	124	162	20	31	133	54	30
1-06	65	130	172	20	31	131	49	27
1-08	67	135	179	20	31	131	50	26
1-10	68	136	177	20	31	131	53	24
1-15	68	135	175	21	31	130	53	19
1-20	70	144	175	20	31	131	48	20
1-25	74	150	174	21	31	125	47	17
1-30	72	148	174	21	31	123	48	16
2-01	74	125	166	22	30	122	55	36
2-04	76	128	166	22	26	111	39	31
2-06	77	130	166	22	26	105	36	25
2-09	77	132	165	22	25	106	32	24
2-13	77	128	158	20	24	102	32	24
2-17	77	128	160	21	28	107	36	22
2-21	77	128	163	21	25	107	35	22
2-29	77	125	161	21	26	106	36	24
2-41	77	124	162	21	24	107	35	22
3-01	79	139	178	19	30	136	52	43
3-02	79	140	178	20	30	126	55	41
3-04	80	140	179	20	30	126	50	45
3-06	79	138	175	20	30	125	43	43
3-08	79	138	174	20	27	125	43	39
3-10	82	143	179	21	31	123	42	34
3-15	84	142	180	20	29	120	41	25
3-20	86	143	179	21	29	120	40	25
3-25	82	142	174	21	30	120	38	25
3-30	82	141	173	21	31	121	38	27
4-01	82	121	150	22	30	112	40	30
4-04	81	122	149	22	31	112	36	33
4-06	83	121	149	22	31	102	32	29
4-09	79	122	149	21	30	105	35	32
4-13	77	117	146	21	29	103	35	31
4-17	75	113	142	21	28	102	35	28
4-21	76	113	144	21	29	102	32	28
4-29	76	111	154	21	29	101	32	25
4-41	78	119	153	21	29	103	34	24

(~ 5 g), previously mixed with a binder [in our case an aqueous solution (~ 2–3 cc) of polyvinyl alcohol] in an aluminum sample holder. A pressure of 5 t/cm² for a few seconds was most commonly applied.

Volatile components (H₂O and CO₂ and organic matter) were collectively determined as loss on ignition (LOI) at 850 °C; a separate CO₂ determination by a gasometric method was also performed (Leone and others 1988). The qualitative mineralogical composition of bulk samples and clay fractions was studied by X-ray diffraction analysis using a Philips PW 1730 automatic X-ray diffractometer. Quantitative estimation of crystalline components was made through a method that combines chemical and X-ray diffraction data (Leoni and others 1988). Data from sedimentological, mineralogical and major chemical analyses are presented and discussed in another paper (Leoni and Sartori 1996b). This study only reports the grain size

Table 2
Simplified mineralogical and grain size composition of the surficial sediments in the Elba-Argentario basin; CO₂ and L.O.I. contents are also given. Data from Leoni and Sartori (1996b).

Qtz quartz, *Feld* plagioclase + K-feldspar, *Carb* calcite + aragonite + dolomite (trace), *Phy* mica-like minerals (mainly illite) + kaolinite + chlorite (chlorite s.s. and "chloritic intergrades") + smectite, *LOI* loss on ignition at 850 °C

