

Alma Mater Studiorum Università di Bologna
Archivio istituzionale della ricerca

Sediment quality assessment in a coastal lagoon (Ravenna, NE Italy) based on SEM-AVS and sequential extraction procedure

This is the final peer-reviewed author's accepted manuscript (postprint) of the following publication:

Published Version:

Sediment quality assessment in a coastal lagoon (Ravenna, NE Italy) based on SEM-AVS and sequential extraction procedure / Pignotti, Emanuela; Guerra, Roberta; Covelli, Stefano; Fabbri, Elena; Dinelli, Enrico.
- In: SCIENCE OF THE TOTAL ENVIRONMENT. - ISSN 0048-9697. - STAMPA. - 635:(2018), pp. 216-227.
[10.1016/j.scitotenv.2018.04.093]

Availability:

This version is available at: <https://hdl.handle.net/11585/656676> since: 2019-01-24

Published:

DOI: <http://doi.org/10.1016/j.scitotenv.2018.04.093>

Terms of use:

Some rights reserved. The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>).
When citing, please refer to the published version.

(Article begins on next page)

This is the final peer-reviewed accepted manuscript of:

Emanuela Pignotti, Roberta Guerra, Stefano Covelli, Elena Fabbri, Enrico Dinelli 2018. Sediment quality assessment in a coastal lagoon (Ravenna, NE Italy) based on SEM-AVS and sequential extraction procedure. Science of The Total Environment, Vol. 635, Pages 216-227

The final published version is available online at:

<https://doi.org/10.1016/j.scitotenv.2018.04.093>

Rights / License:

The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

Sediment quality assessment in a coastal lagoon (Ravenna, NE Italy) based on SEM-AVS and sequential extraction procedure

Emanuela Pignotti ^{a,b,*}, Roberta Guerra ^{b,c}, Stefano Covelli ^d, Elena Fabbri ^{a,b}, Enrico Dinelli ^{a,b}

^a Department of Biological, Geological and Environmental Sciences, University of Bologna, P.zza di Porta San Donato 1, 40100 Bologna, Italy

^b Interdepartmental Research Centre for Environmental Sciences (CIRSA), Via S. Alberto 163, 48123 Ravenna, Italy

^c Department of Physics and Astronomy, University of Bologna, 40127 Bologna, Italy

^d Department of Mathematics and Geosciences, University of Trieste, Via Weiss 2, 34128 Trieste, Italy

* Corresponding author: emanuela.pignotti2@unibo.it

Abstract

Sediments from the Pialassa Piomboni coastal lagoon (NE Italy) were studied to assess the degree of contamination and ecological risk related to trace metals by combining a geochemical characterization of bulk sediments with the assessment of the bioavailable forms of trace metals. With this purpose, sediment contamination (Cd, Cu, Hg, Ni, Pb, and Zn) was assessed by Enrichment Factors (EFs), and potential bioavailability by the Simultaneously Extracted Metals and Acid Volatile Sulfides (SEM-AVS) approach (Cd, Cu, Ni, Pb, and Zn), and by Sequential Extraction Procedure (Co, Cr, Cu, Ni, Pb, and Zn). On average, Cr and Ni exhibited no contamination ($EF \leq 1.5$), and a predominance in the residual fraction of the sediment, indicating natural origin for these metals. Cu, Pb and Zn displayed a local contamination, which resulted in a higher proportion of Cu bound to the reducible and oxidizable fractions (~30% and ~40% as median, respectively), and Pb mostly associated with the reducible phase (~60% as median). Hence, Cu and Pb could be mobilized when environmental conditions become reducing or oxidizing. Zn resulted mainly partitioned into the reducible and residual fractions (~50% as median, in both fractions). The Risk Assessment Code (RAC) indicated that approximately 30% of samples had N10% of total Zn weakly bound to the sediment, suggesting a medium risk of exposure for aquatic organisms. RAC results were consistent with the Σ SEM-AVS findings, pointing to possible adverse effects for aquatic biota in ~30% of samples, with Zn mostly accounting for the total metal bioavailability. Hg showed a moderate to very severe enrichment, indicating that a substantial amount of this metal derives from anthropogenic sources and may pose adverse effects on the aquatic biota of the Pialassa Piomboni lagoon.

Keywords Coastal lagoon, Sediment quality assessment, Sequential extraction procedure, Acid-volatile sulfides, Simultaneously extracted metals, Mercury

1. Introduction

Coastal lagoons are shallow water bodies located between land and sea, characterized by high fluctuations of physical, chemical and biological properties (Pérez-Ruzafa et al., 2013). The dynamics and fragility of these environments are often threatened by human activities (e.g. harbor and industrial activities, fishing, and tourism) mostly concentrated in coastal areas, which can affect both water and sediment quality. Sediments are the compartment of major concern, since they can be an important sink for potentially harmful inorganic and organic contaminants, acting as good scavengers and decreasing their bioavailability (Jonathan et al., 2011). They can also act as a secondary source of contamination when environmental conditions change (e.g. pH, redox potential), releasing contaminants in the water column. Trace metals are included in environmental monitoring programs given their bioaccumulation and toxic effects on aquatic organisms (Roussiez et al., 2011; Arfaeina et al., 2016). Trace metals can occur in sediments in various forms, in association with different geochemical phases that determine their mobility, bioavailability and potential toxicity (Yu et al., 2001). Therefore, knowing their total content in the sediment alone is not exhaustive to assess their potential ecological risk for aquatic organisms (Baran and Tarnawski, 2015; Botwe et al., 2017). Analysis of Simultaneously Extracted Metals (SEM) coupled with the Acid-Volatile Sulfides (AVS) represent a useful approach to determine the potential bioavailability of trace metals. Sulfide minerals bind with trace metals under anoxic conditions, limiting their bioavailability in porewaters (Li et al., 2014). Based on the SEM-AVS model, the mobility of divalent metals (Cd, Cu, Ni, Pb and Zn) is expected to increase if total SEM exceeds AVS content (Zhang et al., 2014). A broader vision of the metal mobility is further given by the analysis of the metal fractionation through a Sequential Extraction Procedure (SEP). This methodology enables the determination of trace metals distribution within different sediment fractions, their mobility and consequent bioavailability.

The aim of this study was to evaluate the sediment quality of the Pialassa Piomboni, a coastal lagoon located in the south-eastern part of the Po delta area (northern Italy) in close connection with the Ravenna harbor, one of the largest commercial harbors in Italy. To this end, the geochemical composition of surficial sediments have been determined to quantify the level of contamination, and SEM-AVS and the SEP analyses have been accomplished to quantify and explain the spatial distribution, bioavailability and potential ecological risk of trace metals (Cd, Cr, Cu, Ni, Pb, Zn).

