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Geochemical anomalies of potentially hazardous elements reflect catchment geology: An example from the Tyrrhenian coast of Italy

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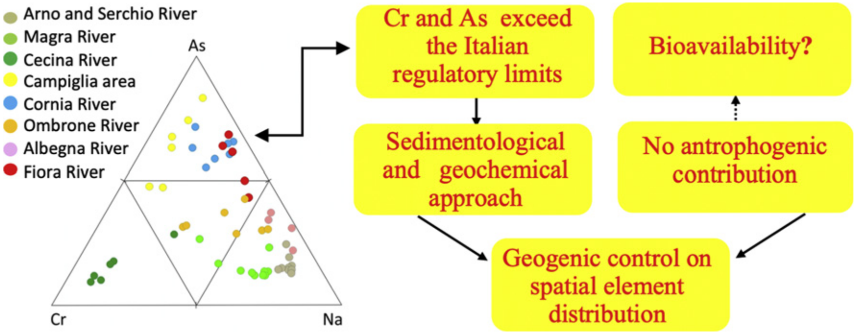
HIGHLIGHTS

- The study is based on an integrated geological, petrographic and geochemical dataset.
- We assessed the geogenic versus anthropogenic origin of potentially hazardous metals.
- Natural concentrations of toxic metals in sediments can exceed regulatory limits.
- Anomalous Cr, Ni and As concentrations are recorded in modern beach sands.
- Natural element abundance is a function of catchment geology and sediment transport.

GRAPHICAL ABSTRACT



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ABSTRACT

Assessing soil contamination by hazardous metals and estimating the extent to which metal concentrations in surficial sediments may pose risks to human health are increasingly important environmental issues. An integrated sedimentological and geochemical study of 57 Holocene beach sands from the shallow subsurface (120–130 cm depth) of the heavily urbanized Tyrrhenian Sea coast of Italy (Tuscany and adjacent coastal stretches) allowed a remarkable compositional heterogeneity to be identified as a function of spatial variations in riverine sediment supply and alongshore sediment dispersal patterns.

Concentrations of Cr, Ni, and As exceeding maximum permissible limits for recreational/industrial sites (150 mg/kg, 120 mg/kg, and 20 mg/kg, respectively) reveal spatial trends that fit the petrography of modern beach sands and closely reflect the geology of river catchments, thus indicating a geogenic origin. Extremely high concentrations of Cr (and Ni), even 10 times greater than threshold values, are interpreted to reflect sediment supply from river catchments rich in ultramafic rocks (ophiolite sequences of Cecina and Campiglia areas), with subsequent transport via the longshore drift. On the other hand, high As concentrations in the Campiglia region and along the southern stretch of coast reflect leaching of felsic volcanic and plutonic parent rocks and hydrothermal products related to the Tuscan and Roman magmatic provinces cropping out in the Fiora, Albegna, and Cornia river catchments.

This study shows that coastal sediment derived from particular source rocks is likely to contain potentially harmful metals in predictable proportions, which may easily exceed maximum allowable concentrations. Assessing spatial distribution of such metals based on catchment geology and sediment transport pathways may help

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separate natural concentrations from the anthropogenic contribution, providing a valuable source of information for appropriate remediation strategies and management options.

1. Introduction

The assessment of soil contamination by potentially toxic metals and the estimate of anthropogenic enrichment represent increasingly important issues, especially in highly vulnerable coastal environments. In Europe, coastal areas are subject to an increasing anthropic pressure: around 86 million people live within 10 km from the coastline and about 200 million people within 50 km from the coastline, respectively (ETC-CCA, 2011; Collet and Engelbert, 2013). In highly permeable sand deposits, pollutants can be leached through the soil profile and may easily pollute groundwater. In finer-grained deposits, they tend to accumulate in topsoil layers and can be toxic to plants and soil microbial biomass (Planquart et al., 1999; Ashworth and Alloway, 2004; Businelli et al., 2009).

To get an accurate depiction of environmental contamination, the distinction between natural metal concentrations and the anthropogenic contribution should be taken into account. Once background values are properly defined, geochemical anomalies can be estimated by subtracting background concentrations from measured metal contents (Reimann and Garrett, 2005; Zhang et al., 2009). It is well established that the definition of background values of potentially toxic metals requires integration of geochemical data with accurate geological studies (Miller, 1997; Box and Wallis, 2002; Tarvainen and Kallio, 2002; Myers and Thorbjornsen, 2004).

Although sediment provenance represents a major controlling factor of natural metal distribution in sediments (Salminen and Tarvainen, 1997; Vital and Stattegger, 2000; Amorosi and Sammartino, 2007; Devesa-Rey et al., 2011), in the vast majority of environmental studies in alluvial and coastal plains, the geological characteristics of river catchments are neglected and the spatial distribution of potentially harmful metals is interpreted on the basis of statistical analysis alone. In this study, which is aimed to investigate the geogenic versus anthropogenic origin of potentially hazardous metals along the Tyrrhenian coast of Italy (Liguria, Tuscany and Latium – Fig. 1) through a combined sedimentological and geochemical approach, we present a set of 57 geochemical analyses from beach sands and use the excellent petrographic datasets by Gandolfi and Paganelli (1975a, 1975b, 1975c, 1984) and Garzanti et al. (2002) from the same area to make geologic inferences on sediment composition.