Sample	Qtz + Feld w. %	Carb w. %	Phy w. %	Gravel w. %	Sand w. %	Silt w. %	Clay w. %	CO ₂ w. %	LOI w. %
15A	8	87	15	4.6	78.3	3.8	13.3	33.89	38.72
15B	3	91	6	14.6	77.7	2.5	5.2	40.34	43.38
16A	22	47	31	2.5	49.9	23.1	24.5	20.44	23.05
16B	16	49	35	0.2	63.2	8.4	28.2	21.37	25.35
16C	3	91	6	5.6	90.6	0.8	3.0	40.05	43.05
17A	20	16	64	<0.1	0.8	27.8	71.4	7.29	12.68
17B	8	69	23	4.4	64.3	9.1	22.2	29.13	37.39
17C	3	93	4	6.5	89.5	1.7	2.3	41.65	44.44
18A	37	28	35	0.3	53.4	12.7	33.6	12.15	15.21
18B	20	17	63	<0.1	0.8	28.3	70.9	7.53	13.28
18C	17	19	64	<0.1	0.2	22.2	77.6	8.34	15.99
18D	16	24	60	<0.1	1.0	19.8	79.2	10.61	15.95
18E	6	75	19	2.0	85.8	2.6	9.6	33.18	34.64
19A	72	20	8	12.7	83.5	0.8	3.0	8.70	9.35
19B	18	33	49	1.4	22.3	17.5	58.8	0.50	13.96
19C	25	17	58	<0.1	3.1	32.0	64.9	7.87	13.33
19D	18	17	65	<0.1	2.6	22.2	75.2	7.51	15.03
19E	14	28	58	<0.1	0.8	20.8	78.4	13.49	18.93
20A	23	17	60	<0.1	3.3	27.7	69.0	7.41	13.32
20B	16	21	63	<0.1	1.1	23.7	75.2	9.01	16.33
20C	15	26	59	<0.1	<0.1	22.0	78.0	11.25	18.42
20D	14	27	59	<0.1	0.9	23.8	75.3	11.97	18.69
21A	38	23	39	1.4	54.7	23.3	20.6	10.43	12.09
21B	26	17	57	<0.1	0.4	52.8	46.8	7.20	12.60
22B	27	18	55	<0.1	0.8	57.5	41.7	8.11	12.56
22C	23	15	62	<0.1	0.3	40.4	59.3	6.94	13.07
23A	36	20	44	0.2	45.2	31.1	23.5	9.02	11.38
23B	33	20	47	<0.1	13.5	46.3	40.2	9.28	12.24
24A	32	19	49	0.2	7.9	49.6	42.3	8.68	11.38
24B	20	14	66	<0.1	0.3	26.9	72.8	6.30	14.36
24C	16	18	66	<0.1	0.7	25.8	73.5	8.01	15.99
24D	14	25	61	<0.1	1.1	24.7	74.2	11.11	18.35
25A	24	17	59	1.8	3.8	33.5	60.9	7.77	14.35
25B	26	16	58	0.1	2.1	49.9	47.9	7.20	12.80
25C	22	15	63	<0.1	0.5	35.6	63.9	6.48	13.46
26A	24	22	54	8.8	32.5	23.0	35.7	9.71	15.20
26B	18	20	62	<0.1	1.2	25.7	73.1	8.48	16.05

and simplified mineralogical data, together with LOI and CO₂ values (Table 2).

Data analysis and evaluation

The choice of methods for data analysis is of great importance when assessing trace element concentrations in sediments for environmental studies. Evaluation of the data on the basis of absolute element concentrations (Table 1) provides significant information in only a few instances. Granulometry and mineralogy are important controlling factors for the abundance of trace elements. In order to reduce the influence of grain size and mineralogy and to provide a good criterion for the choice of a baseline or reference concentration, various methods of

normalization have been proposed (Förstner and Salomons 1984 and literature cited therein; Rule 1986). In the present work it has been found that most trace elements (Ni, Cr, V, Co, Zn, and Pb) are highly correlated with the finest granulometric class (clay) and with the phyllosilicate fraction (expressed as the sum of illite + kaolinite + chlorite + smectite; Table 3) and then it has been regarded as suitable to normalize their contents with this latter fraction. The same criterion had been followed in the studies of the neighboring basins (Leoni and others 1991b, 1995; Leoni and Sartori 1996a). Normalization with respect to the phyllosilicate fraction was performed through calculation of linear regression equations correlating trace element concentration to the phyllosilicate fraction content. This was carried out on the basis of two different criteria according to the element distribution throughout the cores. For the elements Ni, Cr, V,