2. Materials and methods

2.1. Study area

The Pialassa Piomboni lagoon is part of a wetland system formed over the last 250 years together with the northern lagoon area, the Pialassa Baiona, as a result of the dynamic evolution of the Po delta system. It is located 8 km North-East of the city of Ravenna (Fig. 1). The Pialassa Piomboni has a significant relevance from an ecological point of view. It was designated as a Site of Community Importance (SCI) and Special Protection Area (SPA), according to Habitats Directive 92/43/CEE, and it belongs to the Natura 2000 network. However, its western and northern sectors are in connection with the Ravenna harbor area, also known as the Candiano Channel directly flowing in the Adriatic Sea, and are affected by intense and diversified human activities.

The current morphology of the Pialassa Piomboni is the result of both natural and human actions aimed at maintaining the hydrological characteristics of the area (Airoldi et al., 2016). The water depth is shallow in the eastern, central and southern areas (maximum 1.50 m), whereas in the western part and in connection with the main harbor channel, water depth is >10 m. Water circulation is dominated by the tidal flows, which guarantee a natural water exchange, and also by

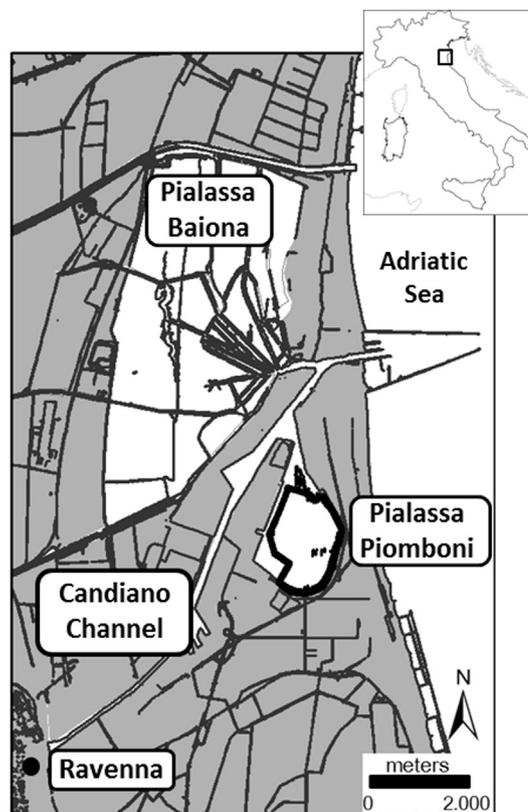


Fig. 1. Map of the study area.

freshwater inputs coming from a number of artificial channels. The most important freshwater input is the San Vitale draining pump, situated in the southern part of the Pialassa Piomboni, which collects municipal wastewaters and agricultural effluents (Farina et al., 1994; Soprani and Giaquinta, 1992). Water quality in this area is poor because of the high amounts of organic compounds and chemical and biological contaminants released by human and harbor activities that occur along the perimeter of the study area (Bandini, 1996; Soprani and Giaquinta, 1992; Migani et al., 2015).

2.2. Sample collection and chemical analysis

Fifty sediment samples were collected over an area of about 3 km² using a 0.1 × 0.1 km regular grid. The top 5-cm of sediment was collected by manual coring; sediment samples were then placed in pre-cleaned glass containers, transported to the laboratory and stored at +4 °C for sample treatment and further analysis.

The sampled sediments were treated with deionized water to remove sea salts; they were then centrifuged, dried in the oven at 60 °C and ground in an agate mortar.

The X-ray fluorescence spectrometer Philips PW1480 with Rh tube was used for the detection of major and trace elements (SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O, P₂O₅, V, Cr, Co, Ni, Cu, Zn, As, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Pb, Th, S, Br, Mo, Sn) on pressed powder pellets, following the matrix correction methods of Franzini et al. (1972, 1975), Leoni and Saitta (1976), and Leoni et al. (1986). Precision and accuracy have been tested including certified reference material SCO-1 (Silty Marine Shale, United States Geological Survey, USGS) in the analytical routine; trace elements determination was better than 5%, except for those elements at 10 ppm or lower (10–15%).

The total Hg content was determined using a Direct Mercury Analyzer (DMA-80, Milestone®) on approximately 30 mg of material according to US-EPA Method 7473. Quality control was tested using Certified Reference Material PACS-2 (Harbour Sediment, NCR-CNRC,

Canada; certified valued $3.040 \pm 0.2 \mu\text{g/g}$). Results obtained were in good agreement with the certified values, with recovery between 98% and 100% ($n = 12$). Loss On Ignition (LOI) was determined gravimetrically after heating 1 g aliquot of sample at 950°C for 12 h.

Acid volatile sulfides (AVS) and simultaneously extracted metals (SEM) were determined following the purge-and-trap method (Allen et al., 1993). An aliquot of sediment (5 g wet weight) was stirred for 1 h with HCl 6 M under constant N_2 flux, and the S^{2-} ions trapped in a 0.5 M NaOH solution were measured spectrophotometrically at 690 nm. The remaining sediment was centrifuged at 3000 rpm for 10 min, and the supernatant was analyzed for Cd, Cu, Pb and Ni by means of a graphite furnace atomic absorption spectrophotometry (GF-AAS, Perkin Elmer Analyst 100) and for Zn by flame atomic absorption spectrophotometry (FAAS). Quality control of AVS extraction was assured by calibrating the procedure against known amounts of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (Durán et al., 2012), and recoveries were within 80–90%. Replicates for 20% of samples were made as part of the quality assurance and the relative standard deviation was always $\pm 10\%$.

Sequential Extraction Procedure (SEP) was applied following the three-step BCR methodology (Rauret et al., 1999; Sahuquillo et al., 1999). The summary of the method steps are: (I) water/acid soluble and exchangeable fraction/carbonate (fraction A), operationally consisting in adding a 0.11 M acetic acid solution to 1 g of sample and shaking at room temperature for 16 h; (II) reducible/bound to Fe–Mn Oxides (fraction B), a 0.5 M of $\text{NH}_2\text{OH}\cdot\text{HCl}$ solution (adjusted to pH 2 by adding HNO_3) was added to the residue from Step I, and the extraction was performed as described in Step I; (III) oxidizable fraction/bound to organic matter (fraction C), where the residue from (II) was added with a 8.8 M H_2O_2 solution and left to digest for 1 h at 90°C , and 1 M NH_4OAc was then added; (IV) residual (fraction R), representing the fraction of the element bound the sediment-forming minerals, defined as the difference between the total content of the element (XRF) and the sum of the first three steps ($R = \text{XRF} - \sum[A + B + C]$).

Blanks (i.e. reagents without the sediment matrix) were run in parallel with each batch of sediment SEP, and Al, Fe, Co, Cr, Cu, Mn, Ni, Pb, and Zn were measured in each fraction by using an iCAP 6200 dual-view ICP Emission Spectrometer (Thermo Scientific). In order to check the accuracy and precision of the BCR extraction, reagent blanks, random sample replicates and reference material BCR-701 (Lake sediment) were analyzed in parallel with sample batches. Measured concentrations in BCR-701 included in the analysis were in good agreement against their certified values (Table S1 of the Supplementary Material), and the standard deviation of replicated samples was on average $\pm 7\%$.