Human exposure to inorganic arsenic or hexavalent chromium is a major public health problem worldwide. High Cr levels along the Cecina River valley, Tuscany (Amorosi et al., 2013; Tassi et al., 2018) and along the Tyrrhenian coast of Liguria (Cosma et al., 1979; Leoni et al., 1991) have been inferred to reflect a possible natural control, though the possible influence of industrial/harbor activities related to shipbuilding and chemical plant has not been ruled out (Bertolotto et al., 2005; Mugnai et al., 2010). High levels of arsenic have been reported from agricultural soils of northern Latium and Mount Amiata, in Tuscany (Tamasi and Cini, 2004), and As concentrations exceeding the regulatory limit for drinking waters have been detected in groundwater from a large area of volcanic origin (Cubadda et al., 2015). However, lack of knowledge about background levels, with few exceptions (Leoni and Sartori, 1996), has resulted in uncertain interpretations (Dinelli et al., 2005; Cortecci et al., 2008; Ungherese et al., 2010).

Previous work on late Holocene alluvial deposits from the Pisa area has shown that metals are typically concentrated in the finest sediment fraction (floodplain clays), whereas coarser crevasse and overbank deposits exhibit invariably lower metal contents (Amorosi et al., 2013). Marked changes in grain size, thus, can lead to biased estimates of spatial metal distribution. To minimize the possible influence of grain size and sediment texture on sediment composition, and thus emphasize the provenance signal, in this study we focused on a particular sedimentary facies, which is representative of a specific (nearshore) subenvironment, between the backshore and the shoreface. All study samples are sands, with only very minor silt and clay proportions. To reduce the possible effects of anthropogenic contamination, we focused entirely on subsurface samples collected inland from the modern shoreline.

2. Geological setting

Based on the distinctive geological features of major river catchments (Geological Map of Tuscany – Fig. 1) and petrographic/mineralogical compositions accurately depicted from modern nearshore sands (Gandolfi and Paganelli, 1975a, 1975b, 1975c, 1984; Garzanti et al., 2002), eight geological provinces, each reflecting particular river transport, were differentiated from north to south (Fig. 1). For detailed geological information, the reader is referred to classic regional and local studies (Giannini and Lazzarotto, 1975; Boccaletti and Coli, 1982; Carmignani and Kligfield, 1990; Rocchi et al., 2003; Molli, 2008; Carmignani et al., 2013).

(1) Magra River, 62 km long, flows from NW Tuscany into the Ligurian Sea. Its catchment is dominated by siliciclastic, deep-marine turbidites (sandstone-marl alternations of the Oligocene Macigno Fm.). A significant volume of mafic and ultramafic (ophiolite) rocks, including serpentinized peridotites and gabbros, is exposed in the Vara River catchment, a western tributary of Magra River.

(2) A similar lithologic composition typifies the catchments of Arno River (241 km), the longest river in Tuscany, and Serchio River (136 km). Thick turbidite foredeep successions are widespread in both watersheds. Three wedge-shaped sediment bodies, Oligocene to Miocene in age, exhibit progressively younger ages in NE direction (Macigno, Cervarola, and subordinate Marnoso-arenacea Formations). Turbidites consist of quartzofeldspathic sandstone-marl alternations, with common metamorphic and sedimentary lithic fragments of Alpine provenance. Sandstones are also abundant along the lower reaches of the Arno River. At the northwestern tip of this province (Apuane area), metamorphic rocks (including low-grade phyllites), metapsammites and porphyroids are present.

(3) A varied lithologic composition, including sandstones, mudstones, limestones, and turbidite successions characterizes the Cecina River system. The abundance of thick ophiolitic sequences, drained by both northern and southern tributaries, represents the diagnostic feature of this catchment.

(4) Minor rivers drain the relatively small Campiglia area, located at the northern margin of the Tuscan magmatic province. Apart from Jurassic limestones and marls, this area includes felsic volcanic and plutonic rocks (monzo-syenogranitic rocks at Campiglia Marittima, rhyolites at S. Vincenzo) emplaced during the Pliocene. Ophiolite rocks crop out NW of Campiglia Marittima, at short distance (< 2 km) from the Tyrrhenian coast (Fig. 1).

(5) Turbidites of Oligo-Miocene age (Macigno Fm.) and large shale, siltstone, and limestone lithosomes are exposed in the Cornia River (50 km) watershed. Felsic volcanic and plutonic rocks of the Tuscan magmatic province, coeval and lithologically similar to those of the Campiglia area, crop out at distinctive