Table 3

Correlation coefficients of trace elements with minerals and grain size fractions. (*Cc* calcite, *Ar* aragonite, *Qtz* quartz, *Pg* plagioclase, *Kf* K-feldspar, *Ill* mica-like minerals (mainly illite), *Ka* kaolinite, *Ch* chlorite s.s. + "chloritic intergrades", *Sm* smectite, *Phy* (Ill + Ka + Ch + Sm), *GR* gravel, *SA* sand, *SI* silt, *CL* clay)

	Ni	Cr	V	Co	Cu	Zn	Pb	As
Cc	-0.56	-0.89	-0.71	-0.71	0.79	-0.73	-0.52	-0.14
Ar	-0.24	-0.56	-0.25	-0.21	0.62	-0.29	-0.23	0.26
Qtz	-0.13	0.39	-0.06	-0.04	-0.68	0.02	-0.14	-0.20
Pg	-0.41	0.19	-0.45	-0.39	-0.56	-0.22	-0.44	-0.38
Kf	-0.76	-0.35	-0.82	-0.76	-0.47	-0.63	-0.66	-0.35
Ill	0.81	0.85	0.93	0.91	-0.52	0.89	0.73	0.29
Ka	0.69	0.76	0.83	0.81	-0.50	0.77	0.54	0.10
Ch	0.77	0.83	0.82	0.83	-0.34	0.88	0.73	0.44
Sm	0.59	0.43	0.66	0.64	-0.42	0.47	0.61	0.17
Phy	0.82	0.82	0.93	0.91	-0.51	0.87	0.75	0.29
GR	-0.76	-0.65	-0.74	-0.77	0.33	-0.58	-0.37	-0.35
SA	-0.81	-0.80	-0.87	-0.86	0.47	-0.86	-0.67	-0.21
SI	0.52	0.66	0.52	0.55	-0.49	0.54	0.17	-0.07
CL	0.83	0.73	0.91	0.88	-0.37	0.86	0.82	0.35

and Co, showing uniform distributions through the cores, data from all the collected samples (both surficial and core sediment) were applied; the data from cores were averaged over the entire core depths. For the elements Zn and Pb, which exhibit weak but distinct enrichments in the uppermost levels of the core columns (Fig. 2), only

data from the three deepest profile subsamples, together with data from some comparable offshore samples (15A, 15B, 16C, 17B, 17C), were used. Since this downcore trend had been interpreted as indicative of faint Zn and Pb pollution, which partly affects the surveyed basin, the baseline or reference concentrations of these metals were established with respect to presumably unpolluted sediments. On the basis of linear regression equations natural and anomalous concentrations were established. The sample population whose metal concentration is within a $\pm 2\sigma$ interval about the best fit line was defined as natural. Metal concentrations occurring outside this interval were regarded as anomalous.

Arsenic does not appear to be significantly correlated with any granulometric class or mineralogical fraction (Table 3); it is likely that its distribution is affected by multiple influences. Therefore the As data have been analyzed in terms of absolute concentrations. Like Pb and Zn, this element shows a slight, but distinct enrichment in the upper layers (Fig. 2); hence, the reference concentration for As was derived from the three deepest core subsamples and the farthest offshore sediment samples. In this case the reference concentration was merely calculated as the average absolute concentration in these samples. For As the concentrations occurring outside the $\pm 2\sigma$ interval about the reference concentration were regarded as anomalous.

Copper is negatively correlated with the phyllosilicate components. Therefore, as with As, normalization with

