

# Environmental Science and Pollution Research

## NATURAL vs ANTHROPOGENIC COMPONENTS IN SEDIMENTS FROM THE PO RIVER DELTA COASTAL LAGOONS (NE ITALY)

--Manuscript Draft--

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<b>Additional Information:</b>	
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# NATURAL vs ANTHROPOGENIC COMPONENTS IN SEDIMENTS FROM THE PO RIVER DELTA COASTAL LAGOONS (NE ITALY)

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## Abstract

The Sacca di Goro and Sacca di Scardovari are two coastal lagoons of the Po River delta facing the northern Adriatic Sea. They are sensitive ecosystems both from the naturalistic and socio-economic point of view, since they are included in a natural park and are high productivity shellfish sites. Bottom sediments from the two lagoons have been analysed for their textural and geochemical (major and trace elements by XRF) composition in order to identify natural backgrounds and anthropogenic inputs. OC, N, and  $\delta^{13}\text{C}_{\text{OC}}$  data have been also carried out by EA-IRMS to highlight the association of heavy metals with inorganic or organic sedimentary components. Results show that abundances of siderophile (Cr, Ni, Co) heavy metals in samples from the two lagoons are generally in the range of those recorded in alluvial sediments from the neighbours, and are associated with the finest (clayey) fraction. Among chalcophile heavy metals Pb and Zn display significant enrichments relative to the local geochemical backgrounds suggesting anthropogenic sources. They appear to be preferentially associated with the sedimentary organic matter that, according to the isotopic composition, is mainly formed by the incorporation of different proportions of macroalgae and macrophytes that have a significant bioaccumulation capacity. Taking into consideration that the ~~presence and bioaccumulation of macroalgae and macrophytes~~ extent of the algal biomass is sensitive to anthropogenic pressure and climatic changes, the trace element budget of sediments from these lagoons has to be monitored in the future, also to assess the impact of heavy metals on shellfish production.

**Keywords:** northern Adriatic lagoons, sediment geochemistry, heavy metals, carbon stable isotopes, organic matter

## Introduction

Deltaic and coastal lagoons are influenced by the interaction between fresh and marine waters and their sediments, and are highly complex systems regulated by an interplay between riverine inflow and tidal currents. They are characterised by multiple physico-chemical and biological processes favoring inorganic and organic sedimentation and bio-accumulation (Khan et al., 2014). In this framework, heavy metals although vital to biota, are potentially toxic when concentrations exceed critical thresholds. The topic has been recently reviewed by Migani et al. (2015) and Borghesi et al. (2016) that provided a detailed geochemical characterisation of surface sediments in the northern Adriatic wetlands around the Po river delta (Fig 1a). Unfortunately, two significant coastal lagoons from the same area such as the Sacca di Goro and the Sacca di Scardovari have not been

investigated, in spite of their importance for the shellfish production (Munari et al., 2009; 2013; Corbau et al., 2016). In this light, the present contribution aims to provide an updated snapshot of the textural and geochemical features of the sediments from the Sacca di Goro and the Sacca di Scardovari (Fig. 1b), in order to implement the knowledge of these important ecosystems. In addition, the paper also reports carbon and nitrogen concentrations and carbon isotopes that are useful tracers for the quantitative and qualitative characterisation of the sedimentary organic matter, and to evaluate its relationships with the heavy metal distribution.

## Materials and Methods

### Outlines of the study area

The Sacca di Goro is a coastal lagoon facing the Northern Adriatic Sea, which receives nutrient rich freshwater from the Po di Goro and the Po di Volano (Marchina et al., 2015; 2016b). It is nowadays the most important farming site for Manila clam (*Tapes philippinarum*) in Italy. The Manila clams were imported at the beginning of the eighties, and nowadays the shellfish activity provides extremely good socio-economic returns (Rossi, 1996). In this framework, the high nutrient input carried out by riverine inflow induces periodic eutrophication processes, reflected in extensive growth of opportunistic green macroalgae leading to summer anoxia and dystrophy (Viaroli et al., 2001). The Sacca di Scardovari is a large embayment comprised between the Po di Tolle and Po di Gnocca. The lagoon is connected to the Adriatic Sea through a wide mouth, partly obstructed by sand banks. Its northern sector receives nutrient-rich, agricultural run-offs, while the southern sector is more influenced by exchanges with seawater and hosts bivalve mollusk (clams and mussels) cultures. Even in this lagoon eutrophication causes seasonal blooms of opportunistic macroalgae in the most sheltered areas.

### Sampling

Sampling has been performed in the year 2015 for the Sacca di Goro and in 2016 for the Sacca di Scardovari, dredging the floor of the lagoon down to approximately 5 cm depth. For the Sacca di Goro, 10 samples (2 to 3 kg) have been collected at approximately equal distance along a W (sample G10)–E (sample G9) longitudinal transect starting from Punta Volano to the main Po di Goro inflow south of Gorino village (Fig. 1). For the Sacca di Scardovari three samples have been collected along a W (sample FF3)–E (sample FF1) inner transect, and two samples from the mouths connecting the lagoon with the Adriatic Sea, one located to the east (sample FF5) and one to the west (sample FF4), the latter very close to the Po di Goro outflow. Samples have been placed in polyethylene bags to be transported to the Laboratories of the Department of Physics and Earth Sciences of the University of Ferrara.

### Methods

Samples were dried in oven at  $T < 60^{\circ}\text{C}$ , separated by hand picking from shells and vegetation detritus. Particle size distribution was estimated by wet sieving and by means of a Micromeritics Sedigraph 5100 to assess the relative percentage of sand, silt and clay fractions, as proposed by

Shepard (1954). Shells of Manila clam from 4 sample locations from the Sacca di Goro and 2 locations from Sacca di Scardovari have been isolated, deprived of soft tissues and treated with hydrogen peroxide to remove tissue remnants and superficial organic films. Sediments (and shells) were powdered in agate mill and an amount of about 4 g of powder was pressed together with boric acid by hydraulic press to obtain powder pellets. A sample aliquot of 0.5–0.6 g of powder was heated for about 12 h in a furnace at 1000 °C in order to determine the Loss On Ignition (LOI). This parameter measures the concentration of volatile species contained in the sample. **The LOI determination has been also carried out at 450 °C to measure the Organic Matter (OM) content of the investigated sediments (e.g., Kennedy et al. 2010).** The Wavelength Dispersion X-Ray Fluorescence (WDXRF) analysis of the powder pellets was carried out using an ARL Advant-XP spectrometer Thermo-Scientific. Calibrations were obtained analyzing certified reference materials, and matrix correction was performed according to the method proposed by Trail and Lachance (1966). Precision and accuracy calculated by repeated analyses of international standards (matrices comparable with the studied samples; Di Giuseppe et al., 2014a) were generally better than 3% for Si, Ti, Fe, Ca and K, and 7% for Mg, Al, Mn and Na. For trace elements at concentration above 10 mg/kg the errors were generally better than 10%. In order to assure the quality of the analyses, the described WDXRF system has been involved in an intercalibration project on the analysis of soils and sediments, that confirmed the reliability of the presented results (Vittori Antisari et al., 2014). Powdered sediments were also investigated for carbon (C) and nitrogen (N) elemental and C isotopic composition using an Elementar Vario Micro Cube Elemental Analyser in line with an ISOPRIME 100 Isotopic Ratio Mass Spectrometer operating in continuous-flow mode. The detection of the distinct isotopic masses of the sample were compared to those of reference CO<sub>2</sub> gases (grade 5 purity) calibrated using a series of reference materials, in turn calibrated against IAEA international standards, such as the limestone JLs-1 (Kusaka and Nakano, 2014), the peach leaves NIST SRM1547 (Dutta et al., 2006), the Carrara Marble (calibrated at the Institute of Geoscience and Georesources of the National Council of Researches of Pisa), and the synthetic sulfanilamide provided by Isoprime Ltd. Mass peaks were recalculated as isotopic ratios by the Ion Vantage software package. Analyses were carried out setting the furnace at 950°C, a temperature that allows the extraction of both organic and inorganic compounds forming the total carbon (TC). Analyses were repeated setting the combustion temperature at 450°C for the extraction of the sole organic carbon (OC) fraction. This temperature allows the complete oxidation of organic matter, whereas calcite and dolomite, the carbonate minerals present in these type of sediments (De Lazzari et al., 2004; Bonardi et al., 2006; Di Giuseppe et al., 2014b), breakdown at higher temperature, above 650 °C (Cuthbert and Rowland, 1947; Manning et al., 2005; Pallasser et al., 2013). The elemental precision estimated by repeated standard analyses, and accuracy estimated by the comparison between reference and measured values, were in the order of 5% of the absolute measured value. Uncertainties increase for contents approaching the detection limit (0.001 wt %). Carbon isotope ratios are expressed in the standard ( $\delta$ ) notation in per mil (‰) relative to the international Vienna Pee Dee Belemnite (V-PDB) isotope standard (Gonfiantini et al., 1995). The  $\delta^{13}\text{C}$  values were characterised by an average standard deviation of  $\pm 0.1\text{‰}$  defined by repeated analyses of the above mentioned standards. Analytical uncertainties increase for low-C signals, and linearity tests indicated that the lowest measured signals are potentially affected by a slight decrease of the certified  $\delta^{13}\text{C}$  values (down to -1.5‰). Further analytical details are reported by Natali and Bianchini (2015).



## Results

Textural features of sediments from Sacca di Goro and Sacca di Scardovari are showed in Fig. 2. In general, Sacca di Goro sediments are coarser in grain size with respect to those from Sacca di Scardovari. On the basis of the Shepard's classification scheme, sediments from Sacca di Goro are mainly sands, with the exception of two silty sands (samples G1 and G7). The grain size distribution along the transect highlights a general decrease in the muddy fraction eastward, with strong local variations in the amount of fine fraction in samples G1 (40%), G3 (15%) and G7 (26%). Samples from the Sacca di Scardovari span from sands (samples FF4 and FF5), through silty sands (sample FF2) to silty clays (samples FF1 and FF3). This indicates a general growth of the fine fraction toward the inner part of the lagoon, and in particular along its levees.

The major and trace element geochemical variation of sediments from the Sacca di Goro and Sacca di Scardovari is reported in Table 1. The major element composition of sediments samples shows that they are characterised by an elevated  $\text{SiO}_2$  content, followed by  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$  suggesting the main silico-clastic nature of the sediments, with minor contribution of carbonates.  $\text{SiO}_2$  is negatively correlated with  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$  and with clay content, suggesting that the coarse fraction is mainly constituted by quartz. The positive correlations of  $\text{Al}_2\text{O}_3$  with  $\text{K}_2\text{O}$  ( $R^2 = 0.77$ ),  $\text{Fe}_2\text{O}_3$  ( $R^2 = 0.94$ ),  $\text{TiO}_2$  ( $R^2 = 0.87$ ), and in turn of all these oxides with the clay content suggest that the finer fraction is dominated by clay minerals including illite, chlorite and smectite.