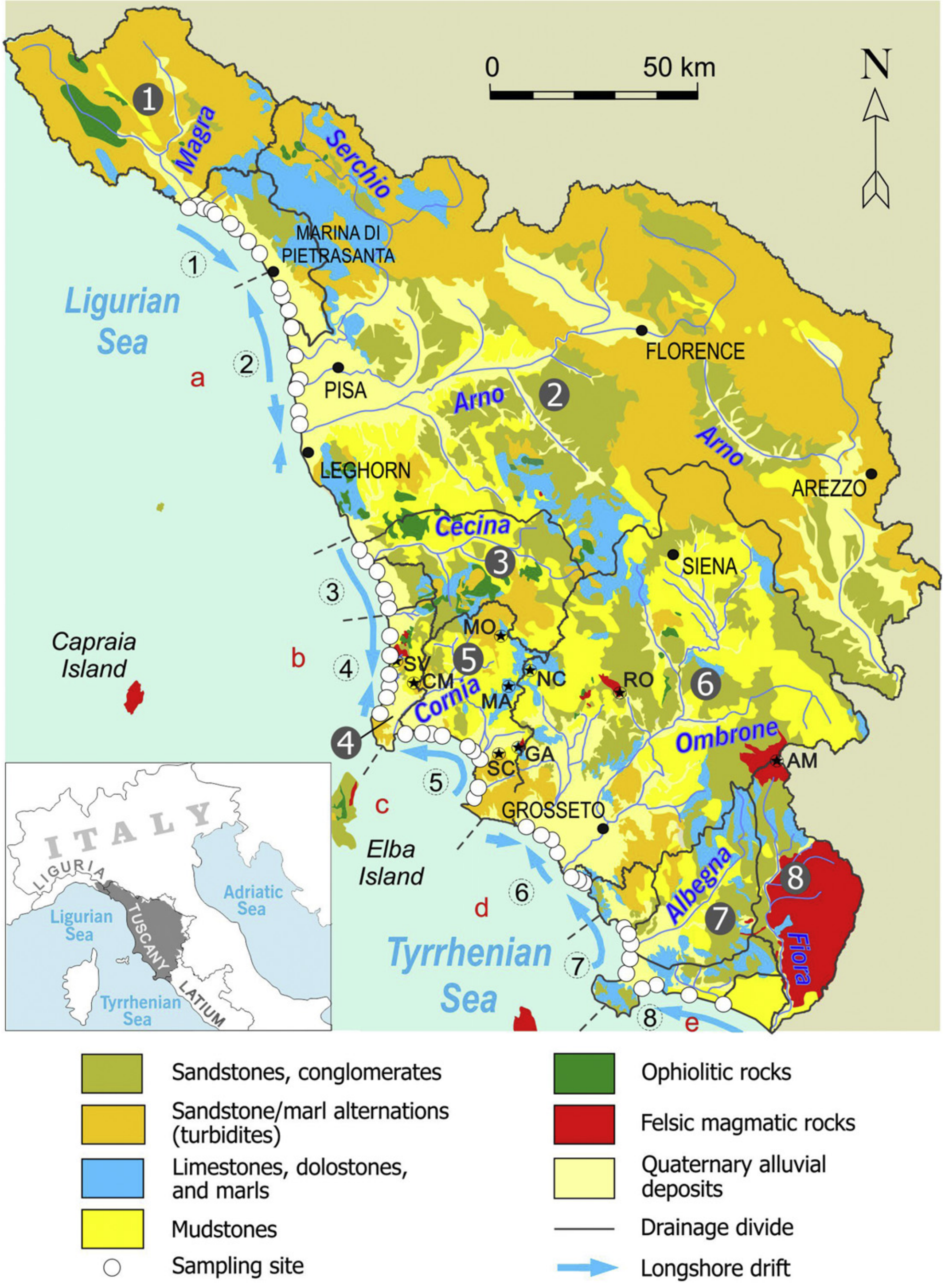

Fig. 1. Geological sketch map of the study area (modified from the Geological Map of Tuscany, 2004), with location of the analyzed beach sands (white dots). Samples are subsurface, pre-industrial beach-ridge deposits collected up to 1 km inland of the modern shoreline, Grey dots indicate river catchments (1: Magra, 2: Arno/Serchio, 3: Cecina, 4: Campiglia, 5: Cornia, 6: Ombrone, 7: Albegna, 8: Fiora). Dashed circles indicate river-influenced sectors as a function of the longshore drift. Red letters indicate physiographic units (a: Northern Tuscany, b: Cecina River, c: Follonica, d: Ombrone River, e: Ombrone River). Stars indicate ore deposits (SV: San Vincenzo, CM: Campiglia Marittima, MO: Monterotondo Marittimo, NC: Niccioleta; MA: Massa Marittima, SC: Scarlino, GA: Gavorrano, RO: Roccastrada, AM: Mt. Amiata).

locations (monzo-syenogranites at Gavorrano and rhyolites at Roccastrada).

(6) Ombrone River, 161 km in length, is the second largest river in Tuscany. Carbonate platform to pelagic sedimentary and metasedimentary successions, thick turbidities (Macigno and Mt. Modino Fm.) sequences, along with Upper Miocene to Quaternary continental and marine mudstones, sandstones, and conglomerates characterize this watershed. The Ombrone River catchment is also fed by volcanic rocks, belonging to the Tuscan magmatic province (Mt Amiata trachydacites and Roccastrada rhyolites).

(7) Carbonate successions crop out extensively in the Albegna river catchment. Pelagic limestones are associated with relatively deep-water sediments (shale and cherts) and shaly to calcareous

turbidites.

(8) In the Fiora river catchment, thick volcanic successions assigned to the Quaternary Roman Magmatic Province crop out. Potassic (trachytes, latites) to ultrapotassic (leucite tephrites to phonolites and leucitites) lavas are associated with abundant carbonate detritus from the Mesozoic platforms. Thick successions of mudstones, sandstones and relatively small conglomerate bodies are also exposed in this watershed.

3. Morphodynamic setting

The stretch of coast investigated in this study is about 400 km long and extends between the mouths of Magra and Fiora Rivers (Fig. 1). It is dominated by low-coast sandy beaches (i.e. strandplains), with small pocket beaches and short stretches with rocky cliffs. Major entry points of fluvial sediment delivered to the Tyrrhenian Sea are from Magra, Serchio, Arno, Cecina, Cornia, Bruna, Ombrone, Albegna and Fiora rivers (see related geological provinces in Fig. 1).

River deltas are of wave-dominated type and their arcuate shapes mostly reflect sand distribution parallel to the coastline due to the longshore currents. Longshore currents form between the wave breaker-zone and the beach, depending on the oblique incoming of waves relative to the coastline. They run parallel to the coast and their direction is controlled by the angle on which the waves approach the coast. Longshore currents cause the longshore drift, which is the transport of sediment along the coast.