2.3. Data analysis

ArcGIS 9.3® software was employed to study the spatial distribution of selected major elements and trace metals in the Pialassa Piomboni lagoon. Dot maps were grouped into five classes, on the basis of percentiles: I class (0–10th); II class (10th–25th); III class (25th–75th); IV class (75th–90th); V class (90th–100th). To obtain the overall spatial patterns, the spatial interpolation method using the Inverse Distance Weighting technique (IDW) was applied to draw interpolated geochemical maps; for a better visualization of their distribution, concentration values were grouped into six classes, according to percentiles: I class (0–10th); II class (10th–25th); III class (25th–50th); IV class (50th–75th); V class (75th–90th); VI class (90th–100th).

Factor analysis was conducted to facilitate interpretation by visualizing the correlations that exist between the original variables (major elements and trace metals) in the sediment. Observations that presented outliers were not considered; variables below the detection limit in over 15% of samples were removed; the remaining variables were standardized, and MATLAB® Software was run for factor analysis.

2.4. Sediment quality assessment

A regional trace metals background was established on the basis of a consistent geochemical dataset, which refers to lagoon areas located in the south-eastern Po delta (Amorosi et al., 2002; Bonanni, 2010; Dinelli et al., 2012). Samples from borehole sections deeper than 1 m were selected, in order to determine the pre-industrial concentrations of trace metals (Huisman et al., 1997). Attention was paid to select samples corresponding to sediments deposited in lagoon environments (according to sedimentary facies analysis and micropaleontological observations), providing a sound reference situation. The regional background values were estimated following the APAT guidelines (APAT, 2006), with the geochemical dataset preliminary tested for distribution and outliers, and then the upper limit of background set as the 95th percentile of cumulative frequency distributions.

The level of contamination of trace metals (Cr, Cu, Hg, Ni, Pb, and Zn) was assessed by the *Enrichment Factor (EF)* calculated in accordance with Müller (1979):

$$EF = \frac{(Me/Al)_{\text{sample}}}{(Me/Al)_{\text{background}}}$$

where (Me/Al) is the ratio of the concentration of the element of interest and the concentration of the normalization element in the sample and in the background reference samples. In this study, Al has been used as a geochemical normalizer since it is a good grain-size proxy useful to compensate the granulometric and mineralogical effects on metal distribution; moreover, it is a conservative element, which is not affected by changes in environmental conditions (Dung et al., 2013). The obtained EFs were interpreted according to six degrees of contamination likely related to anthropogenic inputs: $EF < 1.5$: no enrichment (i.e. no contamination); $EF 1.5\text{--}3$: minor enrichment; $3\text{--}5$: moderate enrichment; $5\text{--}10$: moderately severe enrichment; $10\text{--}25$: severe enrichment; $25\text{--}50$: very severe enrichment, and >50 : extremely severe enrichment (Birch and Olmos, 2008; Celis-Hernandez et al., 2017). In this study, an EF value of 1.5 was chosen as baseline to compensate for lithological effects that can influence the background limit (Zhang and Liu, 2002).

The bioavailability of trace metals (Co, Cr, Cu, Ni, Pb, and Zn) was further analyzed through the Risk Assessment Code (RAC) (Perin et al., 1985), based on the percentage of metal associated with the exchangeable and carbonates fraction in the sediment (fraction A). Trace metals associated with this fraction are easily leachable and thus potentially bioavailable, and may pose a risk on aquatic biota.

According to the RAC approach, the associated risk with this potentially bioavailable fraction was defined by the corresponding criteria: (i) metal bound in fraction A $< 1\%$ (no risk); (ii) between 1 and 10% (low risk); (iii) from 11 to 30% (medium risk); 31–50% (high risk); and $>50\%$ (very high risk) (Jain, 2004; Botwe et al., 2017).

The $\sum\text{SEM-AVS}$ approach was also used as an indicator of the metal bioavailability (Cd, Cu, Ni, Pb, and Zn) and associated with adverse effects on aquatic biota according to US EPA guidelines (US EPA, 2004). This assessment method is based on the assumption that when $\sum\text{SEM-AVS} < 0$ (on a molar basis), there is enough AVS combining phase to react with divalent metals and form insoluble sulfides, which are thus not bioavailable for benthic organisms. On the contrary, when $\sum\text{SEM-AVS} > 0$, the exceeding fraction of metals might exist as free metal ions in porewater and could become potentially bioavailable and toxic for aquatic organisms. Based on this assumption, US EPA proposed the following classification criteria for sediments: no indication of adverse toxic effects when $\sum\text{SEM-AVS} < 0$; possible adverse effects when $0 < \sum\text{SEM-AVS} < 5$; and probable adverse effects when $\sum\text{SEM-AVS} > 5$ (US EPA, 2004; Li et al., 2014).

3. Results and discussion

3.1. Sediment geochemical characterization

Table 1 reports the geochemical composition of the Pialassa Piomboni sediments. The ranges of variation for major elements are limited, whereas a wider scattering occurs for trace elements like Cu, Zn, Pb, Sr, Hg, and S. An insight into the spatial distribution of oxides such as SiO₂, Al₂O₃, CaO and LOI (Fig. S1 of the Supplementary Material) provides key information on the composition of sediments.

Surface sediments from the Pialassa Piomboni lagoon are characterized by a SiO₂ and Al₂O₃ content of 40.2 ± 4.1 wt% and 11.9 ± 1.3 wt%, respectively. The highest Al₂O₃ content is recorded in the northern and southern sectors in tandem with medium to high SiO₂ content, reflecting a sediment composition dominated by clay minerals (e.g. aluminum silicates). Conversely, the high SiO₂ and the lowest Al₂O₃ content is found in the western sector of the lagoon, and these findings are indicative of a predominant sandy fraction enriched in quartz. The lowest content of both SiO₂ and Al₂O₃ was detected in the eastern sector of the lagoon, suggesting a sediment composition depending on other factors. Sediments from the study area reported a CaO content of 14 ± 2 wt%, with the highest and lowest values confined in the central and the southern/northern sectors of the Pialassa Piomboni lagoon, respectively. LOI (mean of 21 ± 3 wt%), which is representative of both carbonate and organic matter content, shows increasing values along a wester-eastern gradient, with the central-eastern sectors being particularly enriched in carbonates and organic matter.

