HEAVY METALS BACKGROUNDS IN SEDIMENTS FROM THE SACCA DI GORO (NE, ITALY)

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Abstract

A textural and geochemical characterization of sediments from the Sacca di Goro lagoon floor has been performed in order to evaluate the present day granulometric distribution and the geochemical budget with respect to literature values. 10 samples have been collected along a WE transect crosscutting the whole Sacca di Goro lagoon in order to explore the maximum lithological variability and to identify geochemical trends. Results show that the present day superficial sediment are coarser in grain size with respect to those studied in the past, in turn implying lower concentrations of Potentially Toxic Elements (PTE). PTE enrichments miming those observed 20 years ago are recorded only locally, in connection with parallel increase of fine fraction and organic matter. Traces of Cu, V and Pb have been also found in the shells of farmed Manila clam (*Ruditapes Philippinarum*) collected within the sediment samples, suggesting PTE bioavailability and accumulation. The comparison of the results with literature data highlights that PTE contents of the Sacca di Goro lagoon deserve more frequent and systematic monitoring both for the high hydrodynamicity of this environment and for the high anthropogenic impact. The analysis of metals in Manila clam shells has a twofold purpose because it represents a further biomarker of the ecosystem, and also provide a geochemical fingerprint of the local shellfish production that could help the traceability in the market, and discrimination from shellfish produced in other area that are not properly controlled from the sanitary point of view.

Keywords: *heavy metals, coastal lagoon, Sacca di Goro, geochemical evolution, biomarker.*

Introduction

The northern Adriatic Sea is characterized by the presence of several coastal lagoons that represent complex ecological systems characterized by a peculiar environmental equilibrium (Migani et al., 2015). Many of these wetlands are affected by natural and anthropogenic stresses that represent a threat for their delicate ecosystems and limit the productivity of the economic activities that are usually related to fishery sectors. In this view, the main negative effects are related to the ongoing climatic changes and to the increase of pollutants produced by anthropogenic activities that influence both the geomorphology and geochemical

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backgrounds characterizing these environments. In this contribution, a particular attention has been devoted to the latter, since one of the main problem recorded in fishery products from these areas is the bioaccumulation of potentially toxic elements (PTE) such as heavy metals. A number of studies dealing with the selective bioaccumulation of heavy metals by the benthic bivalve Manila clam (*Ruditapes Philippinarum*) have been reported in the literature, both for its high economic value and the worldwide farming distribution. Most of these studies (e.g. Baudrimont et al., 2005) claim for an important role played by the sediment geochemical composition in the bioaccumulation of heavy metals in Manila clam, and it becomes therefore of primary importance to identify the total content of these elements in the sediments in which they are cultivated, as well as to define the natural geochemical backgrounds and the complementary anthropogenic contribution (e.g. Migani et al., 2015). In particular, literature data on textural and geochemical composition of the Sacca di Goro sediments (Guerzoni et al., 1984; Fagioli et al., 1991; 1994; Covelli et al., 2000; Dinelli et al., 2000; Simenoni et al., 2000) evidenced that the lagoon is an extremely dynamic sedimentary environment characterized by significant granulometric variability and heavy metal contents. These literature data are very important because they define a snapshot of the Sacca di Goro geochemical condition at ca. 20 years ago, that can be useful to be compared with new investigations in order to evaluate the effect of two decades anthropogenic and climatic impact on the textural and geochemical evolution of the Sacca di Goro sediments.

In this work we therefore present new textural and geochemical analyses carried out on 10 samples of sediment collected along a W-E transect crossing the Sacca di Goro lagoon in the summer of the year 2015, in order to verify the updated geochemical budget of the sedimentary matrices in which Manila clam are farmed. The aim is to understand the origin (natural and anthropogenic backgrounds) of metals associated to these sediments, and to evaluate the extent of their possible transfer to the farmed Manila clams. In this regard, we also analyzed the geochemical composition of Manila clam shells included in the collected sediments, with the aim to identify metal proxies that could serve as site specific tracers of provenance. Such proxies are very important to defend the local production from frauds that bring into the market shellfish of uncertain provenance that is often not properly inspected by food safety controls.