Natural morphologic headlands along the coast of Tuscany confine sediment movement to five distinct physiographic units (a-e in Fig. 1), with their own patterns of longshore drift (Aiello et al., 1975; Anfuso et al., 2011; Cipriani et al., 2013; Anthony, 2018). Petrographic analyses of modern beach sands (Aiello et al., 1975; Gandolfi and Paganelli, 1975a, 1975b, 1975c; Garzanti et al., 2002) have been used to define with accuracy the directions of the longshore drift within the individual physiographic units and to localize zones of convergence. From north to south, the following physiographic units have been identified:

a. The Northern Tuscany unit extends for 63 km from Punta Bianca to the North Leghorns Hills and is fed by Magra, Serchio, and Arno rivers. The longshore drift is southward-trending from the Magra River mouth to Marina di Pietrasanta, where a zone of convergence is recognized. Another convergence area is located south of the Arno River mouth.
b. The Cecina River unit is 43 km long. Sediment supply along this stretch of coast is mainly due to the discharge from the Cecina River. The littoral drift is S-directed and a zone of convergence is identified close to the village of Campiglia Marittima.
c. The Follonica unit, 23 km long, is mainly fed by Cornia River and is characterized by a northward longshore drift.
d. The Ombrone River unit is 32 km long. Along this stretch of coast, sands supplied by the Ombrone and Albegna rivers are redistributed by the N-directed longshore drift. A small convergence area is located in the northernmost sector of this unit.
e. Only the northernmost portion of the Fiora River unit falls in the study area. The sediment drift is northward-trending, from the near Latium coast.

4. Methods

Fifty-seven sampling sites, with average spacing of about 1 sample/7 km, cover the study area. To emphasize the role of major rivers as sediment feeders of the coastal system, we focused sampling on the laterally most continuous sandy beaches (strandplains). On the other hand, no samples were collected along rocky cliffs or within small pocket beaches. Sampling, in general, took place far from the modern beach, in the subsurface of the Holocene coastal plain, within 1 km distance from the modern shoreline.

At each study site, samples (500 g) were collected by hand drilling, at depths of 120–130 cm, to avoid upper potentially contaminated horizons, using Eijkelkamp equipment (01.11.SO hand auger set for heterogeneous soils). Soils in the study area (*Arenosols*) generally have low maturity and thin (<1 m) profiles. Sampling depth in the area was sufficiently deeper to be representative of truly pre-industrial conditions (Romano et al., 2015).

Geochemical analyses were performed at the University of Bologna. The entire sample obtained from the hand auger was oven-dried at 50 °C, powdered and homogenized in an agate mortar and analyzed by X-ray fluorescence (XRF) spectrometry using a Philips PW 1480 spectrometer. The matrix correction methods of Franzini et al. (1972), Leoni and Saitta (1976), and Leoni et al. (1986) were followed. Certified reference material, including samples BR, BCR-1, W1, TB, NIM—P, DR-N, KH and AGV-1 (Govindarajiu, 1989), was also analyzed. The estimated precision and accuracy for trace-element determinations was 5%. For elements with low concentrations (<10 ppm), the accuracy was 10%.

We preferred XRF to aqua-regia inductive coupled plasma mass spectrometry (ICP-MS), because of the proven lower efficiency of aqua regia extractions for the total determination of certain metals, such as Cr and Ni (Sterckemann et al., 1996, Ščančar et al., 2000, Spijker, 2005, Tarvainen et al., 2009, Amorosi and Sammartino, 2011).

Sediment provenance interpretations also relied upon detailed comparison with sand petrographic data by Gandolfi and Paganelli (1975a, 1975b, 1975c, 1984) and Garzanti et al. (2002). We grouped petrographic analyses on a geographic basis into six assemblages that coincide with the coastal stretches marked as 1–6 in Fig. 1. Unfortunately, no petrographic data are available from the southern (Albegna and Fiora) provinces (7–8 in Fig. 1). As a result, only qualitative data were provided for these areas.

As our study samples are not loose sediments from modern beach environments, but they were collected from the subsurface of older (Holocene) beach ridges that are incorporated at present in the coastal plain inland of the coast, we applied to these sediments the same legislation used for soils.

5. Results

The results of XRF analysis are shown in Table 1, where elemental concentrations are summarized through the subdivision of samples into eight coastal segments (Fig. 1). Each group was identified using a combination of catchment geology with the local direction of the littoral drift (Section 3). The environmental significance of geochemical data is documented by red colors, which highlight the stretches of coast where elemental contents are greater than the threshold limit values defined by the Italian regulations (Legislative decree, 03/04/2006, no. 152, Annex 4-V5).

If matched against the maximum permissible levels in soils, elemental contents from the Tyrrhenian cored samples generally lie under these values by a good margin, irrespective of the stretch of coast considered. The opposite, instead, can be observed for particular elements, such as Cr, Ni, and As, which commonly exceeds the threshold limit values (150 mg/kg, 120 mg/kg, and 20 mg/kg, respectively - Table 1). Particularly, average chromium concentrations are up to ten times greater than maximum allowable levels south of the Cecina river mouth, and three times greater along the Campiglia coast. These values are paralleled by nickel concentrations, which also exceeded regulatory limit values up to three times. Significantly high Cr values in beach sands were also recorded along the stretch of coast south of the Magra River. Arsenic, instead, shows anomalously high average concentrations, 2–3 times greater than maximum permissible levels in the Campiglia area and, subordinately, in the southern regions, fed by Cornia, Albegna and Fiora rivers. Cobalt exhibits concentrations higher than its threshold limit value (25 mg/kg) in

Table 1
Average chemical composition of Holocene beach sands, collected at 120–130 cm depth, from eight distinct geological provinces (see Fig. 1). Values that exceed the Italian threshold limit values for soil contamination are marked in red.