In order to evaluate sediment quality in the Pialassa Piomboni lagoon, the spatial distribution of trace metals (Cr, Cu, Hg, Ni, Pb, Zn)

has also been investigated by geochemical mapping (Fig. 2). Chromium shows a fairly homogeneous spatial distribution over the study area with values ranging between 120 and 142 mg/kg (25th–75th percentile). The highest concentrations are registered in the southern and northern portion of the Pialassa Piomboni. Nickel spatial distribution (range: 33–93 mg/kg) reflects that observed for Al₂O₃ and SiO₂, which are indicative of clay minerals (Fig. S1), with the lowest and highest values (<66 mg/kg and >72 mg/kg, respectively) located in the central and the northern/southern sectors, respectively. Copper, lead and zinc display a similar spatial distribution showing increasing concentrations from the western to the eastern sector of the lagoon, ranging from 20 to 187 mg/kg, 11 to 257 mg/kg, and from 81 to 383 mg/kg, respectively. Zinc shows a fairly homogeneous spatial distribution within the Pialassa Piomboni lagoon, with few samples falling in the first class (<10th percentile) or in the last class (>90th percentile), whereas Cu and Pb display a more discontinuous spatial distribution. Copper and lead geochemical maps show several samples associated with very low levels (<10th percentile) surrounded by sediments with higher levels (>75th percentile). Cu and Pb maxima are marked outliers as evidenced by the difference between the 90th percentile and their highest value (55 and 187 mg/kg, and 40 and 257 mg/kg for Cu and Pb, respectively). A previous study conducted by Migani et al. (2015) reported similar levels in the sediments from the Pialassa Piomboni, ranging from 27 to 86 mg/kg, from 91 to 327 mg/kg, and from 8 to 33 mg/kg for Cu, Zn and Pb, respectively. Previous studies on trace metals contamination in the nearby Pialassa Baiona lagoon reported comparable levels with a significant enrichment of Cu, Zn and Pb in the sediments deposited after the 1950s, following the industrial development that begun in the harbor area (Candiano Channel), in close connection with both the Pialassa Piomboni and the Pialassa Baiona lagoons (Matteucci et al., 2005). The high levels of Pb found in our work can be related to atmospheric inputs and waterfowl hunting activities practiced in the Pialassa Piomboni, whereas for Cu and Zn domestic and agricultural effluents as well as the use of paints and galvanization products in the shipyards located in the eastern bank near to the Pialassa Piomboni are also important sources (Misericocchi et al., 1990; Migani et al., 2015). Mercury levels found in our study range from 0.04 to 9.9 mg/kg displaying a spatial distribution pattern different from that observed for Cu, Pb and Zn, with the highest values recorded in the northern sector of the Pialassa Piomboni, and the lowest ones in the southern sector. The Hg geochemical map shows gradually decreasing concentrations along a NE-SW gradient with only few outliers far exceeding the 90th percentile (~4 mg/kg) in the northern sector of the lagoon (Fig. 2). The spatial distribution of Hg suggests a provenance from the Candiano Channel connected to the northern end of the Pialassa Piomboni; the presence of high amounts of clay minerals in this area (as highlighted by the distribution of Al₂O₃ and SiO₂; see Fig. S1) might contribute to partially adsorb this metal in the surface sediments, acting as geochemical barrier and thus determining a pronounced increase of Hg concentrations in this sector. Previous studies on sediment contamination in the Pialassa Baiona lagoon reported even higher concentrations due to the direct discharge of several tons of mercury used as catalyst in a vinyl chloride chemical plant. Even though this chemical plant was shut down in the early 70s, high concentrations of Hg are still detected in surface sediments of the Pialassa Baiona, especially in the southern area close to the discharge input, registering concentrations as high as 57 mg/kg of Hg (Fabbri et al., 1998); 11–43 mg/kg (Matteucci et al., 2005); 0.1–22 mg/kg (Guerra et al., 2014). Lower concentrations have been measured in the central and northern sectors of the Pialassa Baiona (0.4–5.5 mg/kg; Guerra et al., 2009) suggesting Hg dilution due to increasing distance from the source input, and these levels are comparable to those detected in the Pialassa Piomboni in this study. In addition, it must be stressed that Hg is cyclically released from the sedimentary environment to the water column in the most polluted area of the Pialassa Baiona (Covelli et al., 2011).

Table 1

Statistical parameters calculated for the analyzed elements: average, standard deviation, median, minimum value, 25th and 75th percentile, maximum value.

Element	Min	Max	Average	SD	25th	50th	75th
Major oxides^a							
Al ₂ O ₃	8.8	14.0	11.9	1.3	11.3	12.1	12.8
CaO	10.9	20	14	2	13	14	16
Fe ₂ O ₃	2.4	5.8	4.6	0.7	4.4	4.6	5.1
K ₂ O	1.6	2.3	2.0	0.2	1.9	2	2.2
LOI	13	29	21	3	19	21	23
MgO	2.4	4.4	3.9	0.4	3.8	4.0	4.2
MnO	0.11	0.14	0.12	0.01	0.11	0.12	0.13
Na ₂ O	1.3	2.9	1.7	0.3	1.5	1.6	1.7
P ₂ O ₅	0.04	0.17	0.10	0.03	0.08	0.1	0.13
SiO ₂	30.1	53.4	40.2	4.1	38.5	40.3	41.8
TiO ₂	0.32	0.62	0.50	0.06	0.50	0.52	0.56
Trace elements^b							
As	<2	15	4	3	2	3	5
Ba	222	440	325	39	305	323	343
Br	143	1779	659	409	319	571	816
Ce	18	77	52	14	44	54	63
Cr	78	160	128	17	120	125	142
Co	<2	21	13	3	12	14	15
Cu	20	187	42	24	30	37	46
Hg	0.04	9.9	1.7	2.2	0.3	0.8	1.9
La	11	45	28	8	22	29	34
Mo	<2	16	6	3	3	5	8
Nb	4	16	11	3	9	11	12
Ni	33	93	71	13	66	72	80
Pb	11	257	32	35	21	26	32
Rb	73	146	114	20	101	116	129
S	1470	9880	6533	2344	5260	6795	8525
Sn	<2	14	3	2.5	2	2	4
Sr	320	872	447	101	376	416	510
Th	<2	21	8	4	6	8	11
V	53	125	104	17	98	108	116
Y	13	29	22	4	19	22	25
Zn	81	383	167	69	119	151	191
Zr	26	157	96	28	75	98	115

^a wt%.

^b mg/kg.