Considering the geochemical distribution in sediments from the Sacca di Goro along the investigated transect, we observe a general decrease of  $\text{Al}_2\text{O}_3$  (down to 9.02 wt% in sample G8) coupled with an increase in  $\text{SiO}_2$  (up to 62.71 wt% in sample G9) eastward, in parallel with the increase of the sandy fraction. In the Sacca di Scardovari,  $\text{SiO}_2$  is low in samples from the inner part of the lagoon (down to 48.51 wt% in sample FF1) and increase seaward (up to 57.46 wt% in the sandy sample FF5), whereas  $\text{Al}_2\text{O}_3$  displays an antithetic distribution being higher (up to 13.46 wt% in sample FF1) in the inner part that is characterised by finer grain size.

On the whole, the trace element distribution displays relationships with texture and major element compositions. Most heavy metals (Ni, V, Zn, Pb, Cu) show significant correlations with clay content ( $0.60 < R^2 < 0.99$ ), indicating a major affinity with the fine fraction. Therefore, to be compared, sediments have to be plotted against  $\text{Al}_2\text{O}_3$ , which is in turn related to the abundance of clay minerals. In particular, in Fig. 3, the concentration of some siderophile (Cr, Ni, Co) and chalcophile (Zn, Pb, Cu) elements in sediments from the two lagoons have been plotted against the respective  $\text{Al}_2\text{O}_3$  content, to highlight geochemical analogies and differences. Fig. 3 also includes the composition of alluvial sediments from the easternmost Padanian plain deposited in the last millennia (Bianchini et al., 2012; Bianchini et al., 2013; Di Giuseppe et al., 2014b; 2014c) that are free of anthropogenic contribution, thus representing the "geogenic" local background. The geochemical distribution of siderophile elements (and Cu) in sediments from Sacca di Goro and Sacca di Scardovari doesn't display significant enrichments with respect to the values recorded in alluvial sediments at comparable  $\text{Al}_2\text{O}_3$  content. On the other hand, chalcophile elements, such as



Zn and Pb, display distributions characterised by significant trends of enrichment not observed in alluvial sediments. These geochemical trends, similarly observed in Sacca di Goro and Sacca di Scardovari sediments, diverge from those having geogenic origin, plausibly reflecting anthropogenic contributions. Some of these metals have been detected also in Manila clam shells farmed in the Sacca di Goro lagoon (Pb and Cu up to 4 mg/kg, V up to 9 mg/kg), indicating the possible fixation through metabolic processes, and therefore their mobility and bioavailability deserve further investigations.

The ~~total carbon~~ (TC) content displays a lower variability in sediments from the Sacca di Goro, (1.64-2.69 wt%) in comparison with that showed by those from the Sacca di Scardovari (1.72-3.31 wt). The TC isotopic composition ( $\delta^{13}\text{C}_{\text{TC}}$  ‰) of sediments from the Sacca di Goro varies from -1.3 to -5.7‰, whereas that from the Sacca di Scardovari spans over a wider range (from -0.8 to -8.6‰). A precise measurement of the sediment OC content, **indicates that it is generally lower (0.17-0.70 wt%) in the Sacca di Goro with respect to that recorded in the Sacca di Scardovari (0.13-1.55 wt%). This is in agreement with the OM content, which varies from 1.0 to 3.3 wt% in the Sacca di Goro and from 0.7 to 8.8 in the Sacca di Scardovari sediments, showing a remarkable correlation with OC ( $r^2 = 0.94$ , intercept at 0.01).** Nitrogen (N) **is also well** correlated with the OC parameter in the investigated sediments ( $r^2 = 0.96$ , intercept at 0.002), as typically associated with the organic matter (Fig 4a). The distinct OC- $\delta^{13}\text{C}_{\text{OC}}$  trends characterizing samples from the two lagoons **suggests a different nature for their organic matter (Fig. 4b). In particular, the isotopic composition of the organic fraction ( $\delta^{13}\text{C}_{\text{OC}}$ ) of the investigated sediments reveals a marked variation (from -11.2 to -20.2 ‰) in the Sacca di Goro, whereas it is more homogeneous (from -17.1 to -22.0 ‰) in the Sacca di Scardovari.**

N and OC appear scarcely correlated with siderophile heavy metals, whereas they show significant correlations with chalcophile heavy metals. **In particular, among chalcophile elements, Pb and Zn (but not Cu), are better correlated with N and OC with respect to clay content, suggesting their intimate association with the organic matter (Fig. 5).**

## Discussion

The textural and geochemical characterisation of sediments from the Sacca di Goro and Sacca di Scardovari has been carried out with the aim of identifying natural (geogenic) and anthropogenic components in complex environmental systems, such as coastal lagoons. In order to correctly identify these components, the compositions of the investigated sediments have been compared with those of alluvial sediments from the neighbours, which have been considered as the geochemical background of the area. Since heavy metals tend to accumulate in the fine fraction of sediments, their concentration have been normalised to  $\text{Al}_2\text{O}_3$  which is proportional to the clay mineral content. Textural analysis has been also used to confirm the above cited assumptions. The geochemical analysis highlights that siderophile element (Cr, Ni, V, Co) **and Cu** contents of the investigated sediments don't show significant enrichments with respect to the composition of alluvial sediments, showing similar heavy metal/ $\text{Al}_2\text{O}_3$  distributions. On the other hand, some chalcophile elements (Pb **and Zn**, ~~Cu~~) show distinct heavy metal/ $\text{Al}_2\text{O}_3$  enrichment trends with respect to those displayed by in alluvial sediments, suggesting additional inputs. Noteworthy, anomalously high concentrations of chalcophile elements have been recorded in the Sacca di Goro sediments since the nineties (Covelli et al., 2000; Dinelli et al., 2000), and more recently also in

other northern Adriatic wetlands around the Po river delta (Migani et al., 2015). The pollution in Zn in lake and lagoon sediments has been often related to boating activities, since these elements are used as biocide agents in antifouling paints (Migani et al., 2015; Boyle et al., 2016). On the other hand, Pb enrichments is possibly related to more general atmospheric emissions caused by the leaded fuel used until the beginning of this century, and/or caused by hunting, that is a widespread activity in many wetlands (e.g. Li et al., 2007; Migani et al., 2015; Romano et al., 2016). Zn and Pb show more robust correlations with N and OC with respect to those obtained with clay content (Fig. 5). This suggests that in these environments organometallic complexes plays a significant role in the selective sequestration of some heavy metals, as already proposed in the literature (Neto et al., 2000; Zourarah et al., 2007). Moreover, the heavy metal enrichment observed in the sediments of the Sacca di Goro and Sacca di Scardovari could also reflect the specific nature of the organic matter that variously recorded the distinct natural and anthropogenic contributions characterising the two lagoons.

The organic carbon in sediments from Sacca di Goro and Sacca di Scardovari shows a wide spectrum of isotopic compositions ranging from -22.0 to -11.2 ‰. This isotopic range only partially overlap with those recorded previous studies on Adriatic and the Po river prodelta sediments, which never recorded  $\delta^{13}\text{C}_{\text{OC}}$  values higher than -20 ‰ (Faganeli et al., 1987; Boldrin et al., 2005; Ogrinc et al., 2005; Tesi et al., 2006; Miserocchi et al., 2007; Tesi et al., 2007; 2008a; 2008b; 2010; 2012; 2013a; 2013b). In our view, the  $^{13}\text{C}$ -enrichment of OM from Sacca di Goro and Sacca di Scardovari sediments is related to the peculiar sedimentary environment of the investigated lagoons, which is different from those typical of riverine and marine settings. According to the  $\delta^{13}\text{C}_{\text{OC}}$  values, the organic matter of these lagoons is formed by the accumulation of allochthonous (riverine) and autochthonous (macroalgae and macrophytes) components (Fig. 6a). Macroalgae and macrophytes developed in similar environments are characterised by distinct elemental and isotopic signatures, the latter typically having high OC/N ratios and  $\delta^{13}\text{C}_{\text{OC}}$  values (up to -5‰, e.g. Kennedy et al. 2010; McPherson et al., 2015). Macroalgae and macrophytes notoriously bioaccumulate heavy metals (Haritonidis and Malea, 1999; Campanella et al., 2001; Sanchiz et al., 2001; Caliceti et al., 2002; Boubonari et al., 2008; Shams El-Din et al., 2014; Gao et al., 2015) that are subsequently incorporated in the sediments. In order to highlight the heavy metal contribution provided by these algal components to the associated sediments, the OM isotopic fingerprint has been plotted versus chalcophile element ratios reflecting anthropogenic contribution, such as Pb/Cu (Fig. 6b) and Zn/Cu. The observed trends indicate that the Pb (and Zn) anomalies are linked to the relative amount of algal component in the sedimentary OM.

## Conclusions

This work defines the geochemical backgrounds of major and trace elements, including heavy metals, in sediments from Sacca di Goro and Sacca di Scardovari coastal lagoons, which are important sites of shellfish farming. Most elements display natural (geogenic) concentrations strictly related to the geological nature of the sedimentary load delivered by the Po river inflow. For most metals we didn't detect the pollution observed in other coastal sectors of the Northern Adriatic

affected by a marked human impact (Frasconi et al., 1988; Matteucci et al., 2005; Gieskes et al., 2015). Anthropogenic contributions are limited to few chalcophile elements such as Pb and Zn, which appear to be notably enriched with respect to the local backgrounds. The Pb and Zn abundances display enrichment factors, relative to the local geochemical background, up to 3 and 5, respectively. Our comprehensive dataset provides insights on the speciation of heavy metals, indicating that **most** chalcophile elements (differently from siderophile elements **and Cu**), although associated with the finest sediment fraction, appear preferentially bonded to the organic compounds rather than to clay minerals. This is particularly evident for Pb and Zn that show higher correlations with N and OC (proxies of organic matter), rather than with clay and Al<sub>2</sub>O<sub>3</sub> contents (proxies of phyllosilicate minerals). The carbon isotope composition of sedimentary organic matter ( $\delta^{13}\text{C}_{\text{OC}}$ ) suggests that the studied sediments incorporate different proportions of allochthonous (riverine) and autochthonous (macroalgae and macrophyte) components. **The relative amount of these algal components within OM is positively correlated with proxies of anthropogenic contributions such as Zn/Cu and Pb/Cu, thus confirming their role as bioaccumulators.** Similar investigations should be reiterated in the next years to assess if **the variation in algal biomass, related to the ongoing climate change and anthropogenic pressure** (Marchina et al., 2016a; 2016b; 2017), will impact the nature of the sedimentary organic matter, and in turn the heavy metals content of these ecosystems. Future studies should evaluate the mobility and bioavailability of heavy metals in order to protect and safeguard the local shellfish productions, that could be threatened by metal accumulation (Ščančar et al., 2007; Ra et al., 2011; Yang et al., 2013).

