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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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Giovanni Sarti, Irene Sammartino, Alessandro Amorosi

**Geochemical anomalies of potentially hazardous elements reflect
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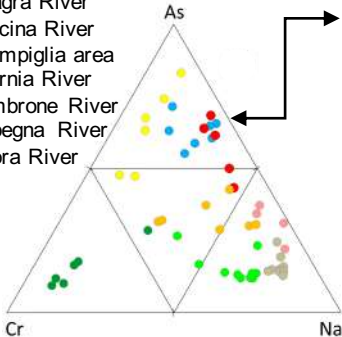
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*Graphical Abstract

- Magra River
- Cecina River
- Campiglia area
- Cornia River
- Ombrone River
- Albegna River
- Fiora River



Cr, Ni and As
exceed the Italian
regulatory limits

Sedimentological
and geochemical
approach

Background values of
potentially toxic
elements

Bioavailability?

No anthropogenic
contribution

Geogenic control on
spatial element
distribution

Highlights

- 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
- Background levels can be assessed on a sedimentological and geochemical basis
- Definition of natural background allows separation of anthropogenic contribution

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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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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 beach sands from 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 reveal spatial trends that fit the petrography of modern beach sands and closely reflect the local geology, 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. Defining reliable background values of such metals based on catchment geology

and sediment transport pathways may help separate natural concentrations from the anthropogenic contribution, delineating soil contamination on a robust basis. This integrated approach also provides 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 pollution, 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 reliable definition of background values of potentially toxic metals requires integration of geochemical data with accurate geological and soil studies (Miller, 1997, Box and Wallis, 2002, Tarvainen and Kallio, 2002, Myers and Thorbjornsen, 2004). 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). However, inter-sample geochemical variability is commonly observed as a function of grain

size (Garzanti et al., 2010), and changes in sediment texture can result in remarkable geochemical heterogeneity (Dinelli et al., 2007).

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 aims at defining background levels 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,b,c; 1984) and Garzanti et al., (2002) from the same area to make geologic inferences on sediment composition. A specific objective is to document that natural elemental abundances can exceed regulatory limits simply as a function of catchment geology and sediment transport mechanisms.

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). Simple

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 depositional (nearshore) sub-environment, between the backshore and the shoreface. The related facies assemblage accumulated under similar hydraulic conditions and exhibits homogeneous (sand) lithology.

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 sand (Gandolfi and Paganelli, 1975a,b,c, 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 Giurassic 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 locations (monzo-syenogranites at Gavorrano and rhyolites at Roccastrada).

(6) Ombrone River, 161 km in length, is the second 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 (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, Cipriani et.al, 2013). Petrographic analyses of modern beach sands (Aiello et al. 1975; Gandolfi and Paganelli 1975a,b,c, Garzanti et al., 2002) have been used to define with accuracy the

161 directions of the longshore drift within the individual physiographic units and to localize zones of
162 convergence. From north to south, the following physiographic units have been identified:

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

177

178

179 **3. Methods**

180

181 Fifty-seven sampling sites, with average spacing of about 1 sample/7 km, cover the study area.
182 To emphasize the role of major rivers as sediment feeders of the coastal system, we focused
183 sampling on the laterally most continuous sandy beaches (strandplains). On the other hand, no
184 samples were collected along rocky cliffs or within small pocket beaches.

185 At each study site, samples were collected by hand drilling, at depths of 120-130 cm, using
186 Eijkelkamp equipment (01.11.SO hand auger set for heterogeneous soils). Soils in the study area
187 generally have low maturity and thin (less than 1 m thick) profiles.

188 Geochemical analyses were performed at the University of Bologna. Samples were oven-dried at
189 50°C, powdered and homogenized in an agate mortar and analyzed by X-ray fluorescence (XRF)
190 spectrometry using a Philips PW 1480 spectrometer. The matrix correction methods of Franzini et
191 al., (1972), Leoni and Saitta, (1976), and Leoni et al., (1986) were followed. The estimated
192 precision and accuracy for trace-element determinations was 5%. For elements with low
193 concentrations (<10 ppm), the accuracy was 10%.

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

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

204

205

206 **4. Influence of catchment lithology on geochemical composition**

207

208 The results of XRF analysis are shown in Table 1, where elemental concentrations are
209 summarized through the subdivision of samples into eight coastal segments (Fig. 1). Each group
210 was identified using a combination of catchment geology with the local direction of the littoral drift

211 (Section 3). The environmental significance of geochemical data is documented by red colors,
212 which highlight the stretches of coast where elemental contents are greater than the threshold limit
213 values defined by the Italian regulations (Italian Legislative decree, 25/10/1999, no. 471, Annex 1;
214 Italian Legislative decree, 03/04/2006, no. 152, Annex 4-V5).