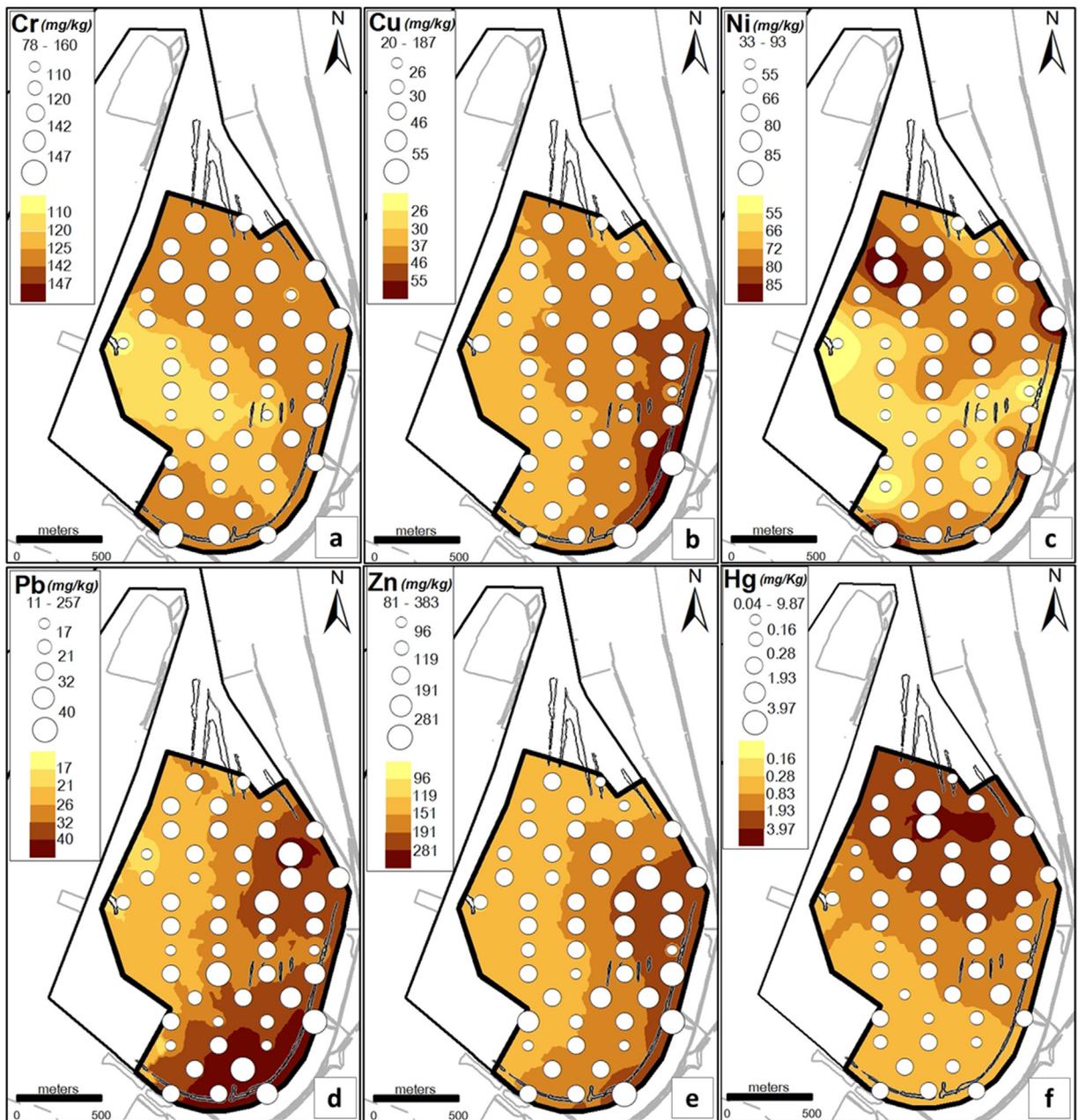


Fig. 2. Spatial distribution maps of Cr (a), Cu (b), Ni (c), Pb (d), Zn (e) and Hg (f).

3.1.1. Factor analysis

Factor analysis was run in order to investigate the multivariate relationship between the studied variables. Table 2 reports the rotated (Varimax) factor loadings obtained for each variable, along with the principal parameters calculated, useful to better evaluate the goodness-of-fit. The selection of factors to be considered was based on eigenvalues >1 . The selected factors explain 82% of the total variance; the high communalities suggest that all analyzed elements are well represented by the selected factors.

Factor 1 explains 37% of the total variance, with a marked bipartition: on one hand, elements with positive factor loadings (Al_2O_3 , Fe_2O_3 , MgO , K_2O , TiO_2 , Co, Nb, Ni, Rb, V, Y, Zr) are related to clay minerals; on the other hand, elements with negative factor loadings (CaO and, to a lower degree, Sr) can be related to carbonates.

Factor 2 accounts for 23% of the total variance and indicates the organic component in sediments (positive values). Indeed, it

includes LOI and P_2O_5 , which can be linked to the organic matter, although P_2O_5 can also have a detrital source that cannot be distinguished from the organic one through this type of analysis. Elements such as S, Br and Mo are also present in this group, since they have a high affinity with organic compounds (De Vivo et al., 2004). Copper and zinc show a very strong relationship with this factor, instead of being related to clay minerals, as it is to be expected in uncontaminated areas (De Vivo et al., 2004; Alloway, 2013) and this reveals the importance of the organic matter in controlling the distribution of these metals. Lead has a high factor score, as well, despite the presence of a very anomalous value. The negative factor scores for SiO_2 , MnO and partly K_2O could indicate the areas where the organic matter deposition is low, in particular those with coarse-grained sediments (SiO_2 and K_2O) and those where more oxidizing conditions allow Mn oxy-hydroxides precipitation.

Table 2

Factor loadings of each variable, communalities, eigenvalues, percentage of variance explained and cumulative variance for each selected factor. Factor loadings are classified as follows: black border for negative values; bold for very high values (>0.7); bold and italic for high values (0.5–0.7); italic for moderate values (0.35–0.5); grey indicates not elevated values (<0.35).

Element	Factor loadings						Communalities
	1	2	3	4	5	6	
Al ₂ O ₃	0.949	-0.153	-0.077	0.100	0.047	-0.006	0.941
CaO	-0.775	0.058	<i>0.470</i>	-0.135	0.156	0.081	0.874
Fe ₂ O ₃	0.890	0.049	0.030	0.102	0.031	0.206	0.849
K ₂ O	0.826	-0.394	-0.293	0.102	0.017	0.044	0.936
LOI	0.047	0.733	0.641	-0.007	0.092	-0.076	0.964
MgO	0.910	0.177	0.150	-0.027	0.041	0.046	0.887
MnO	0.219	-0.488	0.069	0.142	0.242	0.653	0.796
Na ₂ O	-0.204	-0.162	0.032	0.059	-0.898	-0.060	0.882
P ₂ O ₅	-0.067	0.665	-0.049	-0.136	0.252	-0.017	0.532
SiO ₂	-0.219	-0.566	-0.738	0.022	-0.126	-0.021	0.930
TiO ₂	0.954	-0.145	-0.029	-0.056	0.074	0.072	0.945
Ba	-0.154	0.094	-0.756	0.014	0.361	-0.081	0.741
Br	-0.108	0.891	0.217	-0.002	0.063	-0.072	0.861
Ce	<i>0.436</i>	0.027	-0.371	-0.316	-0.387	<i>0.454</i>	0.784
Co	0.860	0.074	0.146	0.013	0.234	0.174	0.852
Cr	0.511	0.221	-0.447	0.305	0.083	0.122	0.624
Cu	0.147	0.872	-0.050	-0.019	0.118	-0.019	0.800
Hg	0.403	0.130	-0.047	0.786	0.173	0.016	0.830
La	0.507	-0.097	-0.134	-0.115	<i>0.352</i>	<i>0.356</i>	0.548
Mo	-0.124	0.819	0.217	0.073	-0.113	0.003	0.751
Ni	0.878	0.323	0.057	0.092	0.081	0.149	0.915
Nb	0.848	0.131	0.075	-0.065	-0.024	-0.100	0.757
Pb	-0.018	0.530	0.291	0.209	-0.190	<i>0.472</i>	0.668
Rb	0.926	-0.059	0.020	0.155	-0.025	0.038	0.888
S	0.196	0.722	0.059	<i>0.418</i>	-0.094	-0.096	0.756
Sr	-0.380	<i>0.423</i>	0.739	<i>0.054</i>	0.225	-0.015	0.922
Th	0.225	0.172	0.020	-0.635	0.316	-0.068	0.589
V	0.847	0.314	0.042	-0.031	0.173	0.099	0.858
Y	0.891	-0.175	-0.126	-0.068	-0.001	-0.007	0.845
Zn	0.069	0.939	-0.060	-0.077	0.040	0.015	0.897
Zr	0.706	-0.126	-0.399	-0.345	-0.066	-0.185	0.831
Eigenvalues	11.454	7.116	2.314	1.802	1.547	1.018	
%Variance explained	37	23	7.5	5.8	5.0	3.3	
%Cumulative variance	37	60	68	74	79	82	