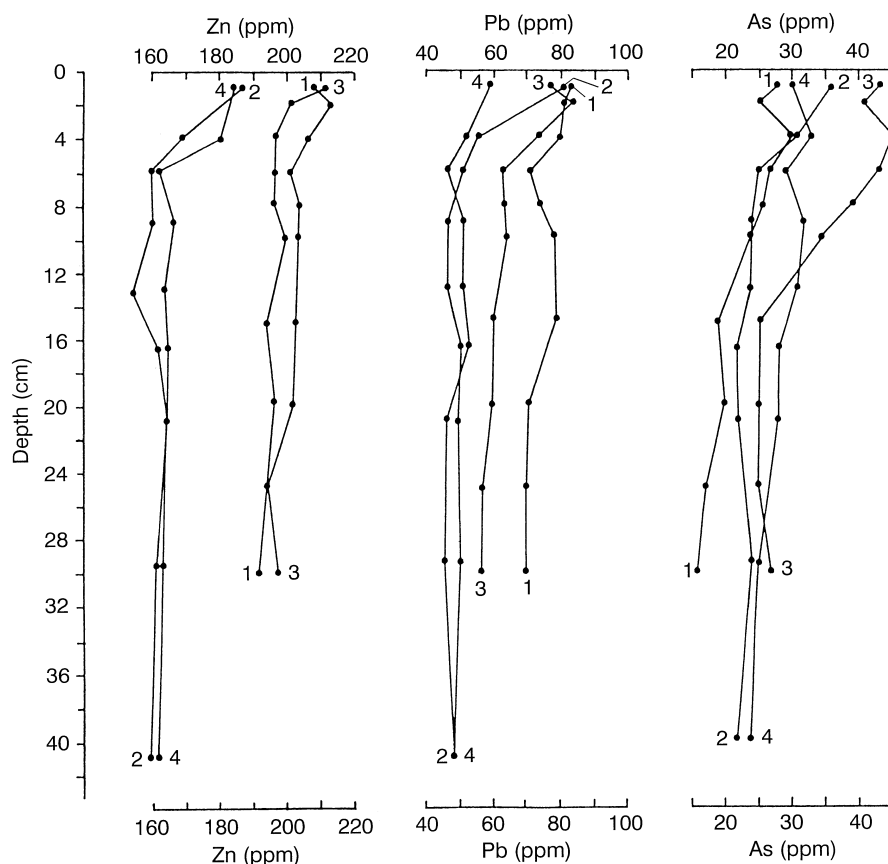


Fig. 2 Zn, Pb, and As concentrations (in ppm) as a function of depth in cores 1, 2, 3, and 4. For Zn and Pb the concentration values have been normalized to 100% of phyllosilicate fraction content; for As, data are plotted as non-normalized concentrations; see text

respect to this mineralogical fraction was not feasible and the baseline or reference concentration had to be derived as an average absolute concentration. Unlike As, for Cu the calculation of such concentration was performed on the basis of data from all the sites, since the metal distribution within the cores appears wholly uniform. Copper concentrations occurring outside the $\pm 2\sigma$ interval about the reference concentration were regarded as anomalous. Table 4 provides a summary of the methods applied to analyze the trace element concentrations; for Ni, V, Cr, Co, V, Pb, and Zn the regression equations which analyze the element concentration/phylosilicate content relationships, the sample groupings utilized for normalization and the correlation coefficients are reported. For most trace elements (except Cu) the distribution pattern within the basin is presented through maps (Figs. 3–6) which highlight the areas where there are concentrations of heavy metals (and As) anomalously higher (or lower) than the natural background. In these maps the difference between the observed metal concentration and the recalculated value from the regression equation (or, in the case of As, from the sediment average concentration) is plotted. For all elements (except As) the applied values are normalized to a 100% phyllosilicate fraction content.

Discussion

Copper

Copper appears to be significantly correlated with carbonates (Table 3). This correlation has been interpreted as an indirect one. Since most carbonates are organic in

Table 4

Methods applied to analyze the trace element concentration (n = number of samples utilized in the calculation of linear regression equations)

a) Normalization with respect to the phyllosilicatic fraction. Linear regression equations, standard deviations (σ) and correlation coefficients (r) from scatterplots of Ni, Cr, Co, V, Pb, and Zn concentrations (Y) vs phyllosilicate fraction (illite + kaolinite + chlorite + smectite) contents (X ; X , Y and σ in ppm)