	Magra R.		Arno-Serchio R.		Cecina R.		Campiglia A.		Cornia R.		Ombrone R.		Albegna R.		Fiora R.	
	Average	±	Average	±	Average	±	Average	±	Average	±	Average	±	Average	±	Average	±
SiO_2 (%)	62.74	1.99	71.38	1.83	49.16	2.58	64.42	8.95	74.96	8.68	54.92	5.89	47.21	2.03	52.05	8.47
TiO_2 (%)	0.35	0.04	0.35	0.09	0.45	0.17	0.27	8.95	0.16	0.04	0.29	0.07	0.21	0.04	0.47	0.18
Al_2O_3 (%)	9.50	0.47	8.87	0.98	5.85	0.38	6.44	2.49	3.66	1.11	6.06	1.00	4.92	1.01	8.41	1.66
Fe_2O_3 (%)	3.83	0.33	2.52	0.38	6.29	0.90	6.67	2.49	1.91	0.61	4.20	0.67	4.13	0.65	5.84	2.27
MnO (%)	0.09	0.02	0.08	0.01	0.18	0.03	0.18	0.12	0.11	0.05	0.16	0.03	0.29	0.03	0.18	0.02
MgO (%)	4.09	0.36	1.79	0.40	11.98	1.53	4.46	3.40	0.98	0.53	2.14	0.38	1.90	0.17	4.15	2.31
CaO (%)	7.82	0.99	5.50	1.00	11.33	1.87	6.87	4.62	8.81	3.48	16.22	3.72	20.56	1.23	15.22	4.55
Na_2O (%)	1.26	0.13	1.75	0.14	0.97	0.19	0.96	0.07	0.69	0.24	0.85	0.20	0.57	0.09	0.82	0.10
K_2O (%)	1.86	0.12	1.91	0.12	0.67	0.21	0.95	0.07	0.88	0.28	1.14	0.24	1.08	0.14	3.21	0.73
P_2O_5 (%)	0.08	0.01	0.07	0.01	0.07	0.01	0.07	0.01	0.04	0.01	0.07	0.01	0.07	0.00	0.13	0.08
LOI (%)	8.37	0.91	5.79	0.90	13.05	1.46	8.70	3.27	7.78	3.12	13.96	2.49	19.07	1.15	9.51	3.42
As (mg/kg)	6	2	6	1	12	1	49	27	22	5	10	2	21	7	27	8
Ba (mg/kg)	304	25	297	21	114	33	101	40	98	27	148	33	136	13	612	86
Ce (mg/kg)	35	5	34	10	15	4	29	20	16	8	26	8	25	8	83	25
Cl (mg/kg)	39	5	38	17	304	502	80	57	443	653	156	182	195	247	58	24
Co (mg/kg)	11	2	7	1	25	3	16	11	4	1	8	1	7	2	12	6
Cr (mg/kg)	221	70	84	17	1460	753	439	258	83	49	158	103	60	14	99	47
Cu (mg/kg)	17	6	9	2	20	3	20	17	5	1	13	1	12	4	8	9
Ga (mg/kg)	10	0	8	1	7	1	7	3	4	1	7	1	6	1	10	2
Ni (mg/kg)	112	16	39	6	376	64	195	150	15	9	40	5	31	7	38	17
Pb (mg/kg)	17	5	15	2	11	1	27	18	11	6	12	1	11	1	24	3
Rb (mg/kg)	67	4	71	6	21	6	40	24	33	8	35	11	30	4	87	34
S (mg/kg)	61	30	44	11	131	64	248	302	116	70	110	41	417	481	318	355
Sc (mg/kg)	10	4	8	4	8	1	14	5	9	3	10	4	8	1	14	7
Sr (mg/kg)	236	26	168	19	244	36	189	88	189	72	326	58	404	27	837	91
V (mg/kg)	46	4	35	7	70	22	46	20	22	6	41	6	40	8	103	58
Y (mg/kg)	15	1	14	3	15	3	18	10	10	3	16	2	19	1	26	7
Zn (mg/kg)	48	7	33	6	62	11	48	19	29	6	44	4	46	9	52	17
Zr (mg/kg)	103	12	111	29	84	19	78	38	56	14	92	13	71	5	237	109

the Cecina area, whereas V exceeds its maximum allowable limit (100 mg/kg) north of Fiora River.

6. Influence of catchment lithology on sediment composition

To get clues about the natural versus anthropogenic origin for such anomalies, with a particular focus on Cr and As, the geochemical composition of the study sands was matched against the geological characteristics of river catchments (Fig. 1). Ternary diagrams based on major and trace element concentrations allow simple graphic discrimination of the eight geological provinces that crop out along the coast of Tuscany, with relatively scarce overlap (Fig. 2A, B). Among major elements, high MgO average values (up to 12% in Table 1) characterize beach sands from the Cecina and Campiglia areas, whereas sand from the southern coast (Albegna, Ombrone, and Fiora river catchments) exhibits the highest CaO values (~ 20% - Table 1 and Fig. 2A). The highest K_2O and Na_2O values are instead characteristic of the wide stretch of coast supplied by Arno, Serchio, and Magra rivers (Fig. 2B).

Fig. 2C shows diagnostic petrographic signatures of six out of eight geological provinces discussed in this work (data from the southern Albegna and Fiora coastal stretches are not available), based on the detailed work by Gandolfi and Paganelli (1984). The sand petrography ternary diagram based on the relative amount of serpentine rock fragments, felsic magmatic rock fragments and feldspars results invariably in distinct fields for the different geological provinces. The Cecina system (and subordinately beach sands supplied by the Magra River catchment) is dominated by ophioliticlastic sands, including abundant serpentinite grains (Garzanti et al., 2002). The Campiglia and Cornia systems exhibit the highest amounts of felsic volcanic and plutonic rock fragments (Fig. 2C). A volcanic detritus made up of felsitic lithic fragments with abundant hypersthene has also been reported from the Fiora River system (Garzanti et al., 2002). The abundance of feldspars (K-feldspar+albite+anortite), likely recycled from foredeep turbidites