Factor 3, corresponding to 7.5% of the total variance, depends primarily on elements such as SiO₂ and Ba, and secondarily on Cr, Zr and Ce, with negative values, and reflects the presence of feldspathic sands in sediments and eventually enrichments related to sorting effect for the presence of heavy minerals (Vital and Stattegger, 2000; Dypvik and Harris, 2001; Garcia et al., 2004; Donnini et al., 2007). LOI, CaO and Sr are represented by this factor in an opposite direction (positive factor loadings), reflecting the different behavior of carbonates, either detrital or biogenic.

Factors 4, 5 and 6 explain very little variability (<6%) and do not contribute with additional information (Preacher and MacCallum, 2002); therefore, they will not be discussed in this section.

Since the majority of data variability (~70%) is explained by the first three factors, their combination can be used to define the main features of the sediments of Pialassa Piomboni lagoon. Fig. 3 reports a combined summary map that identifies the areas of prevalence of the four main sediment components: clays and carbonates (corresponding to Factor 1), organic matter (corresponding to Factor 2) and feldspathic sands (corresponding to Factor 3). The map highlights areas of the Pialassa Piomboni with a dominant composition of sediments. In particular, the northern and southern sectors of the lagoon display a prevalent clayey composition, while the central sector is characterized by a carbonatic belt extending from East to West. Organic matter is predominant in the eastern/middle-eastern sector, partly overlapping with the spatial distribution of carbonate and clayey sediments in the North.

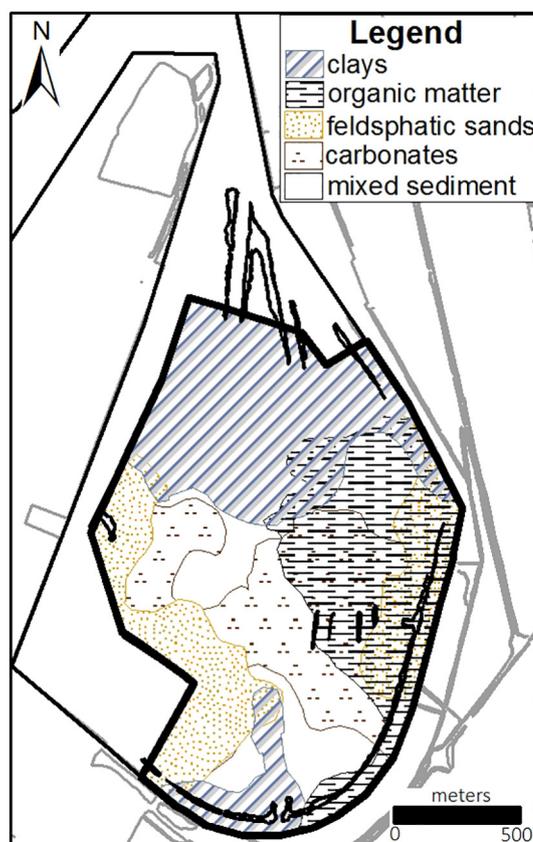


Fig. 3. Map showing surface sediment composition of the Pialassa Piomboni.

Coarse-grained sandy deposits are prevalent on the south-western sector and on the eastern side of the lagoon, partly overlapping with the organic matter distribution.

3.2. SEM-AVS analysis

The results of AVS and SEM analysis are summarized in Table 3. Sulfides concentrations in sediments (AVS) fall in the range between 0.03 and 8.8 μmol/g, and are typical of coastal lagoons located in the Northern Adriatic Sea (Azzoni et al., 2005; Sorokin and Zakuskina, 2012).

Concerning concentrations of the simultaneously extracted metals, Zn is the element that mostly accounts for the total SEM, with a median value of 1.1 μmol/g, quite similar to the ΣSEM median of 1.3 μmol/g. Zn-SEM shows a skewed population data, with a maximum value of 6.1 μmol/g reflecting a skewed ΣSEM population data reaching a maximum of 6.6 μmol/g. Other SEM metals (Cd, Cu, Ni and Pb) are only minor contributors to the total pool of SEM in the sediments, with a

Table 3

Summary table of sulfides (AVS) and simultaneously extracted metals (SEM): range of values (min–max), mean, standard deviation, 25th, 50th and 75th percentile. Values are expressed as μmol/g.

	Min	Max	Mean	SD	25th	50th	75th
AVS	0.03	8.8	3.1	2.8	0.6	2.0	5.0
Cd-SEM	0.001	0.007	0.003	0.001	0.002	0.003	0.004
Cu-SEM	0.005	1.4	0.1	0.2	0.05	0.08	0.2
Ni-SEM	0.04	0.3	0.2	0.05	0.1	0.2	0.2
Pb-SEM	0.02	0.2	0.06	0.03	0.04	0.05	0.1
Zn-SEM	0.2	6.1	1.4	1.2	0.5	1.1	3.5
ΣSEM	0.3	6.6	1.7	1.3	0.8	1.3	2.0
ΣSEM/AVS	0.1	34	2.5	6.2	0.4	0.8	1.5
ΣSEM-AVS	-6.7	2.0	-1.4	2.3	-2.7	-0.5	0.3

total maximum of $<2 \mu\text{mol/g}$, and a median concentration always $<1 \mu\text{mol/g}$.