General outlines on the Sacca di Goro coastal lagoon

Sacca di Goro (Fig. 1) is a shallow coastal lagoon located in the southern part of the Po river delta (44.78–44.83 N and 12.25–12.33 S) with a surface area of 26 km^2 , an average depth of about 1.5 m that is variable in relation to river and seawater inflows (Simeoni et al., 2000). The main fresh water input comes from the Po di Volano canal (about 3.5 10^8 m^3 y^{-1}) that flows directly into the lagoon and from the Po di Goro deltaic branch, which inflow into the lagoon is artificially regulated. Additionally, three irrigation canals, named Giralda, Romanina and Canal Bianco, with similar flows (2.0–5.5 10^7 m^3 y^{-1}), contribute to the overall fresh water input.

Figure 1
Perspective view of the Sacca di Goro lagoon, reporting the sampling sites along a W-E transect.

On the other hand, the Sacca di Goro is connected by two mouths to the Northern Adriatic Sea which variably inflow according to the tidal dynamics. The main sediment input is provided by the solid load of Po di Goro and Po di Volano, with minor contributions from Po di Pila, Po di Tolle and by sediments that rise the Adriatic coastline (Covelli et al., 2000). The floor of the lagoon is flat and, according to survey carried out more than 10 years ago, the sediments mainly include clay/silt in the northern and central zones, prevalent sand near the southern shoreline and sandy mud in the eastern area (Carafa et al., 2007). However, present day spatial distribution of the distinct sedimentary facies is difficult to be defined as a result of the continuous hydrodynamic evolution, which is also affected by numerous manmade hydraulic variations that have been carried out to ameliorate water quality and shellfish productivity. In fact, the lagoon is one of the most important shellfish aquaculture systems in Italy and about 10 km^2 of the aquatic surface are exploited for the Manila clam (*Tapes philippinarum*) farms supporting an annual production between 8000 and 15000 t of clams (Carafa et al., 2007).

Materials and methods

Samples have been collected in May 2015 along a W-E longitudinal transect starting from Punta Volano to the main Po di Goro inflow south of Gorino village. 10 samples (2 to 3 kg) have been collected at approximately equal distance one to each other along this transect, dredging the floor of the lagoon down to approximately 5 cm depth. Samples have been placed in polyethilene bags to be transported to the Laboratories of the Department of Physics and Earth Sciences of the University of Ferrara, then dried in oven at T<60°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 have been isolated, deprived of soft tissues and treated with hydrogen peroxide to remove tissue remnants and superficial organic films. Sediments and shells were finally powdered in agate mill

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and an amounts of about 4 g of powder were pressed with addition of boric acid by hydraulic press to obtain powder pellets. Simultaneously, 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. This parameter measures the concentration of volatile species contained in the sample. The Wavelenght Dispersion X-Ray Fluorescence (WDXRF) analysis of the powder pellets was carried out using an ARL Advant-XP spectrometer Thermo-Scientific. Calibrations were obtained analysing 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 (with 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 ppm 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 isotopic composition using an Elementar Vario Micro Cube Elemental Analyzer in line with an ISOPRIME 100 Isotopic Ratio Mass Spectrometer operating in continuous-flow mode. Results obtained with the analytical protocol defined by Natali and Bianchini (2014; 2015) were presented and discussed in Bianchini et al. (2015).

Results

The textural composition of the 10 investigated sediments (Table 1) highlights that they are characterized by prevalent sand (74-99%), followed by silt (0-28%) and minor clay (0-12%).

Sample	Sand (%)	Silt (%)	Clay (%)
G10	92.2	4.2	3.7
G1	59.9	27.9	12.2
G2	97.9	1.1	1.0
G3	84.7	10.1	5.2
G4	92.6	4.6	2.8
G5	97.5	1.7	0.8
G6	91.6	3.9	4.5
G7	73.8	19.3	7.0
G8	93.1	4.1	2.8
G9	99.5	0.3	0.2

Table 1
Grain size distribution of superficial sediments from the Sacca di Goro lagoon floor.
Please refer to Fig. 1 for sampling position.