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

227 To get clues about the natural versus anthropogenic origin for such anomalies, with a particular
228 focus on Cr and As, the geochemical composition of the study sands was matched against the
229 geological characteristics of river catchments (Fig. 1). Ternary diagrams based on major and trace
230 element concentrations allow simple graphic discrimination of the eight geological provinces that
231 crop out along the coast of Tuscany, with relatively scarce overlap (Fig. 2A, B). Among major
232 elements, high MgO average values (up to 12% in Table 1) characterize beach sands from the
233 Cecina and Campiglia areas, whereas sand from the southern coast (Cornia, Ombrone, and Fiora
234 river catchments) exhibits the highest CaO values (~ 20% - Table 1 and Fig. 2A). High K₂O and
235 Na₂O values are instead characteristic of the wide stretch of coast supplied by Arno and Serchio
236 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 K-feldspar 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 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 Figure 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.

5. 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, such as Cr and 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

263 a very high Cr/V value (45) and an extremely low Y/Ni ratio (0.001 - Turekian and Wedephol,
264 1961). The dotted line roughly corresponds to 5% ultramafic detritus.

265 The Cr/V ratio is commonly used as a key index for sediment provenance from ultramafic source
266 rocks (Feng and Kerrich, 1990, Garver et al., 1996, Bauluz et al, 2000, von Eynatten 2003, Amorosi
267 and Sammartino, 2007, Lužar-Oberiter et al., 2009). High Cr/V levels (> 10 in Fig. 3) from beach
268 sands of the Cecina and Campiglia regions are consistent with the marked abundance of ultramafic
269 lithic fragments reported from the Cecina River system (up to 40% in Gandolfi and Paganelli,
270 (1977), as well as with the southward sediment drift close to the Cecina River mouth (Leoni et al.,
271 1991 - Fig. 1). In the Cecina River system, dense minerals may include up to 40% Cr-spinel, such
272 as chromite, magnesium chromites, and Cr-magnetite (Garzanti et al., 2002). Ophiolite rocks
273 cropping out in the Campiglia area only 2 km from the Tyrrhenian coast (Rocchi et al., 2003 - Fig.
274 1) likely represent an additional source of Cr to the coastal area, as also suggested by the abundance
275 of spinel reported from beach sands south of Cecina by Garzanti et al., (2002).

276 Lower Cr/V values, but still consistent with significant ultramafic input, are recorded by beach
277 samples south of Magra River. Such values likely reflect remarkable input of serpentinite rock
278 fragments at the Magra River mouth and their south-directed transport via the longshore drift (Fig.
279 1).

280

281

282 **6. The natural origin of As**

283

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

287 Magra, Arno/Serchio, Cecina and Ombrone coastal sands exhibit As concentrations below the
288 maximum allowable concentration for parks and residential areas (20 mg/kg in Table 1). If plotted

289 against SiO₂ (Fig. 4A) and CaO (Fig. 4B), which can be used as proxies for siliciclastic and
290 carbonate deposits, respectively, As exhibits obvious inverse and direct linear relationships,
291 respectively, with only slight changes.

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

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

298 The clear relation between As abundance and S/MnO (Fig. 4C) is consistent with its
299 concentration in sulfide minerals other than manganese sulfides. Arsenic sulfides like realgar
300 (As₄S₄), orpiment (As₂S₃), arsenopyrite (FeAsS), and enargite (Cu₃AsS₄) have been reported as
301 common constituents of skarn deposits in the Tuscan region (Tanelli, 1977). The interpretation of a
302 geogenic origin for As along the coast of Tuscany is strongly corroborated by the occurrence of As-
303 rich mineralizations in the Campiglia area (Tanelli et al., 1993, Da Mommio et al., 2010). On the
304 other hand, huge As concentrations (up to 9,000 mg/kg) have been reported from the Roman
305 magmatic province, in the Monte San Pietro area, along Fiora River (De Casa et al., 1996), and are
306 likely to supply As-rich detritus to the Latium coast and to the Tuscany coast via longshore drift.