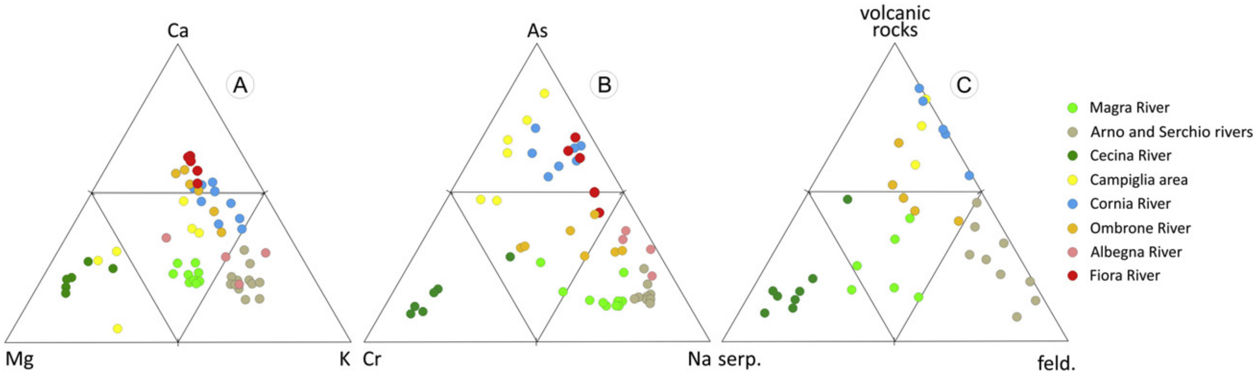

Fig. 2. Ternary plots, showing changes in composition of Holocene beach sand as a function of sediment provenance (the eight geological provinces of Fig. 1 are plotted). A: selected major elements, B: selected trace elements, C: selected mineralogical components (data from Gandolfi et al., 1984).

derived (directly or indirectly) from Alpine sediment sources (Garzanti et al., 2002) typifies the Arno-Serchio system (Fig. 2C). Abundant carbonate lithic fragments suggest additional supply from rocky coasts in the south (Garzanti et al., 2002).

Consistent with the petrographic data shown in Fig. 2C, chromium behaves as Mg and displays its maximum values in the ophiolite-rich Cecina River system (Fig. 2B), whereas the highest As concentrations coincide with maximum amounts of volcanic lithic fragments.

7. The natural origin of Cr and Ni

To assess the possible influence of ophiolite-rich detritus on the spatial distribution and anomalously high concentrations of Cr and Ni along the northern Tyrrhenian coast of Italy, we plotted the ratio between two relatively immobile elements (Cr/V) versus Y/Ni (Hiscott, 1984 - Fig. 3). This diagram enables a semi-quantitative estimate of the proportion of ultramafic rocks in the source region, based on the composition of an ultramafic end-member characterized by a very high Cr/V value (45) and an extremely low Y/Ni ratio (0.001 - Turekian and Wedephol, 1961). The dotted line roughly corresponds to 5% ultramafic detritus (Hiscott, 1984).

The Cr/V ratio is commonly used as a key index for sediment provenance from ultramafic source rocks (Feng and Kerrich, 1990; Garver et al., 1996; Bauluz et al., 2000; von Eynatten, 2003; Amorosi and Sammartino, 2007; Lužar-Oberiter et al., 2009). High Cr/V levels (>10 in Fig. 3) from Holocene beach sands of the Cecina and Campiglia regions are consistent with the marked abundance of ultramafic lithic fragments reported from the Cecina River system (up to 40% in Gandolfi and Paganelli (1977), as well as with the southward sediment drift close to the Cecina River mouth (Leoni et al., 1991 - Fig. 1). In the Cecina River system, dense minerals may include up to 40% Cr-spinel, such as chromite, magnesium chromites, and Cr-magnetite (Garzanti et al., 2002). Ophiolite rocks cropping out in the Campiglia area only 2 km from the Tyrrhenian coast (Rocchi et al., 2003 - Fig. 1) likely represent an additional source of Cr to the coastal area, as also suggested by the abundance of spinel reported from beach sands south of Cecina by Garzanti et al. (2002). We assume olivines, the primary mineral from peridotites, to represent potential carriers for Ni e Co (Herzberg et al., 2016), accounting for concentrations that exceeded regulatory limits for both elements in samples from the Cecina area (Table 1).

Lower Cr/V values, but still consistent with significant ultramafic input, are recorded by beach samples south of Magra River. Such values likely reflect remarkable input of serpentinite rock fragments at the Magra River mouth and their south-directed transport via the longshore drift (Fig. 1).

8. The natural origin of As

The As concentration varies markedly along the Tyrrhenian coast, with generally higher values (commonly higher than threshold limits – Table 1) in the southern (Campiglia, Cornia, Albegna and Fiora) provinces.

Magra, Arno/Serchio, Cecina and Ombrone coastal sands exhibit As concentrations below the maximum allowable concentration for parks and residential areas (20 mg/kg in Table 1). If plotted against CaO (Fig. 4A) and SiO_2 (Fig. 4B), which can be used as proxies for carbonate and siliciclastic deposits, respectively, As exhibits obvious direct and inverse linear relationships, respectively, with only slight changes.

A significantly different behaviour typifies most southern coastal sands, for which no relation can be seen between these variables (Fig. 4A, B). This suggests an origin for As other than from siliciclastic and carbonate rocks.

A simple look at the geological map shows that high As is concentrated in the southern part of the study area, along stretches of coast that are fed by rivers where magmatic rocks are abundant in the catchments. (Table 1 and Fig. 1).