The $\sum \text{SEM}/\text{AVS}$ ratio has been recognized to be a good indicator of the bioavailability of trace metals (Prica et al., 2008; Zhang et al., 2014), and is based on the assumption that divalent metals such as Cd, Cu, Ni, Pb and Zn have a high affinity with sulfides in sediments, especially in anoxic conditions. Sulfides act as good scavengers of divalent metals that are trapped in the solid phase, thus resulting less bioavailable for the resident organisms. When SEM exceed AVS molar content in sediments ($\sum \text{SEM}/\text{AVS} > 1$), they can be released in the sediment porewaters. The ratio of $\sum \text{SEM}/\text{AVS}$ in sediments of the Pialassa Piomboni is highly variable, being comprised between 0.1 and 34, with a median value of 0.8, and thus below the threshold level of 1, indicative of no potential adverse effects on the aquatic biota. According to the $\sum \text{SEM}/\text{AVS}$ ratio, Cd, Cu, Ni, Pb and Zn are potentially bioavailable in 38% of samples with only 6% of samples displaying a $\sum \text{SEM}/\text{AVS} > 10$, indicating that some sediment samples may have potential adverse effects on the aquatic organisms of the Pialassa Piomboni. Another approach used as indicator of metal bioavailability is the difference $\sum \text{SEM}-\text{AVS}$ proposed by Hansen et al. (1996), and applied in several coastal and marine areas (Li et al., 2014; Zhang et al., 2014; Arfaenia et al., 2016), which provides more insights into the extent of AVS binding capacity and the magnitude by which AVS binding can be exceeded. This approach is particularly suitable when AVS concentrations are fairly low, resulting in high $\sum \text{SEM}/\text{AVS}$ ratios, but low $\sum \text{SEM}-\text{AVS}$ differences. $\sum \text{SEM}-\text{AVS}$ ranges between -6.7 and $2.0 \mu\text{mol/g}$, with both median and mean value below 0, confirming low $\sum \text{SEM}$ bioavailability. $\sum \text{SEM}$ concentrations exceed AVS content ($\sum \text{SEM}-\text{AVS} > 0$) in 34% of samples, of which only 6% display SEM-AVS values >1 . In this study, the $\sum \text{SEM}-\text{AVS}$ approach was preferred to the $\sum \text{SEM}/\text{AVS}$ ratio and used for further assessment of metals bioavailability, as $\sum \text{SEM}-\text{AVS}$ difference found in this study better represents the magnitude of $\sum \text{SEM}$ exceeding AVS content (whose exceedance is not so high), which on the other hand is overestimated by the $\sum \text{SEM}/\text{AVS}$ ratio.

3.3. Trace metals fractionation

Since bioavailability and consequent toxicity of trace metals strongly depend on their chemical binding with sediments, metal content in different fractions of sediments (exchangeable, reducible, oxidizable, and residual) was investigated in order to assess their mobility in the solid phase (Fig. 4). Aluminum and iron, which are the major components of the sediment occurring in silicate minerals, are strongly bound to the residual fraction ($\sim 90\%$ and $\sim 80\%$ as median, respectively), highlighting a likely lithogenic origin and thus a negligible mobility. Chromium and nickel are also predominantly bound to the residual fraction of the sediment ($\sim 90\%$ and $\sim 70\%$, respectively), with a likely occurrence in primary and secondary minerals, and are thus the least mobile trace metals; manganese, cobalt and zinc show a similar pattern ($\sim 50\%$ in the residual fraction). Fe shows a slightly higher partition in the reducible fraction ($\sim 10\%$). Mn, and Zn to a lower extent, result weakly bound to the acid extractable/exchangeable phase ($\sim 25\%$ and $\sim 10\%$, respectively), suggesting interactions with carbonates or adsorption onto mineral surfaces; cobalt outliers show partitioning into the weakly-bound phase, as well (Fig. 4a). Lead, zinc and copper are the metals mostly bound to Fe- and Mn oxy-hydroxides (reducible fraction, B), accounting on average for $\sim 60\%$, $\sim 50\%$ and $\sim 30\%$ of their total content, respectively. Co, Mn, Cr and Ni are weakly partitioned into the reducible fraction ($\sim 20\%$, $\sim 1\%$, $\sim 1\%$, and $\sim 10\%$, respectively). Copper, and Co ($\sim 40\%$ and $\sim 30\%$) are mainly bound to the oxidizable phase of the sediment (fraction C), highlighting a great affinity of these trace elements with organic matter. Nickel, lead and zinc are slightly partitioned into this fraction ($\sim 15\%$), with Pb showing a skewed distribution of data with an outlier accounting for $>75\%$ of total Pb, thus reflecting a local anomaly.

In conclusion, considering the sum of A + B + C fractions as the total extractable fraction, Co, Cu and Pb are the most mobile elements in sediments ($\sim 50\%$, $\sim 70\%$ and $\sim 80\%$, respectively), whereas Mn, Co and Zn are the second mobile elements, showing a similar partitioning into the residual phase of the sediment. Conversely, Al, Fe, Cr and Ni are predominantly bound to the residual fraction of the sediment, suggesting a