307

308

309 **7. Factors controlling the spatial distribution of geochemical elements along the** 310 **Tyrrhenian coast**

311

312 Modern beach sands along the northern Tyrrhenian coast of Italy are complex mixtures of
313 detritus fed by a variety of sources (sedimentary, metamorphic and magmatic rocks) and subject to
314 transport and sorting by distinct traction processes (rivers, waves, and longshore currents). This

315 study shows that a strong relation exists between elemental concentrations, sand petrography (Fig.
316 2), and drainage basin composition (Figs. 3 and 4).

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

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

336 In terms of environmental protection measures, it is apparent that a lack of knowledge about
337 background values of potentially harmful elements would define beach sediments along the
338 Tyrrhenian coast as polluted for Cr, Ni and As, resulting in severe restrictions of soil use across
339 wide coastal stretches. Based on detailed geological investigations, this study reveals, instead, that
340 natural concentrations may commonly exceed the threshold limits. To assess the extent to which

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

349

350

351 **8. Conclusions**

352

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

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

367 provinces may account for remarkably high As concentrations within beach deposits of southern
368 Tuscany and Latium.

369 Despite evidence that background values of potentially toxic metals in alluvial and coastal plains
370 may closely reflect catchment lithology and grain size, allowable levels of hazardous metals in soils
371 have been set precisely by the national legislation on protection of the environment irrespective of
372 soil composition. This study shows that background values of potentially harmful elements can be
373 defined accurately as a function of different sediment sources and modes of sediment transport, if
374 sufficiently detailed sedimentological information is available. A lack of accurate geological
375 analysis may result in ambiguous interpretations of measured metal contents, thus preventing the
376 adoption of adequate environmental protection measures by the regulatory bodies.

377

378

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380

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383

384

385

386 **Figure captions**

387

388 Fig. 1. Geological sketch map of the study area (modified from the Geological Map of Tuscany,
389 2004), with location of the analyzed beach sands (white dots). Grey dots indicate river catchments
390 (1: Magra, 2: Arno/Serchio, 3: Cecina, 4: Campiglia, 5: Cornia, 6: Ombrone, 7: Albegna, 8: Fiora).
391 Dashed circles indicate river-influenced sectors as a function of the longshore drift. Red letters
392 indicate physiographic units (a: Northern Tuscany, b: Cecina River, c: Follonica, d: Ombrone River,

393 e: Ombrone River). Stars indicate ore deposits (SV: San Vincenzo, CM: Campiglia Marittima, MO:
394 Monterotondo Marittimo, NC: Niccioleta; MA: Massa Marittima, SC: Scarlino, GA: Gavorrano,
395 RO: Roccastrada, AM: Mt Amiata).

396

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

400

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

403

404 Fig. 4. Scatterplots of CaO (A), SiO₂ (B) and S/MnO (C) versus As. Arsenic shows direct (A) and
405 inverse (B) relations with CaO and SiO₂ in beach sands from Magra, Arno/Serchio, Cecina, and
406 Ombrone river systems, but positive correlation with S/MnO (C) in beach sands from Campiglia,
407 Cornia, Albegna and Fiora river systems.

408

409 Table 1. Average chemical composition of beach sands from eight distinct geological provinces (see
410 Fig. 1). Values that exceed the Italian threshold limit values for soil contamination are marked in
411 red.