Following the Shepard's (1954) classification, the samples are mainly "sands", with the exception of samples G01 and G07 that are "silty sand" and also show the

higher clay content of 12% and 7%, respectively. Although a general decrease in the muddy fraction is observed eastward, strong local variations in the amount of fine fraction produce peaks in samples G01 (40%), G03 (15%) and G07 (26%).
The major and trace element geochemical variation of sediments from the Sacca di Goro and included Manila clam shells is reported in Table 2. The major element composition of sediment samples shows that they are characterized by an elevated SiO_2 content, followed by CaO and Al_2O_3 suggesting the main silico-clastic nature of the sediments, with minor contribution of carbonates. SiO_2 is negatively correlated with CaO, Al_2O_3, Fe_2O_3, MgO and with clay content, suggesting that the coarse fraction is mainly constituted by quartz. The positive correlations of Al_2O_3 with Fe_2O_3 (r^2 = 0.76), MgO (r^2 = 0.68) and clay content (r^2 = 0.76) suggest that the finer fraction is dominated by Fe- and Mg-rich clay minerals such as chlorite, smectite and serpentine. The strong positive correlation of CaO with inorganic carbon content (r^2 = 0.94, data from Bianchini et al., 2015), suggests that this element is almost exclusively associated with the carbonate fraction. As concern the geochemical distribution along the investigated transect, we observe a general decrease of Al_2O_3, Fe_2O_3, P_2O_5 coupled with an increase in SiO_2 in the investigated sediments eastward.

Table 2. *Statistical parameters of the geochemical variations obtained by XRF major and trace element analysis of superficial sediments and included manila clam shells from the Sacca di Goro lagoon floor.*

	Sediments						***Shells***					
	Min	**Median**	**Max**	**Lower Q.**	**Upper Q.**	**St. Dev.**	**Min**	**Median**	**Max**	**Lower Q.**	**Upper Q.**	**St. Dev.**
(wt%)												
SiO_2	**52.24**	**58.34**	**62.31**	**57.43**	**60.39**	**2.76**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
TiO_2	**0.32**	**0.39**	**0.50**	**0.33**	**0.38**	**0.05**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Al_2O_3	**9.16**	**9.74**	**10.48**	**9.24**	**10.08**	**0.44**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Fe_2O_3	**3.34**	**3.74**	**4.09**	**3.27**	**3.70**	**0.27**	**0.48**	**0.49**	**0.49**	**0.48**	**0.49**	**0.01**
MnO	**0.08**	**0.09**	**0.11**	**0.08**	**0.09**	**0.01**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
MgO	**3.40**	**3.77**	**4.29**	**3.85**	**4.24**	**0.29**	**0.16**	**0.17**	**0.18**	**0.16**	**0.18**	**0.01**
CaO	**9.04**	**10.12**	**11.51**	**9.84**	**10.56**	**0.83**	**53.88**	**54.19**	**54.57**	**54.04**	**54.36**	**0.04**
Na_2O	**1.91**	**2.52**	**3.29**	**2.45**	**2.75**	**0.39**	**0.98**	**1.08**	**1.09**	**1.05**	**1.09**	**0.05**
K_2O	**1.90**	**2.08**	**2.15**	**1.91**	**1.98**	**0.07**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
P_2O_5	**0.09**	**0.11**	**0.14**	**0.10**	**0.12**	**0.01**	**0.04**	**0.05**	**0.07**	**0.04**	**0.06**	**0.02**
LOI	**7.49**	**8.50**	**11.44**	**8.40**	**9.64**	**1.14**	**44.16**	**44.16**	**44.16**	**44.16**	**44.16**	**0.00**
(mg/kg)												
Co	**24**	**26**	**30**	**13**	**15**	**2**						
Cr	**125**	**176**	**241**	**157**	**193**	**33**						
Cu	**5**	**10**	**22**	**11**	**17**	**5**	**2**	**3**	**4**	**3**	**4**	**1**
Ni	**66**	**83**	**102**	**75**	**90**	**11**						
Pb	**16**	**18**	**22**	**19**	**22**	**2**	**0**	**3**	**4**	**2**	**3**	**2**
V	**48**	**56**	**79**	**49**	**61**	**10**	**5**	**7**	**9**	**6**	**8**	**1**
Zn	**13**	**23**	**56**	**63**	**82**	**13**						