The clear relation between As abundance and S/MnO (Fig. 4C) is consistent with its concentration in sulfide minerals other than manganese sulfides. Arsenic sulfides like realgar (As_4S_4), orpiment (As_2S_3), arsenopyrite (FeAsS), and enargite (Cu_3AsS_4) have been reported as common constituents of skarn deposits in the Tuscan region (Tanelli, 1977). The interpretation of a geogenic origin for As along the coast of Tuscany is strongly corroborated by the occurrence of As-rich mineralizations in the Campiglia area (Tanelli et al., 1993; Da Mommio et al., 2010). On the other hand, huge As concentrations (up to 9000 mg/kg) have been reported from the Roman magmatic province, in the Monte San Pietro area, along Fiora River (De Casa et al., 1996), and are likely to supply As-rich detritus to the Latium coast and to the Tuscany coast via longshore drift.

The geochemical 'anomaly' in V observed north of Fiora River, in association with high As levels (Table 1), is interpreted to reflect high concentrations of this element in volcanic rocks of the Quaternary Roman Magmatic Province. Vanadium can replace iron in the mineral structure of pyroxene and magnetite or be contained in V-rich minerals (i.e.

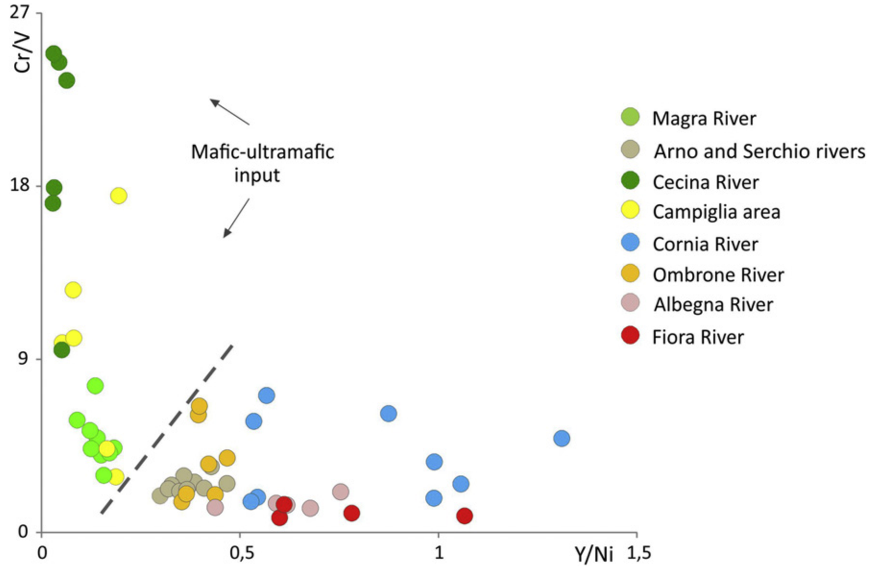

Fig. 3. Scatterplots of Cr/V versus Y/Ni (Hiscott, 1984), showing the likely mafic-ultramafic contribution to Holocene beach sands in the Campiglia area and close to the Cecina and Magra river mouths.