Ni ^a	$Y = 0.79X + 29$	$\sigma = 47$	$r = 0.82$	$n = 37$
Cr ^a	$Y = 1.68X + 39$	$\sigma = 164$	$r = 0.82$	$n = 37$
Co ^a	$Y = 0.32X + 2$	$\sigma = 14$	$r = 0.91$	$n = 37$
V ^a	$Y = 2.14X + 17$	$\sigma = 74$	$r = 0.93$	$n = 37$
Pb ^b	$Y = 0.46X + 11$	$\sigma = 26$	$r = 0.91$	$n = 17$
Zn ^b	$Y = 1.68X + 12$	$\sigma = 27$	$r = 0.98$	$n = 17$

b) Derivation of the absolute average concentration in the bulk sediment. As and Cu average contents (X) and standard deviations (σ) in the bulk sediments (X and σ in ppm)

As ^b	$X = 20$	$\sigma = 6$	$n = 17$
Cu ^a	$X = 31$	$\sigma = 10$	$n = 37$

^a Data from all sites

^b Data from the three deepest sub-samples of each core and from some offshore samples (15A, 15B, 16C, 17B, 17C)

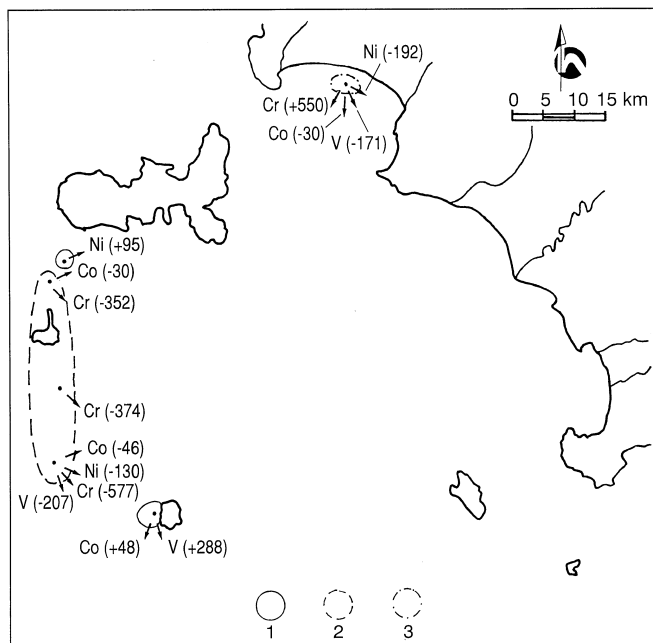


Fig. 3

Areas of anomalous concentrations of Ni, Co, V, and Cr: 1, area of positive anomaly; 2, area of negative anomaly; 3, area of positive anomaly for some elements and negative anomaly for others. Values are differences from background concentration, normalized with respect to 100% of phyllosilicate fraction content; only the differences greater than $|2\sigma|$ are reported (see text)

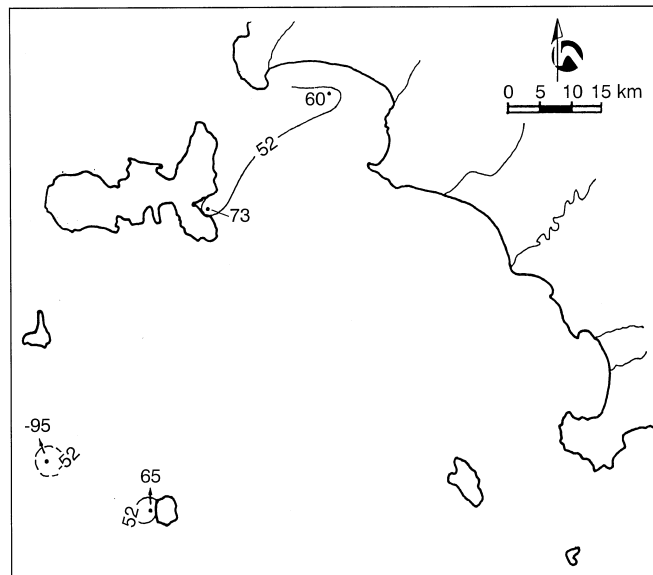


Fig. 4

Areal distribution of anomalous Pb concentrations. Values are differences from background concentration, normalized with respect to 100% of phyllosilicate fraction content; only the differences greater than $|2\sigma|$ are reported (see text). Continuous and dashed lines contour positive and negative anomalies, respectively