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The major element composition of Manila clam shells shows CaO and LOI as major components, confirming that they are mostly composed by calcium carbonate. Notable amounts of Na_2O (0.98-1.09 wt%), FeO (0.48-0.49 wt%) and minor MgO (0.16-0.18 wt%) and P_2O_5 (0.04-0.07 wt %) have been also detected.
The trace element composition of sediment samples reveal variable PTE content, with Co up to 30 mg/kg, Cr up to 240 mg/kg, Ni up to 100 mg/kg, Pb up to 20 mg/kg, V and Zn up to 80 mg/kg. Many investigated PTE show a good affinity with Fe_2O_3 (Cr, r^2 = 0.88; V, r^2 = 0.93; Cu, r^2 = 0.69; Zn, r^2 = 0.88). Cr and V are also well correlated with Al_2O_3 (r^2 of 0.63 and 0.80, respectively), and Co with MgO (r^2 = 0.67), whereas Ni doesn't show any significant correlation with major elements. Chalcophile elements display a good correlation with P_2O_5 (Pb, r^2 = 0.65; Cu, r^2 = 0.78; Zn, r^2 = 0.57), whereas Sr is highly and positively correlated with CaO (r^2 = 0.82). Most of PTE are well correlated with mud content (Cr, r^2 = 0.57; V, r^2 = 0.75; Cu, r^2 = 0.83; Zn, r^2 = 0.75; Pb, r^2 = 0.79) confirming their association with the finer sediment fraction, with the exception of Ni and Co. Coherently with the general trends observed within grain size variation along the investigated transect, we observe a decreasing tendency in the concentration of Cu, Zn, and Pb eastward.
The PTE content of Manila clam shells is in the order of few mg/kg and vary in the following range: V (8 mg/kg) > Pb (4 mg/kg) = Cu (4 mg/kg). No clear relationships have been established between PTE variation in clam and in the associated sediments. It is important to note that no traces of Cr, Ni and Zn have been detected. The most abundant trace element detected in Manila clam shell is represented by Sr (1540-1600 mg/kg) which is a common component of aragonite mineral because it vicariates Ca in carbonates.

Discussion and Conclusions

10 sediment samples have been collected along a W-E transversal transect crossing the whole Sacca di Goro lagoon with the aim to investigate the maximum lithological variability basing on the available textural maps from the literature (e.g. Simeoni et al., 2000). However, granulometric analyses revealed that our samples are only representative of the coarser grain size (clay content < 12%), confirming both the high hydrodynamicity of the Sacca di Goro leading to fast changes in sedimentary features. We suggest that Manila clam intense cultivation exert a strong control on the lagoon floor sediment distribution and erosion (Sgro et al., 2005). In other words, it appears that 20 years of intensive Manila clam farming depleted the substrate in the fine fraction.
The major element geochemistry confirms that Sacca di Goro lagoon floor sediments are very similar to older Po river sediments forming the inland deltaic alluvial plain (Bianchini et al., 2012; 2013; Di Giuseppe et al., 2014b) that, due to their pre-Anthropocene age, can be considered as the PTE background for the investigated samples (Fig. 2). The comparison of the bulk PTE contents between Ferrara alluvial plain and an extensive dataset of Sacca di Goro lagoon sediments (data from this work, Covelli et al., 2000; Dinelli et al., 2000) is reported in Fig. 3.