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## Captions:

**Figure 1** – a) Geographic setting of the Po river delta area showing the location of Sacca di Goro and Sacca di Scardovari coastal lagoons (red box). b) Zoom of the study area reporting the sampling sites (gray circles).

**Figure 2** – Textural classification scheme reporting the sand-silt-clay percentages of the investigated sediments.

**Figure 3** – Siderophile (Cr, Ni, Co) and chalcophile (Zn, Pb, Cu) heavy metals (mg/kg) vs  $\text{Al}_2\text{O}_3$  (wt%) contents of sediments from Sacca di Goro and Sacca di Scardovari from this work (big symbols), and from the literature (small symbols; Covelli et al., 2000; Dinelli et al., 2000) compared with those recorded in alluvial sediments from the neighbouring (easternmost) sector of the Padanian plain (data from Bianchini et al., 2012; Bianchini et al., 2013; Di Giuseppe et al., 2014b; 2014c).

**Figure 4** – OC vs N (a) and  $\delta^{13}\text{C}_{\text{OC}}$  (b) bivariate diagrams of sediments from Sacca di Goro and Sacca di Scardovari coastal lagoons.

**Figure 5** – Pb (a) and Zn (b) distributions related to clay fraction, N and OC content in sediments from Sacca di Goro and Sacca di Scardovari coastal lagoons.

**Figure 6** – OC/N (a) and Pb/Cu (b) vs  $\delta^{13}\text{C}_{\text{OC}}$  bivariate diagrams of sediments from Sacca di Goro and Sacca di Scardovari coastal lagoons. ~~Dashed line encircles samples characterised by high fine fraction (clay+silt > 25%).~~ The composition of Po suspended solid load (shaded field, Corazzari et al., 2016; Natali and Bianchini, 2017) and ~~trends linking those of the~~ different macroalgae and macrophyte components (Komorita et al., 2014; Yamamuro and Kamiya, 2014) are reported to decipher the nature of organic matter, and to highlight the associated Pb anomaly.

**Table 1** – Textural and geochemical composition of sediments from Sacca di Goro and Sacca di Scardovari coastal lagoons. See text for sample locations and analytical details.

# NATURAL vs ANTHROPOGENIC COMPONENTS IN SEDIMENTS FROM THE PO RIVER DELTA COASTAL LAGOONS (NE ITALY)

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## Abstract

The Sacca di Goro and Sacca di Scardovari are two coastal lagoons of the Po River delta facing the northern Adriatic Sea. They are sensitive ecosystems both from the naturalistic and socio-economic point of view, since they are included in a natural park and are high productivity shellfish sites. Bottom sediments from the two lagoons have been analysed for their textural and geochemical (major and trace elements by XRF) composition in order to identify natural backgrounds and anthropogenic inputs. OC, N, and  $\delta^{13}\text{C}_{\text{OC}}$  data have been also carried out by EA-IRMS to highlight the association of heavy metals with inorganic or organic sedimentary components. Results show that abundances of siderophile (Cr, Ni, Co) heavy metals in samples from the two lagoons are generally in the range of those recorded in alluvial sediments from the neighbours, and are associated with the finest (clayey) fraction. Among chalcophile heavy metals Pb and Zn display significant enrichments relative to the local geochemical backgrounds suggesting anthropogenic sources. They appear to be preferentially associated with the sedimentary organic matter that, according to the isotopic composition, is mainly formed by the incorporation of different proportions of macroalgae and macrophytes that have a significant bioaccumulation capacity. Taking into consideration that the extent of the algal biomass is sensitive to anthropogenic pressure and climatic changes, the trace element budget of sediments from these lagoons has to be monitored in the future, also to assess the impact of heavy metals on shellfish production.

**Keywords:** northern Adriatic lagoons, sediment geochemistry, heavy metals, carbon stable isotopes, organic matter

## Introduction

Deltaic and coastal lagoons are influenced by the interaction between fresh and marine waters and their sediments, and are highly complex systems regulated by an interplay between riverine inflow and tidal currents. They are characterised by multiple physico-chemical and biological processes favoring inorganic and organic sedimentation and bio-accumulation (Khan et al., 2014). In this framework, heavy metals although vital to biota, are potentially toxic when concentrations exceed critical thresholds. The topic has been recently reviewed by Migani et al. (2015) and Borghesi et al. (2016) that provided a detailed geochemical characterisation of surface sediments in the northern Adriatic wetlands around the Po river delta (Fig 1a). Unfortunately, two significant coastal lagoons from the same area such as the Sacca di Goro and the Sacca di Scardovari have not been investigated, in spite of their importance for the shellfish production (Munari et al., 2009; 2013;

Corbau et al., 2016). In this light, the present contribution aims to provide an updated snapshot of the textural and geochemical features of the sediments from the Sacca di Goro and the Sacca di Scardovari (Fig. 1b), in order to implement the knowledge of these important ecosystems. In addition, the paper also reports carbon and nitrogen concentrations and carbon isotopes that are useful tracers for the quantitative and qualitative characterisation of the sedimentary organic matter, and to evaluate its relationships with the heavy metal distribution.

## Materials and Methods

### Outlines of the study area

The Sacca di Goro is a coastal lagoon facing the Northern Adriatic Sea, which receives nutrient rich freshwater from the Po di Goro and the Po di Volano (Marchina et al., 2015; 2016b). It is nowadays the most important farming site for Manila clam (*Tapes philippinarum*) in Italy. The Manila clams were imported at the beginning of the eighties, and nowadays the shellfish activity provides extremely good socio-economic returns (Rossi, 1996). In this framework, the high nutrient input carried out by riverine inflow induces periodic eutrophication processes, reflected in extensive growth of opportunistic green macroalgae leading to summer anoxia and dystrophy (Viaroli et al., 2001). The Sacca di Scardovari is a large embayment comprised between the Po di Tolle and Po di Gnocca. The lagoon is connected to the Adriatic Sea through a wide mouth, partly obstructed by sand banks. Its northern sector receives nutrient-rich, agricultural run-offs, while the southern sector is more influenced by exchanges with seawater and hosts bivalve mollusk (clams and mussels) cultures. Even in this lagoon eutrophication causes seasonal blooms of opportunistic macroalgae in the most sheltered areas.

### Sampling

Sampling has been performed in the year 2015 for the Sacca di Goro and in 2016 for the Sacca di Scardovari, dredging the floor of the lagoon down to approximately 5 cm depth. For the Sacca di Goro, 10 samples (2 to 3 kg) have been collected at approximately equal distance along a W (sample G10)-E (sample G9) longitudinal transect starting from Punta Volano to the main Po di Goro inflow south of Gorino village (Fig. 1). For the Sacca di Scardovari three samples have been collected along a W (sample FF3)-E (sample FF1) inner transect, and two samples from the mouths connecting the lagoon with the Adriatic Sea, one located to the east (sample FF5) and one to the west (sample FF4), the latter very close to the Po di Goro outflow. Samples have been placed in polyethylene bags to be transported to the Laboratories of the Department of Physics and Earth Sciences of the University of Ferrara.

### Methods

Samples were dried in oven at  $T < 60^{\circ}\text{C}$ , separated by hand picking from shells and vegetation detritus. Particle size distribution was estimated by wet sieving and by means of a Micromeritics Sedigraph 5100 to assess the relative percentage of sand, silt and clay fractions, as proposed by Shepard (1954). Shells of Manila clam from 4 sample locations from the Sacca di Goro and 2

locations from Sacca di Scardovari have been isolated, deprived of soft tissues and treated with hydrogen peroxide to remove tissue remnants and superficial organic films. Sediments (and shells) were powdered in agate mill and an amount of about 4 g of powder was pressed together with boric acid by hydraulic press to obtain powder pellets. A sample aliquot of 0.5–0.6 g of powder was heated for about 12 h in a furnace at 1000 °C in order to determine the Loss On Ignition (LOI). This parameter measures the concentration of volatile species contained in the sample. The LOI determination has been also carried out at 450 °C to measure the Organic Matter (OM) content of the investigated sediments (e.g., Kennedy et al. 2010). The Wavelength Dispersion X-Ray Fluorescence (WDXRF) analysis of the powder pellets was carried out using an ARL Advant-XP spectrometer Thermo-Scientific. Calibrations were obtained analyzing certified reference materials, and matrix correction was performed according to the method proposed by Trail and Lachance (1966). Precision and accuracy calculated by repeated analyses of international standards (matrices comparable with the studied samples; Di Giuseppe et al., 2014a) were generally better than 3% for Si, Ti, Fe, Ca and K, and 7% for Mg, Al, Mn and Na. For trace elements at concentration above 10 mg/kg the errors were generally better than 10%. In order to assure the quality of the analyses, the described WDXRF system has been involved in an intercalibration project on the analysis of soils and sediments, that confirmed the reliability of the presented results (Vittori Antisari et al., 2014). Powdered sediments were also investigated for carbon (C) and nitrogen (N) elemental and C isotopic composition using an Elementar Vario Micro Cube Elemental Analyser in line with an ISOPRIME 100 Isotopic Ratio Mass Spectrometer operating in continuous-flow mode. The detection of the distinct isotopic masses of the sample were compared to those of reference CO<sub>2</sub> gases (grade 5 purity) calibrated using a series of reference materials, in turn calibrated against IAEA international standards, such as the limestone JLs-1 (Kusaka and Nakano, 2014), the peach leaves NIST SRM1547 (Dutta et al., 2006), the Carrara Marble (calibrated at the Institute of Geoscience and Georesources of the National Council of Researches of Pisa), and the synthetic sulfanilamide provided by Isoprime Ltd. Mass peaks were recalculated as isotopic ratios by the Ion Vantage software package. Analyses were carried out setting the furnace at 950°C, a temperature that allows the extraction of both organic and inorganic compounds forming the total carbon (TC). Analyses were repeated setting the combustion temperature at 450°C for the extraction of the sole organic carbon (OC) fraction. This temperature allows the complete oxidation of organic matter, whereas calcite and dolomite, the carbonate minerals present in these type of sediments (De Lazzari et al., 2004; Bonardi et al., 2006; Di Giuseppe et al., 2014b), breakdown at higher temperature, above 650 °C (Cuthbert and Rowland, 1947; Manning et al., 2005; Pallasser et al., 2013). The elemental precision estimated by repeated standard analyses, and accuracy estimated by the comparison between reference and measured values, were in the order of 5% of the absolute measured value. Uncertainties increase for contents approaching the detection limit (0.001 wt %). Carbon isotope ratios are expressed in the standard ( $\delta$ ) notation in per mil (‰) relative to the international Vienna Pee Dee Belemnite (V-PDB) isotope standard (Gonfiantini et al., 1995). The  $\delta^{13}\text{C}$  values were characterised by an average standard deviation of  $\pm 0.1\text{‰}$  defined by repeated analyses of the above mentioned standards. Analytical uncertainties increase for low-C signals, and linearity tests indicated that the lowest measured signals are potentially affected by a slight decrease of the certified  $\delta^{13}\text{C}$  values (down to -1.5‰). Further analytical details are reported by Natali and Bianchini (2015).