the latter is, in fact, predominantly controlled by the clay mineral assemblage transported by Ombrone River (Leoni and Sartori 1996b). The origin of the anomalously high Cr contents may be traced back to the presence of picotite (a chromium-bearing spinel), observed by Gandolfi and Paganelli (1975) in the Cornia sediments and ascribed by these authors to the erosion of the upper valley mineral deposits. The Montecristo anomaly, which refers to Co and V as well as Pb and As, is by far more important and intriguing than the Follonica anomaly. It is located in an area where the sedimentation conditions are very close to those of the nearby Elba Ridge; the sediments deposited atop the island platform are mostly biogenic sands and gravels with a low amount of very fine-grained clays. The latter are significantly enriched in Co, V, Pb, and As, in strong contrast to the clays of the Elba Ridge, which show low negative anomalies for most of these elements. Furthermore, Montecristo sediments are very rich in Fe and Ti in comparison with texturally equivalent sediments of adjacent areas. This anomalous chemistry cannot be explained on the basis of the sediment mineralogy or by the presence of any heavy metal-bearing mineral deposit on the nearby island (a granodioritic stock). The only likely explanation is to be found in anthropogenic contamination through dumping of waste from a chemical plant. It is well known that for many years a titanium dioxide chemical plant located near Follonica was allowed to discharge into Corsica Channel large amounts of waste made up of very fine amorphous iron and titanium hydroxides ("red muds"), major components of which included significant amounts of heavy metals and As. It is plausible to envisage that whenever weather conditions or the Corsican environmentalists' protests hampered access to the established offshore dumping site, illegal dumping of waste close to Montecristo Island took place.

Lead, zinc, and arsenic

Pb and Zn show strong positive correlations with the phyllosilicate fraction (Table 3). Unlike Ni, Cr, V, and Co, they show definite trends along the core profiles, being slightly enriched in the upper layers of the cores (Fig. 2). For As, whose concentration could not be normalized because of the absence of any significant correlation, the same downcore trend observed for Zn and Pb is evident (Fig. 2). The areal distribution of Zn, Pb, and As anomalous contents in the Elba-Argentario basin is presented in Figs. 4–6.

The main Pb positive anomaly extends over a limited area between Elba Island and the Follonica Gulf (Fig. 4). Data from the sediments of the Elba-Livorno basin (north of the studied area), where it was demonstrated that an important Pb contamination was related to the activities of the big smelting plant at Piombino (Leoni and others 1991b), would also suggest an anthropogenic origin for this anomaly. This hypothesis is supported by the Pb distribution profiles in the cores, which, though not collected in the area of significantly anomalous Pb concentrations, indicate an overall tendency of the basin

sediments to be Pb-enriched in the surficial layers. Close to the Elba coast the Pb anomaly could also be partially related to the influx of natural materials from the eastern Elba Island mineral deposits. Another positive anomaly is located close to Montecristo Island. This anomaly, which overlaps those of Co, V, and As, is most likely of anthropogenic origin. The comments regarding Montecristo enrichments of Co and V can be applied to Pb as well.

The distribution of Zn anomalous concentrations (Fig. 5) is very similar to that of Pb. It differs mainly in the intensity of the anomaly and for the fact that the area covered is wider and spreads further offshore. As for Pb, an important Zn contribution from the nearby industrial center of Piombino, as well as a minor natural influx from Elba mineral deposits, is inferred. Unlike Pb, Zn concentrations in the Montecristo area appear to be normal.