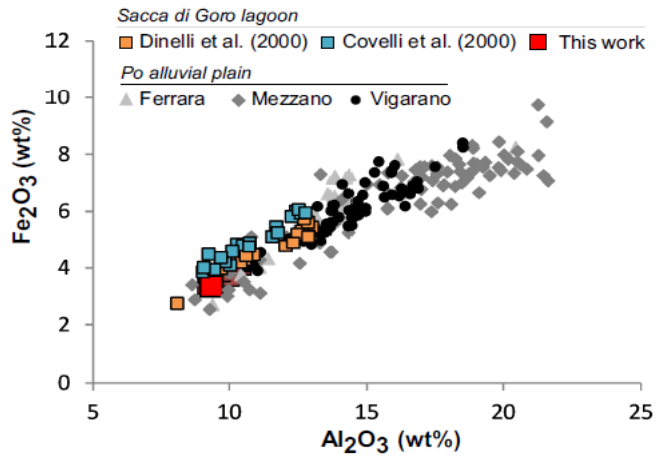

Figure 2
Fe_2O_3 vs Al_2O_3 (wt%) binary diagram of Sacca di Goro sediments compared with Po alluvial plain sediments from the Ferrara province (Mezzano lowland - Di Giuseppe et al., 2014b; Ferrara - Bianchini et al., 2013; Vigarano - Bianchini et al., 2012).

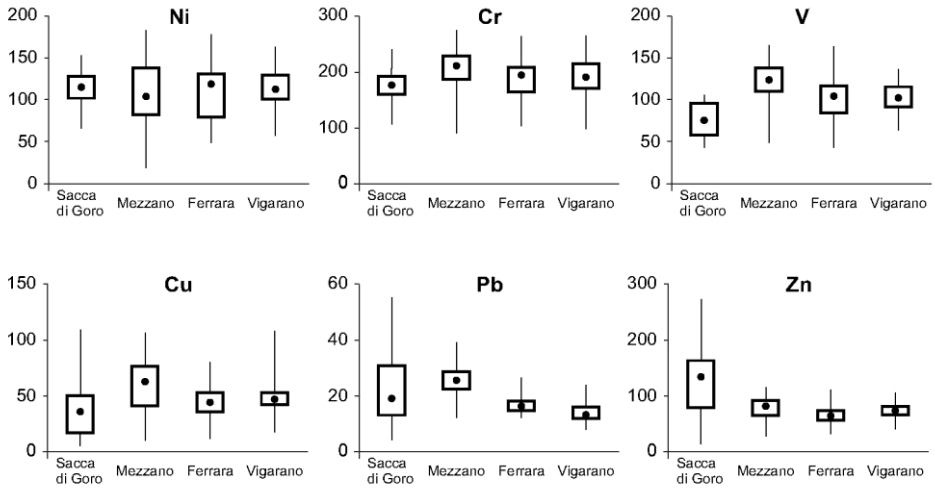

Figure 3. *Box-Plot of heavy metals distribution (Cr, Ni, V, Cu, Pb, Zn – mg/kg) in Sacca di Goro sediments compared with Po alluvial plain sediments from the Ferrara province (Mezzano lowland - Di Giuseppe et al., 2014b; Ferrara - Bianchini et al., 2013; Vigarano - Bianchini et al., 2012). Symbols as in Fig. 2.*

The concentrations of siderophile and lithophile metals in Sacca di Goro lagoon sediments are very similar (Ni, Cr) or lower (V) with respect to those recorded in Po alluvial plain sediments. On the other hand, chalcophile elements (Cu, Pb, Zn) display higher concentrations in Sacca di Goro lagoon sediments, especially for Pb and Zn. The anomalous enrichment in Zn in the upper sediment cores was already recognized by Covelli et al. (2000) who identified an anthropogenic contribution to PTE concentrations in the surficial sediments on the basis of the Zn/Fe ratio. As

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already noted in sediments from the Po alluvial plain (Bianchini et al., 2012; 2013) there is a direct relationships between the concentration of PTE and the clay fraction. Therefore, in order to correctly evaluate anomalous PTE enrichments in Sacca di Goro lagoon sediments, metals are plotted against Al_2O_3 (wt%) to be normalized over grain size (Fig. 4).