412

413

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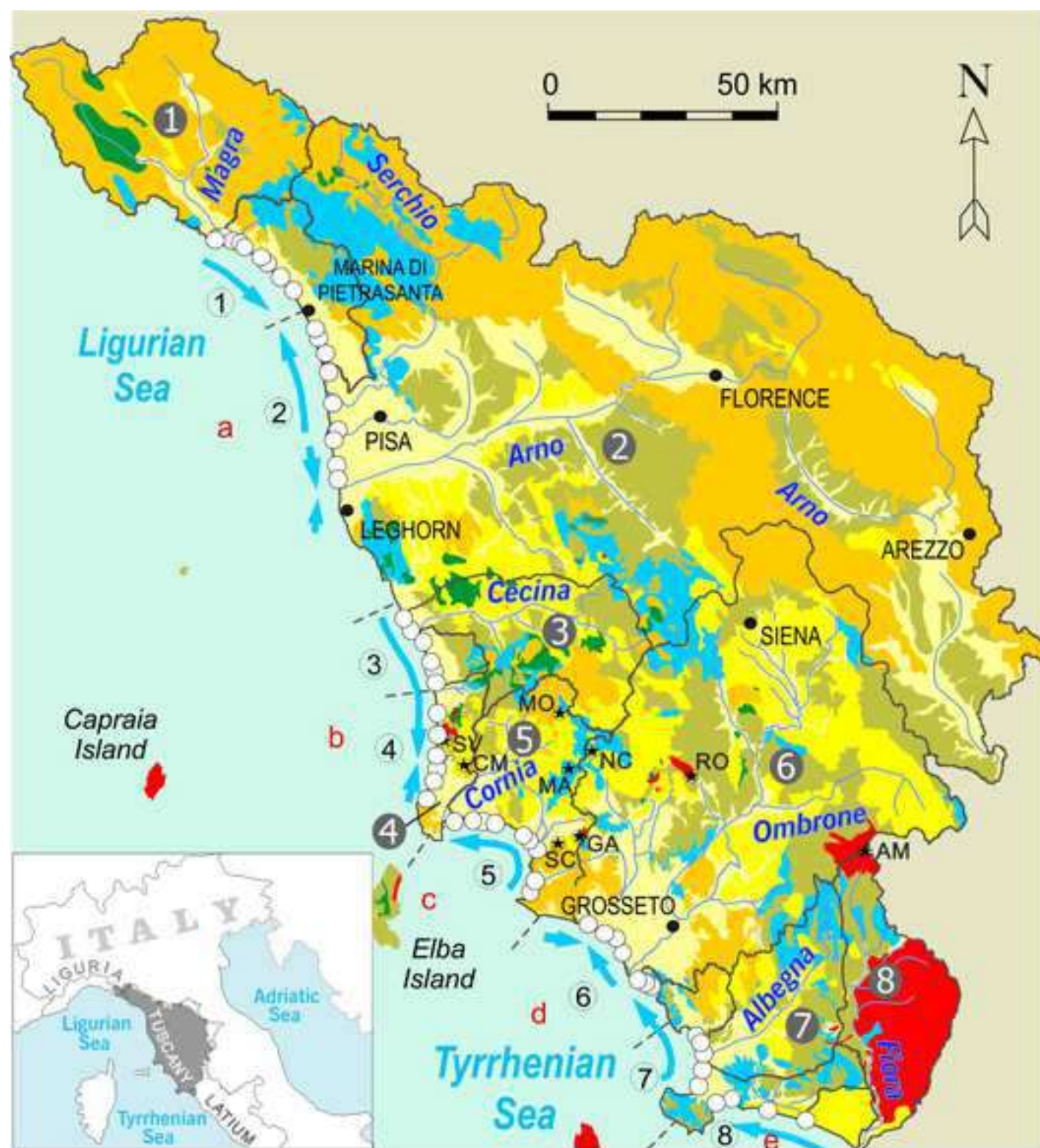
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Table 1

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	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 ₂ O 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 ₂ O 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 ₂ O (%)	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 ₂ O (%)	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 ₂ O 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

Figure 1
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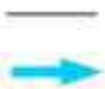
- | | |
|--|---|
|  Sandstones, conglomerates |  Ophiolitic rocks |
|  Sandstone/marl alternations (turbidites) |  Felsic magmatic rocks |
|  Limestones, dolostones, and marls |  Quaternary alluvial deposits |
|  Mudstones | Drainage divide |
|  Sampling site |  Longshore drift |

Figure 2
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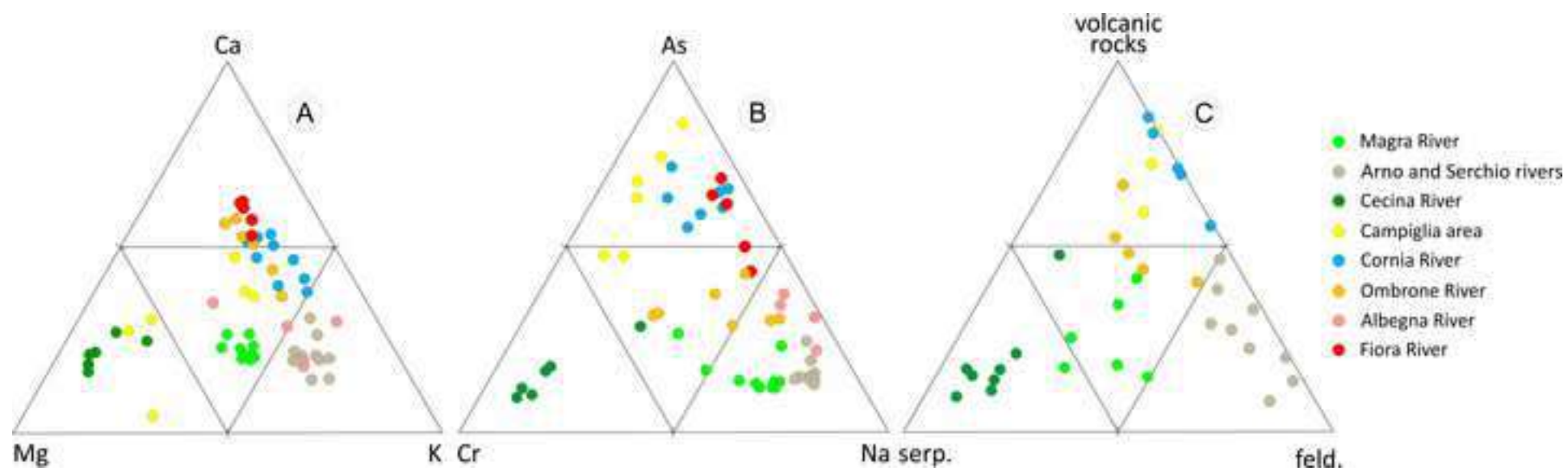