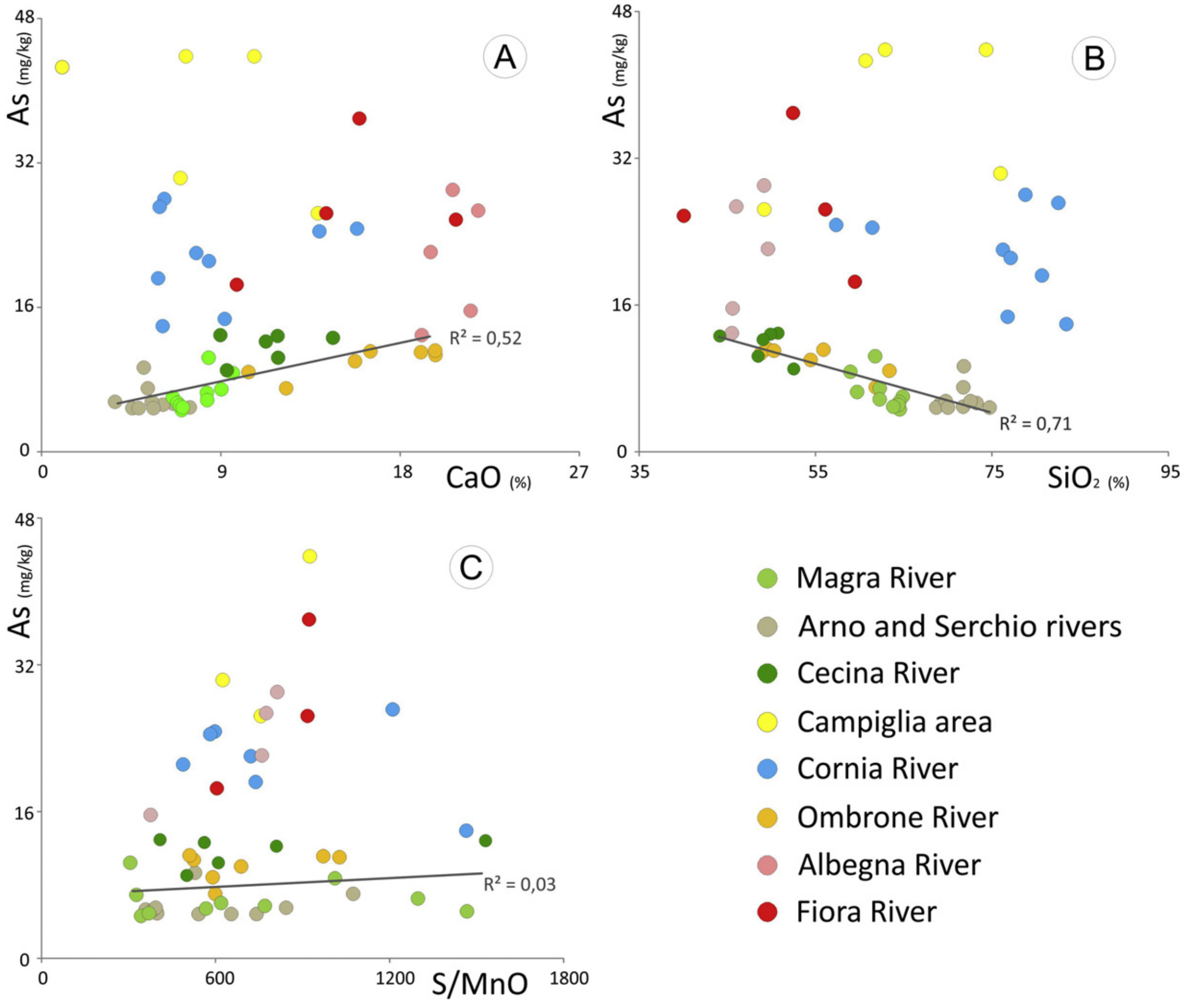

Fig. 4. Scatterplots of CaO (A), SiO_2 (B) and S/MnO (C) versus As. Arsenic shows direct (A) and inverse (B) relations with CaO and SiO_2 in samples from Magra, Arno/Serchio, Cecina, and Ombrone river systems, but positive correlation with S/MnO (C) in samples from Campiglia, Cornia, Albegna and Fiora river systems. Regression lines for samples from the Magra, Arno/Serchio, Cecina and Ombrone river systems highlight linear correlations in A and B.

carnotite and vanadinite) that commonly occur in the volcanic rocks of northern Latium (Cinti et al., 2015).

9. Factors controlling the spatial distribution of geochemical elements along the Tyrrhenian coast

Beach sands along the northern Tyrrhenian coast of Italy are complex mixtures of detritus fed by a variety of sources (sedimentary, metamorphic and magmatic rocks) and subject to transport and sorting by distinct traction processes (rivers, waves, and longshore currents – Garzanti et al., 2002). This study showed the strong relation between: (i) elemental concentrations in Holocene coastal deposits (Fig. 2A, B), (ii) modern beach sand petrography (Fig. 2C), and (iii) drainage basin composition (Figs. 3 and 4).

Geological data may allow pinpointing the sources of geochemical 'anomalies' (Fig. 1). In particular, the spatial distribution of potentially toxic elements appears to be a function of sediment provenance and transport. In the study area, the type of particular source rocks, such as ophiolitic and volcanic successions, is critical to account for significant Cr, Ni and As concentrations. Clear provenance signals are carried by Cr and Ni, hosted preferentially in serpentinite lithic fragments (von Eynatten, 2003; Amorosi, 2012; Garzanti, 2016), and by As, associated with sulfide minerals (Protano et al., 1998; Costagliola et al., 2010). These elements are transported by rivers to fluvial mouths and then concentrated in littoral sands by waves and nearshore processes, following longshore transport along north- or south-directed pathways.

The distance the sediment is transported appears to be another major controlling factor of the geochemical composition of the beach sands. For example, the limited durability of volcanic lithic fragments (Garzanti et al., 2002) can be compensated by their lower selective destruction due to the relatively short transport distance. In the relatively small Campiglia area, despite comparatively small volumes of ophiolitic and magmatic rocks (and related hydrothermal products) cropping out in the catchment (Fig. 1), nearshore sands are markedly enriched in Cr and As (Table 1). Such high Cr and As concentrations are interpreted to reflect proximity of Cr-bearing and As-bearing source rocks to the shoreline. Lack of significant fluvial transport likely favored the high preservation of Cr- and As-bearing lithic fragments, as well as of minerals highly resistant to chemical and physical weathering, such as spinels, resulting in high elemental concentrations in the adjacent, narrow coastal plain.

To assess the extent to which element concentrations in sediments may pose risks to human health, future work should focus on estimating bioavailability of elemental contaminants. While remarkably high amounts of chromium of geogenic origin, even exceeding maximum permissible concentrations, do not imply necessarily high bioavailability (Albanese, 2008; Amorosi et al., 2014), it is possible that highly leachable, potentially harmful elements, such as As, may enter the food chain, exposing local population to exposure to inorganic arsenic via water and also through consumption of food (Cubadda et al., 2015). Specific bioavailability studies, however, are needed to corroborate this hypothesis.

10. Conclusions

Holocene beach sands from the north Tyrrhenian coast of Italy were examined in light of detailed geologic information and a complete petrographic and mineralogical database available from previous work. Metal determinations based on geological criteria showed that elemental contents exceeding the threshold values designated for contaminated areas are not the product of artificial contamination, but reflect primarily the local geological characteristics. Concentrations of Cr, Ni, and As higher than maximum admissible values strictly reflect source-rock composition and sediment transport pathways.

Threshold limit values for Cr and Ni were exceeded in samples from the central coast of Tuscany (Cecina and Campiglia areas), where rivers drain ophiolite-rich catchments. The remarkably high Cr and Ni concentrations reflect river mouth deposits and transport of ophiolitic detritus by the longshore drift along south-directed sediment pathways. Selective concentration of serpentinite rock fragments likely took place in response to diffuse traction processes, including a combination of longshore currents, storms, and waves. On the other hand, felsic volcanic and plutonic lithic fragments and hydrothermal products related to the Tuscan and Roman magmatic provinces may account for remarkably high As concentrations within Holocene beach deposits of southern Tuscany and Latium.

This study showed that the spatial distribution of potentially harmful elements can be defined accurately as a function of different sediment sources and modes of sediment transport, if sufficiently detailed geological information is available. A lack of accurate geological analysis may result in ambiguous interpretations of measured metal contents, thus preventing the adoption of adequate environmental protection measures by the regulatory bodies.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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