## Results

Textural features of sediments from Sacca di Goro and Sacca di Scardovari are showed in Fig. 2. In general, Sacca di Goro sediments are coarser in grain size with respect to those from Sacca di Scardovari. On the basis of the Shepard's classification scheme, sediments from Sacca di Goro are mainly sands, with the exception of two silty sands (samples G1 and G7). The grain size distribution along the transect highlights a general decrease in the muddy fraction eastward, with strong local variations in the amount of fine fraction in samples G1 (40%), G3 (15%) and G7 (26%). Samples from the Sacca di Scardovari span from sands (samples FF4 and FF5), through silty sands (sample FF2) to silty clays (samples FF1 and FF3). This indicates a general growth of the fine fraction toward the inner part of the lagoon, and in particular along its levees.

The major and trace element geochemical variation of sediments from the Sacca di Goro and Sacca di Scardovari is reported in Table 1. The major element composition of sediments samples shows that they are characterised by an elevated  $\text{SiO}_2$  content, followed by  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$  suggesting the main silico-clastic nature of the sediments, with minor contribution of carbonates.  $\text{SiO}_2$  is negatively correlated with  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$  and with clay content, suggesting that the coarse fraction is mainly constituted by quartz. The positive correlations of  $\text{Al}_2\text{O}_3$  with  $\text{K}_2\text{O}$  ( $R^2 = 0.77$ ),  $\text{Fe}_2\text{O}_3$  ( $R^2 = 0.94$ ),  $\text{TiO}_2$  ( $R^2 = 0.87$ ), and in turn of all these oxides with the clay content suggest that the finer fraction is dominated by clay minerals including illite, chlorite and smectite.

Considering the geochemical distribution in sediments from the Sacca di Goro along the investigated transect, we observe a general decrease of  $\text{Al}_2\text{O}_3$  (down to 9.02 wt% in sample G8) coupled with an increase in  $\text{SiO}_2$  (up to 62.71 wt% in sample G9) eastward, in parallel with the increase of the sandy fraction. In the Sacca di Scardovari,  $\text{SiO}_2$  is low in samples from the inner part of the lagoon (down to 48.51 wt% in sample FF1) and increase seaward (up to 57.46 wt% in the sandy sample FF5), whereas  $\text{Al}_2\text{O}_3$  displays an antithetic distribution being higher (up to 13.46 wt% in sample FF1) in the inner part that is characterised by finer grain size.

On the whole, the trace element distribution displays relationships with texture and major element compositions. Most heavy metals (Ni, V, Zn, Pb, Cu) show significant correlations with clay content ( $0.60 < R^2 < 0.99$ ), indicating a major affinity with the fine fraction. Therefore, to be compared, sediments have to be plotted against  $\text{Al}_2\text{O}_3$ , which is in turn related to the abundance of clay minerals. In particular, in Fig. 3, the concentration of some siderophile (Cr, Ni, Co) and chalcophile (Zn, Pb, Cu) elements in sediments from the two lagoons have been plotted against the respective  $\text{Al}_2\text{O}_3$  content, to highlight geochemical analogies and differences. Fig. 3 also includes the composition of alluvial sediments from the easternmost Padanian plain deposited in the last millennia (Bianchini et al., 2012; Bianchini et al., 2013; Di Giuseppe et al., 2014b; 2014c) that are free of anthropogenic contribution, thus representing the "geogenic" local background. The geochemical distribution of siderophile elements (and Cu) in sediments from Sacca di Goro and Sacca di Scardovari doesn't display significant enrichments with respect to the values recorded in alluvial sediments at comparable  $\text{Al}_2\text{O}_3$  content. On the other hand, chalcophile elements, such as

Zn and Pb, display distributions characterised by significant trends of enrichment not observed in alluvial sediments. These geochemical trends, similarly observed in Sacca di Goro and Sacca di Scardovari sediments, diverge from those having geogenic origin, plausibly reflecting anthropogenic contributions. Some of these metals have been detected also in Manila clam shells farmed in the Sacca di Goro lagoon (Pb and Cu up to 4 mg/kg, V up to 9 mg/kg), indicating the possible fixation through metabolic processes, and therefore their mobility and bioavailability deserve further investigations.

The TC content displays a lower variability in sediments from the Sacca di Goro, (1.64-2.69 wt%) in comparison with that showed by those from the Sacca di Scardovari (1.72-3.31 wt). The TC isotopic composition ( $\delta^{13}\text{C}_{\text{TC}}$  ‰) of sediments from the Sacca di Goro varies from -1.3 to -5.7‰, whereas that from the Sacca di Scardovari spans over a wider range (from -0.8 to -8.6‰). A precise measurement of the sediment OC content, indicates that it is generally lower (0.17-0.70 wt%) in the Sacca di Goro with respect to that recorded in the Sacca di Scardovari (0.13-1.55 wt%). This is in agreement with the OM content, which varies from 1.0 to 3.3 wt% in the Sacca di Goro and from 0.7 to 8.8 in the Sacca di Scardovari sediments, showing a remarkable correlation with OC ( $r^2 = 0.94$ , intercept at 0.01). N is also well correlated with the OC parameter in the investigated sediments ( $r^2 = 0.96$ , intercept at 0.002), as typically associated with the organic matter-(Fig 4a). The distinct OC- $\delta^{13}\text{C}_{\text{OC}}$  trends characterizing samples from the two lagoons suggests a different nature for their organic matter (Fig. 4b). In particular, the isotopic composition of the organic fraction ( $\delta^{13}\text{C}_{\text{OC}}$ ) of the investigated sediments reveals a marked variation (from -11.2 to -20.2 ‰) in the Sacca di Goro, whereas it is more homogeneous (from -17.1 to -22.0 ‰) in the Sacca di Scardovari.

N and OC appear scarcely correlated with siderophile heavy metals, whereas they show significant correlations with chalcophile heavy metals. In particular, among chalcophile elements, Pb and Zn (but not Cu), are better correlated with N and OC with respect to clay content, suggesting their intimate association with the organic matter (Fig. 5).

## Discussion

The textural and geochemical characterisation of sediments from the Sacca di Goro and Sacca di Scardovari has been carried out with the aim of identifying natural (geogenic) and anthropogenic components in complex environmental systems, such as coastal lagoons. In order to correctly identify these components, the compositions of the investigated sediments have been compared with those of alluvial sediments from the neighbours, which have been considered as the geochemical background of the area. Since heavy metals tend to accumulate in the fine fraction of sediments, their concentration have been normalised to  $\text{Al}_2\text{O}_3$  which is proportional to the clay mineral content. Textural analysis has been also used to confirm the above cited assumptions. The geochemical analysis highlights that siderophile element (Cr, Ni, V, Co) and Cu contents of the investigated sediments don't show significant enrichments with respect to the composition of alluvial sediments, showing similar heavy metal/ $\text{Al}_2\text{O}_3$  distributions. On the other hand, some chalcophile elements (Pb and Zn) show distinct heavy metal/ $\text{Al}_2\text{O}_3$  enrichment trends with respect to those displayed by in alluvial sediments, suggesting additional inputs. Noteworthy, anomalously high concentrations of chalcophile elements have been recorded in the Sacca di Goro sediments since the nineties (Covelli et al., 2000; Dinelli et al., 2000), and more recently also in other northern



Adriatic wetlands around the Po river delta (Migani et al., 2015). The pollution in Zn in lake and lagoon sediments has been often related to boating activities, since this element is used as biocide agents in antifouling paints (Migani et al., 2015; Boyle et al., 2016). On the other hand, Pb enrichments is possibly related to more general atmospheric emissions caused by the leaded fuel used until the beginning of this century, and/or caused by hunting, that is a widespread activity in many wetlands (e.g. Li et al., 2007; Migani et al., 2015; Romano et al., 2016). Zn and Pb show more robust correlations with N and OC with respect to those obtained with clay content (Fig. 5). This suggests that in these environments organometallic complexes plays a significant role in the selective sequestration of some heavy metals, as already proposed in the literature (Neto et al., 2000; Zourarah et al., 2007). Moreover, the heavy metal enrichment observed in the sediments of the Sacca di Goro and Sacca di Scardovari could also reflect the specific nature of the organic matter that variously recorded the distinct natural and anthropogenic contributions characterising the two lagoons.

The organic carbon in sediments from Sacca di Goro and Sacca di Scardovari shows a wide spectrum of isotopic compositions ranging from -22.0 to -11.2 ‰. This isotopic range only partially overlap with those recorded previous studies on Adriatic and the Po river prodelta sediments, which never recorded  $\delta^{13}\text{C}_{\text{OC}}$  values higher than -20 ‰ (Faganeli et al., 1987; Boldrin et al., 2005; Ogrinc et al., 2005; Tesi et al., 2006; Miserocchi et al., 2007; Tesi et al., 2007; 2008a; 2008b; 2010; 2012; 2013a; 2013b). In our view, the  $^{13}\text{C}$ -enrichment of OM from Sacca di Goro and Sacca di Scardovari sediments is related to the peculiar sedimentary environment of the investigated lagoons, which is different from those typical of riverine and marine settings. According to the  $\delta^{13}\text{C}_{\text{OC}}$  values, the organic matter of these lagoons is formed by the accumulation of allochthonous (riverine) and autochthonous (macroalgae and macrophytes) components (Fig. 6a). Macroalgae and macrophytes developed in similar environments are characterised by distinct elemental and isotopic signatures, the latter typically having high OC/N ratios and  $\delta^{13}\text{C}_{\text{OC}}$  values (up to -5‰, e.g. Kennedy et al. 2010; McPherson et al., 2015). Macroalgae and macrophytes notoriously bioaccumulate heavy metals (Haritonidis and Malea, 1999; Campanella et al., 2001; Sanchiz et al., 2001; Caliceti et al., 2002; Boubonari et al., 2008; Shams El-Din et al., 2014; Gao et al., 2015) that are subsequently incorporated in the sediments. In order to highlight the heavy metal contribution provided by these algal components to the associated sediments, the OM isotopic fingerprint has been plotted versus chalcophile element ratios reflecting anthropogenic contribution, such as Pb/Cu (Fig. 6b) and Zn/Cu. The observed trends indicate that the Pb (and Zn) anomalies are linked to the relative amount of algal component in the sedimentary OM.