The As distribution pattern clearly exhibits a low positive anomaly over a wide belt extending into the central part of the basin (Fig. 6). Previous studies (Leoni and others 1991b, 1995; Leoni and Sartori 1996a) showed that such a belt stretches from south to north to cover most of Tuscany's continental shelf; only the outermost parts, as well as the area of relatively coarse and fast sedimentation close to the coast, appear to be covered by sediments with normal As concentrations. Arsenic concentrations change with depth in all of the cores, showing a more or less sharp increase in the upper part of the profiles. In the Elba-Argentario basin this pattern is particularly evident in cores 2 and 3 (Fig. 2). Such a feature can only be explained as due to an important anthropogenic contribution of As to all of Tuscany's coastal basins. Within the basins' catchment area many As sources related to man's activities could be identified. However, in our opinion, the greatest contribution of As was to be found in the activities of some borate-treating industrial plants of southern Tuscany. The borate minerals worked there are often associated with significant amounts of As sulphides. For many years their purification was achieved through a roasting process, which resulted in an important release of As to the atmosphere. The subsequent influx of As from the atmosphere to all of the ecosystem of coastal Tuscany would explain the diffuse As anomaly present all over the region's continental shelf. The effects of some important coastal contributors, such as the Livorno or Piombino industries, are superimposed on this pattern (basins north of the studied area; Leoni and others 1991b, 1995). As for the Elba-Argentario basin, within the belt of diffuse As anomaly two small maxima, located respectively in the center of the basin and close to eastern Elba Island, stand out. The first maximum is most likely due to the basin's hydrodynamic conditions, which favor the sinking of the finest-grained particulates in this area. The second concentration peak is interpreted as related to the combined effects of anthropogenic As contamination and the influx of natural As-bearing debris from eastern Elba Island mineral deposits.

For the marked positive anomaly close to Montecristo Island, the comments regarding the concentration maxima

of Co, V, and Pb of the same area can be applied to As as well.

Conclusions

1. Compared with the two northernmost basins of Tuscany, the Elba-Argentario basin appears to be the area least affected by anthropogenic contamination from heavy metals. The positive anomalies are few, faint and, most of them, areally restricted. This general pattern is in good agreement with the minor industrialization affecting the basin's watershed.

2. The most important industrial center of the Elba-Argentario basin's catchment is located at Piombino, close to the area's northern boundary. Due to the prevailing winds and surface marine currents, most of the products from the Piombino industrial activities (mainly metallurgical activities) are transported northward beyond Piombino Channel and deposited in the basin north of Elba Island (Leoni and others 1991b).

3. Only minor amounts of the contaminants issued from the Piombino industrial center (mostly Pb, Zn, and As) are distributed in the Elba-Argentario basin. These are regarded as the main cause of the low positive Pb-Zn-As anomaly located between eastern Elba Island and the Follonica Gulf (that is the basin zone closest to Piombino). However, there is reason to believe that this anomaly is partly due also to the accumulation of natural debris originating from erosion of Elba Island mineral deposits.

4. In comparison with the two northernmost basins, the influence of the important and numerous mineral deposits exposed in the watershed of the Elba-Argentario basin seems to be mostly visible in the large scattering of single values and sets of data concerning trace element concentrations, which entails high standard deviations about background levels. Only in a few cases do the latter appear significantly higher in the southern basin than in the northern ones (Leoni and others 1995).

5. It is possible that such high standard deviations could partially obscure the heavy metal trends related to anthropogenic contamination processes; however, this possibility ought not to be overestimated, since the method applied for data evaluation proved to be sensitive enough to reveal even relatively moderate and areally restricted anomalies such as the Co-Pb-As anomaly of Montecristo Island.

6. Accumulation of As from anthropogenic sources, though of low absolute intensity, is the most important contamination process as to areal extent. The inferred major input route, that is the atmospheric pathway, explains the wide distribution of As-contaminated particulates.

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