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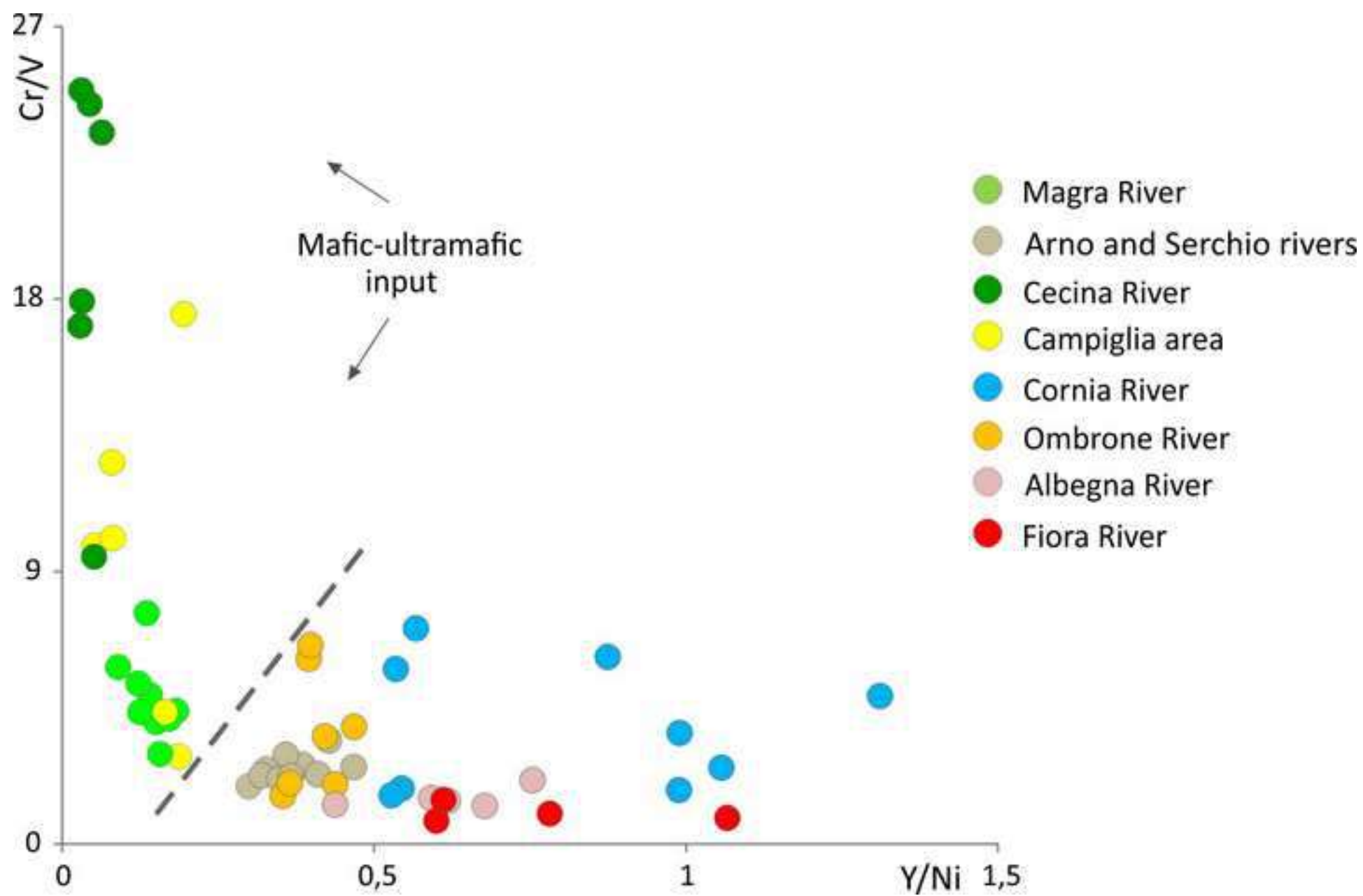
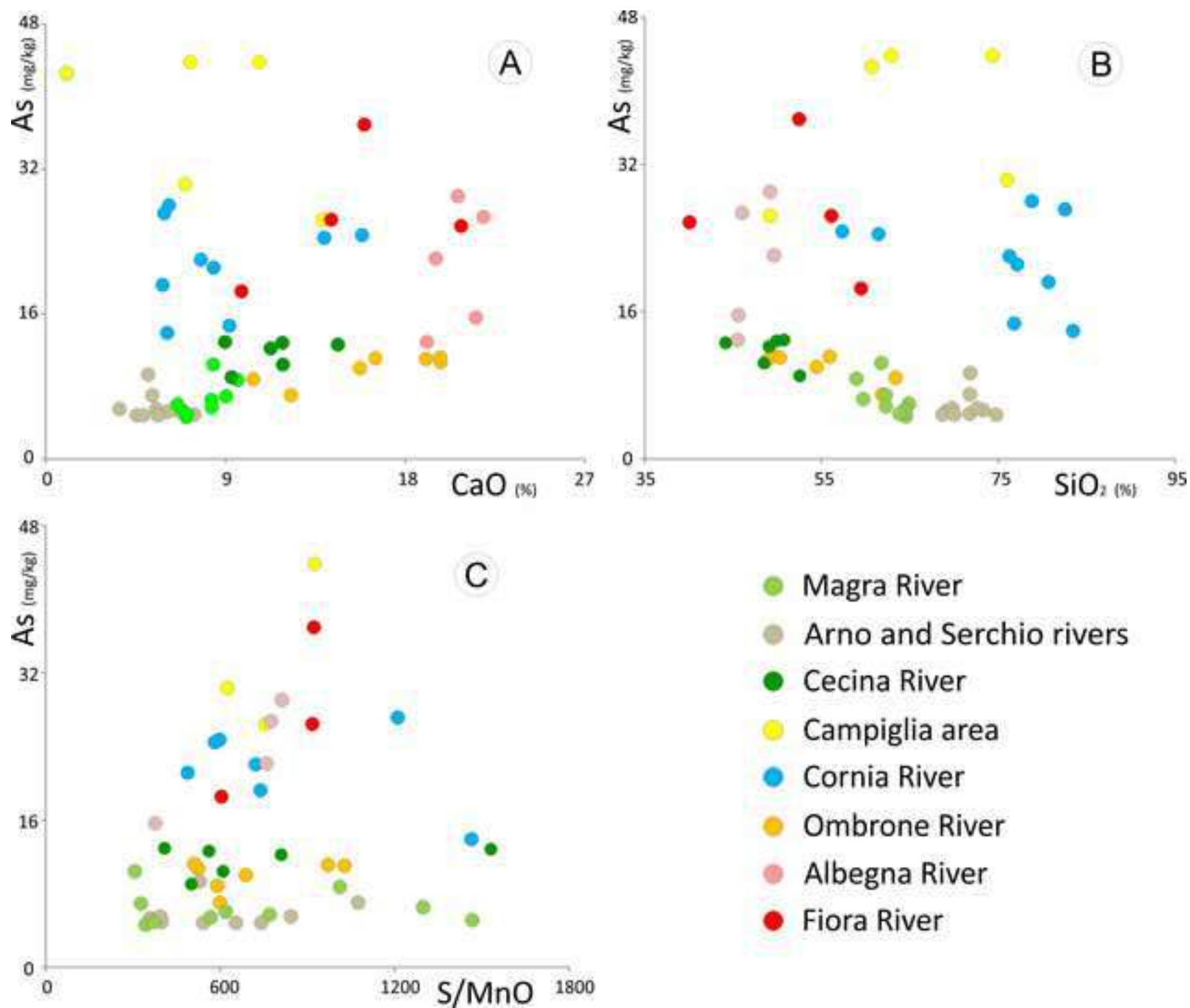


Figure 4
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Declaration of interests

☒ 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.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: