



**TUSCIA UNIVERSITY**  
**DEPARTMENT OF ECOLOGICAL AND BIOLOGICAL SCIENCES**  
**(DEB)**

**PhD COURSE**

Ecology and sustainable management of environmental resources - XXIX cycle

**PhD THESIS**

*Distribution of trace metals in coastal sediments of the physiographical  
unit Capo Linaro - Monte Argentario*

BIO/07

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**2016/2017**



## **Abstract**

Trace metal pollution is a serious threat particularly in the marine environment.

In this context, the present work shows the spatial and temporal assessment of the pollution degree and potential toxicity of trace metal in marine sediments of the coastal area enclosed between Montalto di Castro and Capo Linaro, in northern Latium, Italy.

The distribution pattern and pollution levels of As and Mn in surface sediments highlight two hotspots. These hotspots are due to the naturally high levels of As and Mn in the Mignone River and Marangone Stream as well as the intense human activity in the area including the Torrevaldaliga Nord power plant and the Port of Civitavecchia.

The high Hg concentrations detected in surface sediments confirm the extension of the Hg anomaly of the coastal area of northern Latium, profoundly influenced by the contributions of the Fiora and Mignone Rivers.

Trace metal concentrations detected in soft tissues of *Paracentrotus lividus* reflect the presence of the hotspots and describe a detectable level of bioaccumulation throughout the study area.

Furthermore, the temporal assessment carried out by the analysis of PT50 and MRG50 core samples taken in the southern sector of the study area shows the evolution of the sediment mass accumulation rate values and the trace metal values within the last 60 years.

## **CONTENTS**

|                                                                                                                |           |
|----------------------------------------------------------------------------------------------------------------|-----------|
| <b>Abstract</b>                                                                                                | <b>1</b>  |
| <b>Contents</b>                                                                                                | <b>2</b>  |
| <b>List of tables</b>                                                                                          | <b>5</b>  |
| <b>List of figures</b>                                                                                         | <b>7</b>  |
| <b>Acknowledgements</b>                                                                                        | <b>10</b> |
| <b>1. Introduction</b>                                                                                         | <b>11</b> |
| <b>2. Objectives and scope</b>                                                                                 | <b>14</b> |
| <b>3. Trace-Metal Enrichment and Pollution in Coastal Sediments<br/>in the Northern Tyrrhenian Sea, Italy.</b> | <b>16</b> |
| 3.1 Abstract                                                                                                   | 18        |
| 3.2 Introduction                                                                                               | 18        |
| 3.3 Materials and Methods                                                                                      | 19        |
| 3.3.1 Study area                                                                                               | 19        |
| 3.3.2 Sample Collection and Analysis                                                                           | 22        |
| 3.3.3 Trace-Metal Analysis                                                                                     | 23        |
| 3.4 Results                                                                                                    | 26        |
| 3.5 Discussion                                                                                                 | 34        |
| 3.6 Conclusions                                                                                                | 38        |

|                                                                                                                                                                    |               |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------|
| <b>4. Mercury Enrichment in Sediments of the Coastal Area of Northern Latium, Italy.</b>                                                                           | <b>39</b>     |
| 4.1 Abstract                                                                                                                                                       | 40            |
| 4.2 Introduction                                                                                                                                                   | 40            |
| 4.3 Materials and Methods                                                                                                                                          | 44            |
| 4.4 Results and Discussion                                                                                                                                         | 46            |
| <br><b>5. Concentrations of As, Cd, Cr, Ni, and Pb in the echinoid <i>Paracentrotus lividus</i> on the coast of Civitavecchia, northern Tyrrhenian Sea, Italy.</b> | <br><b>50</b> |
| 5.1 Abstract                                                                                                                                                       | 52            |
| 5.2 Introduction                                                                                                                                                   | 53            |
| 5.3 Materials and Methods                                                                                                                                          | 54            |
| 5.3.1 <i>Paracentrotus lividus</i> as a sentinel organism                                                                                                          | 54            |
| 5.3.2 Study area                                                                                                                                                   | 55            |
| 5.3.2.1 Sedimentological and geochemical setting                                                                                                                   | 56            |
| 5.3.3 Sample collection                                                                                                                                            | 63            |
| 5.3.4 Sample analysis                                                                                                                                              | 64            |
| 5.4 Results                                                                                                                                                        | 65            |
| 5.5 Discussion                                                                                                                                                     | 68            |
| 5.6 Conclusions                                                                                                                                                    | 74            |
| <br><b>6. Temporal distribution of trace metals in recent sediments in the northern Tyrrhenian sea, Italy.</b>                                                     | <br><b>76</b> |
| 6.1 Materials and Methods                                                                                                                                          | 78            |
| 6.1.1 Sample collection                                                                                                                                            | 78            |

|                                            |            |
|--------------------------------------------|------------|
| 6.1.2 Sample analysis                      | 79         |
| 6.2 Results and Discussion                 | 79         |
| 6.2.1 Radionuclide measurements            | 79         |
| 6.2.2 Major and trace elements analysis    | 85         |
| 6.3 Conclusions                            | 96         |
| <b>7. Overall conclusions</b>              | <b>97</b>  |
| <b>8. Future perspectives</b>              | <b>99</b>  |
| <b>Comprehensive literature references</b> | <b>100</b> |

## List of tables

**Table 1:** This table shows the original data set, which includes the pelitic fraction percentages for all surface sediment sampling stations, ranges, averages, standard deviations, ERL and ERM values of Al, Cr, As, Mn, Fe, Ni, Pb and Cu.

**Table 2:** Pearson's correlation of normalized Cr, As, Mn, Fe, Ni, Pb and Cu values detected in surface sediment samples.

**Table 3:** Mean concentrations from the literature for Cr, As, Mn, Ni, Pb, and Cu (mg/kg) in Italian coastal areas.

**Table 4:** This table reports the Hg values detected in surface sediment samples, the pelitic fraction percentage, the Al values, the ratio Hg/Al, the Hg EF values and AEI values in the study area.

**Table 5:** As, Cd, Cr, Ni, and Pb concentrations in sediments from the study area (Scanu 2012; Molino 2013). Dashes indicate “not analyzed”. \*Values below detection limit.

**Table 6:** Sediment enrichment factors in the physiographic unit between Monte Argentario and Capo Linaro.

**Table 7:** Classification of sediments found in the physiographic unit between Monte Argentario and Capo Linaro, according to United States Environmental Protection Agency sediment quality guidelines criteria (Giesy and Hoke, 1990; Long and Morgan, 1990).

**Table 8:** Concentrations ( $\mu\text{g/L}$ ) of As, Cd, Cr, Ni, and Pb in port of Civitavecchia seawater (Molino 2013).

**Table 9:** Concentration of As, Cd, Cr, Ni, and Pb in *P. lividus* from the Civitavecchia area.

**Table 10:** Literature mean concentrations of As, Cd, Cr, Pb, and Ni in *P. lividus* (mg/kg dry weight, whole organism or soft tissues). Minima and maxima are in parentheses.

**Table 11:** Mean concentrations in *P. lividus* (Nascetti et al. 2011a, 2012b, modified). A is a sampling point in the Tarquinia salt marsh north of Mignone River delta, B is a sampling point near the Mignone River delta, and C is a sampling point near sampling station R9.

**Table 12:** PT50 and MRG50 SARs values comparison with literature data for the study area.

**Table 13:** Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, As, Cr, Cu, Ni, Pb and Zn raw values and ERL – ERM, TEL – PEL values of the considered elements.

**Table 14 A:** Pearson's correlation among trace metal values measured in PT50 core.

**Table 14 B:** Pearson's correlation among trace metal values measured in MRG50 core.

## List of figures

**Fig. 1:** This figure shows the study area related to the surface sediment sampling campaign. The study area is located in the northern Tyrrhenian Sea in northern Latium.

**Fig. 2:** Surface sediment sampling locations. Surface sediment samples are located between -50 and -10 m were sampled.

**Fig. 3:** Spatial distribution of the pelitic fraction percentage and Al, Cr, As, Mn, Fe, Ni, Pb and Cu values.

**Fig. 4:** Spatial distributions of Cr, As, Mn, Fe, Ni, Pb and Cu EF values.

**Fig. 5:** Spatial distributions of Cr, As, Mn, Fe, Ni, Pb and Cu Igeo values.

**Fig. 6:** Spatial distribution of the potential toxicity response index (RI).

**Fig. 7:** As and Mn hotspots in the study area including the wind regime at the Torrevaldaliga Nord site and mining waste deposits on the Marangone basin.

**Fig. 8:** Study area and sampling locations related to surface sediment samples campaign for the study of Hg concentrations.

**Fig. 9:** Distribution pattern of pelitic percentage, Al (mg/kg), Hg (mg/kg), Hg/Al, EF, and AEI in coastal sediments of northern Latium.

**Fig. 10:** (*P. Lividus* sampling) study area location in the physiographic unit between Monte Argentario and Capo Linaro.

**Fig. 11:** Sediment samples from the physiographic unit between Monte Argentario and Capo Linaro (A) and the port of Civitavecchia (B). (Scanu 2012, modified; Molino 2013, modified).

**Fig. 12:** Water samples from inside the port of Civitavecchia.

**Fig. 13:** *P. Lividus* sampling plan.

**Fig. 14:** Concentrations (mg/kg) of As, Cd, Cr, Ni, and Pb in *P. lividus* from the Civitavecchia coastal area.

**Fig. 15:** As hotspot between the Port of Civitavecchia and Marangone stream delta (circle), winds at the Torrevaldaliga site, and locations of mine waste deposits.

**Fig. 16:** Spatial distribution of the sampling points in Nascetti et al. (2012b) and in this study.

**Fig. 17:** Bayesian estimation supersedes the t-test analysis of trace metals comparing our results with those of Nascetti et al. (2012b).

**Fig. 18:** PT50 and MRG50 core samples locations.

**Fig. 19:** Total  $^{210}\text{Pb}$  activity values and unsupported  $^{210}\text{Pb}$  values of PT50 and MRG50.

**Fig. 20:** CFCS model results for PT50 and MRG50 cores.

**Fig. 21:** SARs values obtained through the CRS model for PT50 and MRG50 cores.

**Fig. 22:**  $^{137}\text{Cs}$  profile in MRG50 core.

**Fig. 23 A:** Trace metal values measured in PT50 core with respect to TEL and PEL values.

**Fig. 23 B:** Trace metal values measured in MRG50 core with respect to TEL and PEL values.

**Fig. 24:** Pearson's correlation between trace metal values and  $\text{Al}_2\text{O}_3$  and Pearson's correlation between trace metal values and  $\text{Fe}_2\text{O}_3$ .

**Fig. 25 A:** Temporal distribution of As, Cr, Cu, Ni, Pb and Zn values normalized with  $\text{Al}_2\text{O}_3$  concentrations in PT50 core.

**Fig. 25 B:** Temporal distribution of As, Cr, Cu, Ni, Pb and Zn values normalized with  $\text{Al}_2\text{O}_3$  concentrations in MRG50 core.

## Acknowledgements

*This thesis represents the culmination of my work into a topic which has been of interest to me for some 3 years. During this period I have had the privilege of being supported by some excellent people who I pay my thanks to here.*

*Firstly thanks to my PhD tutor, Prof. Marco Marcelli, for his advice and support all the way from my graduate thesis to completion of this PhD.*

*Thanks all the guys of the Laboratory of Experimental Oceanology and Marine Ecology, University of Tuscia (DEB), always willing to help me in difficult times.*

*The results obtained during this years of PhD studies are fruit of the collaboration of several people who contributed to make this PhD possible.*

*In particular, I would like to thank Prof. Maria Violetta Brundo and all her staff (University of Catania, Italy) for the advice and the collaboration.*

*A big thanks goes to Prof. Ian Croudace of the National Oceanography Centre (Southampton, UK) and to all his staff for the great availability, the hospitality and the help that was given to me during the training experience at GAU laboratories.*

*This project probably would not have been possible without the help and support of Dr. Sergio Scanu for his incredibly practical and logical approach to teaching and guiding me day after day.*

*Finally, I must thank my mom and my dad for their patience, advice and abilities to help me take a step back and gain perspective in some of the less exciting moments of the project.*

## **1. Introduction**

The coast is generally defined as the transition area between the environments perennially occupied by marine water bodies and land surfaces. However, this apparently simple definition describes an incredibly complex and differentiated environment.

The high number of chemical, physical and biological agents that characterize these areas consequently leads to identifying several coastal types with unique characteristics dictated by the interaction of environmental factors.

This heterogeneity makes the coastal study an extremely delicate and complex process that requires an extensive knowledge of the considered area.

The high degree of complexity of these areas becomes more complicated when considering the multiple effects and profound changes caused by numerous human activities existing in coastal areas.

Historically, coastal areas have always been considered preferred locations for the development of multiple economic activities. Currently, approximately 44% of the world's population live within 150 kilometers from the shore line, and this number is rising rapidly (UN Atlas of the Oceans).

The strong dynamism of coastal areas, created by the continuous action of marine weather forces and human activities, has resulted in extreme sensitivity of these areas.

Therefore, it is essential to frame the study of coastal areas holistically, taking into account both the events on a local scale, such as coastal erosion, and the boundary conditions, which can have a lasting effect on the Physiographical Unit (the physical framework within which the transport processes of sandy materials remain confined).

In this context, the study of sedimentary contributions from the continent to the sea are of crucial importance: they are constantly affected by weather events (e.g. flooding) and by human activities in the territories of the river basins or directly located on the coast.

Climatic events and the ongoing pressure of human activities lead to qualitative and quantitative changes of sedimentary contributions from the continent to the sea, causing

substantial alterations in the sedimentary balance and the potential increase in organic and inorganic pollutants.

Among the existing inorganic pollutants, trace metals are considered a serious threat in the marine environment due to their toxicity, abundance and persistence.

Trace metals have both natural and anthropogenic origins (Nriagu 1989; Veena et al. 1997). The principal natural source of trace metals is from crustal material that is either weathered on and eroded from the Earth's surface or released into the atmosphere by volcanic activity (Callender 2003). These natural sources of trace metals account for 80% of all the natural sources whereas forest fires and biogenic sources account for 10% each (Nriagu 1990).

Furthermore, there are a multitude of anthropogenic sources of trace metals: rapid industrialization, urbanization, and increased human activity have resulted in an increased quantity of trace metals accumulated in air, water, soil, and sediment as described in several works (Nriagu and Pacyna 1988; Varol 2011; Chaudhari et al. 2012; Suresh et al. 2012; Bastami et al. 2014).

The major anthropogenic source of trace metals is from mining and smelting. Mining activity releases metals to the fluvial environment as tailings and to the atmosphere as metal-enriched dust. Moreover, smelting releases metals to the atmosphere as a result of high temperature refining processes (Callender 2003). Other important anthropogenic sources of trace metals include fossil-fuel combustion, municipal waste incineration, cement production, phosphate mining and the use of commercial fertilizers and pesticides (Nriagu and Pacyna 1988).

Trace metals released from natural and anthropogenic sources are then transported to the marine environment by different pathways including river basin runoff, atmospheric deposition and discharge of sewage (Callender 2003; Gao and Li 2012; Xu et al. 2016).

It is widely shown in the international literature that particular affinity exist between the finer grain size of sediment and the chemical species present in the water column: potentially chemical pollutant, such as trace metals, tend to bond with the pelitic sediment particles, and then they follow the sediment fate (Salomons and Förstner 1984;

Windom et al. 1989; Horowitz 1991; Ligerio et al. 2001; Mil-Homens et al. 2013).

As a result, the final receptors of pollutants in the sea are the depositional areas of the pelitic fraction which are internationally considered as the main "archive integrator" of pollutants reflecting the pollution levels in the water column (Chengxin et al. 2002; Selvaraj et al. 2004; Brondi et al. 2008).

The detailed study of the depositional areas of pelitic fractions can provide important informations regarding the degree of pollution on both spatial and temporal scale and can be used as a valuable tool for assessing the enrichment of trace metals caused by human activities with respect to the "natural geochemical background values" which identify the condition of natural chemical element concentration in a given area (Matschullat et al. 2000; Reimann et al. 2005; Song et al. 2014; Xu et al. 2016).

Furthermore, the assessment of the degree of pollution and the potential toxicity of trace metals in marine sediments assumes a higher value if accompanied by analyses of the biological tissue of "sentinel organisms" or "bio-indicators" strictly connected with the substrate and particularly sensitive to changes induced by polluting agents (Rainbow 1995; Warnau et al. 1998; Soualili et al. 2008).

In the light of the scientific state of the art presented, this PhD work proposes a detailed survey of the pollution degree and potential toxicity of trace metals in the marine coastal environment of the northern Latium, Italy. The results of this study can be usefull to target ecological investigations of the processes of bioaccumulation and biomagnification along the marine food chains in the study area.

## **2. Objectives and scope**

The present work proposes a detailed survey of the pollution degree and potential toxicity of trace metals in marine sediments of the coastal area enclosed between Montalto di Castro and Capo Linaro, in northern Latium, Italy.

This coastal stretch has been chosen as the investigation area because it appears to be the area with the greatest human pressure enclosed between the morphological constraints of the physiographic unit of Capo Linaro - Monte Argentario.

Moreover, given the small number of studies carried out in physiographic unit, this coastal area does not have a complete framework of the distribution, the degree of enrichment and the potential toxicity of marine sediments.

The examined coastal stretch includes the Civitavecchia area which is home to many human activities of national and international importance.

The Port of Civitavecchia is a major hub for national and international commercial traffic and one of the main Italian ports for passenger traffic with over two million passengers in transit each year.

The northern border of the Civitavecchia area hosts the thermal coal power plant ENEL Torvaldaliga North with a total power of 1980 MW. The thermal power plant fueled with natural gas from Tirreno Power consists of two production modules, respectively, with power of 400 and 800 MW.

The study area is also characterized by the alluvial deposits of the Fiora, Marta and Mignone rivers and from several small streams, which influence marine sedimentation during intense rainfall events and during subsequent flooding (Angelucci et al. 1979; Carboni et al. 1980).

The Fiora river basin is affected by cinnabar (HgS), a geologic anomaly of Mt. Amiata, but more so by the Hg extraction that lasted from Etruscan times (the eight to the first century B.C.) to 1980 (Barghigiani et al. 1996).

The areas drained by the Mignone river basin and by the Marangone stream have been the subject of past mining activities related to the extraction of sulphides (Pyrite,

Marcasite and Galena) from the nineteenth century through the early part of the twentieth century (Spadoni et al. 2005; Kreidie et al. 2011).

Considering the different human activities occurring over the years in the hinterlands and the human activities currently located in this coastal stretch, the present study shows a qualitative and quantitative evaluation of the influence of human activities in the examined coastal area with respect to the natural conditions.

In particular, the chemical elements taken into account included trace metals, which are affected by possible changes induced by human activities.

The degree of enrichment and potential toxicity evaluation of marine sediments was performed both spatially and temporally throughout the study area by sampling surface sediments and core samples.

For the enrichment degree and potential toxicity evaluation, numerical thresholds described in US EPA Sediment Quality Guidelines have been used to perform an immediate comparison (Long et al. 1995). Moreover, different indices (enrichment factor, geoaccumulation index, potential toxicity response index, adverse effect index) widely described in the international literature were used (Hakanson 1980; Morillo et al. 2004; Shafie et al. 2013; Muñoz-Barbosa et al. 2012).

The temporal evaluations were carried out assessing the variations of trace metals in a time span which extends from the early 1950s until the present time.

Therefore, this work shows the spatial and temporal assessment of trace metal concentrations in the coastal marine environment of the considered physiographic unit in order to lay a solid foundation for future studies concerning the propagation of chemical pollutant species along the marine food chains in the studied area.

### **3. Trace Metal Enrichment and Pollution in Coastal Sediments in the Northern Tyrrhenian Sea, Italy.**

The first part of the project involved the study of the qualitative and quantitative distribution of some trace metals in surface sediments of the coastal area between Santa Severa and Tarquinia Lido.

In particular it was possible to delineate: (i) the spatial distribution and the current granulometric characteristics of coastal surface sediments of the study area, (ii) the spatial distribution of Cr, As, Mn, Ni, Pb, and Cu associated with surface marine sediments, and (iii) the enrichment degree and the potential toxicity induced by trace metals through the use of some indices (enrichment factor, geo-accumulation index, potential toxicity response index) and by comparison with the US EPA sediment quality guidelines.

The results obtained from the analysis of coastal marine sediments show the abundance of some of these trace metals.

In particular, the results show the presence of two hotspots characterized by high concentrations of As and Mn: (i) the coastal area next to the mouth of the Mignone river, and (ii) the coastal area located between the port of Civitavecchia and the Marangone stream mouth.

The hotspot located in the area near the Mignone river mouth is characterized by high Mn and As values, probably the result of sedimentary productivity and abundance of Mn and As in the territories drained by the Mignone stream.

The contribution of these two elements is due to the geological formations in the same catchment area. Regarding Mn, the sedimentary succession called "the series of Tolfa Flysch and Pietraforte" shows limestone and clay units with discontinuous superposition of clays rich in manganese (Fazzini et al. 1972; Spadoni et al. 2005).

Considering the Mignone basin size and the distribution of prevailing winds near Civitavecchia, it is reasonable to assume that such enrichment is of natural origin and overlaps with the significant contributions from human activities including the

Civitavecchia harbor and the Torrevaldaliga Nord coal-fired power plant.

Several studies have described coal combustion as the main source of anthropogenic As and Mn in natural environments (Nriagu and Pacyna 1988; Yudovich and Ketris 2005; Henke 2009).

The second hotspot, located between the port of Civitavecchia and the Marangone stream mouth, is affected by the presence of abandoned pyrite, marcasite and galena mines, located in the territories drained by the Marangone stream basin (Kreidie et al. 2011).

Urban pollution seems to be a much less important contribution, (e.g., sewage discharges, urban runoff and maritime emissions). The As concentrations and enrichments in this hot spot seem to be dominated by mineral deposits.

Moreover the wind regime and the small size of the Marangone stream basin suggest that emissions of the Torrevaldaliga North plant and of the port of Civitavecchia do not substantially affect the enrichment values of the considered hotspot.

*This Chapter is adapted from a manuscript published in 2015 in “Archives of environmental contamination and toxicology”.*

*Piazzolla D, Scanu S, Frattarelli FM, Mancini E, Tiralongo F, Brundo MV, Tibullo D, Pecoraro R, Copat C, Ferrante M, Marcelli M (2015). Trace-Metal Enrichment and Pollution in Coastal Sediments in the Northern Tyrrhenian Sea, Italy. Arch Environ Contam Toxicol 69(4), 470-481.  
DOI:10.1007/s00244-015-0166-3.*

### **3.1 Abstract**

This study evaluated the distribution pattern and pollution of chromium, arsenic (As), manganese (Mn), nickel, lead, and copper in surface sediments along the northern Latium coast of the Tyrrhenian Sea in Italy. The enrichment factor, geoaccumulation index, and potential toxicity response index were used to evaluate the degree of contamination. These results show As and Mn contamination. The high enrichment and contamination levels of As and Mn are located in two hot spots. These elevations are due to naturally high levels of As and Mn in the Mignone River and the Marangone Stream as well as the intense human activity in the area including the largest energy production site in Europe (Torrevaldaliga Nord coal-fired power plant) and of one of the most important ports for cruise traffic in the Mediterranean Sea.

### **3.2 Introduction**

Trace-metal pollution is a serious threat particularly in the marine environment. Trace metals have both natural and anthropogenic origins with human activities supplementing natural geochemical background values of the pollutants.

Rapid industrialization, urbanization, and increased human activity in coastal areas have resulted in an increased quantity of trace metals accumulated in air, water, soil, and sediment as described in several works (Nriagu and Pacyna 1988; Varol 2011; Chaudhari et al. 2012; Suresh et al. 2012; Bastami et al. 2014). These chemical elements are

transported to the sea by various pathways including river basin runoff, atmospheric deposition, discharge of sewage, industrial emissions, etc.

Trace metals in marine sediments have a particular affinity for finer-particle grain sizes and bind to the surface of fine particles by different processes (Forstner and Wittman 1984; Horowitz 1991; Ligero et al. 2001). They then follow the sedimentary fate of fine particles. The marine depositional areas of the pelitic fraction represent the principal trace metals archive and reflect the pollution levels in the water column (Chengxin et al. 2002; Selvaraj et al. 2004).

Other variations in physical and chemical parameters (e.g., pH, Eh, temperature, and salinity) may cause chemicals to be released from the more stable pelitic deposits. This alters the ecological balance of the surrounding area.

Trace metals are a particular threat for marine ecosystems. They bioaccumulate and biomagnify, which results in the exponential accumulation of toxic elements within various trophic chains and levels (Liu et al. 2009; Zhan et al. 2010; Ghrefat et al. 2011; Gao and Chen 2012). The purpose of this research was to (1) determine the spatial distribution of trace metals (chromium [Cr], arsenic [As], manganese [Mn], nickel [Ni], lead [Pb], and copper [Cu]) associated with marine sediments; and (2) explore the sediment's enrichment and pollution using multiple contamination indices. This evaluates the present contribution of various industrial activities in the area with particular attention given to coal combustion at the Torrevaldaliga Nord power plant and Civitavecchia harbor, which is an important port for cruise traffic in the Mediterranean Sea.

### **3.3 Materials and Methods**

#### **3.3.1 Study area**

The study area is located in the northern Tyrrhenian Sea in northern Latium. It includes the coastal platform that extends from Santa Severa (42.01676 N, 11.95604 E), which is located south of Capo Linaro up to the Tarquinia coastal area (42.22243 N, 11.70495 E)

in the physiographical unit (PU) M. Argentario–Capo Linaro (Fig. 1).

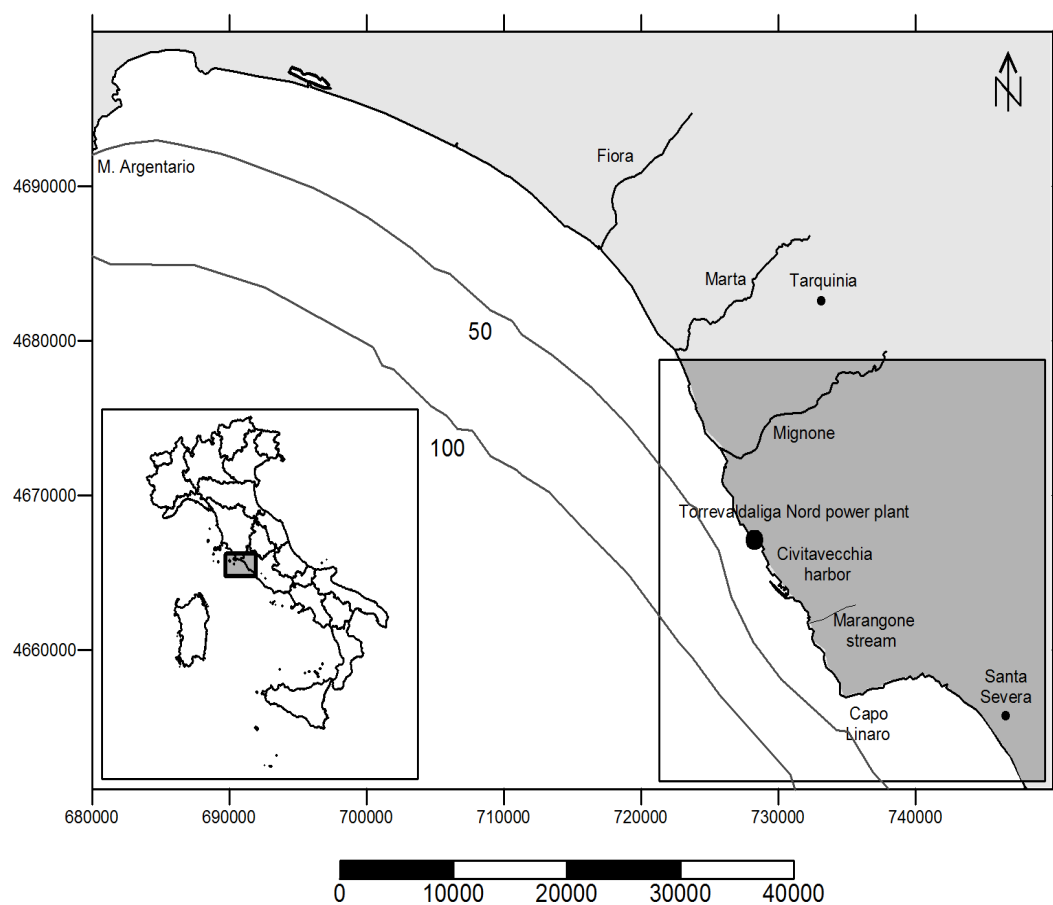
Several investigators have exhaustively described the geological and morphological features of the PU. They have identified a series of stratigraphic marine and/or riverine units that define a series of terraces. These morpho-stratigraphic features are the result of interactions between sea-level glacial fluctuations and lifting of the zone during the Pleistocene (Fazzini et al. 1972; Ambrosetti et al. 1978, 1981; Conato and Dai Pra 1980; Bosi et al. 1990; De Rita et al. 2002; Aureli et al. 2012).

Sediment in the study area mainly comes from the Mignone River and subordinately from other smaller rivers, but these only influence marine sedimentation locally and during high flood phases (Angelucci et al. 1979; Carboni et al. 1980; Tortora 1989a, 1989b).

The Mignone River basin (500 km<sup>2</sup>) is located between the Tyrrhenian margin (to the west) and the Pleistocenic volcanic reliefs of the Sabatini and Cimino–Vicano Mounts. Its complex geological setting includes the presence of many sulphide mineral ores linked to the upwelling of hydrothermal fluids. More than half of the Mignone River basin is set on hilly morphotypes (65 %). Of this, 44 % is marl, 11 % is arenaceous conglomerate, and 10 % is clay. The volcanic formations occupy 15 % of the river basin surface. The sediment is sandy for the conglomeratic formations and clay-like in the marl formations (Spadoni et al. 2005; Scanu 2012). Among the smaller rivers making local contributions, the most important is the Marangone basin. Its delta is located to the south of the Civitavecchia harbor, which has the same geologic characteristics as the Mignone basin. Although modest in size (only 23 km<sup>2</sup>), the Marangone stream basin has abandoned pyrite, marcasite, and galena mines as well as marcasite mine waste deposits and galena small pits (Kreidie et al. 2011).

The Civitavecchia compound located in the study area has the largest energy-production site in Europe as well as one of the most important cruise traffic ports of the Mediterranean sea. The recent history of Civitavecchia (i.e., after World War II) is marked by various industrial activities that have continuously influenced the concentrations of trace metals in all environmental compartments particularly in the

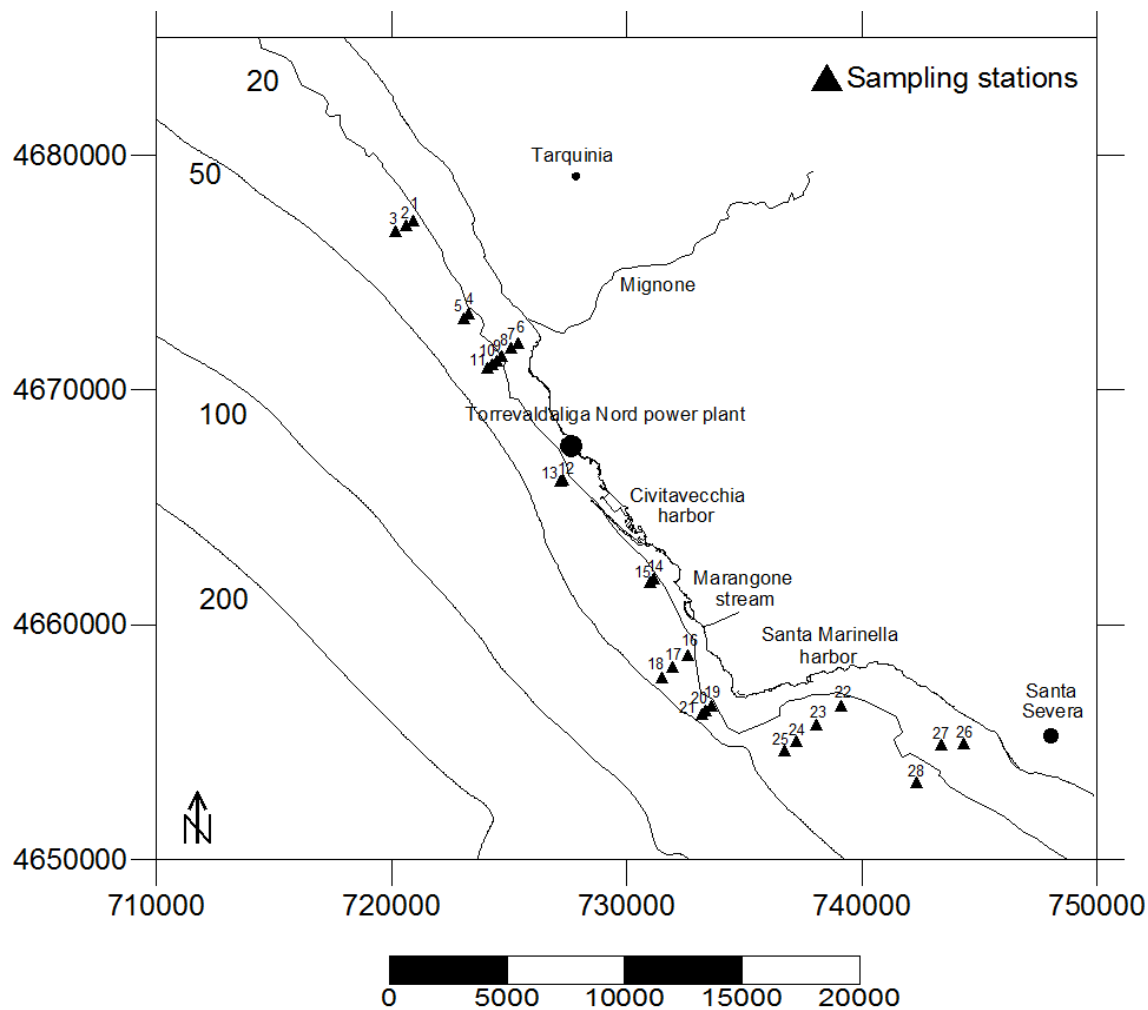
sedimentary matrix. To understand the effective contribution of the anthropic activities in the northern Tyrrhenian Sea—including Cr, As, Mn, Ni, Pb and Cu levels in sediments—one must consider the complex overlap of potential pollution sources. Most important is the Torrevadalliga Nord plant and other industrial stressors such as the Civitavecchia harbour.



**Fig. 1** Study area.

### 3.3.2 Sample collection and analysis

Sediment sampling was performed in July 2013 using a Van Veen grab (18-L volume). Surface sediment samples ( $n = 28$ ) located between -50 and -10 m were sampled (Fig. 2). The surface layer (1 cm) of each sample was subsampled, homogenized, and placed into polyethylene bags. Once transported (at 4 °C) to the laboratory, sediments were dried in an oven at 40 °C for 48 h, crushed, and stored in polyethylene bags for subsequent analysis. Grainsize analysis was performed through wet sieving on sediment samples previously treated with  $\text{H}_2\text{O}_2$  vol. 16 solution (Spagnoli et al. 2014). Surfer 8.0 (Golden Software Inc., USA) was used for drawing the distribution maps of the pelitic fraction percentage as well as the trace-metal concentrations in the surface sediments. Kriging interpolation method was used.



**Fig. 2** Sediment sampling locations.

### 3.3.3 Trace metal analysis

Metal extraction from sediments and analytical determination was performed according to United States Environmental Protection Agency 3051A:2007 and 6010C:2007, respectively. Specifically, 1 g of each analytical sample group was weighed with an analytical scale (Mettler Toledo xs105) and mineralized in a microwave system Ethos Touch Control (MILESTONE S.r.l.—Italy) with a digestion solution prepared using 9 mL of 65 % nitric acid ( $\text{HNO}_3$ ) and 3 mL of 30 % chloridric acid ( $\text{HCl}$ ) (both from Carlo Erba). After mineralization, ultrapure water (Merck) was added to the samples up to 50

mL. The trace metals analysis was performed with an inductively coupled plasma-optical emission spectrometer Optima 2000DV (Perkin Elmer-USA). Standards for the instrument calibration were prepared using a multielement certified reference solution ICP Standard (Merck). The system was calibrated using a calibration line made up of five different concentrations for each element. The linear regression ( $R^2$ ) for the calibration line was between 0.9972 and 0.9989.

Analytical blanks and recovery samples were run in the same way as the real samples, and concentrations were determined using standard solutions prepared in the same acid matrix to validate the calibration. An analytical quality-control procedure was performed with standard reference material NIST-2711a- Montana II Soil with a recovery range between 95 and 110 % for selected metals.

To assess the trace-metal enrichment and contamination degree in sediments, three different indices were used: enrichment factor (EF), geoaccumulation index (Igeo), and potential toxicity response (RI). Moreover, the mean concentrations of Cr, As, Ni, Pb, and Cu were compared with effect range low (ERL) and effect range median (ERM) values (Long et al. 1995).

Finally, Pearson's correlation matrix of raw data set was performed to evaluate the possible correlation between the trace-metal concentrations in the sediment samples. For the Pearson's correlation, all trace-metal values were normalized with aluminum (Al) concentrations to account for grain-size differences.

EF was previously described and used by several investigators (Morillo et al. 2004; Adamo et al. 2005; Vald'es et al. 2005). It is widely used to study the degree of sediment contamination. For normalization of metal concentrations, the EF method normalizes the measured trace metals with respect to a sample reference metal such as iron (Fe) or Al (Ravichandran et al. 1995). In this approach, the Fe or Al is considered as a "proxy" for the clay content (Windom et al. 1989; Din 1992). Al was used for the normalization as described by Lee et al. (1998), Huang and Lin (2003), and Voitke et al. (2003). The enrichment factor is determined by the following equation:

$$EF = (H_s / Al_s) / (H_c / Al_c)$$

where  $H_s$  and  $H_c$  are the sample and background tracemetal concentrations, respectively, and  $Al_s$  and  $Al_c$  are the sample and background reference levels of Al. For background concentrations, the values reported by Turekian and Wedepohl (1961) were used considering the different sedimentary matrix (sandstone or shale). Sakan et al. (2009) suggested that EF values < 1 indicates no enrichment; < 3 indicates minor enrichment; 3 to 5 indicates moderate enrichment; 5 to 10 indicates moderately severe enrichment; 10 to 25 indicates severe enrichment; 25 to 50 indicates very severe enrichment; and > 50 indicates extremely severe enrichment.

Igeo is defined by the following equation:

$$I_{geo} = \log_2 (C_n / k B_n)$$

Here,  $C_n$  is the metal concentrations of the examined sediment samples and  $B_n$  is the metal's geochemical background value. The factor  $k$  (1.5) is the background correction factor due to lithospheric effects (Müller 1969, Rubio et al. 2000; Shafie et al. 2013).

Igeo classifies sediments into 7 classes: Class 0 (practically uncontaminated,  $I_{geo} \leq 0$ ); Class 1 (uncontaminated or moderately contaminated,  $0 < I_{geo} < 1$ ); Class 2 (moderately contaminated,  $1 < I_{geo} < 2$ ); Class 3 (moderate to heavily contaminated,  $2 < I_{geo} < 3$ ); Class 4 (heavily contaminated,  $3 < I_{geo} < 4$ ); Class 5 (heavily to extremely contaminated,  $4 < I_{geo} < 5$ ); and Class 6 (extremely contaminated,  $I_{geo} > 5$ ) (Muller, 1969; Jiang et al., 2014).

The RI was described by Hakanson (1980) and is defined as follows:

$$RI = \sum E_f^i$$

where  $E_f^i$  is the Hakanson potential ecological risk, defined by:

$$E_f^i = C_f^i \times T_f^i$$

where  $T_f^i$  is the response coefficient for the toxicity of the single metal, e.g. Cr = 2, Ni = Cu = Pb = 5, and As = 10 (Hakanson 1980). Term  $C_f^i$  is the monomial contamination factor defined as:

$$C_f^i = C_s^i / C_b^i$$

where  $C_s^i$  and  $C_b^i$  are the trace metal concentrations in the samples and background respectively. The RI grading standards are: RI < 150 = low grade; 150 < RI < 300 = moderate grade; 300 < RI < 600 = severe grade; and RI > 600 = serious grade.

### 3.4 Results

Trace metal concentrations in the surface sediments collected from the study area follow the scheme: Mn > Pb > Cr > Ni > As > Cu.

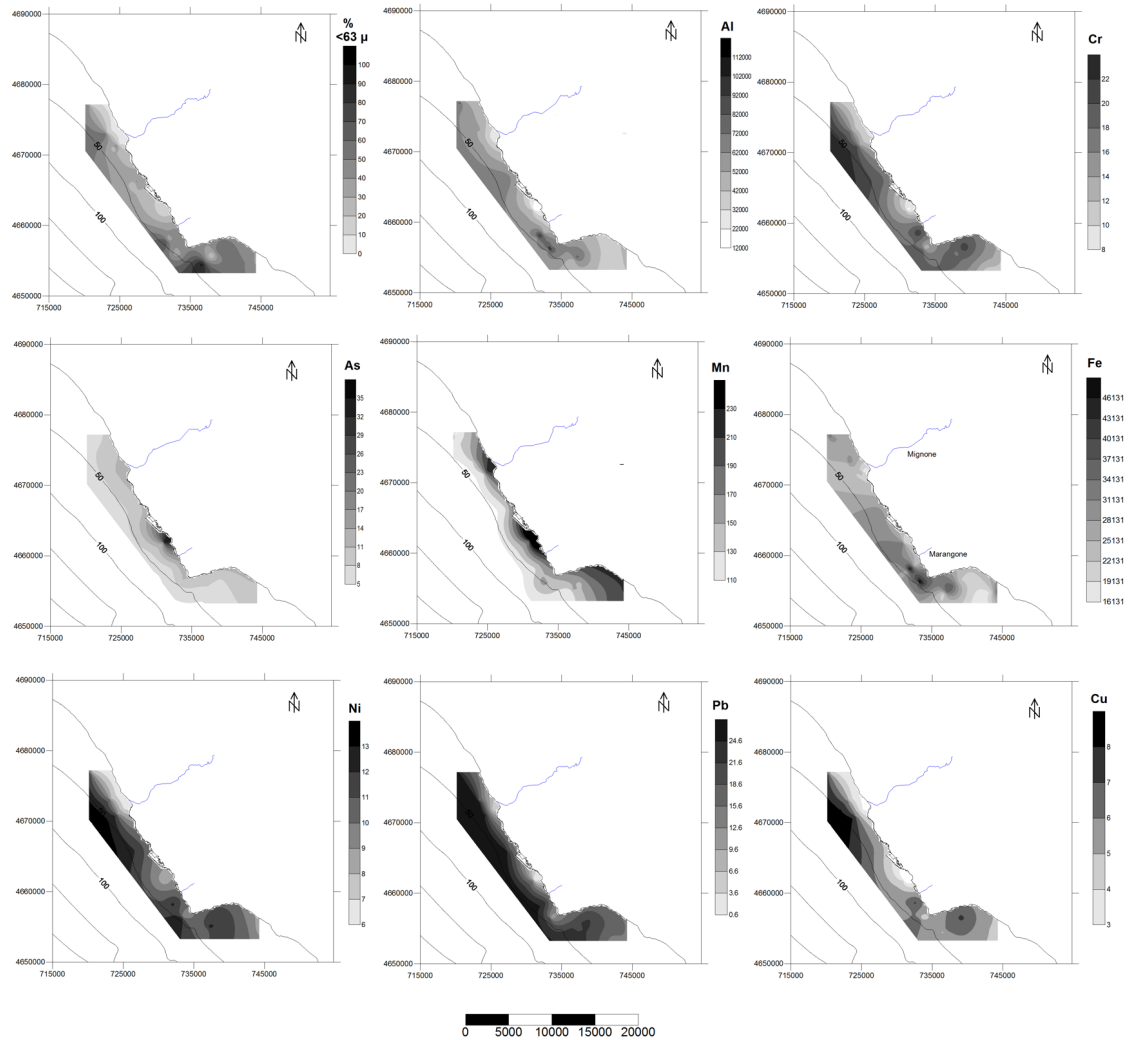
Table 1 shows the original data set, which includes the pelitic fraction percentages for all sediment sampling stations, ranges, averages, standard deviations, ERL and ERM values of the considered elements. Overall, the mean concentrations of all trace metals are below their ERM guidelines. However, the mean concentration of As is above the ERL value (17 sampling stations exceeded the ERL value). This effect represents contamination in most of the sampling locations.

The spatial pattern of metals (Al and Fe included) in sediments as well as the spatial distribution of the pelitic fraction percentages are shown in Figure 3.

| Sampling sites | Location       | Pelitic fraction (%) | Al (mg/kg)       | Cr (mg/kg)   | As (mg/kg)   | Mn (mg/kg)      | Fe (mg/kg)         | Ni (mg/kg)   | Pb (mg/kg)   | Cu (mg/kg)  |
|----------------|----------------|----------------------|------------------|--------------|--------------|-----------------|--------------------|--------------|--------------|-------------|
| ST01           | 4677160 720912 | 15.2                 | 51545            | 12.37        | 6.33         | 115.0           | 26985              | 7.11         | 21.55        | 4.05        |
| ST02           | 4676951 720629 | 45.0                 | 79926            | 13.87        | 5.95         | 105.5           | 35090              | 8.09         | 24.66        | 5.04        |
| ST03           | 4676671 720184 | 43.9                 | 61344            | 20.83        | 7.80         | 137.7           | 24720              | 12.19        | 28.73        | 7.54        |
| ST04           | 4673178 723277 | 15.4                 | 54922            | 13.26        | 9.51         | 163.6           | 30074              | 8.07         | 19.06        | 4.62        |
| ST05           | 4672993 723068 | 54.5                 | 51804            | 17.76        | 9.39         | 131.8           | 23377              | 10.54        | 32.06        | 6.31        |
| ST06           | 4671921 725352 | 6.8                  | 22015            | 10.58        | 12.46        | 224.6           | 17538              | 6.64         | 5.40         | 2.87        |
| ST07           | 4671702 725086 | 3.6                  | 35464            | 11.16        | 14.17        | 217.3           | 24989              | 7.04         | 9.04         | 3.09        |
| ST08           | 4671377 724683 | 28.3                 | 38841            | 13.27        | 11.15        | 171.7           | 20472              | 8.31         | 16.81        | 4.95        |
| ST09           | 4671193 724473 | 58.3                 | 46020            | 13.38        | 9.58         | 134.3           | 22664              | 8.82         | 18.43        | 5.20        |
| ST10           | 4671036 724251 | 20.8                 | 48387            | 14.84        | 9.34         | 102.8           | 22410              | 8.55         | 25.44        | 4.84        |
| ST11           | 4670857 724050 | 26.9                 | 52024            | 20.03        | 9.19         | 122.5           | 23351              | 11.79        | 24.92        | 7.78        |
| ST12           | 4666127 727283 | 42.9                 | 68006            | 19.02        | 7.93         | 117.1           | 29652              | 11.53        | 20.86        | 5.85        |
| ST13           | 4666046 727187 | 25.6                 | 68273            | 19.12        | 9.37         | 118.5           | 29557              | 11.80        | 26.29        | 5.76        |
| ST14           | 4661870 731155 | 11.9                 | 12596            | 7.32         | 35.38        | 356.2           | 19185              | 8.85         | 0.82         | 1.23        |
| ST15           | 4661755 731002 | 15.4                 | 41731            | 11.53        | 14.29        | 191.6           | 32749              | 8.06         | 14.94        | 3.97        |
| ST16           | 4658628 732612 | 49.6                 | 47629            | 21.69        | 9.84         | 164.5           | 23794              | 11.54        | 22.32        | 7.13        |
| ST17           | 4658107 731958 | 30.1                 | 99119            | 19.06        | 7.63         | 137.6           | 47773              | 12.32        | 24.69        | 6.77        |
| ST18           | 4657693 731491 | 71.2                 | 57472            | 17.24        | 6.25         | 123.6           | 26703              | 10.99        | 25.18        | 5.33        |
| ST19           | 4656476 733582 | 43.7                 | 72603            | 12.32        | 11.02        | 146.4           | 39880              | 9.10         | 10.37        | 4.51        |
| ST20           | 4656272 733361 | 33.0                 | 120297           | 18.08        | 6.98         | 137.3           | 55111              | 11.72        | 22.84        | 5.99        |
| ST21           | 4656122 733171 | 30.5                 | 61017            | 18.75        | 8.80         | 168.1           | 35418              | 12.79        | 20.10        | 6.47        |
| ST22           | 4656476 739090 | 60.9                 | 46623            | 21.24        | 7.51         | 182.7           | 22178              | 11.82        | 21.46        | 7.26        |
| ST23           | 4655686 738055 | 18.6                 | 64626            | 17.38        | 7.36         | 143.5           | 34625              | 11.84        | 22.19        | 6.28        |
| ST24           | 4654956 737184 | 51.5                 | 75499            | 19.94        | 7.49         | 155.5           | 37368              | 12.21        | 20.11        | 6.44        |
| ST25           | 4654551 736701 | 93.4                 | 44381            | 18.54        | 5.43         | 116.5           | 20611              | 10.18        | 23.79        | 4.93        |
| ST26           | 4654853 744302 | 36.8                 | 52342            | 12.07        | 9.94         | 213.5           | 34550              | 8.36         | 14.52        | 4.71        |
| ST27           | 4654821 743374 | 48.2                 | 35351            | 13.72        | 10.44        | 199.1           | 19489              | 9.54         | 17.69        | 4.90        |
| ST28           | 4653217 742310 | 51.7                 | 31455            | 11.07        | 8.52         | 194.7           | 16131              | 10.41        | 13.66        | 5.08        |
| Range          |                |                      | 12596 - 120297   | 7.32 – 21.24 | 5.95 – 35.38 | 105.5 – 356.2   | 16131 – 47773      | 7.04 – 12.32 | 5.40 – 32.06 | 2.87 – 7.78 |
| Average ± SD   |                |                      | 55047 ± 22049.76 | 15.69 ± 3.91 | 9.97 ± 5.45  | 160.47 ± 52.067 | 28444.38 ± 9153.09 | 10.01 ± 1.89 | 19.57 ± 7.01 | 5.32 ± 1.48 |
| ERL            |                |                      | -                | 81           | 8.2 (17)     | -               | -                  | 20.9         | 46.7         | 34          |
| ERM            |                |                      | -                | 270          | 70           | -               | -                  | 51.6         | 218          | 270         |

\*(N): number of samples exceeded the ERL value.

**Table 1** Trace metals raw data set.



**Fig. 3** Spatial distribution of the % of pelitic fraction, Al, Cr, As, Mn, Fe, Ni, Pb and Cu.

The results highlight two different patterns: (i) Mn and As concentrations; and (ii) Cu, Pb, Ni, and Cr concentrations.

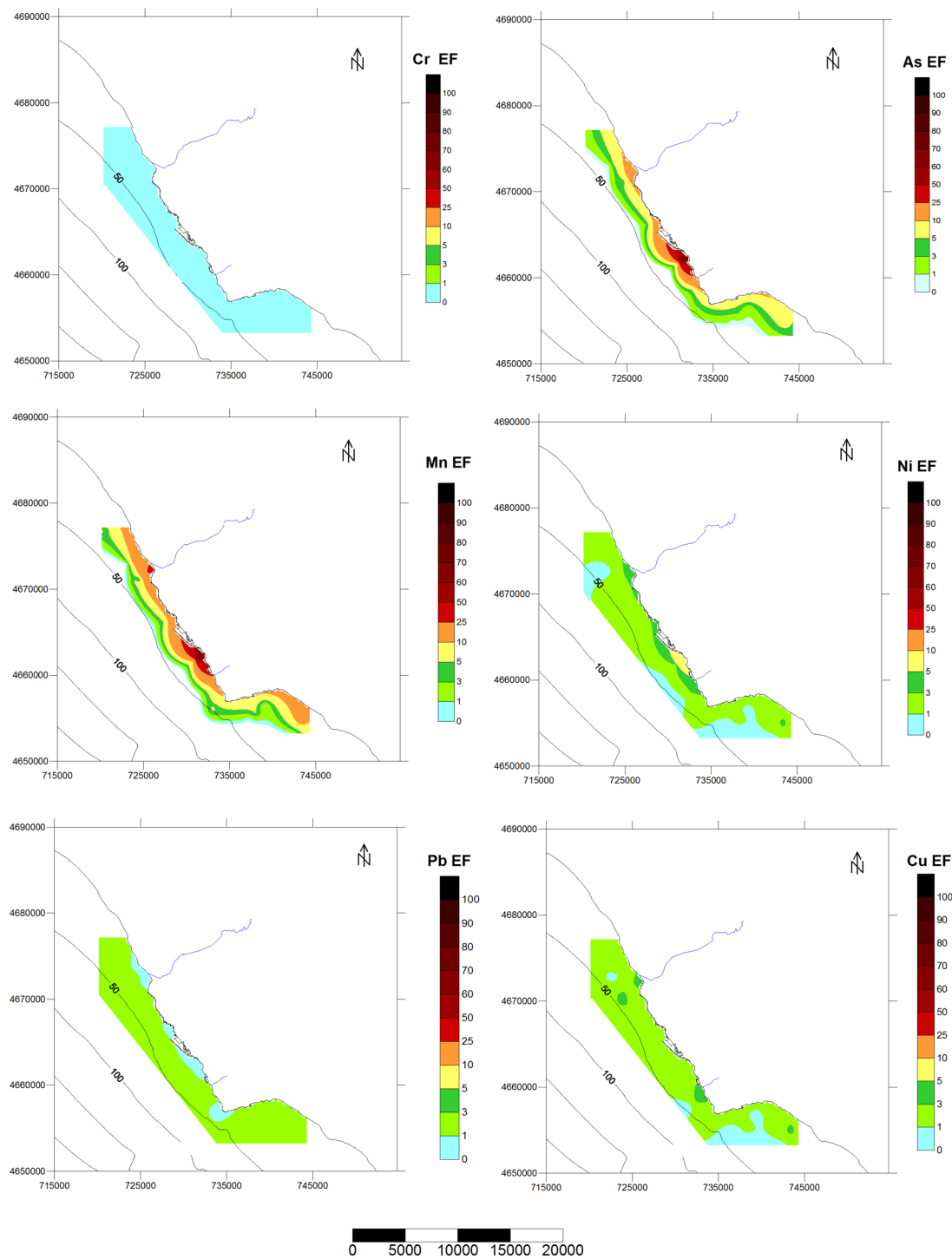
Figure 3 shows that the Mn and As spatial distributions have a different pattern. It is not possible to identify a bathymetric or grain size gradient, and there are two hotspots that affect their distributions. The hotspots are located near the Mignone and Marangone Deltas in the northern and southern part of the study area, respectively.

The Cu, Pb, Ni, and Cr concentrations show a progressive gradient from the coastline up

to the bathymetric depth of -50 m. There is a slight anomaly located near the Santa Marinella touristic harbor. This progressive gradient agrees with the pelitic fraction percentage and Al concentration, which increase with depth. The distribution pattern of Fe is similar to the Al and pelitic fraction distributions.

The calculated EF values follow the scheme:  $Mn > As > Ni > Cu > Pb > Cr$ .

The EF spatial distributions (Fig. 4) of As and Mn follow a similar pattern as the raw data. The As and Mn show a severe enrichment ( $10 < EF < 25$ ) in the area close to the coast. There is extremely severe enrichment ( $EF > 50$ ) near the Marangone Delta. Ni follows a similar pattern to As and Mn, but with lower values; Ni EF is moderately high near the Mignone Delta and moderately severe south of the Civitavecchia harbor near the Marangone Delta. For Cu, there are two moderate enrichment values ( $3 < EF < 5$ ). One is located close to the Mignone River Delta and the other is at the Marangone Stream Delta. The Pb EF pattern follows the pelitic percentage distribution but with lower values near the coast and moderate values away from the coast. However, Cr shows no enrichment.



**Fig. 4** Spatial distributions of EF values.

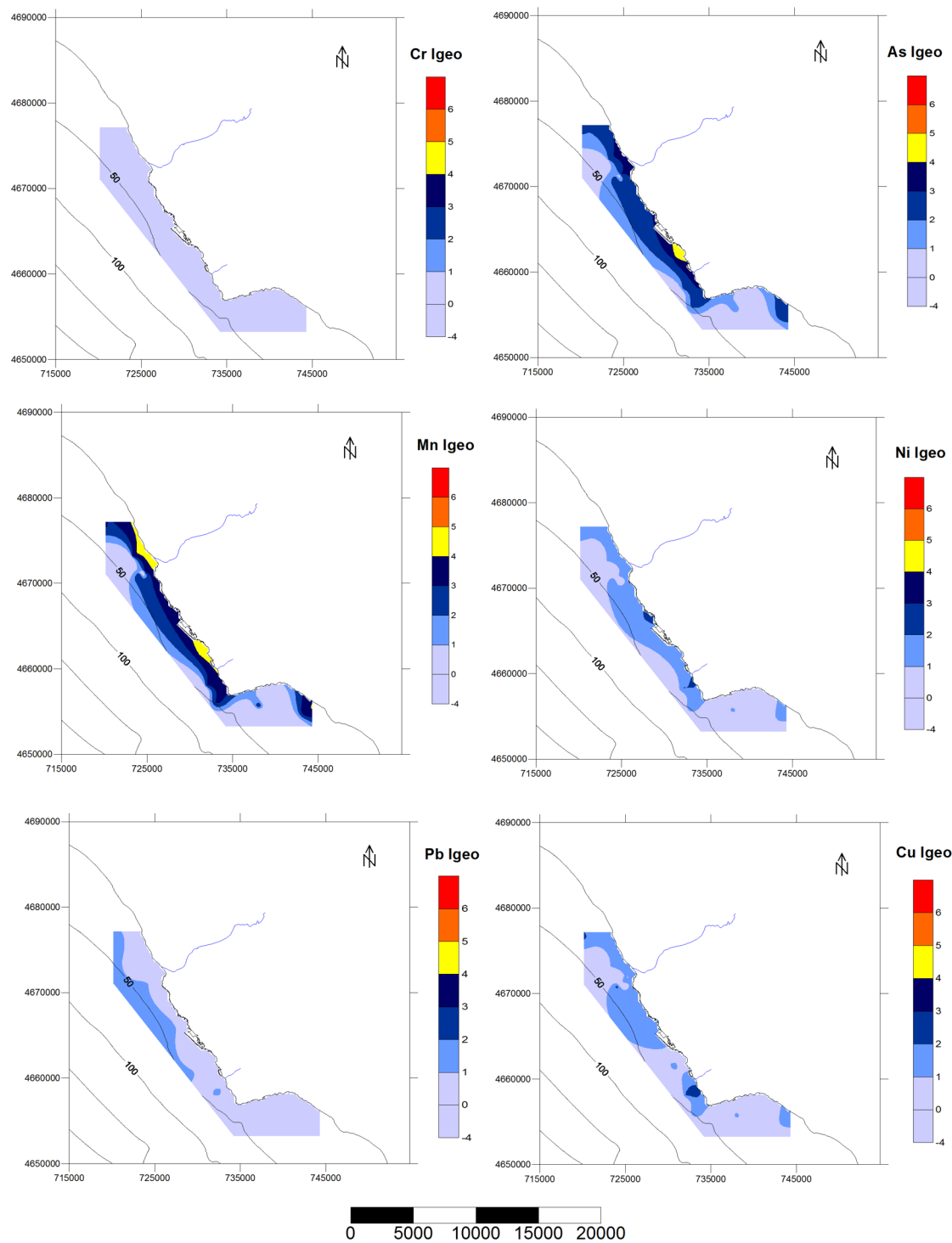
The Igeo results (Fig. 5) follow a similar pattern as the EF data. There is heavy to extreme Mn contamination ( $4 < I_{geo} < 5$ ) near the Mignone River mouth and the Marangone Delta. There is heavy to extreme As contamination near the Marangone Delta and heavy contamination ( $3 < I_{geo} < 4$ ) near the Mignone River Delta. The Ni and Cu Igeo values follow a similar pattern with moderate to heavy Igeo values ( $2 < I_{geo} < 3$ ) near the Marangone Stream. Only Ni is visible with the same Igeo value near the Civitavecchia harbor entrance. The Mignone Delta area shows moderate Igeo values ( $1 < I_{geo} < 2$ ).

The Pb Igeo distribution is similar to the EF distribution with a concentration increases from the coast-line ( $0 < I_{geo} < 1$ ) up to a bathymetric depth of -50 m ( $1 < I_{geo} < 2$ ). The Cr Igeo values show no contamination.

Statistical analyses (i.e., Pearson's correlation matrix) reveal two groups with a strong positive correlation: (i) Mn with As and Ni; and (ii) Ni with As (Table 2).

Positive correlation between the trace metals suggest that metals have common sources, mutual dependence, and identical behavior during transport.

The RI spatial distribution (Fig. 6) reports severe grade of toxicity in the area between the Civitavecchia harbor and the Marangone Delta ( $300 < RI < 600$ ) as well as a moderate grade of toxicity ( $150 < RI < 300$ ) in the coastal area between Capo Linaro and the mouth of the Mignone River.

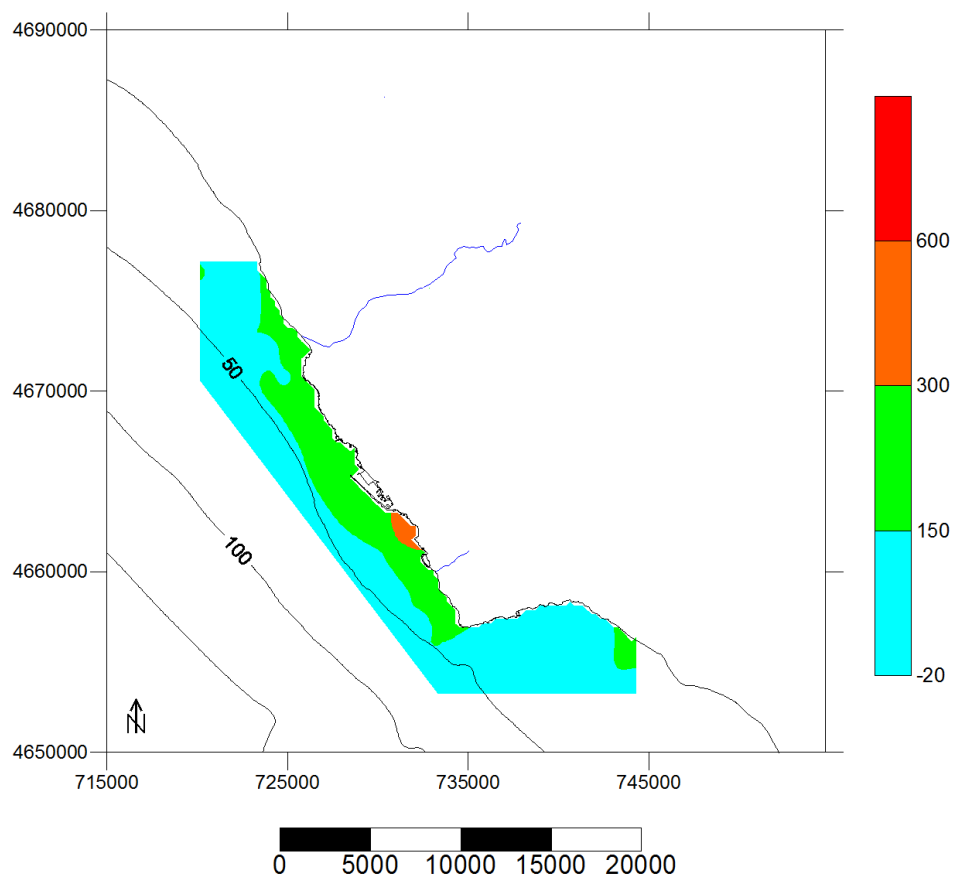


**Fig. 5** Spatial distributions of Igeo values.

|    | Cr    | Mn     | Ni     | Cu    | As     | Pb |
|----|-------|--------|--------|-------|--------|----|
| Cr | 1     |        |        |       |        |    |
| Mn | 0,671 | 1      |        |       |        |    |
| Ni | 0,822 | 0,942* | 1      |       |        |    |
| Cu | 0,731 | 0,154  | 0,410  | 1     |        |    |
| As | 0,604 | 0,981* | 0,916* | 0,051 | 1      |    |
| Pb | 0,204 | -0,438 | -0,196 | 0,592 | -0,456 | 1  |

\*Correlation is significant at 0.01 level

**Table 2** Pearson's correlation of normalized trace-metal values.



**Fig. 6** Spatial distribution of the potential toxicity response RI.

### 3.5 Discussion

Several studies have investigated the concentrations of trace metals in coastal sediments. A compendium of concentrations in Italy is summarized in Table 3.

The average concentration of Cr (15.7 mg/kg) is slightly less than that found in the reference averages and is comparable to the Sardinia values. The As average concentration (9.97 mg/kg) is comparable to other Tyrrhenian coastal areas and are less than the values found in the area to the north of the Mignone river. The Mn average value (160.5 mg/kg) is twice the Sardinia average but is less than the value in the Gulf of Taranto. The average concentrations of Ni (10 mg/kg), Pb (19.6 mg/kg) and Cu (5.3 mg/kg) are far from the average values found in literature.

The results obtained from the coastal surface sediment analysis highlight an abundance trace metals, especially As, Mn, and Ni, and to a lesser extent Cu and Pb. Several studies have described how pollutants, especially trace metals, bind to the finer grain size particles. This facilitates transport and distribution of pollutants in marine sedimentary environments (Forstner and Wittman 1984; Horowitz 1991b; Ligero et al. 2001; Alyazichi et al. 2015). However, the distribution of As and Mn do not conform to the bathymetric and grain size gradients in the study area. Moreover, the mean concentration of As exceeds the ERL value; this effect represents contamination in most of the sampling locations. Our results highlight the presence of two As and Mn hotspots: (i) the coastal area near the Mignone River mouth; and (ii) the coastal area between the Civitavecchia harbor and the Marangone Stream Delta. The distribution of these two trace metals was also confirmed by EF and contamination indices (Igeo and RI).

| Trace metals | Reference                | Site                                               | Range (mg/kg) | Average (mg/kg) |
|--------------|--------------------------|----------------------------------------------------|---------------|-----------------|
| <b>Cr</b>    | Leoni and Sartori, 1996  | Northern Tyrrhenian / Eastern Ligurian Seas, Italy | 18 – 269      | 166.1           |
|              | Adamo et al., 2005       | Port of Naples, Tyrrhenian Sea, Italy              | 10.3 – 161.8  | -               |
|              | Buccolieri et al., 2006  | Gulf of Taranto, Ionian Sea, Italy                 | 75.2 – 102.8  | 85.9            |
|              | Zonta et al., 2007       | Porto Marghera, Venice, Adriatic Sea, Italy        | 14 – 66       | -               |
|              | Acquavita et al., 2010   | Gulf of Trieste, Adriatic Sea, Italy               | 35 – 171      | -               |
|              | Di Leonardo et al., 2014 | Priolo Bay, Ionian Sea, Italy                      | 5.6 – 20.5    | -               |
|              | Schintu et al., 2015     | Sardinia, Italy                                    | 2.41 – 64.1   | 20.03           |
|              | Scanu et al., 2015       | Northern Tyrrhenian Sea, Italy                     | 13 – 53.3     | 34.5            |
| <b>As</b>    | Leoni and Sartori, 1996  | Northern Tyrrhenian / Eastern Ligurian Seas, Italy | 4 – 88        | 20.35           |
|              | Adamo et al., 2005       | Port of Naples, Tyrrhenian Sea, Italy              | 8 – 21        | -               |
|              | Acquavita et al., 2010   | Gulf of Trieste, Adriatic Sea, Italy               | 6.4 – 18.2    | -               |
|              | Di Leonardo et al., 2014 | Priolo Bay, Ionian Sea, Italy                      | 3.1 – 19.7    | -               |
|              | Schintu et al., 2015     | Sardinia, Italy                                    | 2.39 – 22.9   | 7.68            |
|              | Scanu et al., 2015       | Northern Tyrrhenian Sea, Italy                     | 12.6 – 42     | 21.5            |
| <b>Mn</b>    | Buccolieri et al., 2006  | Gulf of Taranto, Ionian Sea, Italy                 | 552 – 2826    | 893             |
|              | Schintu et al., 2015     | Sardinia, Italy                                    | 19.7 – 164.8  | 76.09           |
| <b>Ni</b>    | Leoni and Sartori, 1996  | Northern Tyrrhenian / Eastern Ligurian Seas, Italy | 29 – 118      | 86.63           |
|              | Buccolieri et al., 2006  | Gulf of Taranto, Ionian Sea, Italy                 | 47.9 – 60.7   | 53.3            |
|              | Zonta et al., 2007       | Porto Marghera, Venice, Adriatic Sea, Italy        | 8 – 59        | -               |
|              | Acquavita et al., 2010   | Gulf of Trieste, Adriatic Sea, Italy               | 20 – 231      | -               |
|              | Di Leonardo et al., 2014 | Priolo Bay, Ionian Sea, Italy                      | 19.6 – 74.9   | -               |
|              | Schintu et al., 2015     | Sardinia, Italy                                    | 0.5 – 30.3    | 6.72            |
|              | Scanu et al., 2015       | Northern Tyrrhenian Sea, Italy                     | 12 – 47       | 22.7            |
| <b>Pb</b>    | Leoni and Sartori, 1996  | Northern Tyrrhenian / Eastern Ligurian Seas, Italy | 17 – 58       | 34.79           |
|              | Adamo et al., 2005       | Port of Naples, Tyrrhenian Sea, Italy              | 37 – 314      | -               |
|              | Buccolieri et al., 2006  | Gulf of Taranto, Ionian Sea, Italy                 | 44.7 – 74.8   | 57.8            |
|              | Zonta et al., 2007       | Porto Marghera, Venice, Adriatic Sea, Italy        | 50 – 131      | -               |
|              | Acquavita et al., 2010   | Gulf of Trieste, Adriatic Sea, Italy               | 12 – 170      | -               |
|              | Di Leonardo et al., 2014 | Priolo Bay, Ionian Sea, Italy                      | 1.8 – 7.2     | -               |
|              | Schintu et al., 2015     | Sardinia, Italy                                    | 0.78 – 117.9  | 122.28          |
|              | Scanu et al., 2015       | Northern Tyrrhenian Sea, Italy                     | 4.1 – 58.2    | 26.5            |
| <b>Cu</b>    | Leoni and Sartori, 1996  | Northern Tyrrhenian / Eastern Ligurian Seas, Italy | 14 – 44       | 25.56           |
|              | Adamo et al., 2005       | Port of Naples, Tyrrhenian Sea, Italy              | 40 – 415      | -               |
|              | Zonta et al., 2007       | Porto Marghera, Venice, Adriatic Sea, Italy        | 10 – 92       | -               |
|              | Acquavita et al., 2010   | Gulf of Trieste, Adriatic Sea, Italy               | 14 – 70       | -               |
|              | Di Leonardo et al., 2014 | Priolo Bay, Ionian Sea, Italy                      | 1.5 – 15.7    | -               |
|              | Schintu et al., 2015     | Sardinia, Italy                                    | 0.5 – 202.6   | 29.63           |

**Table 3** Mean concentrations from the literature for Cr, As, Mn, Ni, Pb, and Cu (mg/kg) in Italian coastal areas.

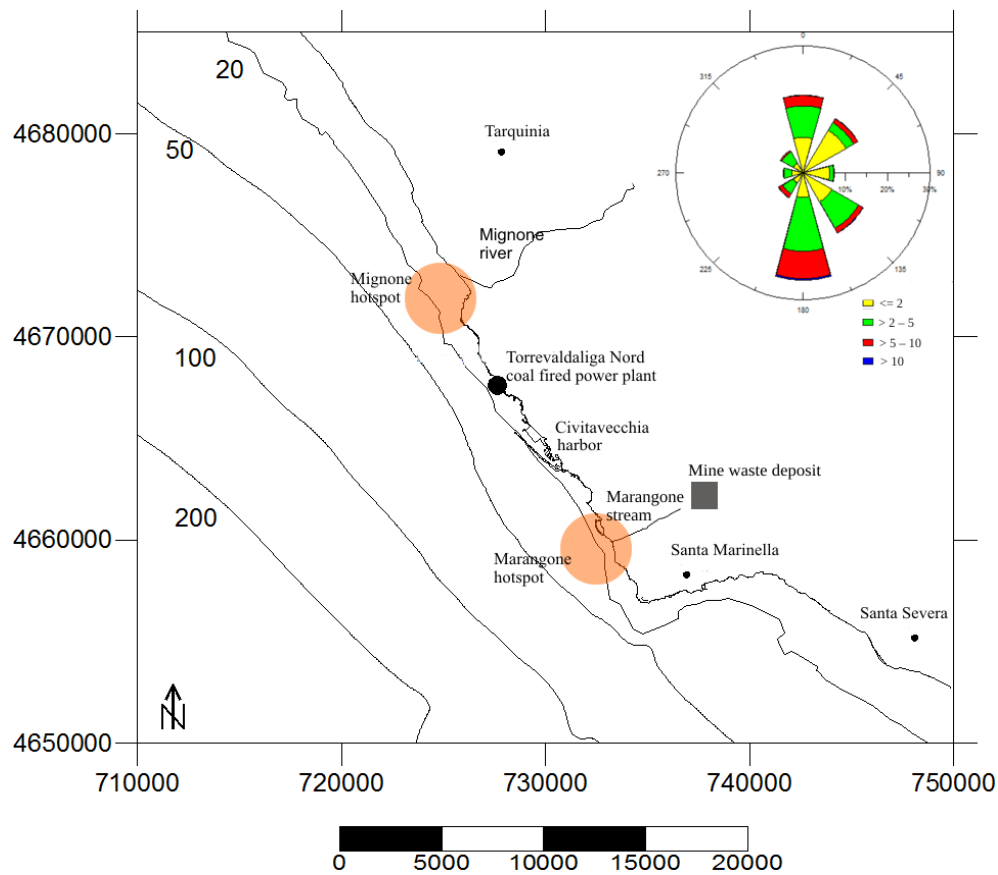
The hotspot located close to the Mignone Delta is likely a result of sedimentary productivity and the abundance of As and Mn in the areas drained by the Mignone River

basin. Spadoni et al. (2005) assessed the abundance of trace metals in stream sediment samples taken from the Mignone River and found average As and Mn values of 44.8 mg/kg and 1168 mg/kg, respectively. These two elements are due to the geological formations present in the Mignone River basin. Regarding Mn, the sedimentary succession called “serie dei Flysch tolfetani e della Pietraforte” (Fazzini et al. 1972) has a clay-like calcareous unit at its bottom that discontinuously overlaps with polychrome manganese rich clay.

This includes the Pietraforte lens and calcareous-marly units that are interbedded with the Mignone formation. Regarding As, high concentrations are found in areas where the sulfide ore mining industry was active up to a few years before this study as well as in the western part of the Mignone River.

This area was seemingly unconnected to the mineralized areas (Spadoni et al. 2005).

Considering the Mignone basin size and the distribution of prevailing winds near Civitavecchia (Fig. 7), it is reasonable to assume that such enrichment is of natural origin and overlaps with the significant contributions from human activities including the Civitavecchia harbor and the Torrevaldaliga Nord coal-fired power plant. Several studies have described coal combustion as the main source of anthropogenic arsenic (Henke 2009; Yudovich and Ketris 2005), and manganese (Nriagu et al. 1988) in natural environments.



**Fig.7** As and Mn hotspots in the study area including the wind regime at the Torrevaldaliga Nord site and mining waste deposits on the Marangone basin.

The hotspot located between the Civitavecchia harbor and the Marangone Stream Delta is influenced by the presence of abandoned mines of pyrite, marcasite, and galena including the presence of marcasite mine waste deposits (Kreidie et al. 2011) in the Marangone basin. Urban pollution seems to be a much less important contribution (e.g., sewage discharges, urban run-off and maritime emissions). As concentrations and enrichments in this hotspot seem to be dominated by mineral deposits. In addition, the wind regime and the small size of the Marangone basin suggest that the Torrevaldaliga Nord power plant should not make significant contributions to the enrichment values of this hotspot though atmospheric fallout.

Considering that the high enrichment and contamination levels of As and Mn are the

result of an overlap between intense human activities with high natural levels of these elements, further geochemical and mineralogical investigations should be performed to quantitatively determine the contribution from anthropogenic sources.

### **3.6 Conclusions**

This study analyzed the concentrations of six trace metals (Cr, As, Mn, Ni, Pb, and Cu) in surface coastal sediments collected from 28 sampling stations in the northern Tyrrhenian Sea.

The Cu, Pb, Ni, and Cr show a progressive gradient (from the coast line up to the bathymetric depth of -50 m) according to previous studies. There was a light anomaly located near the Santa Marinella tourist harbor.

Higher concentrations of Mn and As were found in the area close to the coast. In particular, two hotspots were identified, one located near the Mignone River Delta and another in the coastal area between the Civitavecchia harbor and the Marangone Stream. These Mn and As hotspots were confirmed by EF and contamination indices (Igeo and RI).

These high enrichment and contamination levels are probably the result of overlap between the high natural levels of As and Mn from the Mignone River and the Marangone Stream with intense human activity including the largest energy production site in Europe and one of the most important ports for cruise traffic in the Mediterranean sea. The effects of these anthropic stressors, especially coal combustion at Torvaldaliga Nord, could be more relevant to the northern zone of the study area because the Mignone River basin may suffer from higher atmospheric fallout contributions due to wind regimes.

This complex overlap between the various pollution sources suggests that further geochemical and mineralogical studies are needed to better discriminate between the anthropogenic contributions and naturally high sources.

#### **4. Mercury Enrichment in Sediments of the Coastal Area of Northern Latium, Italy.**

A separate discussion involves the spatial distribution of Hg concentrations in coastal sediments of the examined physiographic unit in view of previous studies conducted in the northern sector of the physiographic unit in the late 1980s and early 1990s (Barghigiani et al. 1981; Barghigiani and Bauleo 1992; Barghigiani and Ristori 1994, 1995).

Specifically the study of Hg concentrations covered the coastal stretch between Santa Severa and the Fiora river mouth, located in Montalto di Castro. The Hg enrichment factor (EF) compared to the crustal background values derived from the literature have been evaluated. Moreover, the possible "adverse effect" on the biotic component through the use of the synthetic index AEI (Adverse Effect Index) was made (Muñoz-Barbosa et al. 2012).

The Hg distribution shows the existence of two anomalies. The first occurs in the northern part of the study area, enclosed between the Fiora river mouth and the Mignone river mouth. The second anomaly occurs in the coastal area south of the port of Civitavecchia, from the Marangone stream mouth to the south of Capo Linaro.

The Hg anomaly located south of the port of Civitavecchia, spatially less extensive than the northern anomaly, is presumably the result of the geological characteristics of the local river basins, characterized by an enrichment of sulphides and by the past presence of extractive mining activities (Spadoni et al. 2005; Kreidie et al. 2011).

Regarding the nature of the northern Hg anomaly, it is reasonable to assume that natural Hg enrichment values are affected by anthropogenic input that overlaps with the already high baseline values.

These values are also affected by the prevailing wind direction and the coastal sediment transport directed from the southeast to the northwest.

*This Chapter is adapted from a manuscript published in 2016 in “Bulletin of environmental contamination and toxicology”.*

*Scanu S, Piazzolla D, Frattarelli FM, Mancini E., Tiralongo F, Brundo MV, Tibullo D, Pecoraro R, Copat C, Ferrante M, Marcelli M (2016). Mercury Enrichment in Sediments of the Coastal Area of Northern Latium, Italy. Bull Environ Contam Toxicol 96(5), 630-637.  
DOI 10.1007/s00128-016-1776-9.*

#### **4.1 Abstract**

The purpose of this study was to evaluate the extent of the Hg geochemical anomaly arising in the Amiata and Tolfa complex to the coastal area of northern Latium and to examine the possible influence on this area by the Mignone River, and by the small coastal basins, which are characterized by both previous mining activities and decades of past industrial impact. The results confirm the extension of the anomaly of concentrations of Hg in the coastal area of northern Latium, with the northern sector influenced by the contributions of the Fiora and Mignone Rivers and the southern sector influenced by the contributions of minor basins. The results show high values of the Adverse Effect Index (AEI) throughout the considered area and highlight the need for further investigation in order to assess the impact of human activities on the present and past values of Hg in marine sediments.

#### **4.2 Introduction**

Today, mercury is re-emerging as a pollutant of concern for both environmental and human health. Current global atmospheric deposition of mercury (Hg) has been estimated to be three times higher than preindustrial levels, reaching values of potential toxicity for many living organisms (Goodsite et al. 2004; Mirlean et al. 2005; Di Leonardo et al. 2006; Selin et al. 2008).

Trace elements, such as Hg, in marine sediments have a particular affinity for finer particle grain sizes, binding to the surface of fine particles by different processes (Ligero et al. 2001) and following fine particles' sedimentary fate. Sediment can receive Hg from both natural and anthropogenic sources such as river basin runoff, atmospheric deposition, discharge of sewage, and industrial emissions.

Rapid industrialization, urbanization, and the increase of human activity in coastal areas has resulted in an increased quantity of pollutants, such as Hg, that accumulate in air, water, soil, and sediment, as described in several works (Nriagu and Pacyna 1988; Varol 2011; Chaudhari et al. 2012; Bastami et al. 2014). Therefore, the study of Hg distribution in coastal sediments is a realistic way to understand the Hg cycle in a marine environment and to explore the history of the possible anthropogenic Hg emissions at the land-ocean interface zone.

In the Mediterranean area, there are some studies of Hg related to the atmospheric compartment (Pyle and Mather 2003), as well as several studies about the Hg distribution in aquatic environments and in dissolved gaseous Hg concentrations (Ferrara et al. 2003; Horvat et al. 2003; Maffucci et al. 2005). But, there is a lack of information about the Hg spatial and temporal distribution in Latium coastal sediments. Northern Tyrrhenian Sea sediments were previously studied by some authors (Leoni and Sartori 1996; Barghigiani et al. 1996; Baldi and Bargagli 1982) and an anomaly of Hg concentration was identified. As the southern Tuscany region has had an extended history as associated with Hg contamination (Rimondi et al. 2012), this study aimed to investigate the concentrations of Hg in the northern Latium coastal area, with particular reference to: (i) the spatial distribution of Hg associated with marine sediments in order to assess the extent of the Hg anomaly, (ii) the degree of Hg in sediments, and (iii) the potential toxicity and adverse effects of Hg in biota.

The study area is located in the Tyrrhenian Sea, in northern Latium, and it included the coastal platform that extends from Santa Severa (42.01676 N–11.95604 E), located south of Capo Linaro, up to the Montalto di Castro coastal area (42.33215 N–11.56786 E), in the physiographic unit Monte Argentario-Capo Linaro (Fig. 8). Regarding the

geomorphological features of this Physiographic Unit, a series of stratigraphic marine and/or riverine units that define a series of terraces were identified. This geomorphological features are the result of interactions between lifting of the zone during the Pleistocene and sea-level glacial fluctuations. (De Rita et al. 2002; Aureli et al. 2012). The seaward margin in this area (begin of the continental slope), can be found at depths between 120 m and 150 m. Moving from the north to the south, the seabed becomes shallower and particularly in the section between Sant'Agostino and Capo Linaro the slope of the continental platform increases (Chiocci and La Monica 1996, La Monica and Raffi 1996). The sediment transport along the shore occurs in a southeast to northwest direction (Anselmi et al. 1976, Berriolo and Sirito 1985, Noli et al. 1996) and it's also confirmed by the northern orientation of the Marta and Mignone rivers.

The study area is characterized by the sedimentary contributions of three important river basins (Fiora, Marta, and Mignone) and, subordinately, from the contributions of other smaller rivers, which influence marine sedimentation only locally and during strong flood phases (Angelucci et al. 1979; Carboni et al. 1980).

The geological features and the sedimentary productivity of these river basins have been exhaustively described in several works (Spadoni et al. 2005; Scanu 2012; Scanu et al. 2015a). The Fiora River basin (which springs from the southern flank of the Monte Amiata) is mainly situated on tuff and volcanic formations, respectively characterized by predominantly sand and clay type sedimentary production. Furthermore, the Amiata district is characterized by several inactive Hg mines (Rimondi et al., 2012). The Marta river basin originates from Lake Bolsena and is mainly covered by volcanic formations, tuff reliefs, lakes and marl. The sedimentary production is clayey for the volcanic formations and sandy for the tuffaceous formations. The Mignone River basin is largely set on hilly topography consisting of marl, arenaceous conglomerate, and clay materials and it includes the presence of many sulphide mineral ores linked to the upwelling of hydrothermal fluids. The sedimentary production is sandy for the conglomeratic formations and clayey for the marl formations (Spadoni et al. 2005, Scanu 2012). The most important local contributions come from the Marangone basin which has the same

geologic characteristics of the Mignone basin. The Marangone small basin is characterized by abandoned iron sulphide (pyrite, marcasite) and galena mines. Furthermore, marcasite mine waste deposits and galena small pits are presents (Kreidie et al. 2011).

Regarding Hg levels in these river basins, several studies have shown that the Fiora River area is affected by cinnabar (HgS), a geologic anomaly of Mt. Amiata, but more so by the Hg extraction that lasted from Etruscan times (the eight to the first century B.C.) to 1980. This gave rise to high soil and vegetation contamination in much of the Amiata area (Barghigiani et al. 1981; Barghigiani and Bauleo 1992; Barghigiani and Ristori 1994, 1995; Rimondi et al. 2012).

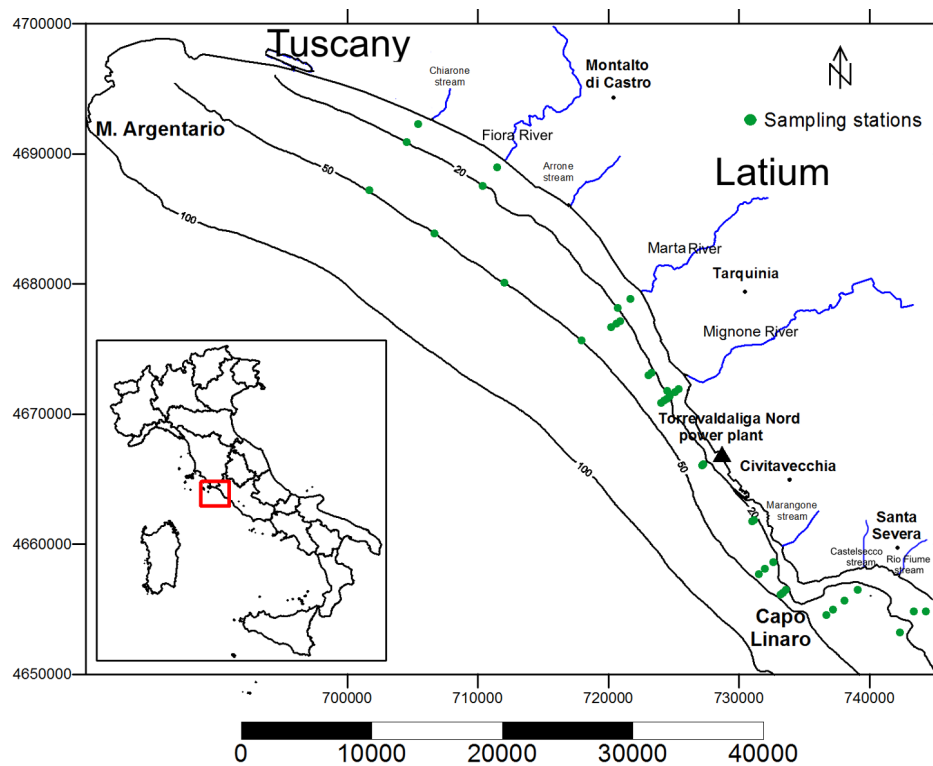


Fig. 8 Study area and sampling locations.

### 4.3 Materials and Methods

Sediment sampling was performed using a Van Veen grab (18 L). A total of 39 surface sediment samples, located between a depth of -50 m and -10 m, were sampled between 2011 and 2013 (Fig. 1). The surface layer (1 cm) of each sample was subsampled, homogenized, and placed into a polyethylene bag. Once transported (at 4 °C ) to the laboratory, sediments were dried in an oven at 40 °C for 48 hours, crushed, and stored in polyethylene bags for subsequent analysis. Grain-size analysis was performed through wet sieving on sediment samples previously treated with 16% solution of H<sub>2</sub>O<sub>2</sub> (Spagnoli et al. 2014).

Hg extraction from sediments and analytical determination was performed according to EPA 3051A:2007 and 6020A:2007, respectively. In particular, for the lab tests, 1 g of each analytical sample group was weighed with an analytical scale (Mettler Toledo xs105) and mineralized in a microwave system, Ethos Touch Control (Milestone S.r.l.-Italy), with a digestion solution prepared with 9 mL of 65% nitric acid (HNO<sub>3</sub>) (Carlo Erba) and 3 mL of 30% chloridric acid (HCl) (Carlo Erba). After mineralization, ultrapure water (Merck) was added to the samples up to 50 mL. The test for Hg analysis was performed with an ICP-MS DRC-e (Perkin Elmer-USA). Standards for the instrument calibration were prepared on the basis of a certified reference solution ICP Standard (Merck). The system was calibrated using a calibration line made up of five points of increasing concentration for each element, with a linear regression ( $R^2$ ) for the calibration line between 0.9972 and 0.9989. Analytical blanks and recovery samples were run in the same way as the real samples, and concentrations were determined using standard solutions prepared in the same acid matrix to validate the calibration. Analytical quality control was performed with standard reference material NIST-2711a-Montana II Soil, with recovery ranging between 95–110%. The cartographic elaborations were made using Surfer 8 (Golden Software, USA) and the Kriging interpolation method was used. To assess the Hg enrichment degree in sediments, enrichment factor (EF) has been used in other studies. It has been previously described by several authors (Morillo et al. 2004; Adamo et al. 2005; Vald'es et al. 2005) and is widely used to study sediment-

contamination degree. For the normalization of Hg concentrations in EF aluminum was used, as previously described by Huang and Lin (2003) and Woitke et al. (2003). The enrichment factor is determined as:

$$EF = (H_s / Al_s) / (H_c / Al_c),$$

where  $H_s$  and  $H_c$  are the sample and background trace metal concentrations, respectively, and  $Al_s$  and  $Al_c$  represent the sample and background reference of aluminum contents.

As background concentrations, the values described by Turekian and Wedepohl (1961) were used because of the different sedimentary matrix (Sandstone or shale). Values of EF less than 1 indicate no enrichment, of less than 3 indicate minor enrichment, of equal to 3–5 indicate moderate enrichment, of equal to 5–10 indicate moderately severe enrichment, of equal to 10–25 indicate severe enrichment, of equal to 25–50 indicate very severe enrichment, and of greater than 50 indicate extremely severe enrichment (Sakan et al. 2009).

In order to assess the potential ecological risk and toxicity of Hg, the measured concentrations in the sediment samples were compared with the effects range low (ERL) and the effects range medium (ERM) values. These numerical values are sediment quality guidelines (SQGs) originally determined by Long and Morgan (1990) and later refined by Long et al. (1995). The ERL was calculated as the lower 10th percentile of “effects” concentrations and the ERM as the 50th percentile of “effects” concentrations. Moreover, AEI values described by Muñoz-Barbosa et al. (2012) were calculated using the following equation:

$$AEI = [X] / [TEL],$$

where X is the metal concentration, and TEL is the Threshold Effect Levels derived by Long et al. (1995). If AEI is less than or equal to 1 then the metal concentration in the sample is not high enough to produce adverse effects in biota. However, if AEI is greater than or equal to 1 then the metal concentration in the sample could produce adverse

effects (Muñoz-Barbosa et al. 2012).

#### **4.4 Results and Discussion**

The results are shown in Table 4 and the superficial distribution patterns of pelitic fraction, Al, Hg, Hg/Al, EF, and AEI are reported in Figure 9. The maximum concentration is 2.20 mg/kg (M11), while the minimum is concentration is 0.03 mg/kg (M25). The average value for the area is 0.62 mg/kg, but there is great variability in the data. Overall, the mean Hg concentration is above the ERL value. Moreover, eight sampling stations exceed the ERM value.

The distribution pattern of Hg clearly shows the existence of two Hg anomalies. The first occurs in the northern part of the study area, near the Fiora River delta, that extends to the coastal area of the Mignone River delta, north of Civitavecchia. The second occurs in the coastal area south of the Port of Civitavecchia, from the Marangone Stream delta to the south of Capo Linaro. The central stretch of coastline, corresponding to the urban area of Civitavecchia, shows rather low values of Hg. There is also a decreasing gradient in Hg values with increasing depth.

The distribution of EF values shows that the northern coastal area is characterized by severe enrichments, with maximum values at the Fiora River delta (very severe enrichment,  $EF > 60$ ), while the southern area has enrichments from severe to moderately severe, corresponding to the coastal area south of the Port of Civitavecchia towards Santa Severa. In general, enrichment values show a distribution with maximum values at the north and south end of the study area and minimal values in the central coastal area of Civitavecchia.

The distribution of AEI values shows a similar pattern to EF values in the coastal area of Civitavecchia that is enclosed between two areas having values well above the limit of possible adverse effect.

The concentrations of Hg and the other indices show that the anomaly of Hg of the southern Tuscany extends further south than Cape Linaro. More specifically, the coastal

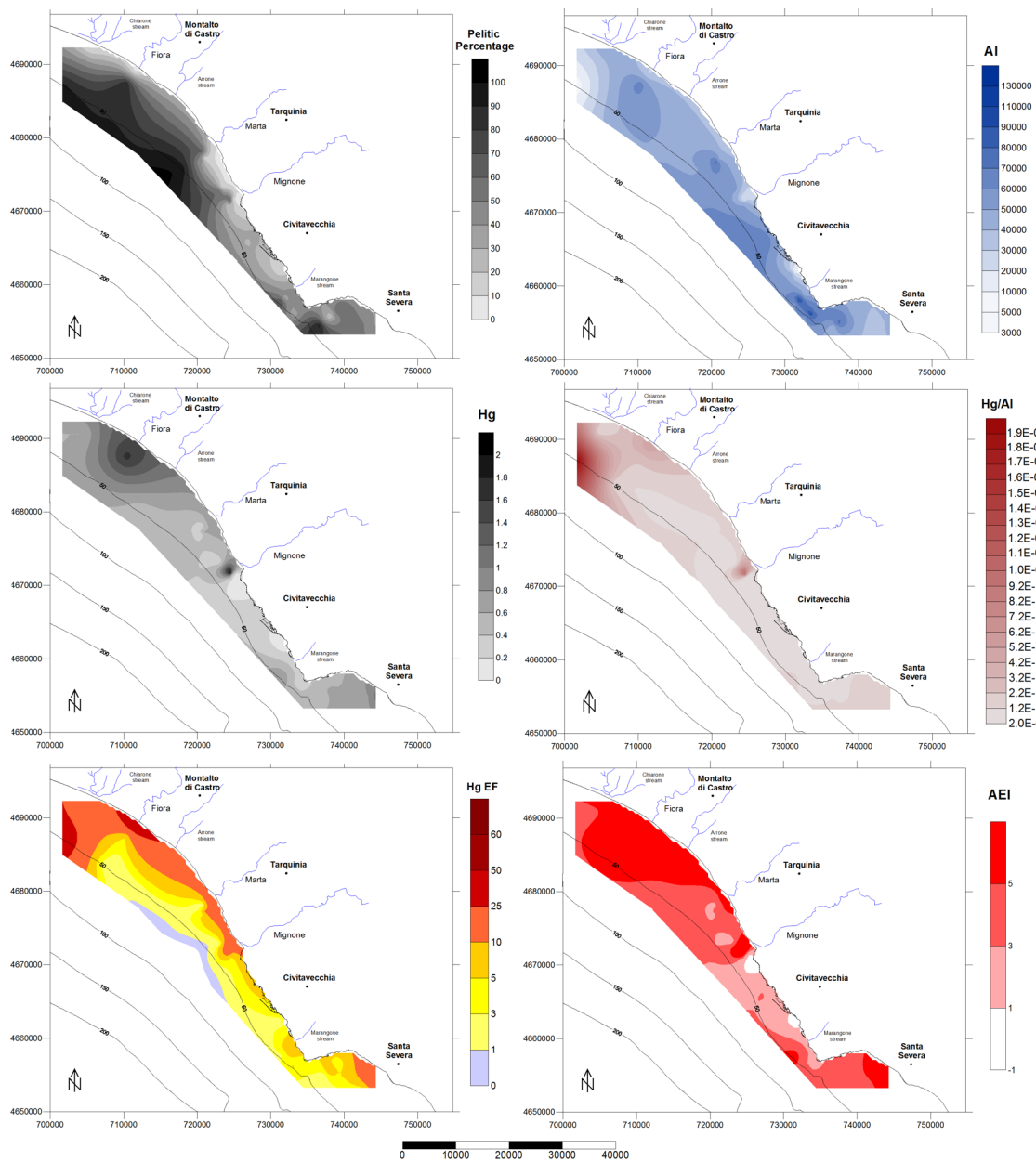
area south of the Port of Civitavecchia is characterized by a second geochemical anomaly of Hg, spatially smaller than the northern one.

Considering the coastal area south of the Port of Civitavecchia, it is reasonable to assume that the Hg anomaly is due to the geological characteristics of the minor local basins that are all characterized by enrichment of sulfides and past mining activities (Kreidie et al. 2011; Scanu et al. 2015b; Spadoni et al. 2005; Piazzolla et al. 2015). The same geogenic origin is presumable for the northern Hg anomaly from the Fiora River delta to Mignone River mouth. The Amiata district, that is part of the "circum-Mediterranean Hg belt" (Bargagli et al. 1986), has several inactive Hg mines with the extraction of cinnabar being completely stopped by the 1980's. Assuming the geogenic nature of Hg anomalies it is appropriate to consider the possibility that the concentrations are also influenced by anthropogenic inputs which overlap with the already high baseline values. The main potential anthropogenic source of Hg in the area is the coal fired power plant of Torrevaldaliga Nord with an installed capacity of 1,980 MW and more than 4 million tons of coal burned per year (National Entity for Electricity 2014). Hg is a volatile element emitted to the atmosphere through flue gas generated in coal power plants and it tends to be adsorbed onto the atmospheric dust particles, which are subsequently deposited in the aqueous and terrestrial systems by dry or wet deposition (Haykiri-Acma et al. 2011; Tang et al. 2013). This fallout can affect hydrographic basins and can lead to an enrichment of Hg in coastal marine environment. In this context, the main river basins of the area (Fiora, Marta and Mignone), may be subject to emissions from the Torrevaldaliga Nord coal fired power plant also considering the prevailing wind direction and the coastal sediment transport (Scanu et. 2015a; Scanu et. 2015b; Piazzolla et al. 2015).

The study area characteristics imply to deepen the knowledge of the source of the enrichment of Hg in marine sediments through the quantification of the real weight of the anthropogenic sources even in the high values of natural origin.

| Sampling stations | Location |         | Pelitic % | Al (mg/kg) | Hg (mg/kg)  | (Hg/Al) | EF   | AEI  |
|-------------------|----------|---------|-----------|------------|-------------|---------|------|------|
|                   | x        | y       |           |            |             |         |      |      |
| M1                | 705441   | 4692270 | 8.2       | 49800      | 0.9         | 1.8E-05 | 15.1 | 6.9  |
| M2                | 704539   | 4690881 | 36.8      | 33900      | 0.59        | 1.7E-05 | 14.5 | 4.5  |
| M3                | 701682   | 4687213 | 92.8      | 3200       | 0.63        | 2.0E-04 | 39.4 | 4.8  |
| M4                | 711487   | 4688958 | 8.9       | 28400      | 1.44        | 5.1E-05 | 42.3 | 11.1 |
| M5                | 710384   | 4687529 | 86.5      | 64600      | 1.69        | 2.6E-05 | 5.2  | 13   |
| M6                | 706688   | 4683882 | 86.0      | 48300      | 0.79        | 1.6E-05 | 3.3  | 6.1  |
| M7                | 712012   | 4680106 | 83.3      | 50000      | 0.44        | 8.8E-06 | 1.8  | 3.4  |
| M8                | 721657   | 4678853 | 20.7      | 36100      | 0.75        | 2.1E-05 | 17.3 | 5.8  |
| M9                | 720710   | 4678152 | 61.8      | 48500      | 0.31        | 6.4E-06 | 1.3  | 2.4  |
| M10               | 717923   | 4675650 | 97.1      | 48600      | 0.61        | 1.3E-05 | 2.5  | 4.7  |
| M11               | 724509   | 4671761 | 61.8      | 18000      | 2.2         | 1.2E-04 | 24.4 | 16.9 |
| M12               | 720912   | 4677160 | 15.2      | 51545      | 0.63        | 1.2E-05 | 10.2 | 4.9  |
| M13               | 720629   | 4676951 | 45.0      | 79926      | 0.34        | 4.3E-06 | 3.6  | 2.6  |
| M14               | 720184   | 4676671 | 43.9      | 61344      | 0.36        | 5.8E-06 | 4.8  | 2.7  |
| M15               | 723277   | 4673178 | 15.4      | 54922      | 0.39        | 7.1E-06 | 5.9  | 3.0  |
| M16               | 723068   | 4672993 | 54.5      | 51804      | 0.33        | 6.5E-06 | 1.3  | 2.6  |
| M17               | 725352   | 4671921 | 6.8       | 22015      | 0.46        | 2.1E-05 | 17.2 | 3.5  |
| M18               | 725086   | 4671702 | 3.6       | 35464      | 0.24        | 6.8E-06 | 5.7  | 1.9  |
| M19               | 724683   | 4671377 | 28.3      | 38841      | 0.52        | 1.3E-05 | 11.2 | 4.0  |
| M20               | 724473   | 4671193 | 58.3      | 46020      | 0.66        | 1.4E-05 | 2.9  | 5.1  |
| M21               | 724251   | 4671036 | 20.8      | 48387      | 0.55        | 1.1E-05 | 9.5  | 4.2  |
| M22               | 724050   | 4670857 | 26.9      | 52024      | 0.41        | 8.0E-06 | 6.6  | 3.2  |
| M23               | 727283   | 4666127 | 42.9      | 68006      | 0.38        | 5.6E-06 | 4.7  | 2.9  |
| M24               | 727187   | 4666046 | 25.6      | 68273      | 0.41        | 6.0E-06 | 5.0  | 3.2  |
| M25               | 731155   | 4661870 | 11.9      | 12596      | 0.03        | 2.0E-06 | 1.7  | 0.2  |
| M26               | 731002   | 4661755 | 15.4      | 41731      | 0.14        | 3.4E-06 | 2.9  | 1.1  |
| M27               | 732612   | 4658628 | 49.6      | 47629      | 0.43        | 9.1E-06 | 7.6  | 3.3  |
| M28               | 731958   | 4658107 | 30.1      | 99119      | 0.61        | 6.2E-06 | 5.1  | 4.7  |
| M29               | 731491   | 4657693 | 71.2      | 57472      | 0.81        | 1.4E-05 | 2.8  | 6.2  |
| M30               | 733582   | 4656476 | 43.7      | 72603      | 0.27        | 3.7E-06 | 3.1  | 2.1  |
| M31               | 733361   | 4656272 | 33.0      | 120297     | 0.46        | 3.8E-06 | 3.2  | 3.6  |
| M32               | 733171   | 4656122 | 30.5      | 61017      | 0.42        | 6.9E-06 | 5.7  | 3.2  |
| M33               | 739090   | 4656476 | 60.9      | 46623      | 0.58        | 1.3E-05 | 2.5  | 4.5  |
| M34               | 738055   | 4655686 | 18.6      | 64626      | 0.64        | 9.9E-06 | 8.3  | 4.9  |
| M35               | 737184   | 4654956 | 51.5      | 75499      | 0.54        | 7.2E-06 | 1.4  | 4.2  |
| M36               | 736701   | 4654551 | 93.4      | 44381      | 0.58        | 1.3E-05 | 2.6  | 4.4  |
| M37               | 744302   | 4654853 | 36.8      | 52342      | 1.09        | 2.1E-05 | 17.4 | 8.4  |
| M38               | 743374   | 4654821 | 48.2      | 35351      | 0.79        | 2.2E-05 | 18.7 | 6.1  |
| M39               | 742310   | 4653217 | 51.7      | 31455      | 0.62        | 2.0E-05 | 4.0  | 4.8  |
| Range             |          |         |           |            | 0.03 – 2.2  |         |      |      |
| Average ± Sd      |          |         |           |            | 0.62 ± 0.41 |         |      |      |
| ERL               |          |         |           |            | 0.15        |         |      |      |
| ERM               |          |         |           |            | 0.71        |         |      |      |
| TEL               |          |         |           |            | 0.13        |         |      |      |

**Table 4** Hg, pelitic fraction percentage, Al, Hg/Al, EF, and AEI values in the study area.



**Fig. 9** Distribution pattern of pelitic percentage, Al (mg/kg), Hg (mg/kg), Hg/Al, EF, and AEI in coastal sediments of northern Latium.

## **5. Concentrations of As, Cd, Cr, Ni, and Pb in the echinoid *Paracentrotus lividus* on the coast of Civitavecchia, northern Tyrrhenian Sea, Italy.**

The study of pollution and contamination of the marine environment must necessarily be set according to an ecosystem approach that takes into account the possible changes in both the abiotic and biotic compartments.

In this context, trace metal contamination is one of the main problems encountered in the field of marine ecotoxicology.

The assessment of trace metal concentrations in biological tissues is essential for the evaluation of the propagation of these pollutant species within the bodies and through the food chain. Moreover, it is possible to quantify the damage on the single organisms and on the communities (Beyer and Meador 2011).

The analysis of concentrations of chemical elements in biological tissues provides important information on the spatial distribution of the pollutants, their temporal trends and pollution propagation along the trophic chains governed by processes of bioaccumulation and biomagnification (Beyer and Meador 2011).

It is widely described in the international literature that the analysis of the concentrations of pollutants in soils and marine sediments provides in itself important information about the distribution both in space and time of the degree of pollution in a specific area. However, the evaluation of the potential toxicity of the chemical elements taken into account in the sedimentological analysis assumes an extremely high value and accuracy when accompanied by analyses of the biological tissue of the so-called "sentinel organisms" or "bio-indicators", animal or vegetable organisms which are particularly sensitive to changes induced by external polluting agents (Warnau et al. 1998; Soualili et al. 2008).

In this context, and as a part of this PhD project, it was possible to study the bioaccumulation of trace metals As, Cd, Cr, Ni, and Pb in the soft tissues of *Paracentrotus lividus* in the coastal area of Civitavecchia.

This echinoid was chosen as a sentinel organism for its sedentary habits and recognized

for its sensitivity to pollutants. *P. lividus* has been used in several studies as a biological indicator of local pollution, able to accumulate trace metals as a function of the level of environmental contamination.

The results of this study showed primarily a bioaccumulation of As and Cr and to a lesser extent of Pb and Ni in the tissues of *P. lividus*.

The As concentrations, and to a lesser extent Cr concentrations, detected in the *P. lividus* tissues confirm the presence of spatial gradients highlighted by the analysis of the concentrations of the same chemical elements in coastal sediments of the area. This is probably due to the presence of geochemical anomalies of As.

The inverse spatial distribution of As in respect to the anomaly highlighted by the Pb and Ni concentrations measured in the tissues of *P. lividus*, indicates the possible contribution of different human activities existing in the study area.

*This Chapter is adapted from a manuscript published in 2015 in “Regional studies in marine science”.*

*Scanu S, Soetebier S, Piazzolla D, Tiralongo F, Mancini E, Romano N, Marcelli M (2015). Concentrations of As, Cd, Cr, Ni, and Pb in the echinoid Paracentrotus lividus on the coast of Civitavecchia, northern Tyrrhenian Sea, Italy. Regional Studies in Marine Science 1, 7-17.*

*DOI:10.1016/j.rsma.2015.02.001.*

## **5.1 Abstract**

This work assessed the levels of As, Cd, Cr, Ni, and Pb in soft tissues (gonads and gut) of specimens of *Paracentrotus lividus* (Lamarck 1816) collected from the coast of Civitavecchia, in the northern Tyrrhenian Sea. The average levels, in order of concentration, were 14.64 mg/kg As, 3.58 mg/kg Cr, 1.18 mg/kg Pb, 1.15 mg/kg Ni, and 0.07 mg/kg Cd. Dry weight concentrations described bioaccumulation of As and Cr, and, to a lesser extent, Ni and Pb. A hotspot of As at the station near the delta of Marangone stream reflected the effect of mine waste deposits of galena, pyrite, and marcasite in this basin. The As concentration in the northern part of the study area increased closer to the Mignone delta, and according to the prevailing winds, this could reflect enrichment from the combustion of coal at the Torrevaldaliga power plant. Comparing data with the literature, As in marine sediments show a ratio of 0.7 in the tissues of *P. lividus* from the Civitavecchia area. These results were also compared to those found in *P. lividus* in an environmental biomonitoring program currently ongoing to control the emissions from the coal-fired power plant in Torrevaldaliga Nord, highlighting a substantial quantitative correspondence. In view of the presence of various industrial activities in the study area that can influence the enrichment of these elements, this work emphasizes the need for performing further studies aimed at assessing the actual contribution of anthropogenic activities even when the background concentrations in marine sediments and marine organisms are high, because burning coal is considered the major anthropogenic source

of many trace elements especially As.

## 5.2 Introduction

Contamination of the marine environment by trace metals is one of the major problems of environmental toxicology. The potential impact on humans from the consumption of seafood raises concern because of the ability of certain elements to bioaccumulate and biomagnify along the trophic chain (Thibaud et al. 1982; Orlando 1985).

Trace metals are naturally present in air, water, soil, and food. Human activities, especially since the industrial revolution, have led to a continuous release of trace metals into the environment, causing progressive enrichment in all environmental compartments and organisms, compared to natural background values.

Coastal oceans are often heavily impacted by metal pollution because land use in the coastal zone often becomes rapidly developed and heavily industrialized. Furthermore, the coastal ocean is a transition zone that receives not only anthropogenic inputs from land uses, but is also affected by naturally-occurring metals from erosional processes, leading to metals reaching the coastal ocean through rivers.

The need to carry out an assessment of the contamination by trace metals in the coastal area of Civitavecchia is linked to the high rate of industrialization in the area. Civitavecchia is characterized by the presence of the largest energy production site in Europe and by the most important port for cruise traffic in the Mediterranean Sea. Its recent history, after World War II, was marked by industrial activities of various kinds that continuously influenced concentration of trace metals in all environmental compartments. In the present work the analytical results of the levels of As, Cd, Cr, Ni, and Pb in soft tissues of *Paracentrotus lividus* are correlated with literature data.

*P. lividus* was chosen as a sentinel organism because of its sedentary habits and acknowledged sensitivity to pollutants and heavy metals. It has been used in several studies as a biological–biochemical indicator of local pollution, capable of accumulating metals as a function of the level of contamination in the environment (Warnau et

al. 1998; Soualili et al. 2008).

Determining the sources of metal pollution in the study area is complicated by the interplay of current and historical industrial activities with the presence of two local geological anomalies (As and mercury; Baldi and Bargagli 1984; Scanu 2012). The use of *P. lividus* as a biological indicator of local pollution, however, in this context, can highlight which elements are bioavailable to marine organisms.

### **5.3 Materials and Methods**

#### **5.3.1 *Paracentrotus lividus* as a sentinel organism**

The characteristics that an organism must possess to be a good bioindicator are manifold, including limited mobility, easy identification, abundance, longevity, availability for sampling, tolerance to changes in environmental physico-chemical parameters, ample tissues for analysis, and ability to accumulate metals with a simple correlation with the average concentration in the environment (Rainbow 1995). *P. lividus* has been used as a sentinel organism in many studies and in several biomonitoring studies because it has an important ecological role in various ecosystems, especially in the Mediterranean Sea. *P. lividus* colonizes *Posidonia oceanica* meadows, *Cymodocea nodosa*, and rocky substrates with algae where its grazing activities can locally control the dynamics of algae and seagrasses (Lozano et al. 1995; Tomas et al. 2006). Its sedentary habit and sensitivity to pollutants has led to its use as a biological-biochemical indicator of local pollution (Warnau et al. 1998; Coteur et al. 2001; Bayed et al. 2005) as well as a bioindicator for heavy metals accumulation in parallel with the accumulation in sediments and *P. oceanica* (Soualili et al. 2008; Warnau et al. 1995a,b, 1998).

In Civitavecchia, there is a series of studies of trace metals in the tissues of *P. lividus*. These works are an integral part of the monitoring activities carried out with the aim to monitor the potential environmental effects of the emissions from the coal-fired power

plant of Torrevaldaliga Nord (Nascetti et al. 2011a, 2012b). In this study, total metal concentration in homogenized soft tissues (gonads and gut) was analyzed.

### 5.3.2 Study area

The study area is enclosed within the physiographic unit (PU) between Monte Argentario and Capo Linaro in northern Latium, Italy. The PU is bounded on the south by terraces and mountains south of Civitavecchia and on the north by terraces north of the mouth of the Mignone River. The remainder is dominated by alluvial plains. The appearance of the coast is intimately related to the morphology of the seabed as the isobaths show a very articulate pattern with the presence of a rocky bottom and reliefs. The outcrops consist mainly of cemented fossiliferous calcarenite (the bench of the middle-upper Pleistocene) and arenaceous-marly flysch (sandstone of the upper Cretaceous), which is also present in the mainland (Chiocci and La Monica 1996).

The corresponding mainland is characterized by small water-sheds, the Fiora, Arrone, Marta, and Mignone rivers. These basins provide the coastal terrigenous inputs generated by the erosion of the Plio-Quaternary volcanic outcrops of the Vulsini, Sabatini, and Vicani mountains and of the Cerite-Tolfetano complex (clay, marly, and calcarenitic flysch; La Monica and Raffi 1996).

The Mignone River basin (500 km<sup>2</sup>) is placed between the Tyrrhenian margin on the west and the Pleistocenic volcanic reliefs of the Sabatini and Cimino-Vicano Mountains. It is a complex geological setting that includes many sulfide mineral ores linked to the upwelling of hydrothermal fluids. The Mignone River basin is more than half (65%) set on hilly morphotypes: (44%) marl, (11%) arenaceous conglomerate, and (10%) clay, and the volcanic formations occupy 15% of the river basin surface (Spadoni et al. 2005).

Among the smaller rivers with local contributions, the most important is the Marangone basin, located to the south of the port of Civitavecchia, sharing the geologic characteristics of the Mignone basin. In particular, the Marangone stream basin, although modest in size (only 23 km<sup>2</sup>), is characterized by abandoned pyrite, marcasite,

and galena mines, the latter two with mine waste deposits (Kreidie et al. 2011).

The coastal area is characterized by urban and industrial zones with the exception of the northern and southern parts of the study area. The area to the north is also affected by the proximity of one of the biggest energy production sites in Europe, the Tirreno Power combined cycle power plant (gas fueled) and ENEL Torrevaldaliga Nord, fueled by coal. Torrevaldaliga Nord is one of the biggest coal-fired power plants in Italy.

#### 5.3.2.1 Sedimentological and geochemical setting

The assessment of bioaccumulation of metals and metalloids in tissues of marine organisms cannot be separated from the analysis of the environmental conditions, particularly those related to the concentrations of these elements in sediments and seawater. In the considered PU, sedimentary processes are influenced by the continental terrigenous input from rivers and by bioconstruction (cemented fossiliferous calcarenite) and *P. oceanica* meadows. These are particularly important because they generate, in certain areas, low hydrodynamic conditions, favoring the storage of fine sediments.

From a mineralogical point of view, the distribution of heavy and light minerals seems to indicate the existence of a SE to NW littoral drift (Anselmi et al. 1979) and the predominant migration of material toward the NW is also confirmed by concentrations of mercury in marine sediments in the area between the Mignone delta and the Argentario peninsula (Baldi and Bargagli 1984; Scanu 2012).

The area is also characterized by two geochemical anomalies of cinnabar (HgS) from the Monte Amiata complex in the northern sector and the terrigenous contributions of Mignone River from the Cerite-Tolfetano complex in the southern part (Scanu 2012).

Some authors (Barghigiani et al. 1996) have shown that the mercuriferous anomaly has been further enhanced over time by centuries of cinnabar mining activity. The area is also characterized by a second geochemical anomaly, spatially stackable with the mercuriferous one but relative to the concentrations of As (Scanu 2012; Kreidie et al. 2011; Spadoni et al. 2005) (see Fig. 10).

Assuming that sedimentological and geochemical data for the area south of the Mignone delta are rather scarce, we report the concentrations in sediments of some trace metals at different sampling points in the PU (Fig. 11 and Table 5).

To assess trace metal enrichment and degree of contamination at sediment sampling points, the enrichment factor (EF) was calculated as previously described by several authors (Morillo et al. 2004; Adamo et al. 2005; Vald'es et al. 2005; Table 6). Aluminum was used to normalize metal concentrations in the EF, as previously described in Lee et al. (1998), Huang and Lin (2003) and Wotke et al. (2003). The EF was determined using:

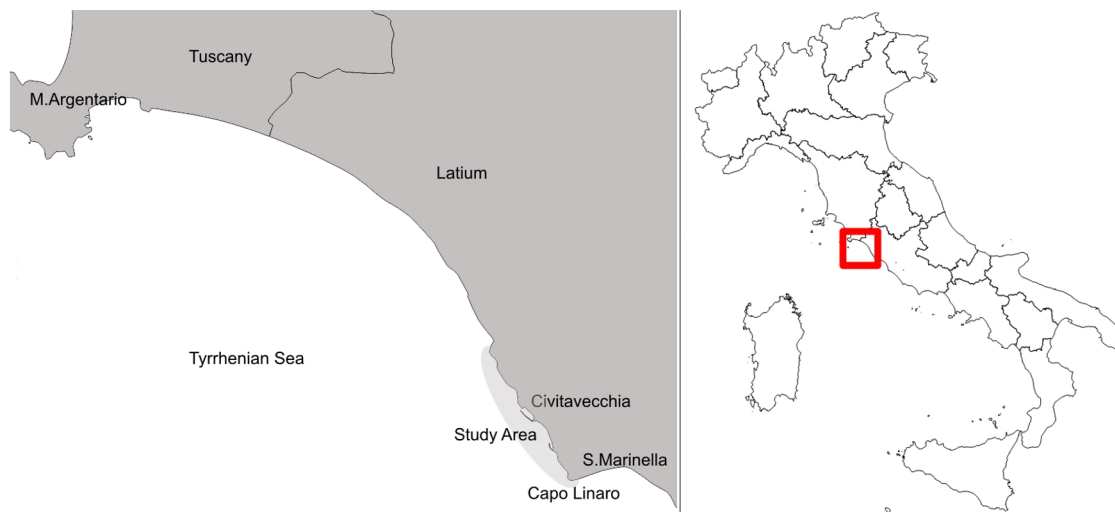
$$EF = (H_s/Al_s)/(H_c/Al_c)$$

where  $H_s$  and  $H_c$  are the sample and background trace metal concentrations, respectively, and  $Al_s$  and  $Al_c$  represent the sample and background references for aluminum.

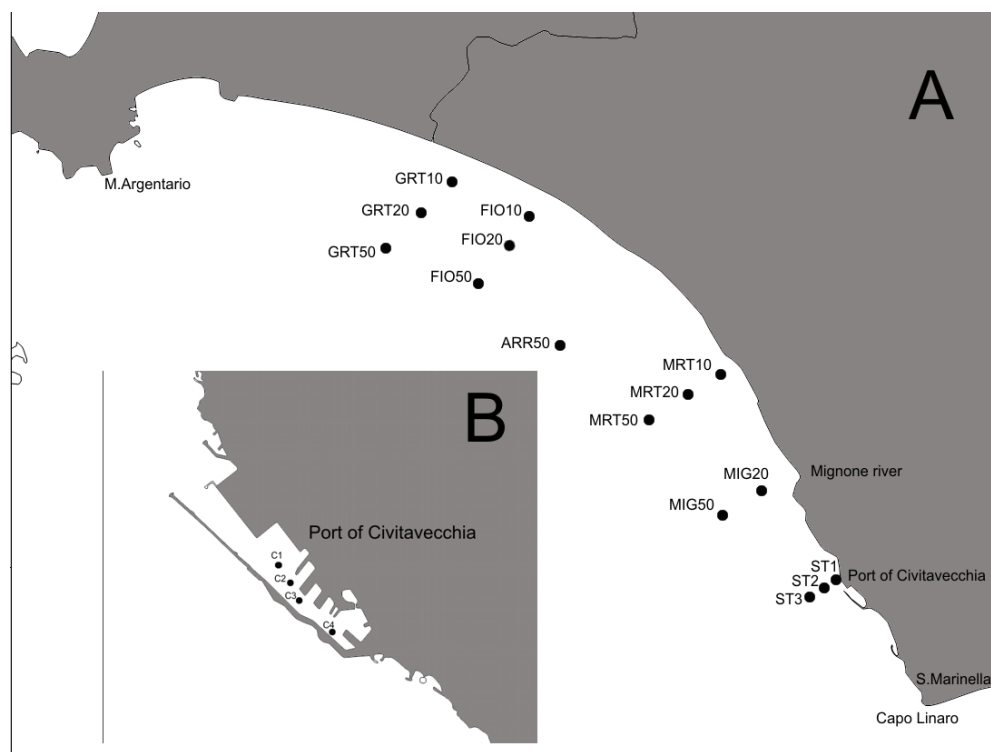
The values determined by Turekian and Wedepohl (1961), were used for background concentrations, depending on the sedimentary matrix (sandstone or shale).

As suggested by Sakan et al. (2009), EF values less than 1 indicate no enrichment; between 1 and 3, minor enrichment; between 3 and 5, moderate enrichment; between 5 and 10, moderately severe enrichment; between 10 and 25, severe enrichment; between 25 and 50, very severe enrichment; and greater than 50, extremely severe enrichment.

Trace metal concentrations were compared to those reported in sediment quality guidelines (SQGs). The main purpose of the SQGs is to protect the marine environment from potentially toxic effects of contaminants associated with sediments and can be useful for assessing the potential that contaminants in sediments can induce biological effects (Spencer and MacLeod 2002). They classify sediments into three main groups: non-polluted, moderately polluted, and extremely polluted (Giesy and Hoke 1990; Table 7).



**Fig. 10** Study area location in the physiographic unit between Monte Argentario and Capo Linaro.



**Fig. 11** Sediment samples from the physiographic unit between Monte Argentario and Capo Linaro (A) and the port of Civitavecchia (B). (Scanu 2012, modified; Molino 2013, modified).

| AREA                                                  | Station | As   | Cd    | Cr   | Ni   | Pb   |
|-------------------------------------------------------|---------|------|-------|------|------|------|
| North of Mignone River delta                          | GRT50   | 21   | 0.01* | -    | -    | 33   |
|                                                       | GRT20   | 23   | 0.01* | -    | -    | 17.3 |
|                                                       | GRT10   | 19.5 | 0.01* | -    | -    | 35   |
|                                                       | FIO50   | 23   | 0.01* | -    | -    | 33   |
|                                                       | FIO20   | 15.6 | 0.01* | -    | -    | 30   |
|                                                       | FIO10   | 21   | 0.01* | -    | -    | -    |
|                                                       | ARR50   | 20   | 0.01* | -    | -    | 30   |
|                                                       | MRT50   | 18.4 | 0.01* | -    | -    | 32   |
|                                                       | MRT20   | 19   | 0.01* | -    | -    | 27   |
|                                                       | MRT10   | 18   | 0.01* | -    | -    | 18.3 |
|                                                       | MIG50   | 20   | 0.01* | -    | -    | 31   |
|                                                       | MIG20   | 42   | 0.01* | -    | -    | 14   |
| Between Mignone River delta and Port of Civitavecchia | ST1     | 12.8 | 0.26  | 15.2 | 20   | 12   |
|                                                       | ST2     | 19.5 | 0.95  | 38.6 | 33.7 | 38.4 |
|                                                       | ST3     | 22.8 | 1.2   | 52.7 | 47   | 50.3 |
| Inside Port of Civitavecchia                          | C1      | 12.6 | 0.017 | 23   | 12   | 4.1  |
|                                                       | C2      | 22.1 | 0.023 | 46   | 14   | 9.3  |
|                                                       | C3      | 17.2 | 0.017 | 13   | 13   | 4.5  |
|                                                       | C4      | 40.6 | 0.053 | 53.3 | 19   | 58.2 |
| mean                                                  |         | 21.5 | 0.4   | 34.5 | 22.7 | 26.5 |
| std.dev                                               |         | 7.6  | 0.5   | 17.3 | 13.0 | 14.8 |

**Table 5** As, Cd, Cr, Ni, and Pb concentrations in sediments from the study area (Scanu 2012; Molino 2013). Dashes indicate “not analyzed”. \*Values below detection limit.

| EF           | As    | Cd   | Cr  | Ni   | Pb   |
|--------------|-------|------|-----|------|------|
| <b>GRT50</b> | 164.1 | 7.8  | -   | -    | 36.8 |
| <b>GRT20</b> | 17.0  | 0.7  | -   | -    | 1.8  |
| <b>GRT10</b> | 9.8   | 0.5  | -   | -    | 2.5  |
| <b>FIO50</b> | 11.9  | 0.5  | -   | -    | 2.4  |
| <b>FIO20</b> | 6.0   | 0.4  | -   | -    | 1.7  |
| <b>FIO10</b> | 18.5  | 0.9  | -   | -    | -    |
| <b>ARR50</b> | 10.0  | 0.5  | -   | -    | 2.1  |
| <b>MRT50</b> | 9.5   | 0.5  | -   | -    | 2.4  |
| <b>MRT20</b> | 9.8   | 0.5  | -   | -    | 2.0  |
| <b>MRT10</b> | 12.5  | 0.7  | -   | -    | 1.8  |
| <b>MIG50</b> | 11.0  | 0.6  | -   | -    | 2.4  |
| <b>MIG20</b> | 58.3  | 1.4  | -   | -    | 2.8  |
| <b>ST1</b>   | 38.6  | 78.5 | 1.3 | 30.2 | 5.2  |
| <b>ST2</b>   | 9.6   | 46.9 | 0.5 | 8.3  | 2.7  |
| <b>ST3</b>   | 8.1   | 42.8 | 0.5 | 8.4  | 2.6  |
| <b>C1</b>    | 9.7   | 1.3  | 0.5 | 4.6  | 0.5  |
| <b>C2</b>    | 10.9  | 1.1  | 0.6 | 3.4  | 0.7  |
| <b>C3</b>    | 13.4  | 1.3  | 0.3 | 5.0  | 0.5  |
| <b>C4</b>    | 25.8  | 3.4  | 1.0 | 6.0  | 5.3  |

**Table 6** Sediment enrichment factors in the physiographic unit between Monte Argentario and Capo Linaro.

| <b>SQG</b>          | <b>As</b>                 | <b>Cd</b>  | <b>Cr</b>                   | <b>Ni</b>                   | <b>Pb</b>                   |
|---------------------|---------------------------|------------|-----------------------------|-----------------------------|-----------------------------|
| Non polluted        | <3                        | -          | <25                         | <20                         | <40                         |
| moderately polluted | 3 – 8                     | -          | 25-75                       | 20-50                       | 40-60                       |
| extremly polluted   | >8                        | >6         | >75                         | >50                         | >60                         |
| <b>GRT50</b>        | 21<br>extremly polluted   | 0.01<br>-  | -<br>-                      | -<br>-                      | 33<br>Non polluted          |
| <b>GRT20</b>        | 23<br>extremly polluted   | 0.01<br>-  | -<br>-                      | -<br>-                      | 17.3<br>Non polluted        |
| <b>GRT10</b>        | 19.5<br>extremly polluted | 0.01<br>-  | -<br>-                      | -<br>-                      | 35<br>Non polluted          |
| <b>FIO50</b>        | 23<br>extremly polluted   | 0.01<br>-  | -<br>-                      | -<br>-                      | 33<br>Non polluted          |
| <b>FIO20</b>        | 15.6<br>extremly polluted | 0.01<br>-  | -<br>-                      | -<br>-                      | 30<br>Non polluted          |
| <b>ARR50</b>        | 20<br>extremly polluted   | 0.01<br>-  | -<br>-                      | -<br>-                      | 30<br>Non polluted          |
| <b>MRT50</b>        | 18.4<br>extremly polluted | 0.01<br>-  | -<br>-                      | -<br>-                      | 32<br>Non polluted          |
| <b>MRT20</b>        | 19<br>extremly polluted   | 0.01<br>-  | -<br>-                      | -<br>-                      | 27<br>Non polluted          |
| <b>MRT10</b>        | 18<br>extremly polluted   | 0.01<br>-  | -<br>-                      | -<br>-                      | 18.3<br>Non polluted        |
| <b>MIG50</b>        | 20<br>extremly polluted   | 0.01<br>-  | -<br>-                      | -<br>-                      | 31<br>Non polluted          |
| <b>MIG20</b>        | 42<br>extremly polluted   | 0.01<br>-  | -<br>-                      | -<br>-                      | 14<br>Non polluted          |
| <b>ST1</b>          | 12.8<br>extremly polluted | 0.26<br>-  | 15.2<br>Non polluted        | 20<br>moderately polluted   | 12<br>Non polluted          |
| <b>ST2</b>          | 19.5<br>extremly polluted | 0.95<br>-  | 38.6<br>moderately polluted | 33.7<br>moderately polluted | 38.4<br>Non polluted        |
| <b>ST3</b>          | 22.8<br>extremly polluted | 1.2<br>-   | 52.7<br>moderately polluted | 47<br>moderately polluted   | 50.3<br>Non polluted        |
| <b>C1</b>           | 12.6<br>extremly polluted | 0.017<br>- | 23<br>Non polluted          | 12<br>Non polluted          | 4.1<br>Non polluted         |
| <b>C2</b>           | 22.1<br>extremly polluted | 0.023<br>- | 46<br>moderately polluted   | 14<br>Non polluted          | 9.3<br>Non polluted         |
| <b>C3</b>           | 17.2<br>extremly polluted | 0.017<br>- | 13<br>Non polluted          | 13<br>Non polluted          | 4.5<br>Non polluted         |
| <b>C4</b>           | 40.6<br>extremly polluted | 0.053<br>- | 53.3<br>moderately polluted | 19<br>Non polluted          | 58.2<br>moderately polluted |
| <b>Mean</b>         | 21.5<br>extremly polluted | 0.1<br>-   | 34.5<br>moderately polluted | 22.7<br>moderately polluted | 26.5<br>Non polluted        |

**Table 7** Classification of sediments found in the physiographic unit between Monte Argentario and Capo Linaro, according to United States Environmental Protection Agency sediment quality guidelines criteria (Giesy and Hoke, 1990; Long and Morgan, 1990).

Results confirmed that the study area was affected by an anomaly in concentrations of As in marine sediments with rather great enrichment. According to SQGs, Cd, Cr, and Ni were moderately enriched, but confined inside the port of Civitavecchia or in the surrounding sediments.

Molino (2013) also considered the concentrations of trace metals in the harbor seawater (see Table 8 and Fig. 12):

Bibliographic data concerning the concentrations of the considered trace elements in sediments follow the sequence  $Cr > Pb > Ni > As > Cd$ , and all but Cd had very similar concentrations.

The only available data for seawater were related to harbor waters, and followed the sequence  $Ni > Pb > Cr > Cd > As$ , which shows no correspondence with the analytical results in sediments and biota.

At present, no data can be found for trace metals in the tissues of *Posidonia oceanica* or algae in the studied coastal area. Mercury concentrations were not considered in this work because in the analytical method used for soft tissues analysis, it has a tendency to evaporate, giving understated values.

| Station | As   | Cd   | Cr   | Ni   | Pb   |
|---------|------|------|------|------|------|
| A1      | 0.09 | 0.41 | 0.68 | 20.4 | 18.8 |
| A2      | 0.3  | 0.31 | 0.31 | 11.4 | 6.7  |
| A3      | 0.63 | 0.44 | 2.15 | 25.7 | 19.7 |
| A4      | 0.35 | 0.4  | 1    | 19.9 | 21.6 |
| A5      | 0.19 | 0.63 | 0.42 | 16.7 | 11.2 |
| A6      | 0.23 | 0.36 | 0.52 | 14.8 | 10.2 |
| A7      | 0.28 | 0.65 | 0.76 | 19.2 | 23   |
| A8      | 0.09 | 0.38 | 0.18 | 8.1  | 7    |
| mean    | 0.27 | 0.45 | 0.75 | 17   | 14.8 |

**Table 8** Concentrations ( $\mu\text{g/L}$ ) of As, Cd, Cr, Ni, and Pb in port of Civitavecchia seawater (Molino 2013).



**Fig. 12** Water samples from inside the port of Civitavecchia.

### 5.3.3 Sample collection

The sampling plan (Fig. 13) aimed at characterizing the entire stretch of coastline to compare local values with previously reported data representing other Mediterranean waters, particularly in the area of Civitavecchia. The arrangement of sampling points (from R1 in the southern part to R9 in the northern part of the study area) was chosen to be able to cover the various environmental features and coastal anthropogenic stressors (rivers, urban areas, electric power plants, and waste discharges).

The specimens of *P. lividus* were collected by hand at nine sampling points from October 2013 to February 2014, with a minimum of five individuals taken from each station, totaling 53 individuals. Stations at 2 m depth were chosen in order to take account of different biological community types (R2 is characterized by natural hard bottom and R9 by the presence of *P. oceanica* meadows).

The samples were brought to  $-10\text{ }^{\circ}\text{C}$  before measuring the diameter. To prevent contamination, ceramic spoon was used to remove soft tissues from the exoskeletons. Samples were homogenized, dried in an oven at  $70\text{ }^{\circ}\text{C}$  for about 48 h, then stored in

separate polyethylene containers for analysis.

#### 5.3.4 Sample analysis

The mechanically homogenized samples, by using Tube Ultra Turrax (IKA), were subsequently oven mineralized with an oxidizing mixture ( $\text{HNO}_3 + \text{H}_2\text{O}$ ). Quantification of the metals, after optional dilution, was carried out using ICP-MS following the method reported by Salvo et al. (2014). The data are normalized to mg/kg, thus not in dependence of number of animals and the quantification limit for each metal was of 0.010 mg/kg dry weight. The uncertainties were 10% for As, 9% for Cd, 15% for Cr, 18% for Ni, and 20% for Pb.

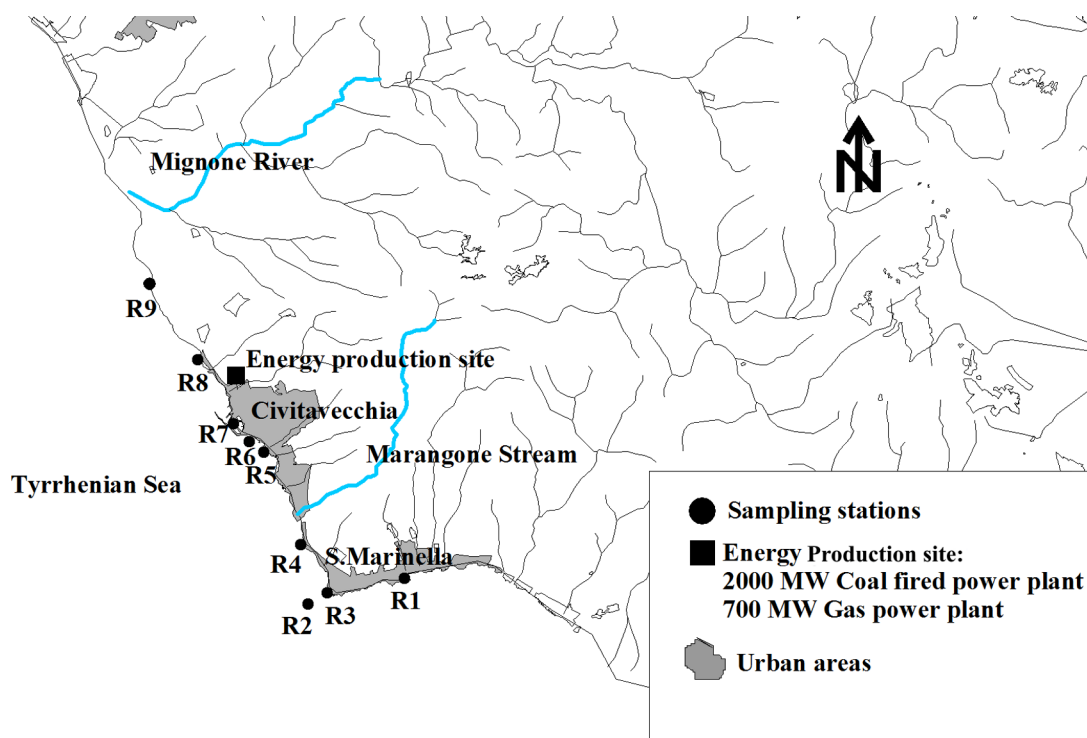


Fig. 13 Sampling plan.

## 5.4 Results

Concentrations (mg/kg dry weight) are summarized in Table 9 and shown in Fig. 14.

The maximum concentration of As was found to be 42.7 mg/kg (station R4) and the minimum was 0.01 mg/kg (station R3). Peak concentrations were found at stations R1, R4, R7, and R9. Aside from the peak values at R1 and R4, As seems to show an increasing gradient from R5 toward the north.

The maximum concentration of Cd was found to be 0.13 mg/kg (station R1 at the port of Santa Marinella) and decreases toward the north, reaching the lowest values closest to the urban area of Civitavecchia. The minimum, 0.04 mg/kg, was found at R4 and R5. Concentration profiles indicate the lowest concentrations of Cd in the urbanized area of Civitavecchia rather than at either the extreme northern or southern ranges of the sampling area.

Cr presented two peaks: 14.8 mg/kg at R4 and 8.7 mg/kg at R1 (the port of Santa Marinella). Concentrations were lower at the other stations, and the minimum of 0.2 mg/kg was found at R8. As with As, its maximum concentration was at R4. No gradient with respect to the urban area of Civitavecchia was found.

Ni also presented a maximum concentration at R4 (2.9 mg/kg). A second peak was found at R1 (2.3 mg/kg), R6 and R7 presented similar values (1.3 and 1.4 mg/kg) and the minimum was at R8 (0.2 mg/kg), similar to Cr.

The highest concentrations of Pb seemed to correspond to urbanized sampling points, peaking at R6 (3.33 mg/kg) and R7 (3.01 mg/kg). The minimum value was at R4 (0.23 mg/kg).

The mean concentrations across all sampling stations followed the sequence  $As > Cr > Pb > Ni > Cd$ .

| Station            | Lat.       | Long.     | biological community type                       | Environmental features | individuals number | median diameter (cm) | As (mg/kg)         | Cd (mg/kg)         | Cr (mg/kg)       | Ni (mg/kg)       | Pb (mg/kg)         |
|--------------------|------------|-----------|-------------------------------------------------|------------------------|--------------------|----------------------|--------------------|--------------------|------------------|------------------|--------------------|
| R1                 | 42.034205  | 11.872036 | Artificial infralittoral rocky bottom community | wharf                  | 5                  | 4                    | 22.1               | 0.13               | 8.7              | 2.3              | 0.33               |
| R2                 | 42.03143   | 11.831561 | Natural pebbles bottom community                | natural hard bottom    | 8                  | 4.5                  | 3.9                | 0.1                | 0.6              | 0.4              | 0.57               |
| R3                 | 42.030847  | 11.8331   | Artificial infralittoral rocky bottom community | wharf                  | 5                  | 3.8                  | 0.01               | 0.08               | 0.6              | 0.7              | 0.53               |
| R4                 | 42.04893   | 11.819799 | Artificial infralittoral rocky bottom community | inland sea             | 5                  | 3.3                  | 42.7               | 0.04               | 14.8             | 2.9              | 0.23               |
| R5                 | 42.0865517 | 11.796294 | Mesolittoral rocky bottom community             | breakwater             | 5                  | 3                    | 5.6                | 0.04               | 0.6              | 0.4              | 1.18               |
| R6                 | 42.088605  | 11.791116 | Infralittoral rocky bottom community            | wharf                  | 6                  | 3.8                  | 5.9                | 0.07               | 2.5              | 1.3              | 3.33               |
| R7                 | 42.094221  | 11.786006 | Infralittoral rocky bottom community            | harbor                 | 5                  | 3.6                  | 16.9               | 0.05               | 2.5              | 1.4              | 3                  |
| R8                 | 42.118035  | 11.768006 | Infralittoral rocky bottom community            | wharf                  | 5                  | 3.8                  | 8                  | 0.05               | 0.2              | 0.2              | 0.7                |
| R9                 | 42.145088  | 11.742997 | <i>Pocillopora oceanica</i>                     | natural hard bottom    | 9                  | 4.1                  | 26.7               | 0.07               | 2                | 0.7              | 0.78               |
| Range (mean)       |            |           |                                                 |                        |                    |                      | 0.01 - 42.7 (14.6) | 0.04 - 0.13 (0.07) | 0.2 - 14.8 (3.6) | 0.2 - 2.9 (1.15) | 0.23 - 3.33 (1.18) |
| standard deviation |            |           |                                                 |                        |                    |                      | 13.8               | 0.03               | 4.9              | 0.9              | 1.2                |

**Table 9** Concentration of As, Cd, Cr, Ni, and Pb in *P. lividus* from the Civitavecchia area.

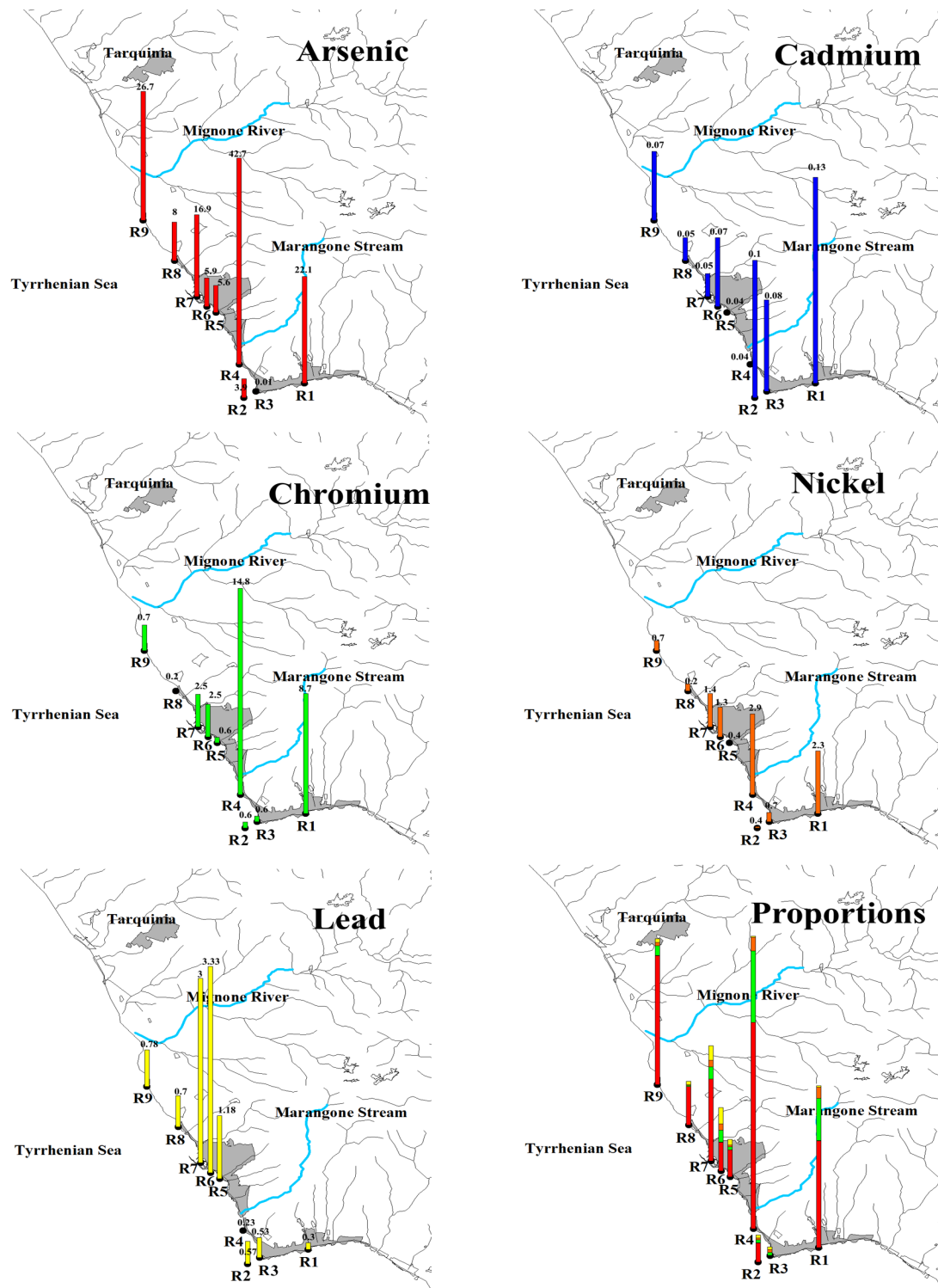


Fig. 14 Concentrations (mg/kg) of As, Cd, Cr, Ni, and Pb in *P. lividus* from the Civitavecchia coastal area.

## 5.5 Discussion

Several studies have investigated the concentrations of metals and metalloids in *P. lividus*. A compendium of concentrations in the Mediterranean sea is summarized in Table 10.

| Element   | Reference                 | Site                     | mg/kg                     |
|-----------|---------------------------|--------------------------|---------------------------|
| <b>As</b> | Deudero et al. 2007       | Balearic Islands (Spain) | 1.6 (0.7 – 4.1)           |
|           | Salvo et al 2014          | Sicily (Italy)           | 7.35 (1.14 – 21.56)       |
|           | Pinsino et al. 2001       | Pianosa (Apulia, Italy)  | 18                        |
|           |                           | Caprara (Apulia, Italy)  | 15                        |
| <b>Cd</b> | Deudero et al. 2007       | Balearic Islands (Spain) | 0.67 (0.14 – 1.6)         |
|           | Salvo et al 2014          | Sicily (Italy)           | 1.32 (1.18 – 1.52)        |
|           | Warnau et al. 1998        | Corsica (France)         | 3.47                      |
|           |                           | Ischia (Campania, Italy) | 3.41                      |
|           |                           | Marseille (France)       | 3.51                      |
|           | Soulalili et al. 2008     | Algiers beach (Algeria)  | 0.14                      |
|           | Storelli et al. 2001      | Apulia (Italy)           | 0.24                      |
| <b>Cr</b> | Papadopoulou et al. 1976  | Greece                   | 4.8                       |
|           | Deudero et al. 2007       | Balearic Islands (Spain) | 1.6 (0.4 – 3.2)           |
|           | Salvo et al 2014          | Sicily (Italy)           | 2.43 (0.92 – 4.17)        |
|           | Warnau et al. 1998        | Corsica (France)         | 0.9                       |
|           |                           | Ischia (Campania, Italy) | 2.01                      |
|           |                           | Marseille (France)       | 1.27                      |
| <b>Ni</b> | Deudero et al. 2007       | Balearic Islands (Spain) | 1.7 (0.8 – 2.7)           |
|           | Salvo et al 2014          | Sicily (Italy)           | 1.69 (0.72 – 4.31)        |
| <b>Pb</b> | Deudero et al. 2007       | Balearic Islands (Spain) | 3 (0.8 – 6.7)             |
|           | Salvo et al 2014          | Sicily (Italy)           | 4.61 (1.28 – 20.74)       |
|           | Sheppard and Bellamy 1974 | Naples (Campania, Italy) | 20 reference site (Italy) |
|           |                           | Naples (Campania, Italy) | 42 polluted site (Italy)  |
|           | Soulalili et al. 2008     | Algiers beach (Algeria)  | 6.14                      |
|           | Warnau et al. 1998        | Corsica (France)         | 2.25                      |
|           |                           | Ischia (Campania, Italy) | 3.02                      |
|           |                           | Marseille (France)       | 2.68                      |
|           | Storelli et al 2001       | Apulia (Italy)           | 0.86                      |

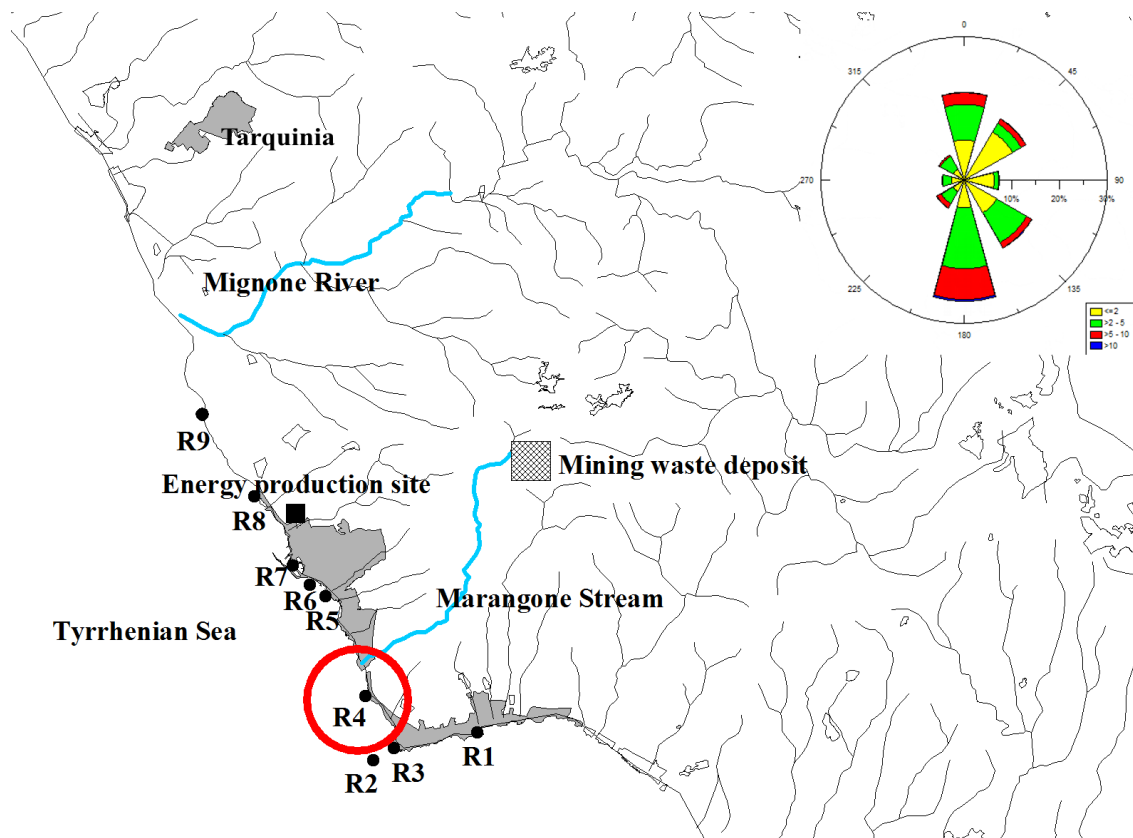
**Table 10** Literature mean concentrations of As, Cd, Cr, Pb, and Ni in *P. lividus* (mg/kg dry weight, whole organism or soft tissues). Minima and maxima are in parentheses.

The average concentration of As found in *P. lividus* was 14.6 mg/kg, a value greater than that found in the literature, except for that reported by (Pinsino et al., 2008). The average concentration of Cr was 3.58 mg/kg, also greater than that found in the literature, except for that reported by Papadopoulou et al. (1976). The average concentration of Pb was 1.18 mg/kg, within the reference averages and far from the 42 mg/kg found in highly polluted sites in Italy (Sheppard and Bellamy 1974). Cd concentrations were within the reference averages, indicating a substantial absence of contamination in soft tissues of *P. lividus*. Finally, the average concentration of Ni was 1.15 mg/kg, slightly less than that found in the reference averages.

Samples of *P. lividus* from R1 and R4 were found to have peak concentrations of As, Cr, and Ni and samples from R6 and R7 were found to have peak concentrations of Pb. Compared to existing reference data, we show substantial contamination of As and Cr, with maximum levels that should be of concern.

Overall, our results show bioaccumulation in *P. lividus* of As and to a lesser extent of Cr, Ni, and Pb. Observed concentration patterns of Cr, Ni, and Pb seem to have the typical characteristics of industrial areas. In particular, the concentration gradient of Pb shows the influence of urban emissions with decreasing values at the extremes of the study area. The same pattern can be seen in the concentration patterns of Cr and Ni with the exceptions of the values at R1 and R4. The high values for these two metals at these points can be typical of port environments (antifouling chemicals, fuel spills, and maritime traffic), taking into account the small size of the port of Santa Marinella.

In detail, our results highlight the presence of an As hotspot in the coastal area between the Port of Civitavecchia and the Marangone stream delta. This hotspot seems to be influenced by the presence of abandoned pyrite, marcasite and galena mines, particularly marcasite mining waste deposits (Kreidie et al. 2011) in the Marangone basin as concentrations and enrichment in this area are dominated mainly by elements indicative of mineral release. Winds and the small size of the Marangone basin suggest that the Torvaldaliga Nord power plant does not present a significant contribution through atmospheric fallout (Fig. 15).



**Fig. 15** As hotspot between the Port of Civitavecchia and Marangone stream delta (circle), winds at the Torrevaldaliga site, and locations of mine waste deposits.

The data also seemed to indicate that Pb concentrations are descriptive of the influence of urban activities on the coastal environment and that Cr and Ni concentrations, because they overlap with industrial activities such as power plants and maritime transport activities, are descriptive of the combustion of fossil fuels and the use of anti-fouling chemicals in port areas.

It should be noted that As was the most abundant element in *P. lividus* at all sampling stations with the exception of R3, and that it showed an increasing gradient as the stations became more northerly, with the exception of stations R1 and R4.

Torrevaldaliga coal combustion emissions, the presence of mine waste deposits, and the small dimension of Marangone basin (23 km<sup>2</sup>), along with the prevailing wind direction

are probable influences of contamination levels in the northern part of the study area as coal combustion is the main source of anthropogenic As in natural environments (Henke 2009; Yudovich and Ketris 2005).

To test this assumption, we compared our results with data collected since 2010 by an environmental monitoring program in which *P. lividus* was analyzed for concentrations of As, Cd, Cr, Ni, and Pb at three sampling stations located north of the study area and adjacent to ours (Nascetti et al. 2011a, 2012b).

To make the comparison (Table 11 and Fig. 16), it was necessary to convert the values obtained by Nascetti et al., from wet weight to dry weight using the following formula:

$$DW/WW = \text{conversion factor (specific for each species)}.$$

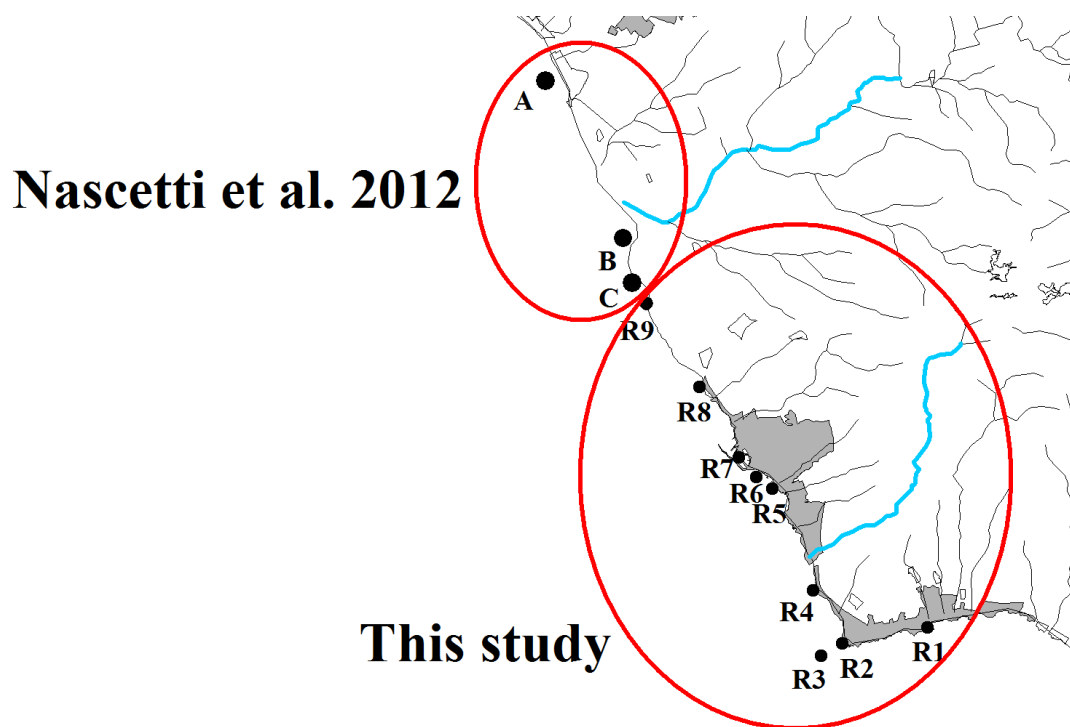
The conversion factors are derived by calculating the moisture content of the organisms used (Ahmed, 1991). For *P. lividus* it was experimentally calculated as 9.3.

We found that all the values reported by Nascetti et al. (2012b) exceeded the average concentrations used as references (Table 10), and were far above the references for As, Cr, and Ni (Table 11). This pattern is in agreement with our results.

From a quantitative point of view, the confirmed high values of As and Cr north of Civitavecchia in the proximity of the Torrealvaldliga Nord power plant suggest that long term monitoring activities should continue to adequately assess temporal trends.

| Station | 2011    |         |        |        |         |         |         |         |        |        |
|---------|---------|---------|--------|--------|---------|---------|---------|---------|--------|--------|
|         | As (WW) | As (DW) | Cd(WW) | Cd(DW) | Cr (WW) | Cr (DW) | Ni (WW) | Ni (DW) | Pb(WW) | Pb(DW) |
| A       | 2.22    | 20.6    | 0.1    | 0.93   | 1.1     | 10.3    | 0.9     | 8.4     | 0.34   | 3.2    |
| B       | 1.58    | 14.7    | 0.12   | 1.12   | 0.3     | 3.1     | 0.15    | 1.4     | 0.12   | 1.1    |
| C       | 1.58    | 14.7    | 0.07   | 0.65   | 0.7     | 6.1     | 0.15    | 1.4     | 0.3    | 2.8    |
|         | 2012    |         |        |        |         |         |         |         |        |        |
|         | As (WW) | As (DW) | Cd(WW) | Cd(DW) | Cr (WW) | Cr (DW) | Ni (WW) | Ni (DW) | Pb(WW) | Pb(DW) |
| A       | 8.26    | 76.8    | 0.002  | 0.02   | 0.7     | 6.1     | 0.13    | 1.2     | 0.07   | 0.7    |
| B       | 3.71    | 34.5    | 0.002  | 0.02   | 0.7     | 6.0     | 0.002   | 0.02    | 0.15   | 1.4    |
| C       | 2.74    | 25.5    | 0.11   | 1.02   | 1.19    | 11.1    | 0.5     | 4.8     | 0.002  | 0.02   |

**Table 11** Mean concentrations in *P. lividus* (Nascetti et al. 2011a, 2012b, modified). A is a sampling point in the Tarquinia salt marsh north of Mignone River delta, B is a sampling point near the Mignone River delta, and C is a sampling point near sampling station R9.



**Fig. 16** Spatial distribution of the sampling points in Nascetti et al. (2012b) and in this study.

To compare concentration distribution results with those reported by Nascetti et al. (2012b), we performed the Bayesian estimation supersedes the t-test (BEST) (Kruschke 2013).

This approach allows an estimation of the distributions of credible values for the means of each group and their differences using Bayesian estimation and the Markov chain Monte Carlo method (MCMC).

Using a Bayesian posterior probability distribution, it is possible to determine the probability that the true difference in means is above (or below) an arbitrary comparison value, which in this case, was set at zero. The process of MCMC sampling generates representative sample of credible parameter values from the posterior distribution. The 95% highest density interval (HDI) shows where the bulk of the most credible values fall. Every value inside the HDI has higher probability density than any value outside the HDI (Kruschke 2013).

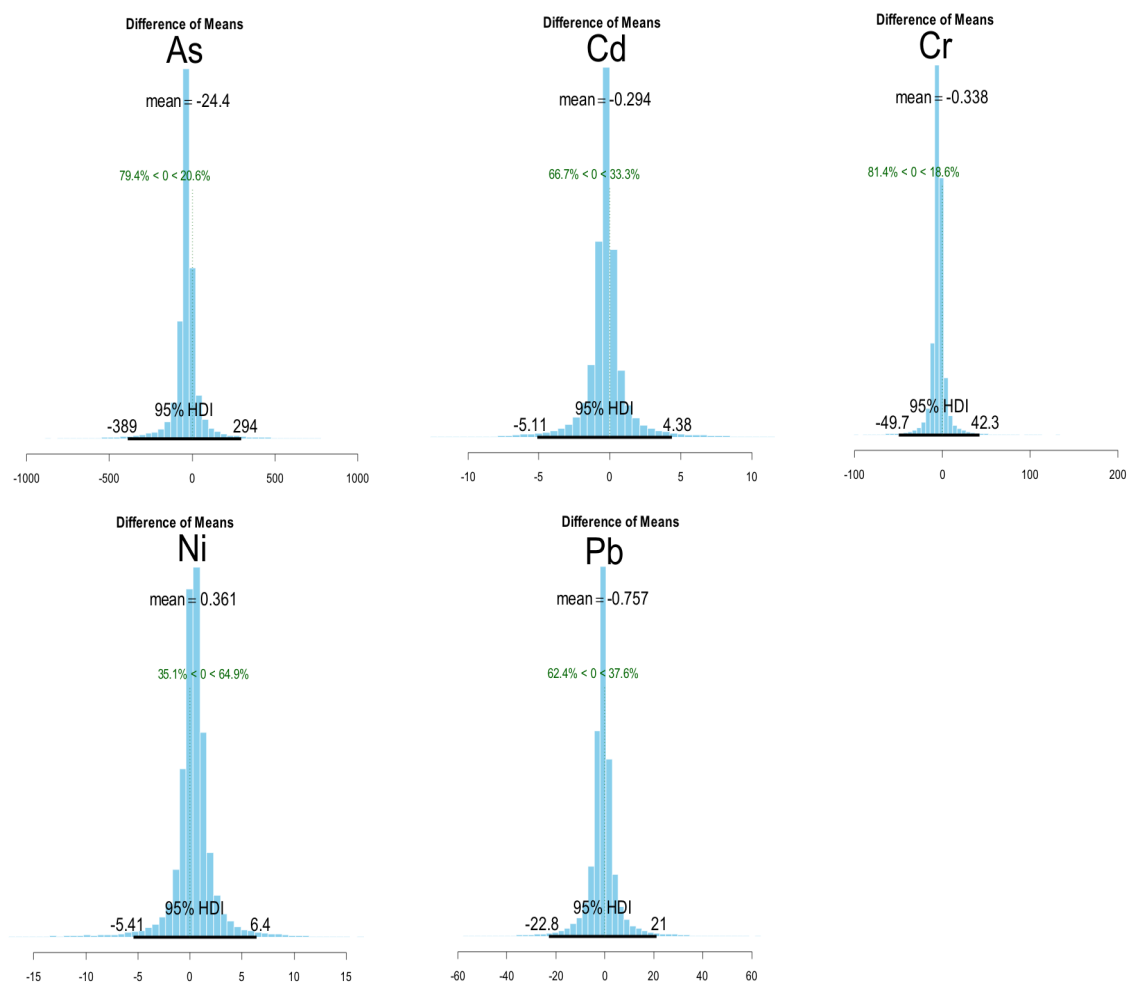
The results show that for As, Cd, Cr, and Pb, we obtained lower means than did Nascetti et al. (2012b). The greatest evidence was for As (79.4% probability) and Cr (81.4% probability). We obtained higher means for Ni (Fig. 17).

From the spatial distribution of the sampling points (Fig. 16), we show a greater mean concentration of As, Cd, Cr, and Pb in the northern part of the study area. Ni may have showed an opposite result because the urban environment had a greater influence in the southern part (urban runoff, sewage discharges, maritime traffic emissions) than the northern part. Means differences in As are shifted toward the north despite the hotspot near the Marangone delta, reinforcing the need for in-depth studies to determine the effective weight of the fallout contribution from the Torrevaldaliga Nord.

Nevertheless, the data clearly indicate that As is present in the tissues *P. lividus* at rather high mean levels. The average concentration in the tissues of *P. lividus* is 0.7 times the amount found in sediments, confirming the influence of the sediment background in the measured levels of As in this organism.

Overall, it can be said that *P. lividus* bioaccumulates mainly As and Cr, presumably because of the bioavailability from the sedimentary matrix and that such high As levels

can represent a potential threat as a result of human consumption.



**Fig. 17** Bayesian estimation supersedes the t-test analysis of trace metals comparing our results with those of Nascetti et al. (2012b).

## 5.6 Conclusions

In this paper, the dry weight concentrations of As, Cd, Cr, Ni, and Pb were analyzed in the gonads and gut of *P. lividus* found in the coastal area of Civitavecchia. The average concentrations, in order of abundance, were 14.64 mg/kg As, 3.58 mg/kg Cr, 1.18 mg/kg Pb, 1.15 mg/kg Ni, and 0.07 mg/kg Cd. These concentrations describe bioaccumulation

of As and Cr, and to a lesser extent, of Ni and Pb, in *P. lividus*. A comparison with the literature shows that around Civitavecchia, higher levels of As and Cr were found. A specific comparison with those found by Nascetti et al. (2011a, 2012b) in the same area shows a substantial quantitative correspondence. In general, it can be deduced that the high concentrations reflect an As geochemical anomaly in the coastal area of Civitavecchia because the ratio between the concentration in soft tissue of *P. lividus* and the surrounding sediments is 0.7. In particular, an As hotspot in the Marangone stream area reveals a strong influence of mine wastes located in this basin, and the increasing gradient toward the north indicates an effect from emissions of the Torrevaldaliga Nord coal fired power plant. The high bioaccumulation of As, and to a lesser extent, Cr, suggests the need for further research aimed at assessing the actual contribution of industrial activities, particularly coal combustion, on the level of contamination in marine organisms. Another topic that should be further investigated is the potential contamination of primary producers (such as algae and *P. oceanica*) and the possibility that As can biomagnify up the food chain.

## **6. Temporal distribution of trace metals in recent sediments in the northern Tyrrhenian sea, Italy.**

The potential pollution and contamination level assessment of a given coastal area can not ignore a careful consideration and understanding of the geological and natural geochemical features of the area.

The consequences of heavy industrialization, especially after World War II, are manifested through chemical and physical changes in environmental compartments that suffer from considerable enrichment of potentially chemical pollutant species.

From this perspective, the definition of the so-called "natural geochemical background values" which identifies the condition of natural chemical element concentration in a given area is particularly important, regardless of the variations of the chemical pollutant species concentrations potentially caused by anthropogenic impacts.

In order to define the geochemical background values, the choice of an appropriate helpful environmental matrix is crucial.

Additionally, in order to evaluate the marine environment pollution degree, the study of the depositional areas of pelitic sediments is fundamental.

It is widely shown in the international literature that particular affinity exist between the finer grain size of sediment and the chemical species present in the water column. Potentially chemical pollutant elements tend to bond with the pelitic sediment particles, and as a result, they follow the sediment fate (Horowitz 1991; Salomons and Förstner 1984).

For this reason, the marine pelitic depositional areas are internationally considered as the main "archive integrator" of all chemical and physical processes occurring in the water column (Brondi et al. 2008).

Consequently, the temporal analysis of pelitic sedimentary environments can be used to trace the natural "pre-impact" levels.

In light of the above considerations a temporal assessment of trace metals was carried out by analyzing the data obtained from a sampling campaign carried out in May 2015,

which involved sampling of two sediment cores in the southern sector of the study area. Therefore, this chapter reports some results concerning the sediment accumulation rate values (SARs) and the trace metal values measured in PT50 and MRG50 core samples. The temporal assessment of trace metals distribution in the study area is still under completion and it will be deepened through the analysis of trace metal concentrations in deeper sediment horizons in order to obtain detailed informations about the mining activities contribution that have occurred in the study area.

## 6.1 Materials and Methods

### 6.1.1 Sample collection

The sediment sampling was performed in May 2015 by collecting two sediment core samples using a UWITEC gravity corer (diameter: 90 mm). The two core samples were located at -50 m depth, near the port of Civitavecchia (PT50) and near the Marangone stream (MRG50). Once transported (at 4 °C) to the laboratory, the cores were immediately cut at intervals of 1 cm. Figure 18 reports the locations of the two sediment core samples.

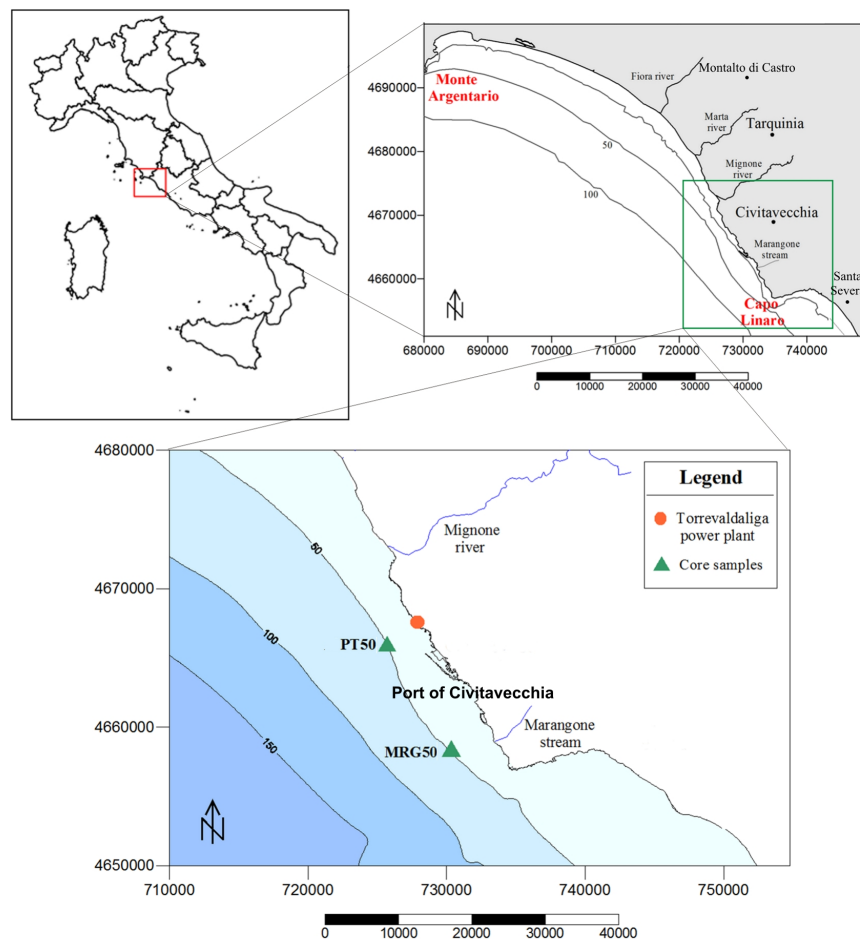


Fig. 18 PT50 and MRG50 core samples locations.

### 6.1.2 Sample analysis

The radiochronological measurements and trace elements analysis were carried out at the National Oceanography Center (NOC) in Southampton, UK.

First of all, the core sections were freeze-dried and stored in polyethylene bags. Subsequently, the radiochronological measurements were performed in a three cm interval starting from the first section of each core for a total of 13 subsamples for PT50 core and 12 subsamples for MRG50 core. More specifically, approximately 20 g of dried samples were transferred into 20 ml polythene scintillation vials and counted for 12 h using a Canberra well-type high purity germanium (HPGe) detectors.

Major and trace elements analysis of sediment sections were performed on eight sections from each core (section 1-2-3-4-5-10-20-30) by WD-XRF using a Philips MagiX-Pro XRF spectrometer. Samples were homogenised by grinding and compressed into powder pellets in accordance with the methodology proposed by Croudace and Williams-Thorpe (1988). A certified reference sample (BCR-1, USGS Geochemical Reference materials) was used as a control.

## **6.2 Results and Discussion**

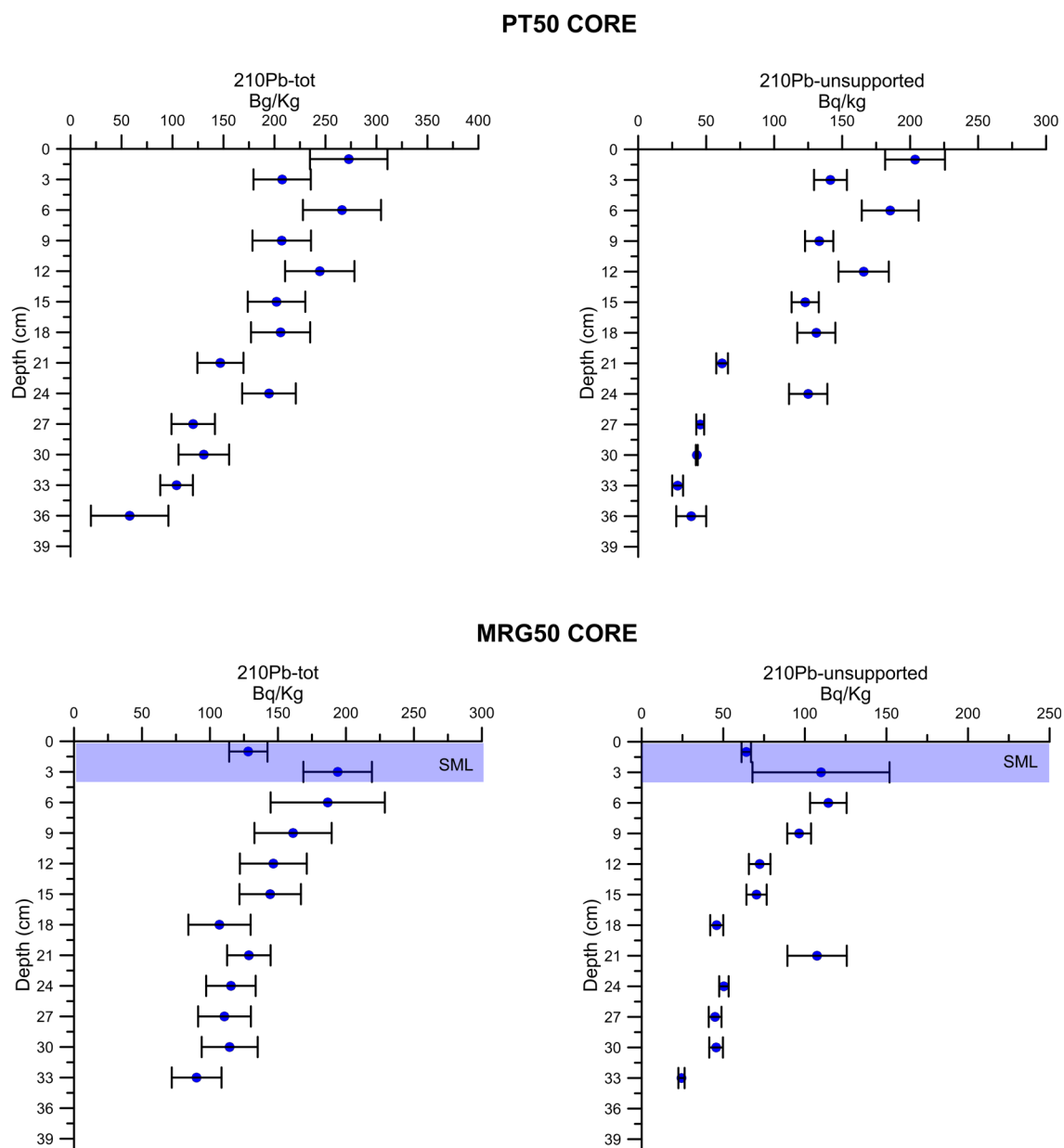
### 6.2.1 Radionuclide measurements

$^{210}\text{Pb}$  is an important tool for estimating the age of sediments and sedimentary mass accumulation rates (SARs) (Appleby and Oldfield 1978; Goldberg 1963; Koide et al. 1972) due to his relatively short half-life (22.3 years) and the adsorption properties of fine sediments.

Figure 19 reports the total  $^{210}\text{Pb}$  activity values and unsupported  $^{210}\text{Pb}$  values of PT50 and MRG50 respect to depth. The unsupported or “excess”  $^{210}\text{Pb}$  is the  $^{210}\text{Pb}$  derived by dry or wet deposition generated by  $^{222}\text{Rn}$  decay in air or by  $^{222}\text{Rn}$  decay in water column. The unsupported  $^{210}\text{Pb}$  was calculated by subtracting the nearest neighbouring  $^{226}\text{Ra}$  measurement from each total  $^{210}\text{Pb}$  value (Appleby and Oldfield 1978).

The maximum unsupported  $^{210}\text{Pb}$  activity detected was  $203.6 \text{ Bq kg}^{-1}$  for PT50 (section

1) and  $114.4 \text{ Bq kg}^{-1}$  for MRG50 (section 6).



**Fig. 19** Total  $^{210}\text{Pb}$  activity values and unsupported  $^{210}\text{Pb}$  values of PT50 and MRG50.

The two core samples exhibited an irregular but approximately exponential decreasing activity profile of total  $^{210}\text{Pb}$  and unsupported  $^{210}\text{Pb}$  with respect to depth.

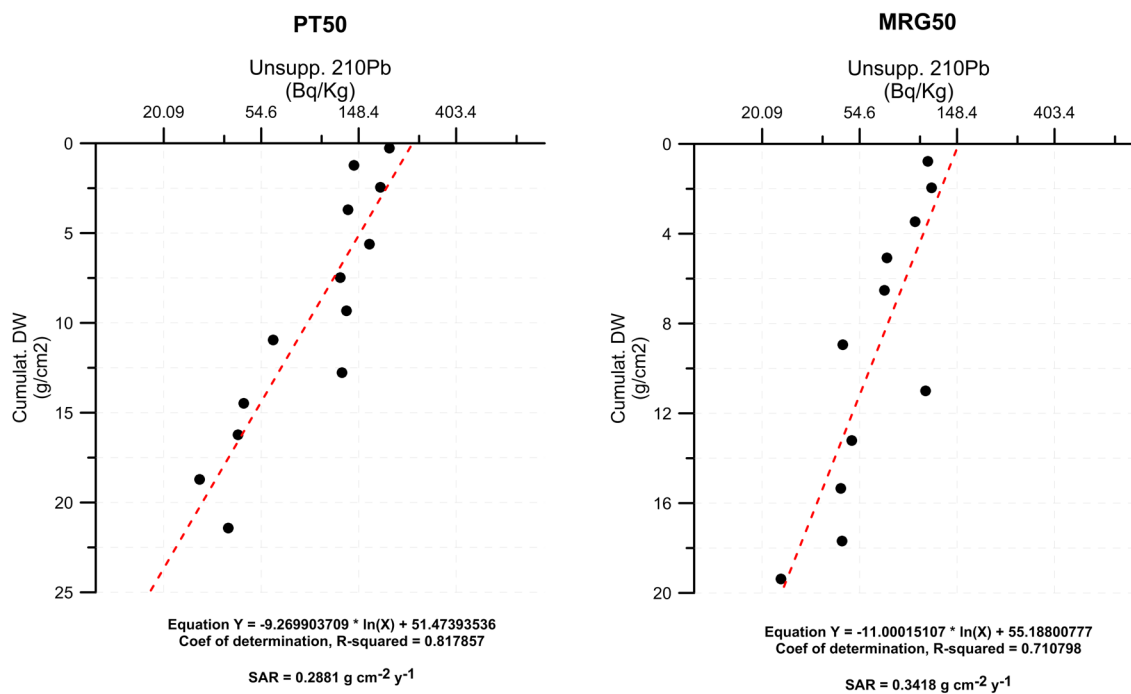
From the visual inspection of the MRG50  $^{210}\text{Pb}$  profiles is possible to see low activity values of total  $^{210}\text{Pb}$  and unsupported  $^{210}\text{Pb}$  in the first 3 cm sections.

This trend in the surface layers of MRG50 is identifiable as a Sediment Mixed Layer (SML), diagnosed by a dilution of  $^{210}\text{Pb}$  concentrations (Blais et al. 2015). This dilution of the  $^{210}\text{Pb}$  concentrations could be related to an increase in sedimentation rates in recent years. However, the most common process resulting in sediment mixing is bioturbation, a general term referring to physical mixing of sediments by the burrowing and feeding activities of benthic organisms (Boudreau 1997; Burdige 2006, Blais et al. 2015).

In this work PT50 and MRG50 cores were dated using the CRS interpretation model (Appleby and Oldfield 1978; Robbins et al. 1978).

The CRS model assumes constant input of  $^{210}\text{Pb}$  and a core that is long enough to include all of the measurable atmospheric source  $^{210}\text{Pb}$ . Since the second assumption is not satisfied in the two cores (background has not been achieved), it is not normally possible to apply the CRS model. However, it is possible to calibrate the CRS model against the CFCS model (Appleby and Oldfield 1978; Robbins et al. 1978), and therefore allow the CRS model to be used. With the CRS model calibrated, ages at the bottom of all sections in the two cores were calculated.

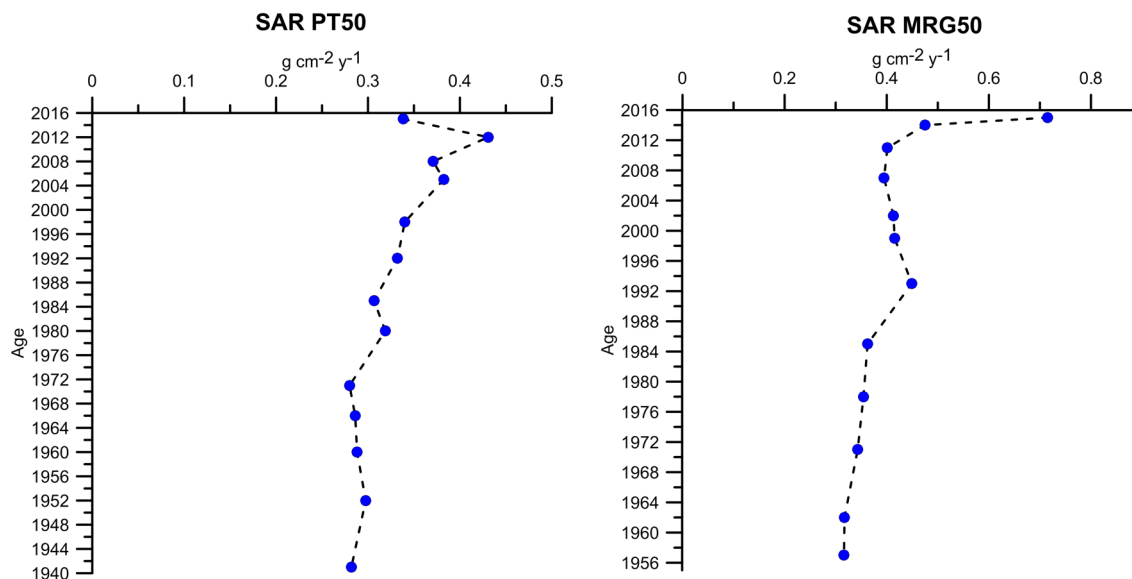
In the CFCS model, the unsupported  $^{210}\text{Pb}$  was calculated by subtracting the nearest neighbouring  $^{226}\text{Ra}$  measurement from each total  $^{210}\text{Pb}$  value. Subsequently, regression between unsupported  $^{210}\text{Pb}$  (plotted in logarithm) and cumulative dry mass was performed. For PT50 core, the CFCS model predicts ( $R^2 = 0.82$ ) a sediment mass accumulation rate of  $0.29 \text{ g cm}^{-2} \text{ y}^{-1}$ . For MRG50 core the CFCS model applied to sections 3 - 33 predicts ( $R^2 = 0.72$ ) an average sediment accumulation rate of  $0.34 \text{ g cm}^{-2} \text{ y}^{-1}$  (Figure 20). SARs values were calculated as described by Yuan et al. (2014).



**Fig. 20** CFCS model results for PT50 and MRG50 cores.

The SARs values calculated by the CFCS model were used for the calibration of the CRS model. The SARs values obtained through the CRS model ranged between 0.28 and 0.43 g cm<sup>-2</sup> y<sup>-1</sup> for PT50 and between 0.32 and 0.71 g cm<sup>-2</sup> y<sup>-1</sup> for MRG50.

Figure 21 shows SARs values obtained through the CRS model for PT50 and MRG50 cores.



**Fig. 21** SARs values obtained through the CRS model for PT50 and MRG50 cores.

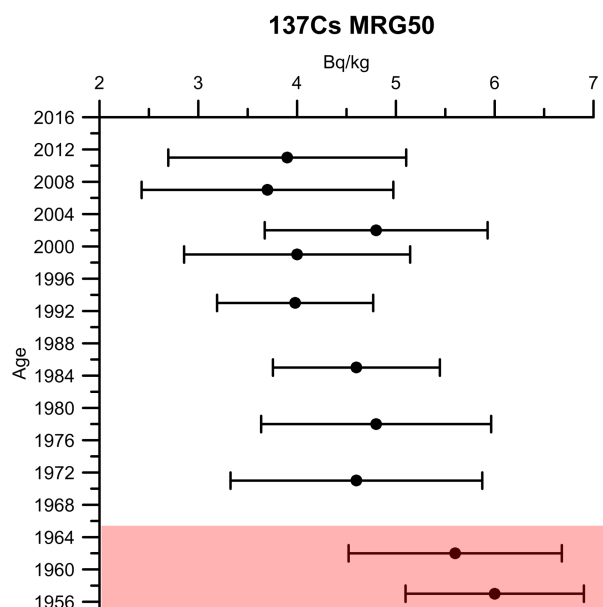
Since <sup>210</sup>Pb dating is not always unambiguous, the method requires the support of dates determined from stratigraphic records of artificial radionuclides such as <sup>137</sup>Cs.

Peak activities of <sup>137</sup>Cs in a sediment profile may be useful to mark the ages of sediment deposited from the mid 1950s to early 1960s (<sup>137</sup>Cs source is the fallout from nuclear bomb tests) or in 1986 (fallout from the Cheronobyl accident). However, in many cases <sup>137</sup>Cs profiles are not stable enough over time to reliably reconstruct a detailed depositional history or to determine a sedimentation rate (Klaminder et al. 2012) as in PT50 core in which <sup>137</sup>Cs profile is difficult to interpretate.

The <sup>137</sup>Cs profile of MRG50 core (Figure 22) could be interpreted assuming that:

- The <sup>137</sup>Cs profile in MRG50 core doesn't show a peak in corrspondence of the Cheronobyl accident (1986).
- The CRS model for the bottom sections shows that the MRG50 core has not reached the onset of nuclear bomb tests.
- The <sup>137</sup>Cs peak in MRG50 core is inside the mid 1950s – 1960s according to the CRS model ages.

In light of the above assumptions the CRS model shows a correspondence with the  $^{137}\text{Cs}$  profile.



**Fig. 22**  $^{137}\text{Cs}$  profile in MRG50 core.

The results obtained through the use of  $^{210}\text{Pb}$  in PT50 and MRG50 cores are comparable with the results obtained by the analysis of three sediment cores taken in the northern sector of the study area near the Mignone, Marta and Fiora rivers at -50m depth (Scanu 2012) (Table 12).

| Cores ID | Mean SARs values (CRS)<br>$\text{g cm}^{-2} \text{y}^{-1}$ | Mean SARs values (CFCS)<br>$\text{g cm}^{-2} \text{y}^{-1}$ |                                |
|----------|------------------------------------------------------------|-------------------------------------------------------------|--------------------------------|
| GRT50    | 0.42                                                       | 0.41                                                        | Scanu 2012, Scanu et al. 2015a |
| MRT50    | 0.36                                                       | 0.33                                                        |                                |
| MIG50    | 0.55                                                       | 0.51                                                        |                                |
| PT50     | 0.33                                                       | 0.29                                                        | This study                     |
| MRG50    | 0.41                                                       | 0.34                                                        |                                |

**Table 12** SARs values comparison with literature data for the study area.

Generally, the SARs values confirm a lower sediment supply for the southern sector of the physiographic unit Capo Linaro - Monte Argentario and this is in agreement with the distribution of the major river basins in the northern part of the study area (Mignone, Marta and Fiora rivers).

### 6.2.2 Major and trace elements analysis

Table 13 shows  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , As, Cr, Cu, Ni, Pb and Zn values and numerical sediment quality guidelines (SQGs) ERL – ERM and TEL – PEL values of the considered elements.

|              | Sections   | $\text{Al}_2\text{O}_3$ (%) | $\text{Fe}_2\text{O}_3$ (%) | As (ppm) | Cr (ppm) | Cu (ppm) | Ni (ppm) | Pb (ppm) | Zn (ppm) |
|--------------|------------|-----------------------------|-----------------------------|----------|----------|----------|----------|----------|----------|
| <b>MRG50</b> | 1          | 14.768                      | 6.472                       | 23.4     | 114      | 29.9     | 35.9     | 37.6     | 93.6     |
|              | 2          | 14.811                      | 6.5                         | 20       | 119.3    | 30.4     | 37       | 42.4     | 94       |
|              | 3          | 14.919                      | 6.453                       | 18.2     | 117.7    | 29.8     | 36.9     | 40.5     | 95.9     |
|              | 4          | 15.032                      | 6.536                       | 18.6     | 118.7    | 30.6     | 38.4     | 43.1     | 95.9     |
|              | 5          | 15.154                      | 6.547                       | 16.2     | 122.6    | 30.2     | 39.1     | 45.4     | 97.9     |
|              | 10         | 14.913                      | 6.28                        | 13.5     | 117      | 29.9     | 39.3     | 45.5     | 93.7     |
|              | 20         | 15.137                      | 6.445                       | 14.2     | 119.3    | 31.5     | 38.6     | 47.9     | 98.8     |
|              | 30         | 15.365                      | 6.59                        | 15       | 119.3    | 32.3     | 40.8     | 50       | 100.8    |
| <b>PT50</b>  | 1          | 13.787                      | 5.769                       | 15.2     | 105      | 28.2     | 35.8     | 37.2     | 84.1     |
|              | 2          | 14.082                      | 5.925                       | 16.7     | 107.7    | 28.6     | 34.8     | 35.2     | 84.9     |
|              | 3          | 14.266                      | 6.065                       | 16.9     | 111.2    | 27.9     | 36.8     | 39.2     | 88.3     |
|              | 4          | 14.481                      | 6.141                       | 16.1     | 114.4    | 28.6     | 37.7     | 39.9     | 88.2     |
|              | 5          | 14.494                      | 6.117                       | 15.5     | 115.3    | 27.5     | 36.9     | 39.8     | 90.1     |
|              | 10         | 15.128                      | 6.535                       | 16.4     | 119.6    | 30.3     | 38       | 43.7     | 97.5     |
|              | 20         | 15.337                      | 6.586                       | 17       | 118.1    | 31       | 39       | 48.8     | 100.1    |
|              | 30         | 15.802                      | 6.814                       | 18       | 121.3    | 33.7     | 41.5     | 52.6     | 103.7    |
|              | <b>ERL</b> |                             |                             | 8.2      | 81       | 34       | 20.9     | 46.7     | 150      |
|              | <b>ERM</b> |                             |                             | 70       | 270      | 270      | 51.6     | 218      | 410      |
|              | <b>TEL</b> |                             |                             | 7.24     | 52.3     | 18.7     | 15.9     | 30.2     | 124      |
|              | <b>PEL</b> |                             |                             | 41.6     | 160      | 108      | 42.8     | 112      | 271      |

**Table 13**  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , As, Cr, Cu, Ni, Pb and Zn raw values and ERL – ERM, TEL – PEL values of the considered elements.

Trace metal values measured in the sections of PT50 and MRG50 cores show slight variations (Table 13). As, Cr, Ni, Pb, Cu and Zn values measured in PT50 show a slight decreasing trend starting from the deepest sections up to the most recent ones.

Cu, Ni, Pb, and Zn values measured in MRG50 show a slight decreasing trend starting from the deepest sections up to the most recent ones while As values show an opposite trend. Cr values measured in MRG50 show a different trend respect to the other considered elements.

The ERL - ERM values (effects range low and effects range medium) were determined by Long and Morgan (1990). A large data set for each chemical was assembled and concentrations not associated with an effect were excluded; the ERL was calculated as the lower 10th percentile of the data set and the ERM was calculated as the 50th percentile of the data set.

TEL - PEL values (threshold effects level and probable effects level) were determined by the Florida Department of Environmental Protection (FDEP, 1994). The method was similar to the method for deriving ERL - ERM values, but both effect and no effect data were used to calculate TEL and PEL numerical values.

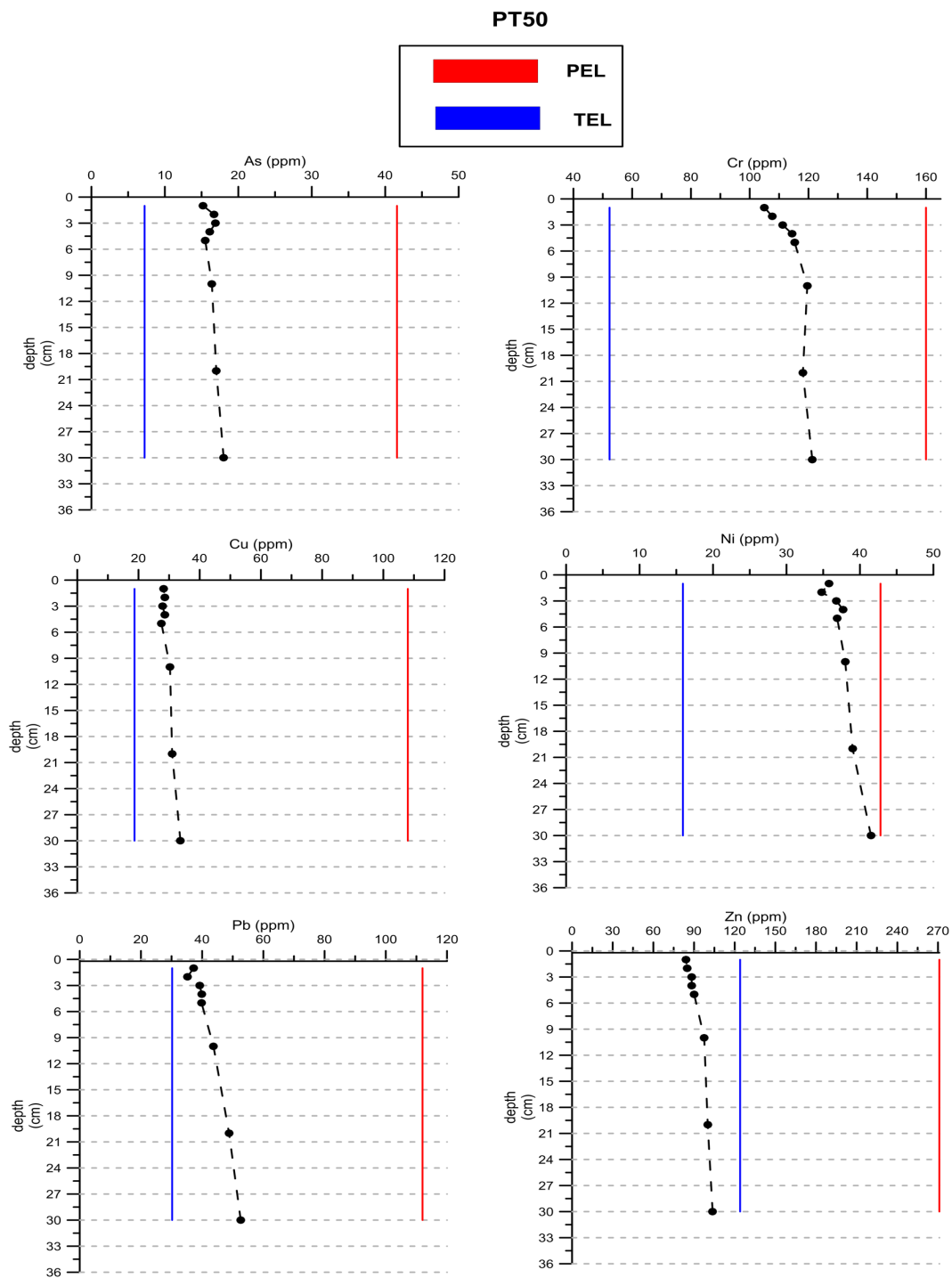
The TEL (or ERL) and PEL (or ERM) values define three concentration ranges for a chemical element:

- (1) Rarely associated with adverse effects ( $x < \text{TEL or ERL}$ ).
- (2) Occasionally associated with adverse effects ( $\text{TEL or ERL} < x < \text{PEL or ERM}$ ).
- (3) Frequently associated with adverse effects ( $x > \text{PEL or ERM}$ ).

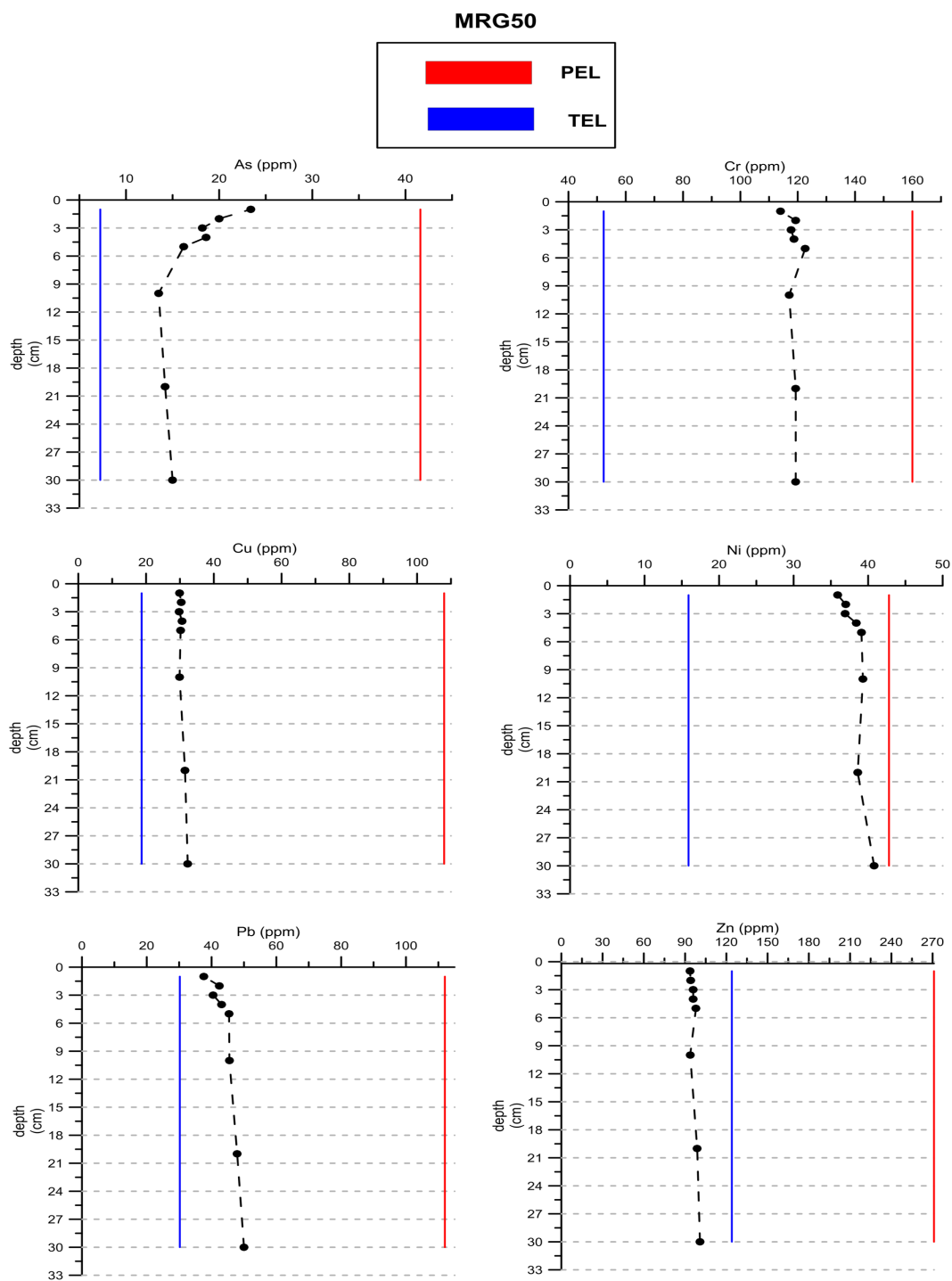
As described in Table 13, As concentrations exceed the ERL and TEL values in all the sections of the two core samples. Ni and Cr exceed the ERL and TEL values in all the sections of the two core samples. Pb exceeds the ERL value in section 20 and 30 of MRG50 and PT50 cores. Cu concentrations exceed the TEL value in all the sections of the two core samples but are below the ERL value in all the sections of the two core samples. Zn concentrations are below the ERL and TEL values in all the sections of the

two core samples.

However, trace metal values result to be below the ERM and PEL values in all the sections of the two cores. This effect indicates a no relevant toxicity of the samples (Alebic-Juretic, 2011). Figure 23 A and 23 B shows trace metal values with respect to TEL and PEL values.



**Fig. 23 A** Trace metal values measured in PT50 core with respect to TEL and PEL values.



**Fig. 23 B** Trace metal values measured in MRG50 core with respect to TEL and PEL values.

The content of trace metals originated from the same or similar source have usually a significant correlation (Rodríguez et al. 2008). The correlation between the trace metals content in sediments can be considered as an indicator of whether the source of heavy metal was the same or not.

In this study Pearson's correlation analysis was used to analyze the correlation among the different trace metals measured in the sections of PT50 and MRG50 core samples. Tables 14 A and 14 B show the Pearson's correlation results among trace metals.

In PT50 a positive correlation is visible among Cr, Ni, Cu, Pb, and Zn concentrations. The only exception to this are As concentrations. The As concentrations show significant correlation only with the Cu concentrations.

In MRG50 core a positive correlation is visible between Pb and Ni values and between Pb and Cu values. Zn values are positive correlated with Ni, Cu and Pb values. As values show a strong negative correlation with Ni and Pb.

Positive correlation between trace metals suggests that these trace metals have common sources, mutual dependence and identical behavior during transport (Ren et al. 2015). Negative correlations suggest that they do not share the above mentioned metal traits with each others. The absence of correlation among trace metals suggests that the content of trace metals are not controlled by a single factor. However it is controlled by a combination of geochemical support phases and their mixed associations (Suresh et al. 2012).

In light of these considerations Cr, Ni, Cu, Pb, and Zn concentrations measured in PT50 seem to have a common source. In MRG50 Ni and Cu seem to have a common source with Pb; Zn seems to have a common source with Ni, Cu, and Pb. The As concentrations measured in PT50 and MRG50 suggest that As content is not controlled by a single factor.

|    | Cr                                 | Ni      | Cu      | Pb      | As      | Zn |
|----|------------------------------------|---------|---------|---------|---------|----|
| Cr | 1                                  |         |         |         |         |    |
| Ni | 0.86629                            | 1       |         |         |         |    |
| Cu | 0.71715                            | 0.87581 | 1       |         |         |    |
| Pb | 0.855                              | 0.96778 | 0.91274 | 1       |         |    |
| As | 0.56614                            | 0.67312 | 0.78459 | 0.6991  | 1       |    |
| Zn | 0.91836                            | 0.92096 | 0.89201 | 0.97177 | 0.69606 | 1  |
|    | Positive correlation at 0.05 level |         |         |         |         |    |
|    | Positive correlation at 0.01 level |         |         |         |         |    |
|    | Negative correlation at 0.05 level |         |         |         |         |    |
|    | Negative correlation at 0.01 level |         |         |         |         |    |

**Table 14 A** Pearson's correlation among trace metal values measured in PT50 core.

|    | Cr                                 | Ni       | Cu      | Pb       | As       | Zn |
|----|------------------------------------|----------|---------|----------|----------|----|
| Cr | 1                                  |          |         |          |          |    |
| Ni | 0.55264                            | 1        |         |          |          |    |
| Cu | 0.33661                            | 0.66903  | 1       |          |          |    |
| Pb | 0.6066                             | 0.93073  | 0.79313 | 1        |          |    |
| As | -0.50663                           | -0.83397 | -0.4408 | -0.86789 | 1        |    |
| Zn | 0.58898                            | 0.71071  | 0.83918 | 0.78258  | -0.54618 | 1  |
|    | Positive correlation at 0.05 level |          |         |          |          |    |
|    | Positive correlation at 0.01 level |          |         |          |          |    |
|    | Negative correlation at 0.05 level |          |         |          |          |    |
|    | Negative correlation at 0.01 level |          |         |          |          |    |

**Table 14 B** Pearson's correlation among trace metal values measured in MRG50 core.

Trace metal concentrations in coastal marine sediments are largely determined by inorganic material resulting from physical and chemical weathering of landmasses.

Inorganic detritus is composed of silicate minerals such as quartz, feldspar, micas and clay minerals, smaller amounts of metal oxides and sulfide phases. Clay minerals are finer and tend to bond more metals than coarser material (Windom et al. 1989).

Therefore, variations in trace metal concentrations have often been related to the grain size effect. For this reason, metal concentrations were normalized using a normalizing factor whose concentration is not affected by anthropogenic processes (Daskalakis and O'Connor 1995).

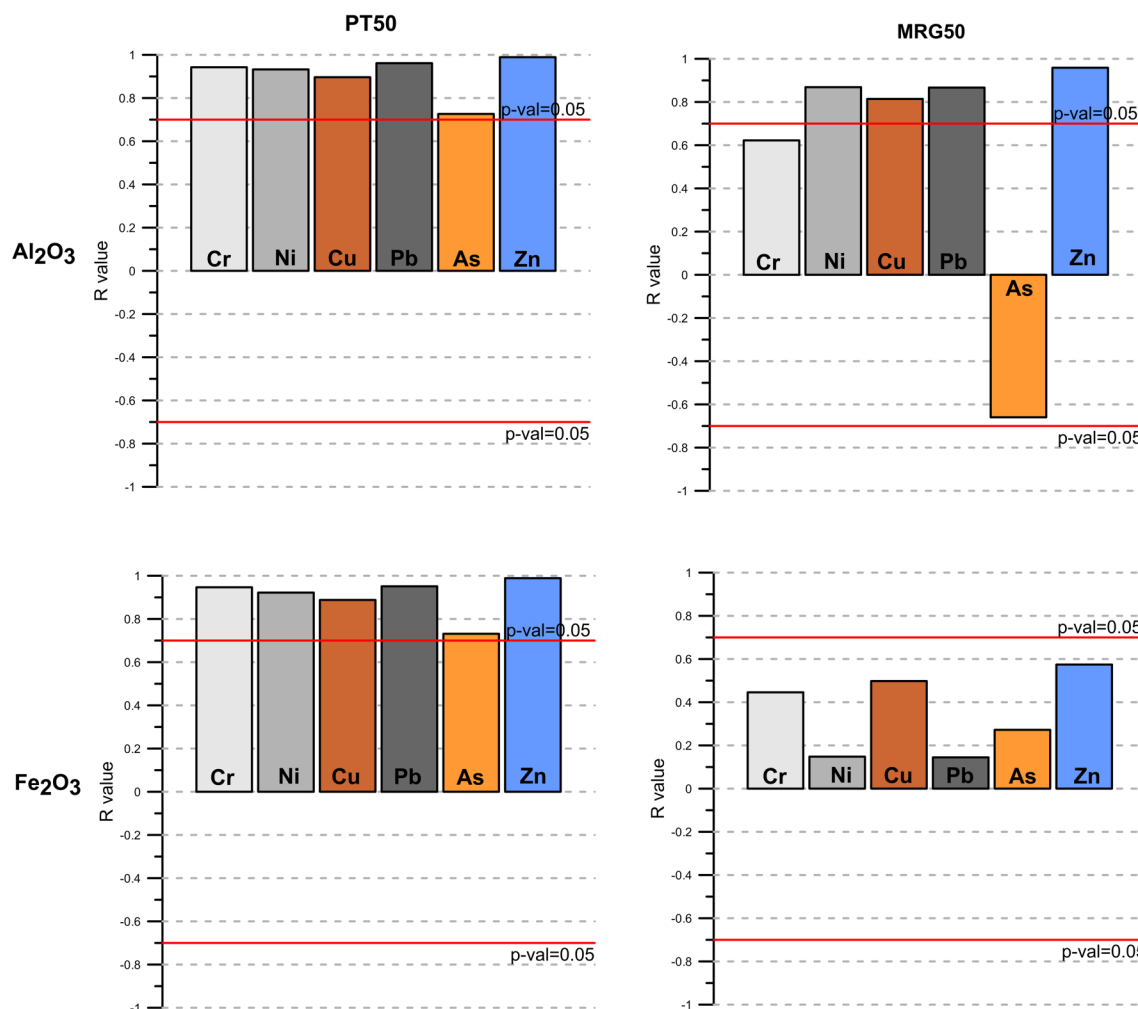
The two well established categories of normalizing factors are granulometric and geochemical factors. Granulometric techniques are based on normalisation against total weight percent of fine sediments ( $< 63 \mu\text{m}$ ) or the total clay size sediments ( $< 4 \mu\text{m}$ ) (Loring, 1991).

Geochemical methods are based on the comparison between metal concentration in sediment and the concentration of reference elements such as aluminium, chromium, iron, organic carbon and lithium (Windom et al. 1989; Loring 1990, 1991; McMurtry et al. 1995; Daskalakis and O'Connor 1995; Balls et al. 1997; Tam and Yao 1998). Aluminium and iron are considered as a “proxy” for the clay content (Windom et al. 1989; Din 1992).

In light of the above considerations Figure 24 shows the Pearson correlation between trace metal values and  $\text{Al}_2\text{O}_3$  and the Pearson correlation between trace metal values and  $\text{Fe}_2\text{O}_3$ .

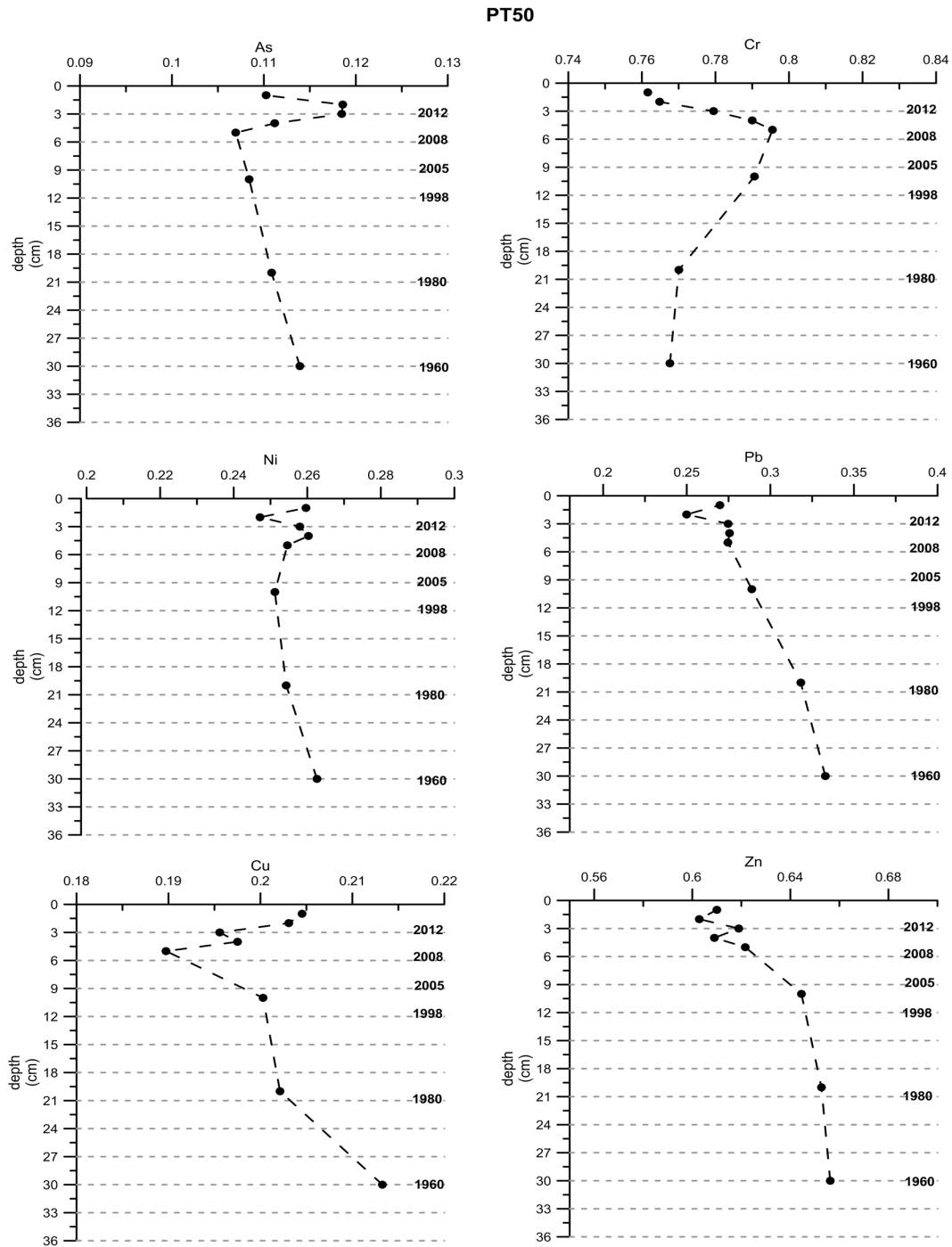
Trace metal values measured in PT50 core show a significant correlation ( $p\text{-val} = 0.05$ ) with  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  values. Ni, Cu, Pb and Zn values measured in MRG50 core show a significant correlation ( $p\text{-val} = 0.05$ ) with  $\text{Al}_2\text{O}_3$  values. However, Cr and As values measured in MRG50 core does not show a significant correlation with  $\text{Al}_2\text{O}_3$  values.

Furthermore, trace metal values measured in MRG50 does not show a significant correlation with  $\text{Fe}_2\text{O}_3$  values.



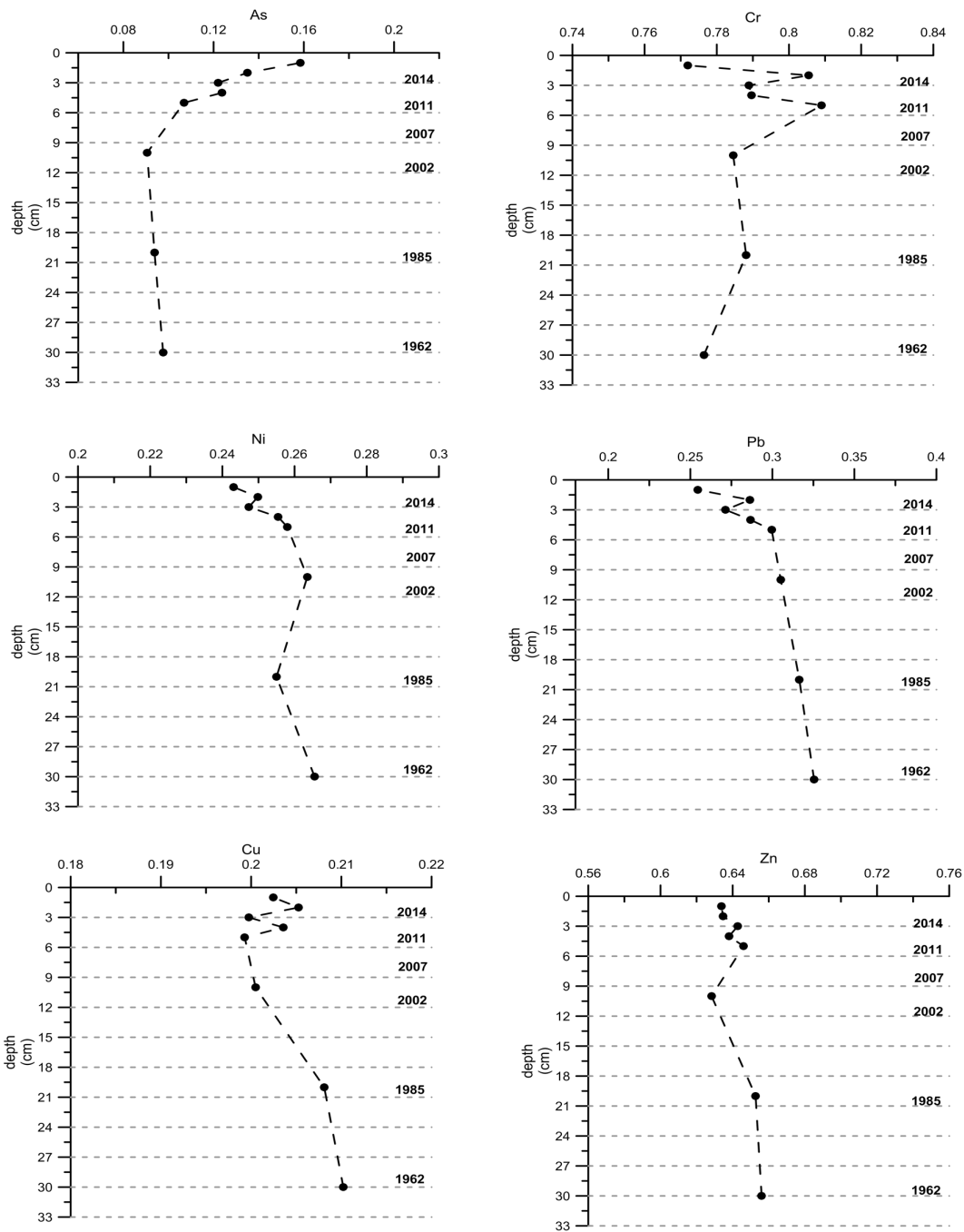
**Fig. 24** Pearson's correlation between trace metal values and  $\text{Al}_2\text{O}_3$  and Pearson's correlation between trace metal values and  $\text{Fe}_2\text{O}_3$ .

From these correlations is clear that the best normalizing factor appears to be  $\text{Al}_2\text{O}_3$ . Looking at the correlation results between trace metals and  $\text{Al}_2\text{O}_3$  values all the considered trace metals in the two cores are linked to the fine sediment fractions except for As and Cr in MRG50 core. In light of the results obtained, trace metal were normalized using the  $\text{Al}_2\text{O}_3$  values. Figures 25 A and 25 B show the temporal distribution of As, Cr, Cu, Ni, Pb and Zn values normalized with  $\text{Al}_2\text{O}_3$  concentrations.



**Fig. 25 A** Temporal distribution of As, Cr, Cu, Ni, Pb and Zn values normalized with  $Al_2O_3$  concentrations in PT50 core.

# MRG50



**Fig. 25 B** Temporal distribution of As, Cr, Cu, Ni, Pb and Zn values normalized with  $\text{Al}_2\text{O}_3$  concentrations in MRG50 core.

PT50 shows a slight decrease trend of Pb and Zn normalized values from the deepest sections up to the recent ones. Ni normalized values are almost constants in all the core sections. Cr normalized values show an increase from the early 1980s up to the early 2000s. As and Cu normalized values show a decreasing trend from the early 1960s up to the early 2000s and an increase in the top of the core (Figure 25A).

MRG50 shows slight variations of Ni, Cu, Pb and Zn normalized values down-core profiles. As and Cr normalized values show a different trend especially in the first 10 cm of the core (Figure 25B). However, As and Cr do not show a good correlation with  $Al_2O_3$  values (Figure 24). This indicate that the variations of As and Cr values in MRG50 core are not linked with the fine sediment variations.

### **6.3 Conclusions**

The temporal assessment of trace metal concentrations was carried out by the analysis of PT50 and MRG50 core samples taken in the coastal area of Civitavecchia at a depth of -50 m. The chronology of sediment cores covers 60 years and trace metal values measured in the sections of the two core samples result to be below the ERM and PEL values. This effect indicates a no relevant toxicity of the samples.

The results of the Pearson's correlation analysis show that all the considered trace metals in the two core samples are linked to the fine sediment fractions except for As and Cr values measured in MRG50 core.

Moreover, trace metal values recorded in PT50 and MRG50 core samples do not show considerable variations attributable to the existing industrial activities during the considered period.

The absence of evident signs of recent human impact on trace metal values can be attributable to the preponderant influence of the geochemical anomalies and to the past mining activities that have occurred in the study area.

However, further geochemical and mineralogical studies are needed to confirm these hypothesis.

## 7. Overall conclusions

This PhD work aimed to assess the pollution degree and potential toxicity of trace metals in marine sediments of the coastal area enclosed between Montalto di Castro and Capo Linaro, in northern Latium, Italy.

The spatial assessment of the distribution, pollution degree and potential toxicity of trace metals highlighted the presence of two hotspots of As and Mn and the presence of two anomalies of Hg.

The hotspots are largely due to naturally high levels of As and Mn in the Mignone River and Marangone Stream. However, the overlap between the high natural levels of As and Mn with intense human activity in the area including the Torrevaldaliga Nord coal-fired power plant and the Port of Civitavecchia can not be excluded. Moreover, the distribution pattern and pollution level of Hg in surface sediments confirm the extension of the anomaly of concentrations of Hg in the coastal area of northern Latium, with the northern sector influenced by the contributions of the Fiora and Mignone Rivers and the southern sector influenced by the contributions of minor basins.

The distribution of trace metals highlighted from the surface sediments analysis were confirmed by the analysis of trace metals in soft tissues of specimens of *Paracentrotus Lividus*. In particular, the measured levels of As in *P. Lividus* tissues showed a strong correspondence with the As values in marine sediments and confirm the presence of the hotspots. In addition, Pb values detected in *P. lividus* tissues highlighted the clear influence of urban pollution in the studied coastal area.

The temporal assessment of trace metal concentrations in coastal sediments showed the sedimentary accumulation rates and pollution status during the last 60 years. Trace metal values do not show considerable variations attributable to the existing industrial activities during the considered time span. The comparison with the numerical thresholds ERL-ERM and TEL-PEL certifies a condition of no relevant toxicity of the samples in the sedimentary layers. However, the values of Hg detected in surface sediment analysis exceeded the ERM value in several sampling stations.

The absence of significant variations of trace metal concentrations in coastal sediments does not necessarily imply the absence of influence of industrial activities that succeeded over the years in this coastal area. The absence of significant variations in trace metal concentrations can be due to the preponderant influence of mining activities that have occurred in the territories of the hydrographic basins of the study area. The effects of mining activities and the natural distinctive geochemical nature of the territory make difficult to detect any other enrichment of trace metals attributable to the influence of recent human activities of different types compared to the mining activities in the considered time span.

The results of this study highlight the need to deeply assess the current status of the territories in which mines and mine-waste deposits are located in order to verify the state of abandonment and to plan actions that could have a retaining effect on the enrichment degree detected in the marine environment in light of the geochemical nature of the territory and the presence of anomalies in the studied area.

## **8. Future perspectives**

The assessment of the pollution degree and potential toxicity of chemical elements associated with marine sediments is a relatively understudied issue in the coastal marine platform of the northern Latium.

The results obtained during this PhD study contribute to increase knowledge about the distribution and the degree of toxicity of trace metals related to the marine sediments in order to lay a solid foundation for future studies concerning the propagation of chemical pollutant species along the marine food chains in the studied area.

From a quali-quantitative point of view, the presence of natural geochemical anomalies of As, Mn and Hg in the study area was confirmed. These anomalies are due to the geochemical province of the Monte Amiata district and the Cerite - Tolfetano complex.

In light of the results obtained, it would be appropriate to focus future analysis to the qualitative and quantitative assessment of the influence of past mining activities carried out in the territories of the hydrographic basins of the study area. These investigations would be useful in order to trace the local pre-mining geochemical background values.

The informations acquired would lead to a better qualitative and quantitative assessment of the contribution of recent human activities to the degree of enrichment and potential toxicity of marine sediments in the area.

Moreover, the study of the spatial and temporal distribution of more chemical species (e.g. PAHs, PCBs) in marine sediments in relation to the existing human activities in the study area would be particularly helpful for a better discrimination of the weight of each potential pollutant source throughout the marine coastal platform of northern Latium.

## **Comprehensive literature references**

Adamo P, Arienzo M, Imperato M, Naimo D, Nardi G, Stanzione D (2005). Distribution and partition of heavy metals in surface and sub-surface sediments of Naples city port. *Chemosphere* 61, 800–809.

Ahmed, Farid E (1991). Seafood Safety Committee on Evaluation of the Safety of Fishery Products. National Academy, Washington, D.C.