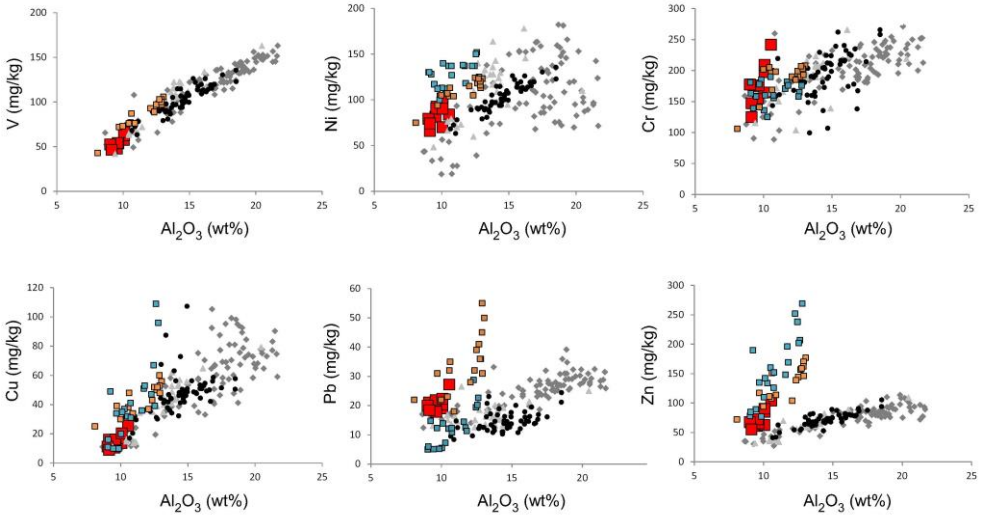

Figure 4. *Heavy metals contents (Cr, Ni, V, Cu, Pb, Zn– mg/kg) vs Al_2O_3 (wt%) binary diagram of Sacca di Goro sediments compared with Po alluvial plain sediments from the Ferrara province (Mezzano lowland - Di Giuseppe et al., 2014; Ferrara - Bianchini et al., 2013; Vigarano - Bianchini et al., 2012). Symbols as in Fig. 2.*

As already noted by the absolute concentration, the V distribution in the Sacca di Goro samples is similar to that of the background along with the various grain sizes, whereas Ni and Cr show deviation toward slightly higher concentrations at low Al_2O_3 content (10-12 wt%) in comparison with values recorded in Po alluvial plain sediments. Coherently, the distribution of V and Cr show an higher correlation with silt (r^2 of 0.75 and 0.60, respectively) with respect to the clay (r^2 of 0.67 and 0.45, respectively), whereas the Ni distribution doesn't show any correlation with the grain size. Although these data mainly imply a geogenic origin of these PTE, a possible additional anthropogenic contribution (e.g. for Cr) seem to be accumulated in the form of metal-clay complexes as suggested in other lagoons impacted by human activities (Maanan et al., 2004).

Chalcophile element distribution in Sacca di Goro lagoon show instead strong deviations from the background alluvial sediments, which are decidedly more marked for Pb and Zn. The Cu, Pb and Zn distributions in the Sacca di Goro sediments show well defined trends with Al_2O_3 (wt%) content, which are characterized by higher slope with respect to that observed in the Po alluvial sediments. This suggests a strong association of Cu, Pb and Zn with the finest

fraction. The distribution of chalcophile elements show correlation values generally growing with decreasing grain size, confirming the strong association of Cu, Pb and Zn with the finest fraction. Notably, these chalcophile elements display an excellent correlation coefficient when plotted against the carbon isotopic composition ($\delta^{13}C$ ‰, data from Bianchini et al., 2015 - Cu, r^2 = 0.99; Zn, r^2 = 0.90; Pb, r^2 = 0.89), which is a tracer of the percentage of organic matter in the investigated sediments. Moreover, they show high correlation among themselves ($r^2 \geq 0.77$) which is maximum between Zn and Cu (r^2 = 0.90), thus suggesting that these elements have a common origin and are influenced by the same factors and processes. As recently evidenced by Boyle et al. (2016), the enrichment of Cu and Zn in bottom lake sediments can derive from intense boating, an activity directly linked to the continue intensification of fishery in the Sacca di Goro lagoon.