## Conclusions

This work defines the geochemical backgrounds of major and trace elements, including heavy metals, in sediments from Sacca di Goro and Sacca di Scardovari coastal lagoons, which are important sites of shellfish farming. Most elements display natural (geogenic) concentrations strictly related to the geological nature of the sedimentary load delivered by the Po river inflow. For most metals we didn't detect the pollution observed in other coastal sectors of the Northern Adriatic

1 affected by a marked human impact (Frasconi et al., 1988; Matteucci et al., 2005; Gieskes et al.,  
2 2015). Anthropogenic contributions are limited to few chalcophile elements such as Pb and Zn,  
3 which appear to be notably enriched with respect to the local backgrounds. The Pb and Zn  
4 abundances display enrichment factors, relative to the local geochemical background, up to 3 and 5,  
5 respectively. Our comprehensive dataset provides insights on the speciation of heavy metals,  
6 indicating that most chalcophile elements (differently from siderophile elements and Cu), although  
7 associated with the finest sediment fraction, appear preferentially bonded to the organic compounds  
8 rather than to clay minerals. This is particularly evident for Pb and Zn that show higher correlations  
9 with N and OC (proxies of organic matter), rather than with clay and Al<sub>2</sub>O<sub>3</sub> contents (proxies of  
10 phyllosilicate minerals). The carbon isotope composition of sedimentary organic matter ( $\delta^{13}\text{C}_{\text{OC}}$ )  
11 suggests that the studied sediments incorporate different proportions of allochthonous (riverine) and  
12 autochthonous (macroalgae and macrophyte) components. The relative amount of these algal  
13 components within OM is positively correlated with proxies of anthropogenic contributions such as  
14 Zn/Cu and Pb/Cu, thus confirming their role as bioaccumulators. Similar investigations should be  
15 reiterated in the next years to assess if the variation in algal biomass, related to the ongoing climate  
16 change and anthropogenic pressure (Marchina et al., 2016a; 2016b; 2017), will impact the nature of  
17 the sedimentary organic matter, and in turn the heavy metals content of these ecosystems. Future  
18 studies should evaluate the mobility and bioavailability of heavy metals in order to protect and  
19 safeguard the local shellfish productions, that could be threatened by metal accumulation (Ščančar  
20 et al., 2007; Ra et al., 2011; Yang et al., 2013).

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## 37 Captions:

38 **Figure 1** – a) Geographic setting of the Po river delta area showing the location of Sacca di Goro  
39 and Sacca di Scardovari coastal lagoons (red box). b) Zoom of the study area reporting the sampling  
40 sites (gray circles).

41 **Figure 2** – Textural classification scheme reporting the sand-silt-clay percentages of the  
42 investigated sediments.

43 **Figure 3** – Siderophile (Cr, Ni, Co) and chalcophile (Zn, Pb, Cu) heavy metals (mg/kg) vs  $\text{Al}_2\text{O}_3$   
44 (wt%) contents of sediments from Sacca di Goro and Sacca di Scardovari from this work (big  
45 symbols), and from the literature (small symbols; Covelli et al., 2000; Dinelli et al., 2000) compared  
46 with those recorded in alluvial sediments from the neighbouring (easternmost) sector of the  
47 Padanian plain (data from Bianchini et al., 2012; Bianchini et al., 2013; Di Giuseppe et al., 2014b;  
48 2014c).

49 **Figure 4** – OC vs N (a) and  $\delta^{13}\text{C}_{\text{OC}}$  (b) bivariate diagrams of sediments from Sacca di Goro and  
50 Sacca di Scardovari coastal lagoons.



**Figure 5** – Pb (a) and Zn (b) distributions related to clay fraction, N and OC content in sediments from Sacca di Goro and Sacca di Scardovari coastal lagoons.

**Figure 6** – OC/N (a) and Pb/Cu (b) *vs*  $\delta^{13}\text{C}_{\text{OC}}$  bivariate diagrams of sediments from Sacca di Goro and Sacca di Scardovari coastal lagoons. The composition of Po suspended solid load (Corazzari et al., 2016; Natali and Bianchini, 2017) and those of the different macroalgae and macrophyte components (Komorita et al., 2014; Yamamuro and Kamiya, 2014) are reported to decipher the nature of organic matter, and to highlight the associated Pb anomaly.

**Table 1** – Textural and geochemical composition of sediments from Sacca di Goro and Sacca di Scardovari coastal lagoons. See text for sample locations and analytical details.

Figure 1

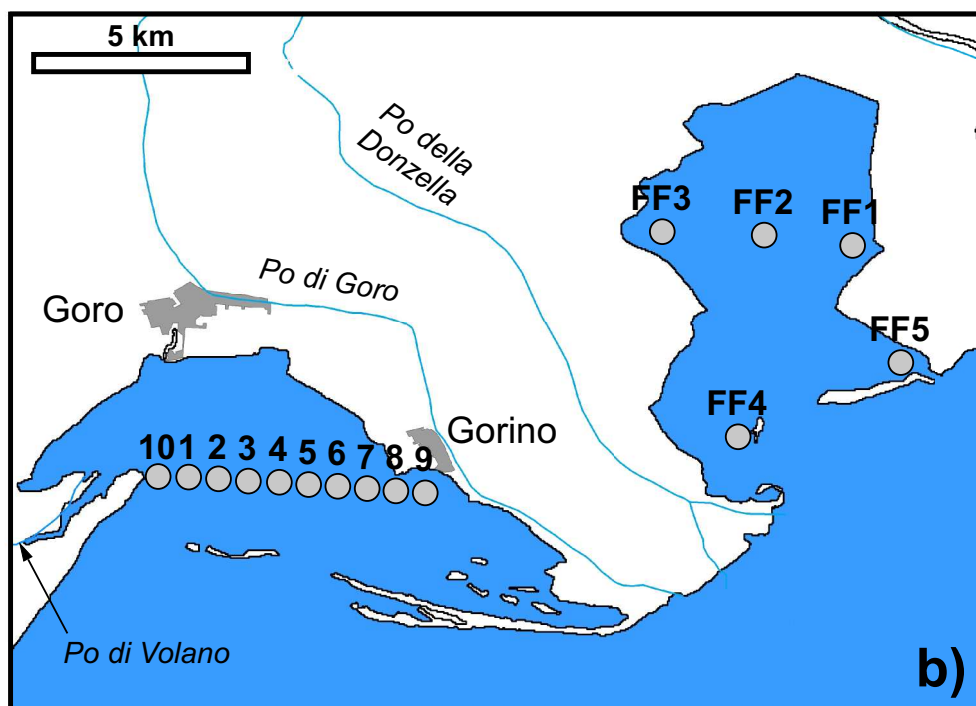
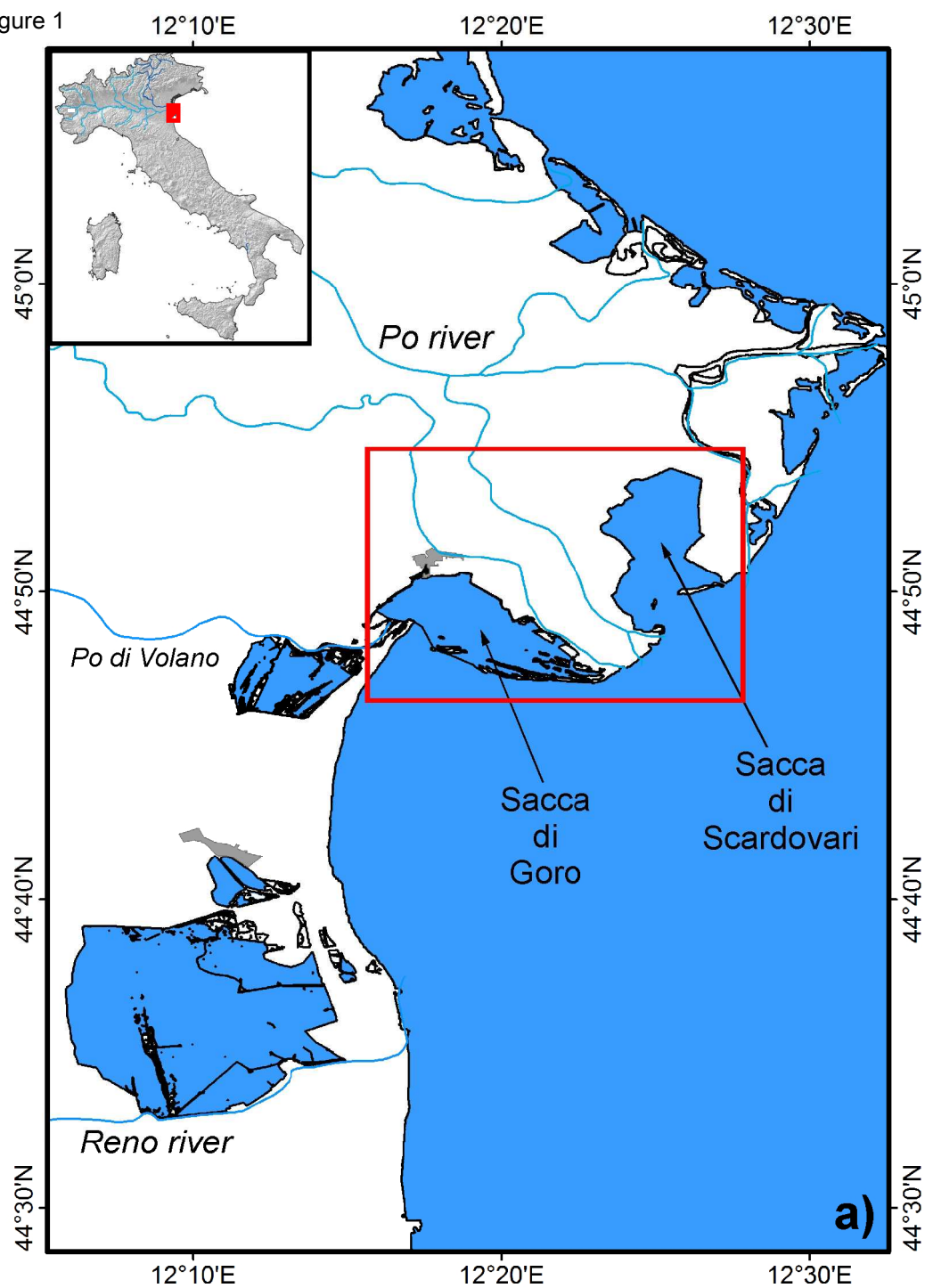