Alebic-Juretic A (2011). Polycyclic aromatic hydrocarbons in marine sediments from the Rijeka Bay area, Northern Adriatic, Croatia, 1998–2006. *Mar Poll Bull* 62(4), 863-869.

Alyazichi Y, Jones B, McLean E (2015). Spatial and temporal distribution and pollution assessment of trace metals in marine sediments in Oyster Bay, NSW, Australia. *Bull Environ Contamin Toxicol* 94, 52-57.

Ambrosetti P, Carboni MG, Conti MA, Costantini A, Esu D, Gandin A, Girotti O, Lazzarotto A, Mazzanti R, Nicosia U, Parisi G, Sandrelli F (1978). Evoluzione paleogeografica e tettonica nei bacini Tosco-Umbro-Laziali nel Pliocene e nel Pleistocene inferiore. *Mem Soc Geo It* 19, 573-580.

Ambrosetti P, Bartolini C, Bosi C (1981). L'evoluzione geologica e morfologica quaternaria dell'area adiacente la bassa valle del Fiume Fiora. *Geogr Fisic Dinam Quat* 4, 104-143.

Angelucci A, Borelli GB, Burrigato F, Tortora P (1979). Risultati preliminari delle indagini “placers” nel tratto di piattaforma continentale compreso tra Torre Valdaliga ed il promontorio dell'Argentario. *Atti del Convegno Scientifico Oceanografia e Fondi*

Marini (Roma, CNR) 1-13, 5-7.

Anselmi B, Brondi A, Ferretti O, Rabottino L (1976). Studio mineralogico e sedimentologico della costa compresa fra Ansedonia e la foce del Fiume Mignone. Soc It Min Petr Rendiconti 32, 311-348.

Anselmi B, Benvegnù F, Brondi A, Ferretti O (1979). Studi sui parametri geologici rilevanti ai fini della determinazione della contaminazione ambientale del territorio nazionale. Comitato Nazionale Energia Nucleare, RT/PROT (79) 14, 1-9.

Appleby PG, Oldfield F (1978). The calculation of  $^{210}\text{Pb}$  dates assuming a constant rate of supply of unsupported  $^{210}\text{Pb}$  to the sediment. Catena 5, 1-8.

Aureli D, Contardi A, Giaccio B, Modesti M, Palombo MR, Rozzi R, Sposato A, Trucco F (2012). Straight-Tusked Elephants in the Middle Pleistocene of northern Latium: Preliminary report on the Ficoncella site (Tarquinia, central Italy). Quat Int 255, 29-35.

Baldi F, Bargagli R (1982). Chemical leaching and specific surface area measurements of marine sediments in the evaluation of mercury contamination near cinnabar deposits. Mar Env Res 6, 69-82.

Baldi F, Bargagli R (1984). Mercury pollution in marine sediments near a chlor-alkali plant: distribution and availability of the metal. Sci Total Environ 39, 15-26.

Baldi F, D'Amato ML (1986). Mercury pollution in marine sediment cores near cinnabar deposits and a chlor.alkali plant. Sci Total Environ 57, 111-120.

Balls PW, Hull S, Miller BS, Pirie JM, Proctor W (1997). Trace metal in Scottish estuarine and coastal sediments. Mar Pollut Bull 34, 42 – 50.

Bargagli R, Barghigiani C, Maserti BE (1986). Mercury in vegetation of the Mount Amiata area (Italy). *Chemosphere* 15, 1035–42.

Barghigiani C, Ferrara R, Seritti A, Petrosino A, Masoni A, Morelli E (1981). Determination of Reactive, Total and Particulate Mercury in the Coastal Waters of Tuscany (Italy) by Atomic Fluorescence Spectrometry. *Proc Ves Journbes Etud Pollut C.I.E.S.M.* 1980, 127- 130.

Barghigiani C, Bauleo R (1992). Mining area environmental mercury assessment using *Abies alba*. *Bull Environ Contam Toxicol* 49, 31-36.

Barghigiani C, Ristori T (1994). Mercury levels in agricultural products of Mt. Amiata (Tuscany, Italy). *Arch Environ Contam Toxicol* 26, 329-334.

Barghigiani C, Ristori T (1995). The distribution of mercury in a Mediterranean area. In: C.J. Watras and J.W. Huckabee (Eds), *Mercury Pollution: Integration and Synthesis*. Lewis Publisher, Boca Raton. pp. 41.

Barghigiani C, Ristori T, Lopez-Arenas J (1996). Mercury in marine sediment from contaminated area of the northern Tyrrhenian Sea: <20  $\mu$ m grain-size fraction and total sample analysis. *Sci Total Environ* 192, 63–73.

Bastami KD, Bagheri H, Kheirabadi V, Zaferani GG, Teymori MB, Hamzehpoor A, Soltani F, Haghparast S, Harami SRM, Ghorghani NF, Ganji S (2014). Distribution and ecological risk assessment of heavy metals in surface sediments along southeast coast of the Caspian Sea. *Mar Poll Bull* 81, 262-267.

Bayed, A., Quiniou, F., Benrha, A., Guillou, M., 2005. The *Paracentrotus lividus* populations from the northern Moroccan Atlantic coast: growth, reproduction and health

condition. J. Mar. Biol. Assoc. UK 85, 999–1007.

Berriolo G, Sirito G (1985). Studio Generale sul regime delle spiagge laziali e delle isole pontine. Italia, Savona: Studio Volta, Regione Lazio: 97-99.

Beyer WN, Meador JP (Eds.) (2011). Environmental contaminants in biota: interpreting tissue concentrations. CRC Press.

Blais JM, Rosen MR, Smol JP (2015). Using natural archives to track sources and long-term trends of pollution: an introduction. In Environmental Contaminants (pp. 1-3). Springer Netherlands.

Bosi C, Palieri L, Sposato A (1990). Guida all'escursione sui terrazzi e linee di costa del litorale del Lazio settentrionale. AIQUA, CNR, Centro di studio per la Geologia Tecnica, Roma, pp. 1E25.

Boudreau BP (1997) Diagenetic models and their implementation: modeling transport and reactions in aquatic sediments. Springer, Berlin

Brondi A, Di Maio A, Marcelli M (2008). Principi logici per il monitoraggio dell'ambiente costiero. Geologia dell'Ambiente 2, 19-35.

Buccolieri A, Buccolieri G, Cardellicchio N, Dell'Atti A, Di Leo A, Maci A (2006). Heavy metals in marine sediments of Taranto Gulf (Ionian Sea, Southern Italy). Mar Chem 99, 227–235.

Burdige DJ (2006). Geochemistry of marine sediments. Princeton University Press, Princeton.

Callender E (2003). Heavy metals in the environment-historical trends. *Treatise on geochemistry* 9, 612.

Camargo JA (2002). Contribution of Spanish–American silver mines (1570–1820) to the present high mercury concentrations in the global environment: a review. *Chemosphere* 48, 51–57.

Carboni MG, Matteucci R, Tortora P (1980). La piattaforma costiera dell’alto Lazio: dalla foce del fiume Marta a Torre Sant’Agostino. *Atti Soc Tosc Sci Nat Mem* 87, 193–230.

Chaudhari PR, Gupta R, Gajghate DG, Wate SR (2012). Heavy metal pollution of ambient air in Nagpur City. *Environ Monit Assess* 184, 2487–2496.

Chiocci FL, La Monica GB. (1996). Elementi di oceanografia fisica e chimica, biologia e geologia marina, clima meteomarinico, dinamica dei sedimenti ed apporti continentale: analisi sismostratigrafica della piattaforma continentale. In: *Il Mare del Lazio*. Regione Lazio, Roma, Italia: Tip. Borgia: 40-61.

Conato V, Dai Pra G (1980). Livelli marini pleistocenici e neotettonica fra Civitavecchia e Tarquinia (Italia Centrale). *Geo Rom* 19, 181-194.

Coteur G, Danis B, Fowler SW, Teysié JL, Dubois P, Warnau M (2001). Effects of PCB’s on reactive oxygen species (ROS) production by the immune cells of *Paracentrotus lividus* (Echinodermata). *Mar Pollut Bull* 42, 667–672.

Chaudhari PR, Gupta R, Gajghate DG, Wate SR (2012). Heavy metal pollution of ambient air in Nagpur City. *Env Mon Ass* 184, 2487–2496.

Chengxin F, Yuxin Z, Zhijun J (2002). Characteristics of the Pollution of Heavy Metals in the Sediments of Yilihe River, Taihu Basin. *J Lake Sci* 14, 235-241.

Croudace IW, Williams-Thorpe O (1988). A low dilution, wavelength-dispersive x-ray fluorescence procedure for the analysis of archaeological rock artefacts. *Archaeometry* 30(2), 227–236.

Daskalakis KD, O'Connor TP (1995). Normalization and elemental sediment contamination in the coastal United States. *Environ Sci Technol* 29(2), 470– 7.

De Rita D, Fabbri M, Mazzini I, Paccara P, Sposato A, Trigari A (2002). Volcanoclastic sedimentation in coastal environment: the interplay between volcanism and Quaternary sea level change (Central Italy). *Quat Int* 95-96, 141-154.

Deudero S, Box A, March D, Valencia JM, Grau AM, Tintora J, et al. (2007). Temporal trends in benthic invertebrate species from the Balearic Islands. Western Mediterranean. *J Mar Pollut* 54, 1545–1558.

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

Di Leonardo R, Mazzola A, Tramati CD, Vaccaro A, Vizzini S (2014). Highly contaminated areas as sources of pollution for adjoining ecosystems: The case of Augusta Bay (Central Mediterranean). *Mar Poll Bull* 89, 417 – 426.

Din TB (1992). Use of aluminum to normalize heavy metal data from estuarine and coastal sediments of straits of Melaka. *Mar Poll Bull* 24, 484–491.

Fazzini P, Gelmini R, Mantovani MP, Pellegrini M (1972). Geologia dei Monti della Tolfa (Lazio settentrionale; province di Viterbo e Roma). Mem Soc Geo It 11, 65-144.

Ferrara R, Ceccarini C, Lanzillotta E, Gaørdfeldt K, Sommar J, Horvat M, Logar M, Fajon V, Kotnik J (2003). Profiles of dissolved gaseous mercury concentration in the Mediterranean seawater. Atmos Environ 37 (S1), S85–S92.

Florida Department of Environmental Protection, 1994. Approaches to the assessment of sediment quality in Florida coastal waters: development and evaluation of sediment quality assessment guidelines, prepared for Office of Water Policy, Tallahassee, FL, by MacDonald Environmental Sciences, Ltd., Ladysmith, British Columbia, Canada.

Forstner U, Wittman GTW (1984). Metal Pollution in Aquatic Environment. Berlin: Springer-Verlag.

Gao XL, Li PM (2012). Concentration and fractionation of trace metals in surface sediments of intertidal Bohai Bay, China. Mar Poll Bull 64, 1529–1536.

Gao X, Chen C-T.A (2012). Heavy metal pollution status in surface sediments of the coastal Bohai Bay. Wat Res 46, 1901–1911.

Goldberg ED (1963). Geochronology with  $^{210}\text{Pb}$ . Radioactive dating, 121-131. Vienna: IAEA.

Goodsite ME, Plane JMC, Skov H (2004). A theoretical study of the oxidation of  $\text{Hg}^0$  to  $\text{HgBr}_2$  in the troposphere. Environ Sci Technol 38, 1772–1786.

Ghrefat HA, Abu-Rukah Y, Rosen MA (2011). Application of geoaccumulation index and enrichment factor for assessing metal contamination in the sediments of Kafrain

Dam, Jordan. *Env Mon Ass* 178, 95–109.

Giesy JP, Hoke RA (1990). Freshwater sediment quality criteria: toxicity bioassessment. In: Baudo, R. (Ed.), *Sediments: Chemistry and Toxicity of Inplace Pollutants*. Lewis publishers, Chelseae, p. 391.

Guo, Weihua Liu, Xianbin Liu, Zhanguang, Li, Guofeng (2010). Pollution and potential ecological risk evaluation of heavy metals in the sediments around Dongjiang Harbor, Tianjin. *Procedia Env Sci* 2, 729–736.

Hakanson L (1980). Ecological risk index for aquatic pollution control. A sedimentological approach. *Wat Res* 14, 975–1001.

Hammerschmidt CR, Fitzgerald WF (2004). Geochemical controls on the production and distribution of methylmercury in near-shore marine sediments. *Environ Sci Technol* 38, 1487–1495.

Haykiri-Acma H, Yaman S, Ozbek N, Kucukbayrak S (2011). Mobilization of some trace elements from ashes of Turkish lignites in rain water. *Fuel* 90, 3447–55.

Henke K (2009). *Arsenic: Environmental Chemistry. Health Threats and Waste Treatment*. John Wiley & Sons Ltd, p. 164.

Horowitz AJ (1991). *A Primer on Sediment-Trace Element Chemistry*, 2nd Edition. Lewis Publishers.Inc., Chelsea MI. p. 136.

Horvat M, Kotnik J, Logar M, Fajon V, Zvonaric T, Pirrone N (2003). Speciation of mercury in surface and deep-sea waters in the Mediterranean Sea. *Atmos Environ* 37 (S1), S93–S108.

Huang KM, Lin S (2003). Consequences and implication of heavy metal spatial variations in sediments of the Keelung River drainage basin, Taiwan. *Chemosphere* 53, 1113–1121.

Jiang X, Teng A, Xu W, Liu X (2014). Distribution and pollution assessment of heavy metals in surface sediments in the Yellow Sea. *Mar Poll Bull* 83, 366-75.

Klaminder J, Appleby P, Crook P, Renberg I (2012) Post-deposition diffusion of  $^{137}\text{Cs}$  in lake sediment: implications for radiocaesium dating. *Sedimentology* 59, 2259–2267.

Koide M, Soutar A, Goldberg D (1972). Marine geochronology with  $^{210}\text{Pb}$ . *Earth Planet Sci Lett* 14, 442-446.

Kreidie N, Armiento G, Cibir G, Cinque G, Crovato C, Nardi E, Pacifico R, Cremisini C, Mottana A (2011). An integrated geochemical and mineralogical approach for the evaluation of arsenic mobility in mining soils. *J Soils Sed* 11, 37-52.

Kruschke JK (2013). Bayesian estimation supersedes the t test. *J Exp Psychol [Gen]* 142 (2), 573–603.

La Monica, G. B. & Raffi R. (1996). Morfologia e sedimentologia della spiaggia e della piattaforma continentale interna. In: *Il Mare del Lazio. Regione Lazio Assessorato Opere e Reti di Servizi e Mobilità*. Roma, Italia: Università degli Studi La Sapienza: 62-105.

Lee CL, Fang MD, Hsieh MT (1998). Characterization and distribution of metals in surficial sediments in southwestern Taiwan. *Mar Poll Bull* 36, 464–471.

Leoni L, Sartori F (1996). Heavy Metals and Arsenic in Sediments from the Continental

Shelf of the Northern Tyrrhenian/Eastern Ligurian Seas. Mar Environ Res 41, 73 – 98.

Ligero RA, Ramos-Lerate I, Barrera M, Casas-Ruiz M (2001). Relationships between sea-bed radionuclide activities and some sedimentological variables. J Env Rad 57, 7–19.

Long ER, Morgan LG (1990). The potential for biological effects of sediment-sorbed contaminants tested in the National Status and Trends Program. NOAA Technical Memorandum NOS OMA 52. NOAA Office of Oceanography and Marine Assessment, Seattle, WA: 220.

Long ER, MacDonald DD, Smith SL, Calder FD (1995). Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Env Manag 19, 81–97.

Long ER, Ingersoll CG, MacDonald DD (2005). Calculation and uses of mean sediment quality guideline quotients: a critical review. Environ. Sci. Technol. 40, 1726–1736.

Loring DH (1990). Lithium—a new approach for the granulometric normalization of trace metal data. Mar Chem 29, 155– 68.

Loring DH (1991). Normalization of heavy-metal data from estuarine and coastal sediments. J Mar Sci 48, 101– 15.

Lozano J, Galera J, Lopez S, Turon X, Palacin C, Morera G (1995). Biological cycles and recruitment of *Paracentrotus lividus* (Echinodermata: Echinoidea) in two contrasting habitats. Mar Ecol Prog Ser 122, 179–191.

Liu C, Xu J, Liu C, Zhang P, Dai M (2009). Heavy Metals in the Surface Sediments in

Lanzhou Reach of Yellow River, China. *Bull Environ Contamin Toxicol* 82, 26–30.

Maffucci F, Caurant F, Bustamante P, Bentivegna F (2005). Trace element (Cd, Cu, Hg, Se, Zn) accumulation and tissue distribution in loggerhead turtles (*Caretta caretta*) from the western Mediterranean Sea (southern Italy). *Chemosphere* 58, 535–542.

Matschullat J, Ottenstein R, Reimann C (2000) Geochemical background—can we calculate it? *Environ Geol* 39(9), 990–1000.

McMurtry GM, Wiltshire JC, Kauahikaua JP (1995). Heavy metal anomalies in coastal sediments of Oahu, Hawaii. *Pac Sci* 49, 452–70.

Mil-Homens M, Costa AM, Fonseca S, Trancoso MA, Lopes C, Serrano R, Sousa R (2013). Natural heavy metal and metalloid concentrations in sediments of the Minho River estuary (Portugal): baseline values for environmental studies. *Environ monit assess* 185(7), 5937–5950.

Mirlean N, Lamed ST, Nikora V, Tavares Kuñter, V (2005). Mercury in lakes and lake fishes on a conservation-industry gradient in Brazil. *Chemosphere* 60, 226–236.

Molino C (2013). Marine antifouling in harbour environments: ecotoxicity and role of some trace metals in two case studies. Department of Biological and Ecological Sciences, Master of Science in Conservation of Nature Specialising in Marine Environment. (Graduation thesis), Tuscia University, Viterbo.

Morillo J, Usero J, Gracia I (2004). Heavy metal distribution in marine sediments from the southwest coast of Spain. *Chemosphere* 55, 431–442.

Muhua F, Jiangping L, Long Y, Li Jianjun L (2003). Ecological Risk Evaluation of

Heavy Metals of Marine Sediment in Liaodong Bays Shallow Waters. *Mar Sci* 27, 52-56.

Müller G (1969). Index of geo-accumulation in sediments of the Rhine River. *Geojournal* 2, 108–118.

Muñoz-Barbosa A, Gutiérrez-Galindo EA, Daesslé LW, Orozco-Borbón MV, Segovia-Zavala JA (2012). Relationship between metal enrichments and a biological adverse effects index in sediments from Todos Santos Bay, northwest coast of Baja California, México. *Mar Pollut Bull* 64, 405–409.

Nascetti G, Onofri S, Zucconi L, Mosesso P, Munzi S, Ripa C, Ferrari C, Angeletti D, Scialanca F, Pepe G, Buonadonna P (2011a and 2012b). Monitoring activities for the environmental impact assessment of Torrevaldaliga Nord coal fired power plant. (Azioni di monitoraggio ambientale per la valutazione dell’impatto dovuto alla riconversione a carbone della Centrale Enel di Civitavecchia Torvaldaliga Nord). Annual Reports of the Civitavecchia Environmental Observatory.

National Entity for Electricity (ENEL) (2014). Impianto termoelettrico Torrevaldaliga Nord. Dichiarazione Ambientale.  
[https://www.enel.it/itit/documents/azienda/ambiente/dichiarazioni\\_ambientali/Dichiarazione\\_Ambientale\\_Aggiornamento\\_2014.pdf](https://www.enel.it/itit/documents/azienda/ambiente/dichiarazioni_ambientali/Dichiarazione_Ambientale_Aggiornamento_2014.pdf)

Nelson CH, Pierce DE, Leong KW, Wang FFH (1975). Mercury distribution in ancient and modern sediment of northeastern Bering Sea. *Mar Geol* 18, 91–104.

Noli A, De Girolamo P, Sammarco P (1996). Parametri meteomarini e dinamica costiera: oceanografia e chimica, biologia e geologia marina, clima meteomarinico, dinamica dei sedimenti e apporti continentali. In: *Il Mare del Lazio*. Ass. Opere e reti di servizi e

mobilità, Regione Lazio, Roma, Italia: Università degli Studi di La Sapienza.

Nriagu JO, Pacyna JM (1988). Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature* 333, 134 – 139.

Nriagu JO (1989). A global assessment of the natural sources of atmosphere trace metals. *Nature* 338, 47–49.

Nriagu JO (1990). Global metal pollution. *Environment* 32, 7–33.

Orlando E (1985). Heavy metals marine pollution assessment through the use of biological indicators. (Valutazione dell'inquinamento marino da metalli pesanti tramite l'uso di indicatori biologici). *Oebalia* XI, 93–100.

Papadopoulou C, Kanias GD, Kassinati EM (1976). Stable elements of radioecological importance in certain echinoderm species. *Mar Pollut Bull* 7, 143–144.

Piazzolla D, Scanu S, Frattarelli FM, Mancini E, Tiralongo F, Brundo MV, Tibullo D, Pecoraro R, Copat C, Ferrante M, Marcelli M (2015). Trace-Metal Enrichment and Pollution in Coastal Sediments in the Northern Tyrrhenian Sea, Italy. *Arch Environ Contam Toxicol* 69 (4), 470-481

Pinsino A, Della Torre C, Sammarini V, Bonaventura R, Amato E, Matranga V (2008). Sea urchin coelomocytes as a novel cellular biosensor of environmental stress: a field study in the Tremiti Islands Marine Protected Area, southern Adriatic Sea, Italy. *Cell Bio Toxicol* 24, 541–552.

Pyle DM, Mather TA (2003). The importance of volcanic emissions for the global atmospheric mercury cycle. *Atmos Environ* 37, 5115–5124.

Rainbow RS (1995). Biomonitoring of heavy metal availability in the marine environment. *Mar Pollut Bull* 31, 183–192.

Ravichandran M, Baskaran M, Santschi PH, Bianchi T (1995). History of trace metal pollution in Sabine-Neches Estuary, Beaumont, Texas. *Env Sci Tech* 29, 1495–1503.

Reimann C, Garrett RG (2005). Geochemical background—concept and reality. *Sci total environ* 350(1), 12-27.

Ren J, Shang Z, Tao L, Wang X (2015). Multivariate analysis and heavy metals pollution evaluation in Yellow River surface sediments. *Polish Journal of Environmental Studies*, 24(3).

Rimondi V, Gray JE, Costagliola P, Vaselli O, Pierfranco L (2012). Concentration, distribution, and translocation of mercury and methylmercury in mine-waste, sediment, soil, water, and fish collected near the Abbadia San Salvatore mercury mine, Monte Amiata district, Italy. *Sci Total Environ* 414, 318-327.

Robbins JA, Edgington DN and Kemp ALW (1978). Comparative <sup>210</sup>Pb, <sup>137</sup>Cs, and pollen geochronologies of sediments from Lakes Ontario and Erie. *Quat Res* 10, 256–278.

Rodríguez JA, Nanos N, Grau JM, Gil L, LópezArias M (2008). Multiscale analysis of heavy metal contents in Spanish agricultural topsoils. *Chemosphere* 70, 1085–1096. doi:10.1016/j.chemosphere.2007.07.056, 2008.

Rubio B, Nombela MA, Vilas F (2000). Geochemistry of major and trace elements in sediments of the Ria de Vigo (NW Spain): an assessment of metal pollution. *Mar Poll*

Bull 40, 968–980.

Sakan SM, Djordjevic DS, Manojlovic DD, Polic PS (2009). Assessment of heavy metal pollutants accumulation in the Tisza river sediments. J Env Manag 90, 3382–3390.

Salomons W, Förstner U (1984). Metals in hydrocycle. Springer-Verlag, New-York Berlin Heidelberg, p 349.

Salvo A, Potorti AG, Cicero N, Bruno M, Lo Turco V, Di Bella G, et al. (2014). Statistical characterization of heavy metal contents in *Paracentrotus lividus* from Mediterranean Sea. Natural Product Res. 28 (10), 718–726.

Scanu S (2012). Geocronologia (210Pb) dei sedimenti recenti della piattaforma costiera del Lazio settentrionale: stima del rateo di accumulo sedimentario e distribuzione spaziale e temporale delle concentrazioni di alcuni metalli in traccia (As, Hg, Pb, Al e Zn). Viterbo, Italy: University of Tuscia. Ph.D. thesis, 9-12.

Scanu S, Paladini de Mendoza F, Piazzolla D, Marcelli M (2015a). Anthropogenic impact on river basins: temporal evolution of sediment classes and accumulation rates in the northern Tyrrhenian Sea, Italy. Oceanol Hydrobiol Stud. 44, 74-86

Scanu S, Soetebier S, Piazzolla D, Tiralongo F, Mancini E, Romano N, Marcelli M (2015b). Concentrations of As, Cd, Cr, Ni, and Pb in the echinoid *Paracentrotus lividus* on the coast of Civitavecchia, northern Tyrrhenian Sea, Italy. Regional Studies in Marine Science 1, 7 – 17.

Scanu S, Piazzolla D, Manfredi Frattarelli F, Mancini E, Tiralongo F, Brundo MV, Tibullo D, Pecoraro R, Copat C, Ferrante M, Marcelli M (2016). Mercury Enrichment in Sediments of the Coastal Area of Northern Latium, Italy. Bull Environ Contam

Toxicol 96(4), DOI 10.1007/s00128-016-1776-9.

Selin NE, Jacob DJ, Yantosca RM, Strode S, Jaegle L, Jaegle L, Sunderland EM (2008). Global 3-D land-ocean atmosphere model for mercury: present-day versus preindustrial cycles and anthropogenic enrichment factors for deposition. Glob Biogeochem Cycle 22 GB2011.

Selvaraj K, Mohan RV, Piotr S (2004). Evaluation of Metal Contamination in Coastal Sediments of the Bay of Bengal, India: Geochemical and Statistical Approaches. Mar Poll Bull 49, 174-185.

Shafie NA, Aris AZ, Zakaria MP, Haris H, Lim WY, Isa NM (2013). Application of geoaccumulation index and enrichment factors on the assessment of heavy metal pollution in the sediments. J Env Sci 48, 182-190.

Sheppard CRC, Bellamy DJ (1974). Pollution of the Mediterranean around Naples. Mar Pollut Bull 5 (3), 42–44.

Song Y, Choi MS, Lee JY, Jang DJ (2014). Regional background concentrations of heavy metals (Cr, Co, Ni, Cu, Zn, Pb) in coastal sediments of the South Sea of Korea. Sci Total Environ 482–483, 80–91.

Soualili D, Dubois P, Gosselin P, Pernet P, Guillou M (2008). Assessment of seawater pollution by heavy metals in the neighbourhood of Algiers: use of the sea urchin, *Paracentrotus lividus*, as a bioindicator. ICES J Mar Sci 65, 132–139.

Spadoni M, Voltaggio M, Cavarretta G (2005). Recognition of areas of anomalous concentration of potentially hazardous elements by means of a subcatchment-based discriminant analysis of stream sediments. J Geoch Explor 87, 83–91.

Spagnoli F, Dinelli E, Giordano P, Marcaccio M, Zaffagnini F, Frascari F (2014). Sedimentological, biogeochemical and mineralogical facies of Northern and Central Western Adriatic Sea. *J Marine Syst* 139, 183-203.

Spencer KL, MacLeod CL (2002). Distribution and partitioning of heavy metals in estuarine sediment cores and implications for the use of sediment quality standards. *Hydrol. Earth Syst Sci* 6, 989–998.

Storelli MM, Storelli A, Marcotrigiano GO (2001). Heavy metals in the aquatic environment of the Southern Adriatic Sea, Italy: macroalgae, sediments and benthic species. *Environ. Int.* 26 (7–8), 505–509.

Suresh G, Ramasamy V, Meenakshisundaram V, Venkatachalapathy R, Ponnusamy V (2011). Influence of mineralogical and heavy metal composition on natural radionuclide contents in the river sediments. *Appl Radiat Isot* 69, 1466–1474.

Suresh G, Sutharsan P, Ramasamy V, Venkatachalapathy R (2012). Assessment of spatial distribution and potential ecological risk of the heavy metals in relation to granulometric contents of Veeranam lake sediments, India. *Ecotox Environ Safety* 84, 117-124.

Tang Q, Liu G, Zhou C, Sun R, (2013). Distribution of trace elements in feed coal and combustion residues from two coal-fired power plants at Huainan, Anhui, China. *Fuel* 107, 315-322.

Thibaud Y, Alzieu C, Heral M, Feuillet M (1982). Influences des peintures antisalissures a base d'organostanniques sur la calcification de la coquille de l'huitre *Crassostrea gigas*. *Revue des Travaux de l'Institut des Pêches Maritimes* 45, 101–116.

Tam NFY, Yao MWY (1998). Normalization and heavy metal contamination in mangrove sediments. *Sci Total Environ* 216, 33–9.

Tomas F, Álvarez-Cascos D, Turon X, Romero J (2006). Differential element assimilation by sea urchins *Paracentrotus lividus* in seagrass beds: implications for trophic interactions. *Mar Ecol Prog Ser* 306, 125–131.

Tortora P (1989a). I fondali antistanti la costa di Montalto di Castro (alto Lazio): caratteristiche ed evoluzione tardo-quadernaria. *Il Quadernario* 2, 175-187.

Tortora P (1989b). La sedimentazione olocenica nella piattaforma continentale interna tra il Promontorio di Monte Argentario e la Foce del Fiume Mignone (Tirreno centrale). *Giornale di Geologia* 51, 93-117.

Turekian KK, Wedepohl DH (1961). Distribution of the elements in some major units of the earth's crust. *Bull Geo Soc America* 72, 175-192.

Vald'es J, Vargas G, Sifeddine A, Ortlieb L, Guinez M (2005). Distribution and enrichment evaluation of heavy metals in Mejillones Bay (23S), Northern Chile: geochemical and statistical approach. *Mar Poll Bull* 50, 1558–1568.

Varol M (2011). Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques. *J Hazard Mat* 195, 355-364.

Warnau M, Ledent G, Temara A, Bouquegneau JM, Jangouxatc M, Dubois P (1995a). Heavy metals in *Posidonia oceanica* and *Paracentrotus lividus* from seagrass beds of the north-western Mediterranean. *Sci Total Environ* 171, 95–99.

Warnau M, Ledent G, Temara A, Bouquegneau JM, Jangoux M, Dubois P (1995b). Experimental Cd contamination of the echinoid *Paracentrotus lividus*: influence of exposure mode and distribution of the metal in the organism. Mar Ecol Prog Ser 116, 117–124.

Warnau M, Biondo R, Temara A, Bouquegneau JM, Jangoux M, Dubois P (1998). Distribution of heavy metals in the echinoid *Paracentrotus lividus* from the Mediterranean *Posidonia oceanica* ecosystem: seasonal and geographical variations. J Sea Res 39, 267–280.

Windom HL, Smith RG Jr, Rawlinson C (1989). Particulate trace metal composition and flux across the south eastern US continental shelf. Mar Chem 27, 283–297.

Windom HL, Schropp SJ, Calder FD, Ryan JD, Smith RG, Burney LC, Lewis FG, Rawlinson CH (1989). Natural trace metal concentrations in estuarine and coastal marine sediments of the southern United States. Environ Sci Technol 23(3), 314–20.

Veena B, Radhakrishnan CK, Chacko J (1997). Heavy metal induced biochemical effects in an estuarine teleost. Indian J Mar Sci 26, 74–78.

Woitke P, Wellmitz J, Helm D, Kube P, Lepom P, Litherat P (2003). Analysis and assessment of heavy metal pollution in suspended solids and sediments of the river Danube. Chemosphere 51, 633–642.

Xu G, Liu J, Pei S, Hu G, Kong X (2016). Sources and geochemical background of potentially toxic metals in surface sediments from the Zhejiang coastal mud area of the East China Sea. J Geochem Explor 168, 26–35.

Yuan F, Depew R, Soltis-Muth C (2014). Ecosystem regime change inferred from the

distribution of trace metals in Lake Erie sediments. Scientific reports, 4.

Yudovich YE, Ketris MP (2005). Arsenic in coal: a review. Inter J Coal Geo 61, 141–196.

Zhan S, Peng S, Liu C, Chang Q, Xu J (2010). Spatial and temporal variations of heavy metals in surface sediments in Bohai Bay, North China. Bull Environ Contamin Toxicol 84, 482–487.

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

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