The strong relationships between these elements and organic matter highlights an association in the form of organometallic complexes (Zourarah et al., 2007; Baptista Neto et al., 2000). The high levels of Pb and Zn recorded in Sacca di Goro sediments and their association with organic matter can represent a threat for the food safety of Manila clam cultivation, due to the possible metal mobilization and bioaccumulation. The quantification and understanding of oxygen undersaturation at the sediment/water interface deserve further investigation for the Sacca di Goro lagoon, as it represent a process which has already been inferred as possible cause of metal mobilization in similar environments (Baudrimont et al., 2005).

On the other hand, this study highlights that textural, and related geochemical, variations occurred in the Sacca di Goro lagoon sediments over the last 20 years, and suggests that similar but more detailed study along with the whole lagoon is needed in order to update and better define the nowadays sediment characterization and PTE budgets.

As concern the possible utilization of geochemical markers for the Manila clam traceability, the presented data indicate that the relatively high values of Cu, Pb and V typical of the coexisting sediments seem to be transferred to the shells, with an extent that could be site specific. In this light, differently from most of the literature which deals on soft tissues analysis for bioaccumulation studies, we think that traceability could be better defined by the geochemical investigations of shells, that represent a more reliable archive which potentially record interaction between the biota and the living environment. For this reason, further investigation will imply the use of more accurate and precise analytical techniques (such as ICP-MS) that allow to measure a wider metal spectrum, also in shells where concentrations are extremely low, with the aim of identify a multielement traceability card for the Manila clam farmed in different lagoons.

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TENORI DI FONDO DEI METALLI PESANTI NEI SEDIMENTI DELLA SACCA DI GORO (ITALIA SETTENTRIONALE)

Riassunto

Questo lavoro riporta una recente caratterizzazione geochimica e tessiturale dei sedimenti superficiali della laguna costiera della Sacca di Goro con lo scopo di valutare le variazioni granulometriche e del budget degli Elementi Potenzialmente Tossici (PTE) rispetto ai valori riportati in letteratura. Sono stati raccolti 10 campioni di sedimenti lungo un transetto WE che attraversa tutta la laguna con lo scopo di esplorare la massima variabilità litologica e possibili trend di variazione geochimica. I risultati mostrano che i sedimenti superficiali attuali sono tessituralmente più grossolani rispetto a quelli campionati in passato nelle stesse aree e ciò implica generalmente contenuti inferiori di PTE. Arricchimenti simili a quelli identificati circa 20 anni fa si riscontrano solo localmente, in parallelo ad aumenti della frazione fine e sostanza organica del sedimento. Sono state riscontrate anche tracce di Cu, V e Pb nei gusci della vongola filippina (*Ruditapes Philippinarum*) campionati assieme ai sedimenti e ciò suggerisce biodisponibilità ed accumulo di questi elementi. La comparazione dei risultati con i dati di letteratura suggerisce la necessità di un monitoraggio più frequente del contenuto di PTE dei sedimenti della Sacca di Goro, sia per l'elevata idrodinamicità che per l'elevato impatto antropico che caratterizzano questo ambiente. L'analisi dei metalli nei gusci della vongola filippina risulta importante sia per identificare biomarkers di questo ecosistema che per fornire una possibile firma geochimica della produzione locale di venericoltura e differenziarla sul mercato da altre produzioni che non sono propriamente controllate dal punto di vista igienico-sanitario.

Parole chiave: *metalli pesanti, laguna costiera, Sacca di Goro, evoluzione geochimica, biomarker*