Figure 2

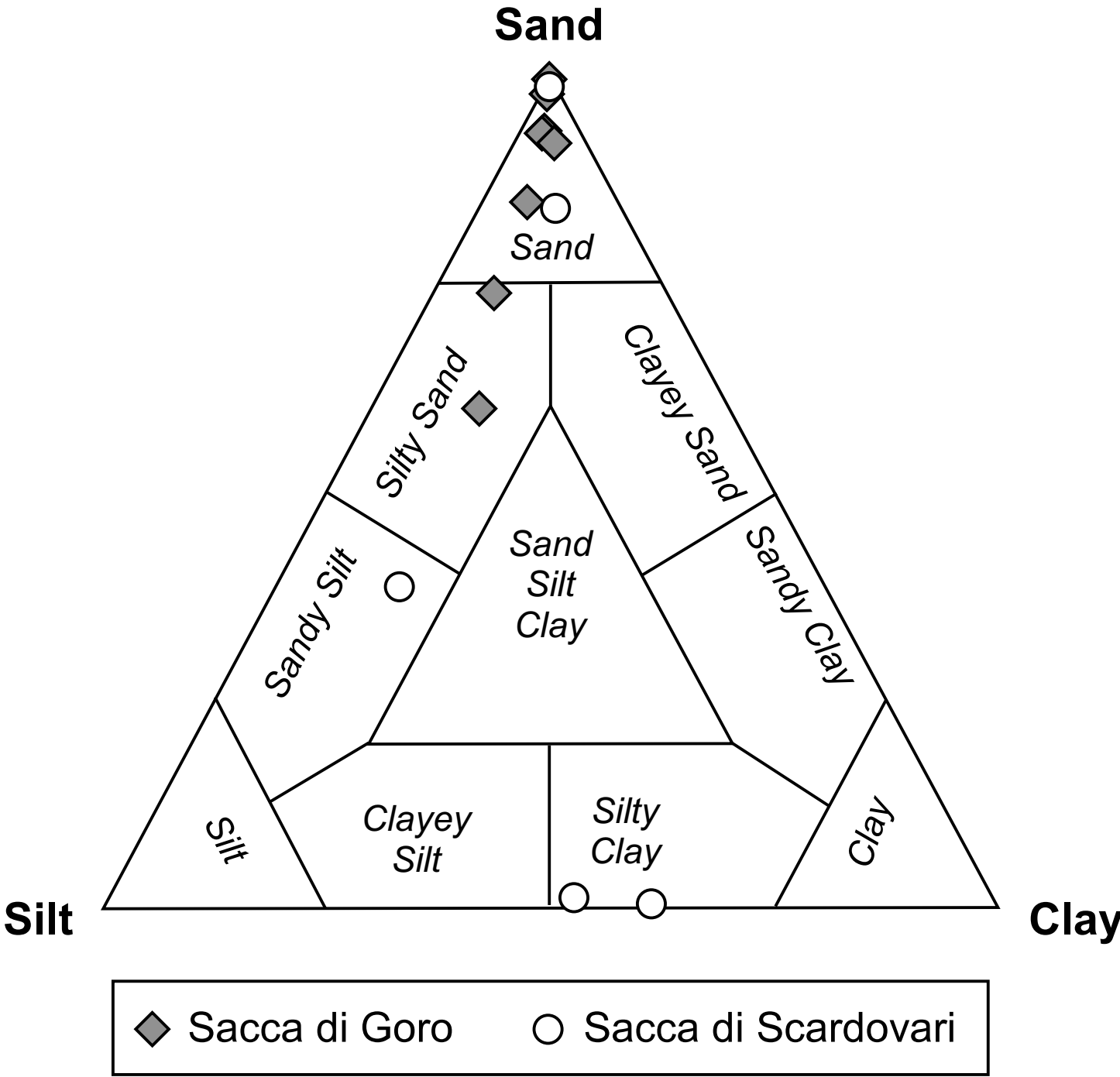


Figure 3

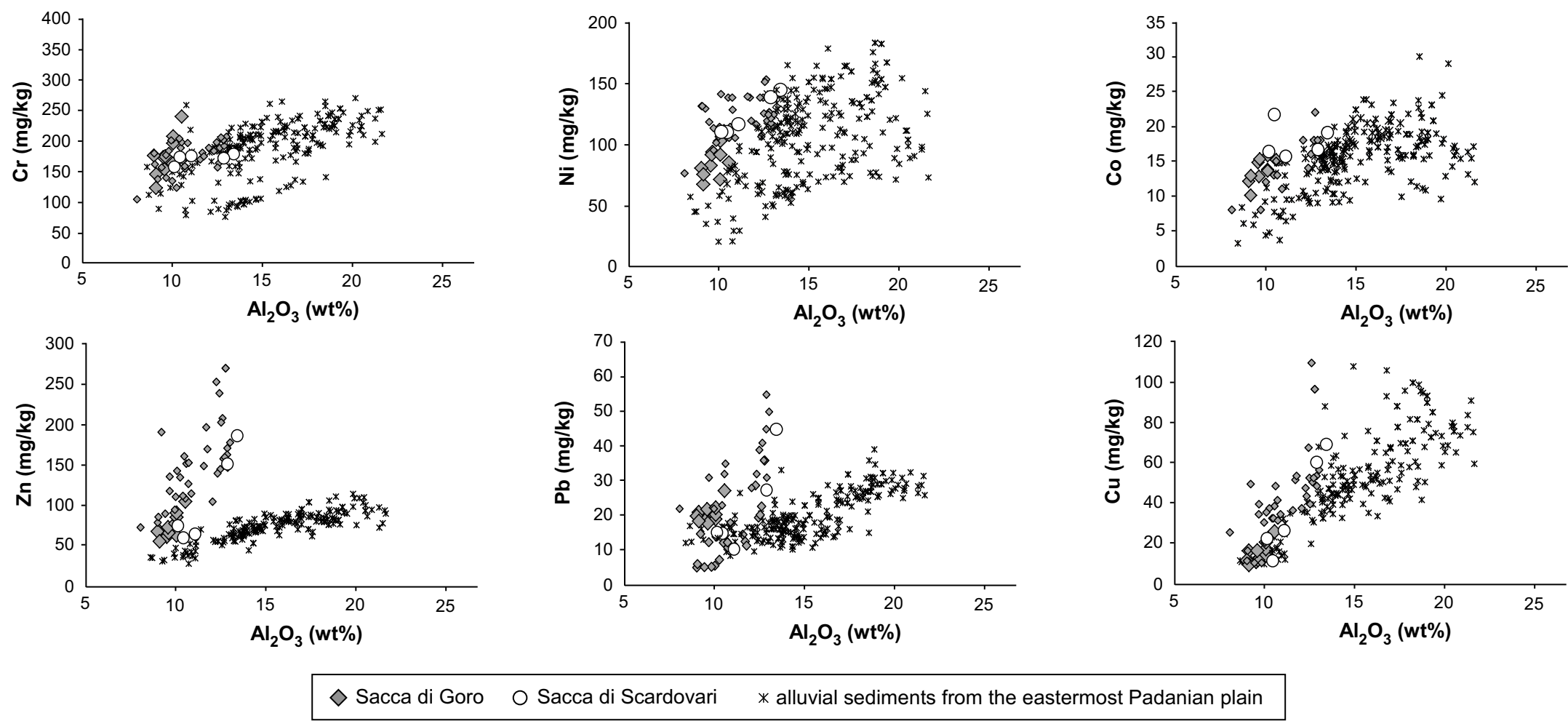


Figure 4

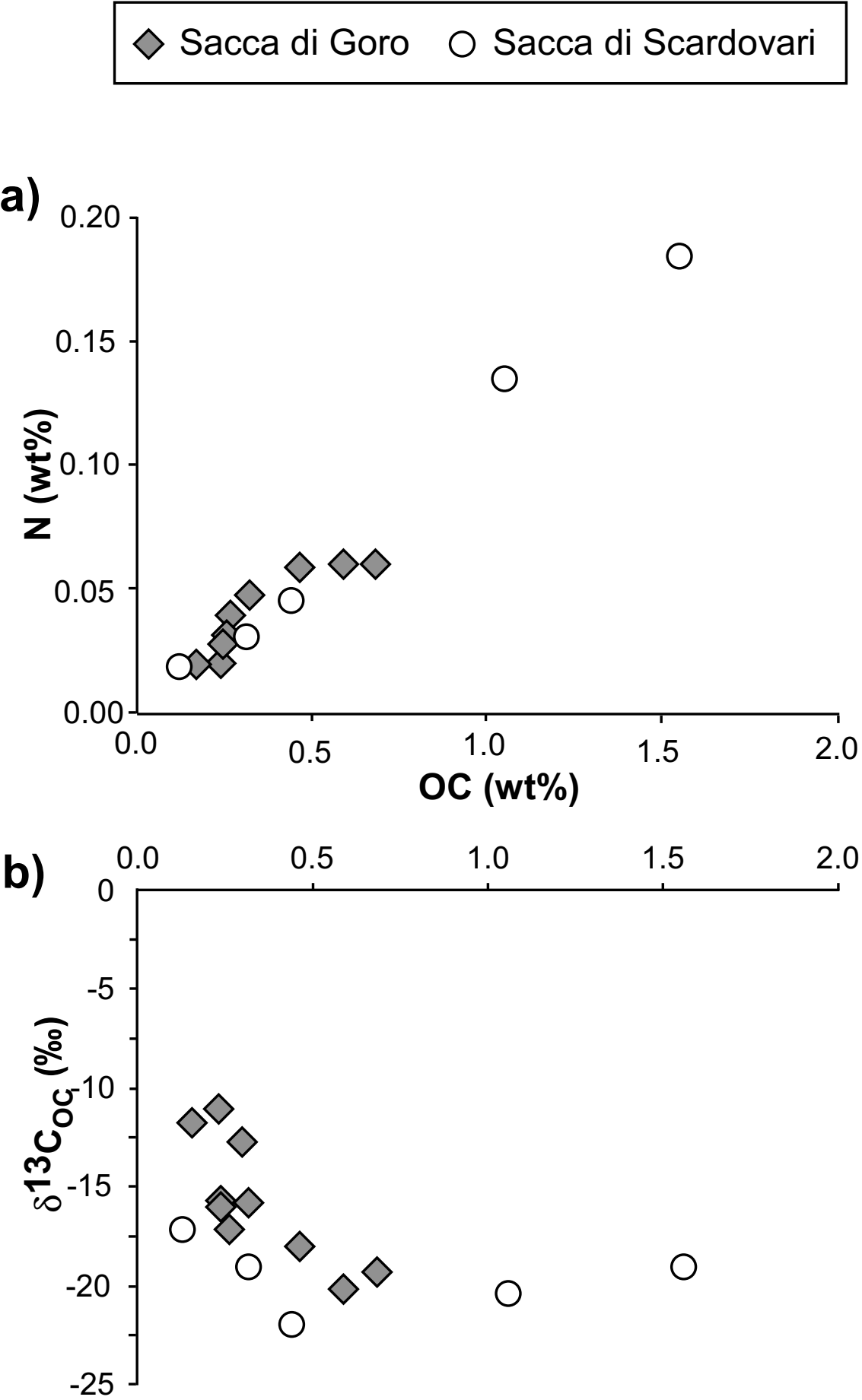
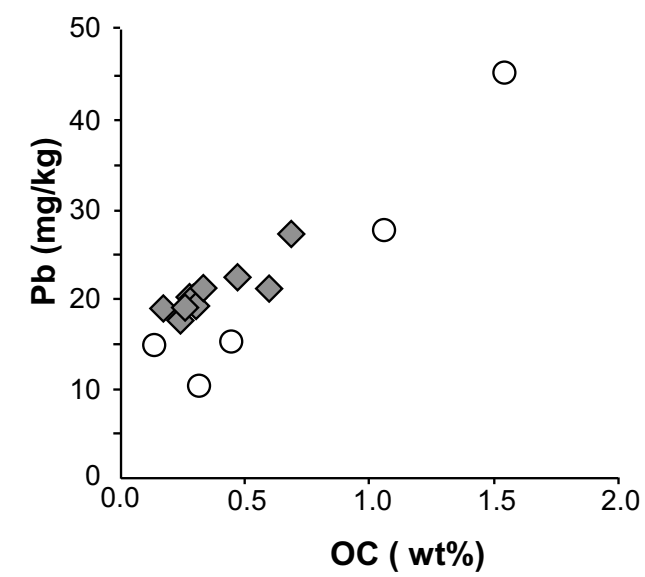
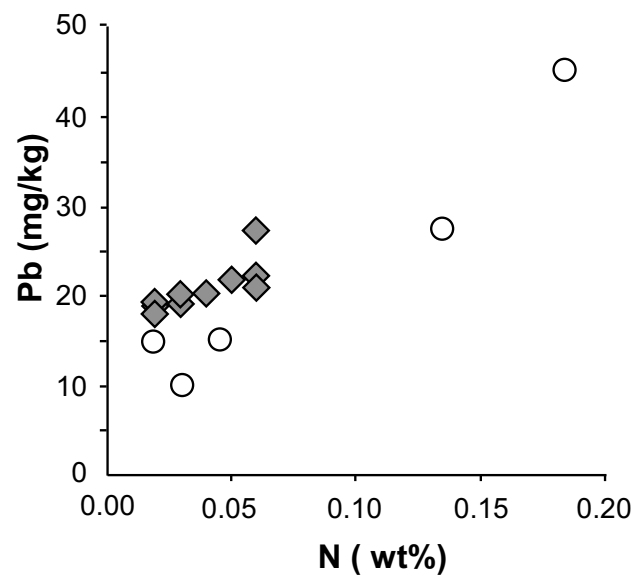
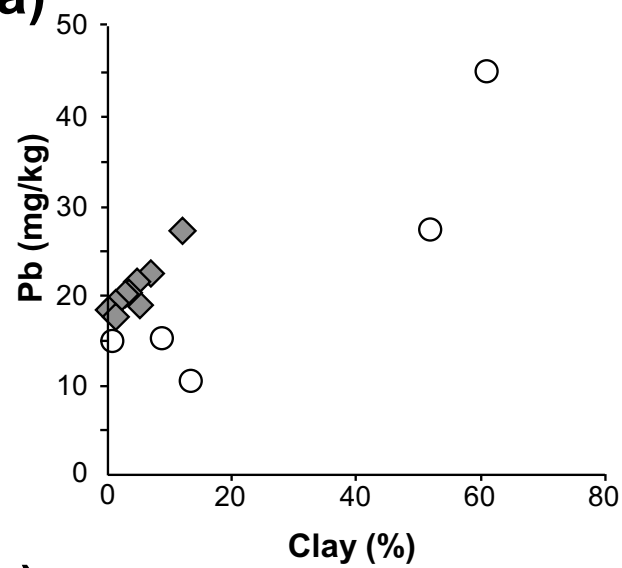


Figure 5

**a)**



**b)**

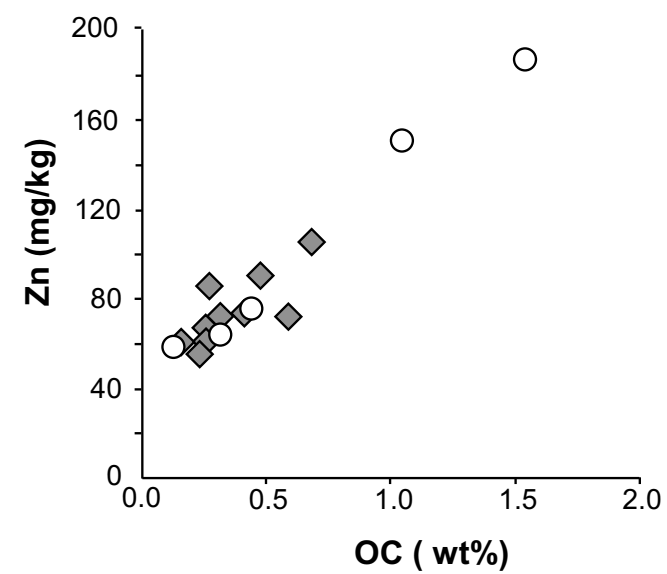
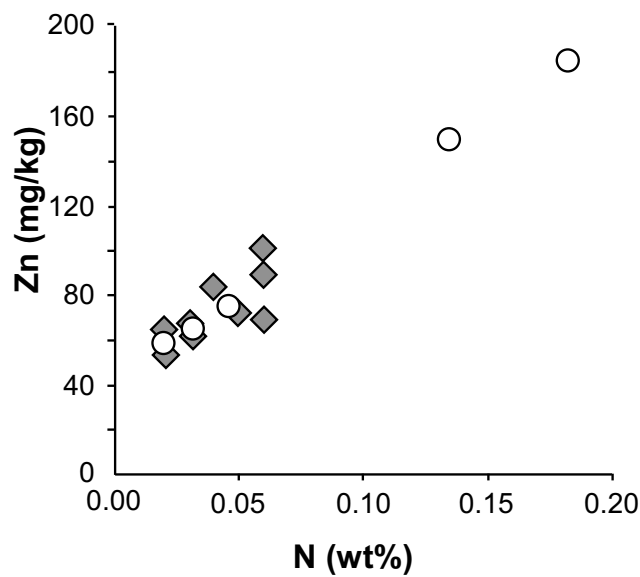
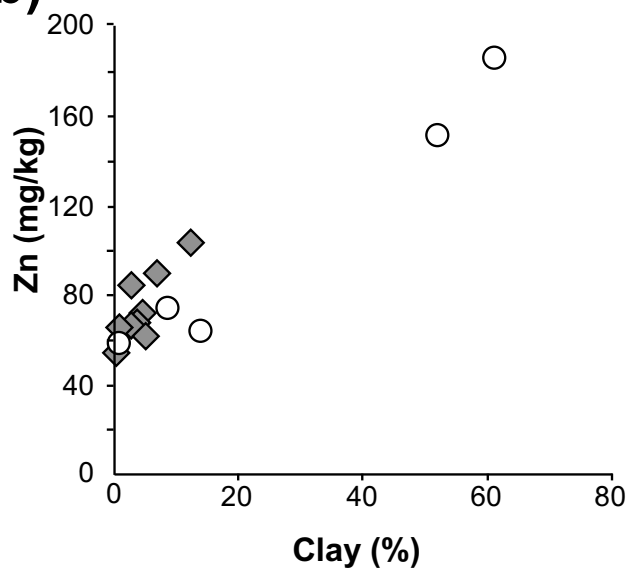


Figure 6

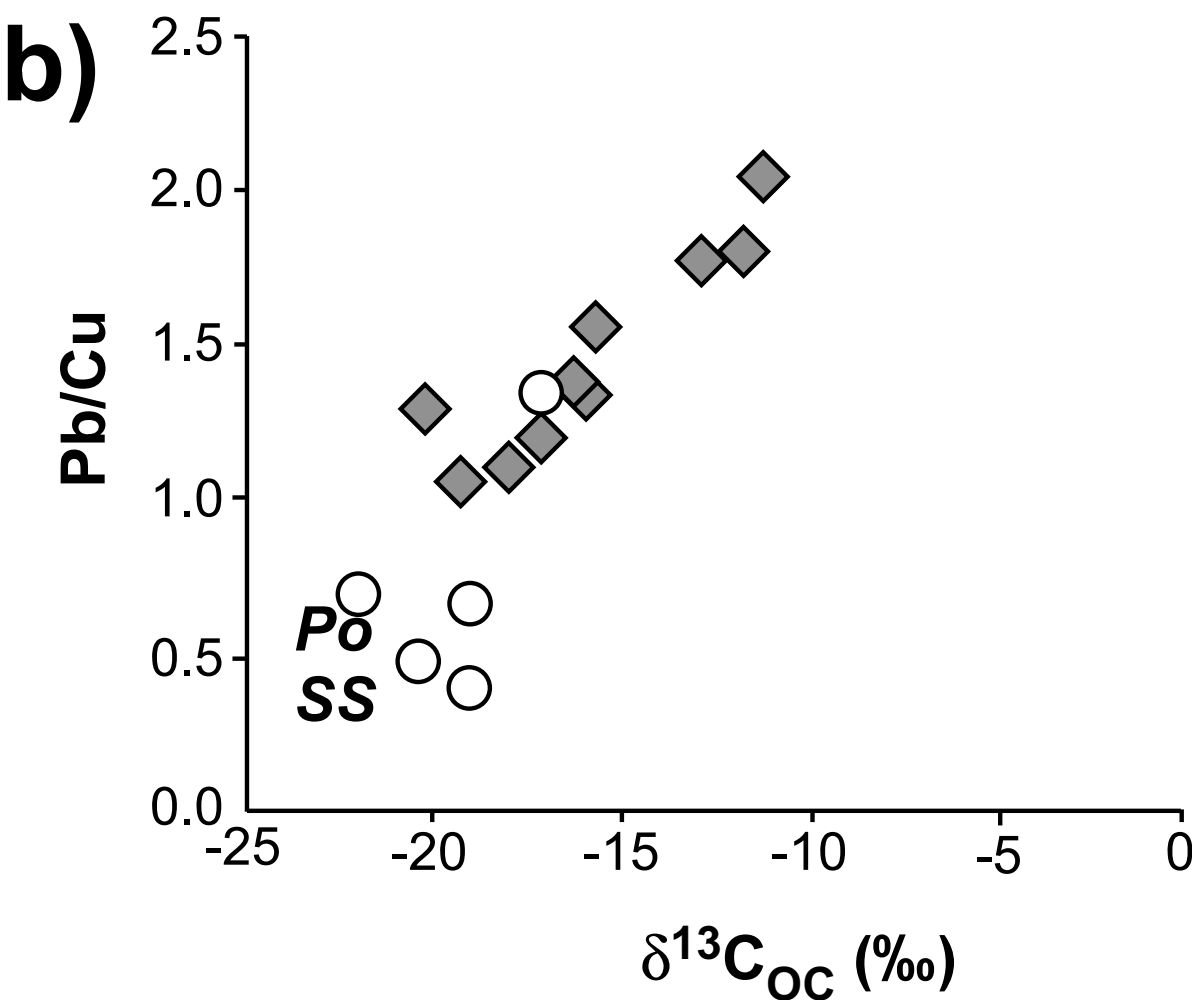
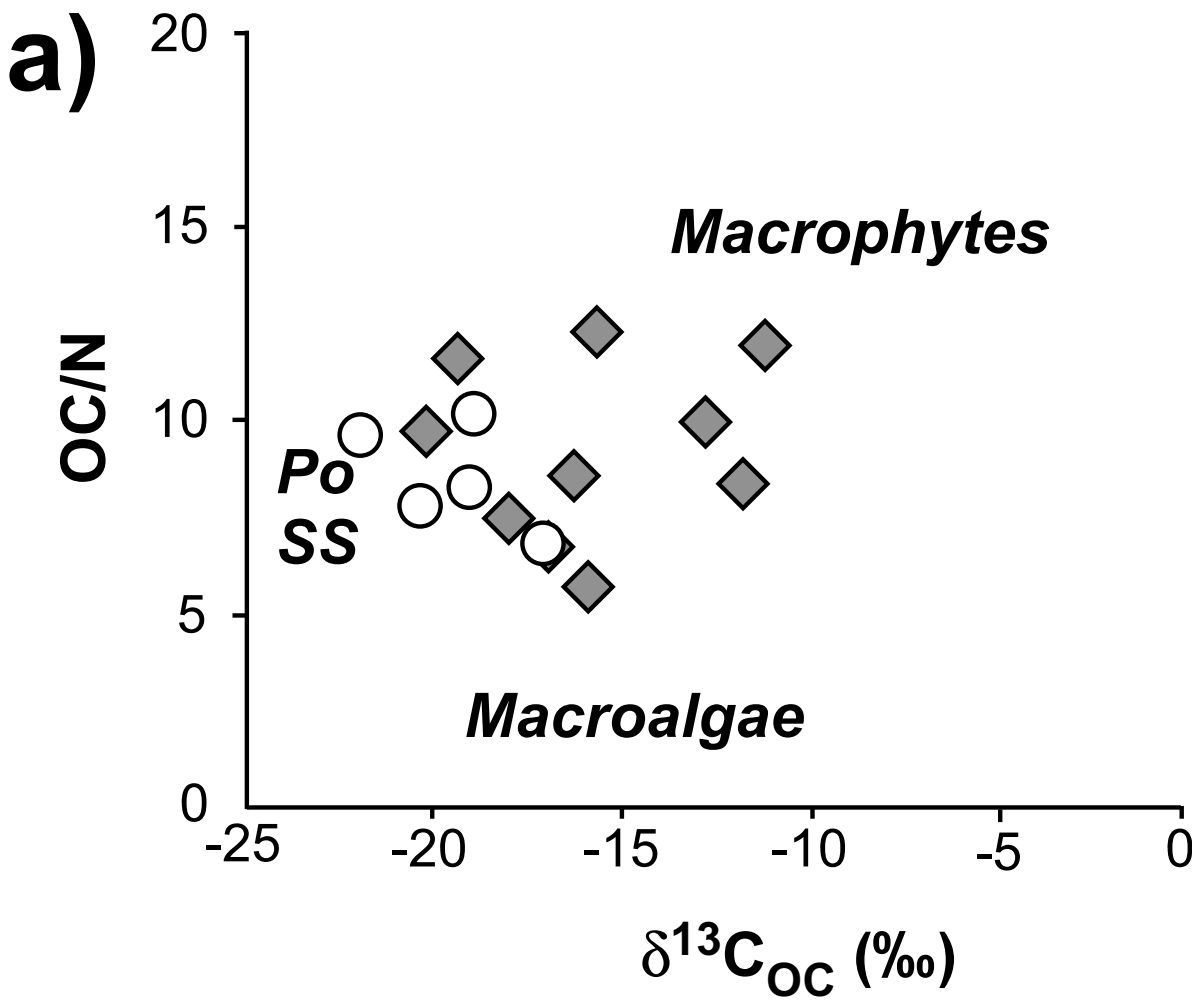




Table 1

	Sacca di Goro										Sacca di Scardovari				
	G10	G1	G2	G3	G4	G5	G6	G7	G8	G9	FF1B	FF2B	FF3B	FF4B	FF5B
<b>Sand (%)</b>	92.2	59.9	97.9	84.7	92.6	97.5	91.6	73.8	93.1	99.5	0.7	38.7	1.2	98.3	84.0
<b>Silt</b>	4.2	27.9	1.1	10.1	4.6	1.7	3.9	19.3	4.1	0.3	38.1	47.4	46.8	0.8	7.4
<b>Clay</b>	3.7	12.2	1.0	5.2	2.8	0.8	4.5	7.0	2.8	0.2	61.3	13.9	52.0	0.9	8.6
<b>SiO<sub>2</sub> (wt%)</b>	58.24	52.17	59.27	58.19	57.18	60.25	60.43	56.41	60.58	62.71	48.42	53.76	48.74	57.63	59.12
<b>TiO<sub>2</sub></b>	0.33	0.45	0.33	0.38	0.36	0.37	0.32	0.41	0.35	0.29	0.59	0.54	0.6	0.48	0.41
<b>Al<sub>2</sub>O<sub>3</sub></b>	9.13	10.56	9.54	10.07	10.08	9.64	9.6	10.08	9.02	9.14	13.43	11.09	12.89	10.45	10.14
<b>Fe<sub>2</sub>O<sub>3</sub></b>	3.02	4.13	3.26	3.33	3.82	3.38	3.38	3.8	3.31	2.96	5.41	3.86	5.18	3.62	3.61
<b>MnO</b>	0.09	0.09	0.08	0.07	0.09	0.08	0.08	0.08	0.08	0.07	0.1	0.09	0.11	0.1	0.08
<b>MgO</b>	3.66	4.64	4.41	4.08	4.27	4.08	3.92	4.15	3.82	3.74	4.6	4.52	4.53	4.84	4.07
<b>CaO</b>	11.43	11.32	9.87	10.41	10.08	9.93	9.27	10.61	9.83	8.99	9.11	11.43	10.11	11.1	9.7
<b>Na<sub>2</sub>O</b>	2.42	3.22	2.77	3.02	2.57	2.09	2.38	2.52	2.7	2.59	0.82	1.28	0.88	1.64	1.58
<b>K<sub>2</sub>O</b>	1.90	1.88	1.92	1.94	2.00	1.99	2.01	1.95	1.81	1.96	2.45	1.91	2.36	1.98	1.98
<b>P<sub>2</sub>O<sub>5</sub></b>	0.13	0.14	0.10	0.11	0.11	0.11	0.11	0.12	0.1	0.09	0.12	0.17	0.11	0.2	0.12
<b>LOI</b>	9.69	11.44	8.45	8.38	9.48	8.12	8.55	9.93	8.45	7.49	14.92	11.35	14.49	7.94	9.18
<b>Ba (ppm)</b>	265	260	272	280	274	286	263	274	257	280	314	269	316	296	290
<b>Ce</b>	30	45	30	31	35	32	30	42	30	30	55	40	47	35	34
<b>Co</b>	10	15	15	14	16	15	13	14	12	13	19	16	17	22	16
<b>Cr</b>	125	241	175	165	198	176	155	209	178	147	180	177	173	175	159
<b>Cu</b>	16	26	11	14	17	11	16	20	11	9	69	26	60	11	22
<b>Ga</b>	10	13	10	11	12	10	11	12	10	10	18	8	15	9	9
<b>Hf</b>	2	4	3	3	3	3	4	3	3	2	2	3	3	2	2
<b>La</b>	15	23	15	17	16	19	15	25	20	22	30	31	34	25	22
<b>Nb</b>	9	10	8	8	10	9	9	10	9	8	9	5	6	7	5
<b>Nd</b>	15	19	13	16	16	16	14	17	16	15	22	23	23	22	21
<b>Ni</b>	66	84	81	70	102	93	90	90	79	74	143	115	137	109	109
<b>Pb</b>	21	27	19	19	20	18	22	22	20	18	45	10	27	15	15
<b>Rb</b>	69	75	70	72	80	71	77	76	69	70	99	43	70	61	52
<b>Sc</b>	8	10	9	8	9	10	7	11	7	5	13	9	12	10	10
<b>Sr</b>	338	316	296	297	293	302	286	303	293	282	229	158	164	260	182
<b>Th</b>	5	7	4	5	6	6	6	5	5	5	7	6	8	4	6
<b>V</b>	47	71	48	57	63	54	54	66	52	46	116	73	108	57	60
<b>Y</b>	17	24	17	17	19	21	17	22	19	16	14	12	11	18	10
<b>Zn</b>	67	104	61	62	85	66	72	90	67	55	186	64	151	59	74
<b>Zr</b>	136	280	115	133	139	162	129	192	159	99	117	118	93	133	76
<b>N (wt%)</b>	0.06	0.06	0.02	0.03	0.04	0.02	0.05	0.06	0.03	0.02	0.18	0.03	0.13	0.02	0.05
<b>TC</b>	2.54	2.69	1.75	2.02	2.09	1.85	1.87	2.25	1.89	1.64	3.31	2.46	3.20	1.72	2.15
<b>OC</b>	0.59	0.68	0.17	0.26	0.27	0.25	0.32	0.47	0.30	0.24	1.55	0.32	1.05	0.13	0.44
<b>OM</b>	2.9	3.3	1.4	1.6	1.7	1.4	1.9	3.3	1.9	1.0	8.8	1.4	4.4	0.7	1.8
<b>δ<sup>13</sup>C<sub>TC</sub> (‰)</b>	-5.7	-5.7	-1.5	-2.5	-3.2	-1.9	-3.5	-4.1	-1.8	-1.3	-8.6	-2.1	-7.8	-0.8	-4.9
<b>δ<sup>13</sup>C<sub>OC</sub></b>	-20.2	-19.4	-11.7	-16.3	-17.1	-15.7	-15.9	-18.0	-12.8	-11.2	-19.1	-19.0	-20.4	-17.1	-22.0