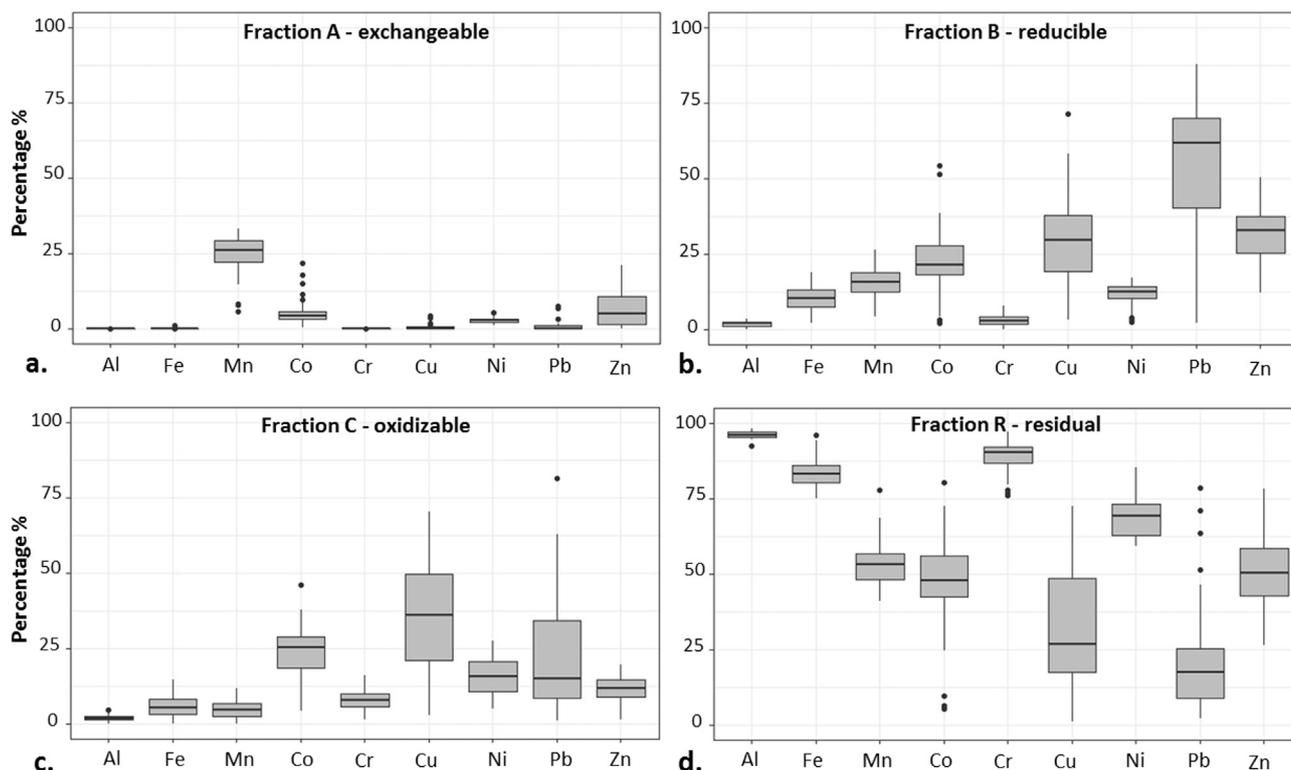


Fig. 4. Percentage of partitioning of Al, Fe, Mn, Co, Cr, Cu, Ni, Pb, Zn in the exchangeable fraction A (a), reducible fraction B (b), oxidizable fraction C (c) and residual fraction R (d).

lithogenic origin, and thus low mobility, regardless pH and redox conditions.

Geochemical mapping (Fig. 5) shows that Mn has a homogeneous spatial distribution, and is equally partitioned between the weakly-bound and residual phases of sediments, with the highest mobile proportion localized in the northern and south-eastern sectors of the Pialassa Piomboni lagoon, in tandem with carbonate sediments and clay minerals. Hence, a peak concentration of 335 mg/kg of Mn could be released if changes in pH occurred (Table S2 of the Supplementary Material). Spatial distribution of Mn bound to the reducible phase of sediment is similar to that of clay minerals within the lagoon, though

lower concentrations with respect to the weakly-bound phase are registered (maximum of 268 mg/kg). Cobalt bound to the oxidizable fraction of the sediment (organic matter and sulfides), appears to be spatially condensed in the northern and central-eastern sectors of the Pialassa Piomboni; under oxic conditions, as high as 6 mg/kg of Co could be released due to organic matter degradation. In the western sector, Co predominance in the residual phase matches the spatial distribution of the carbonatic belt, as well as that of feldspathic sands, and thus a low mobility of this trace metal is expected in this area of the lagoon. Copper affinity to organic matter in the oxidizable phase of the sediment is particularly evident in the north-eastern sector of the lagoon (Fig. 5c).

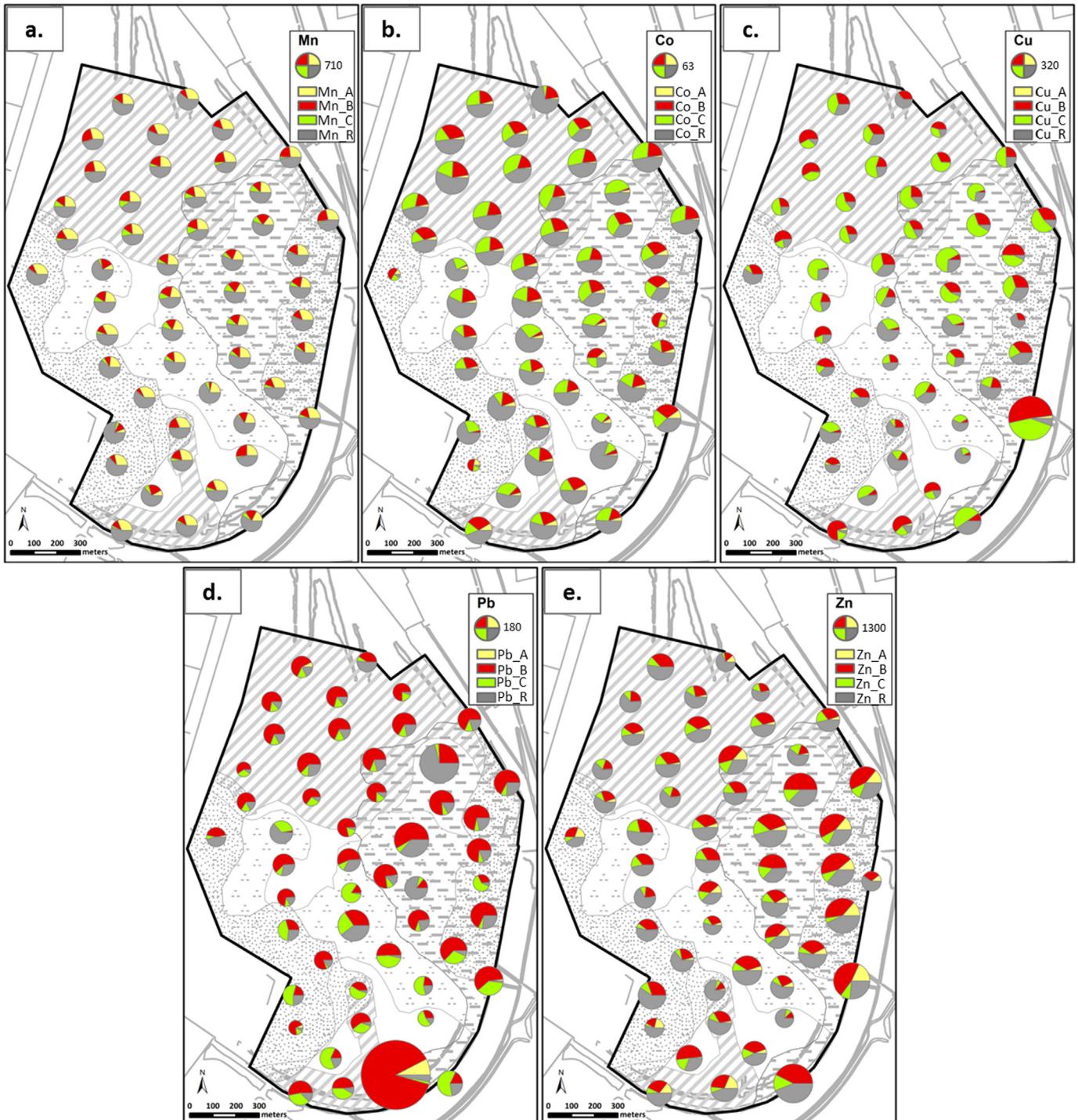


Fig. 5. Distribution maps of percentage of elements in the different fractions obtained by SEP analysis: Mn (a), Co (b), Cu (c), Pb (d), Zn (e). The legend of sediment composition in the background is the same as Fig. 3, previously reported.

Clayey sediments are associated with the Cu fraction bound to the reducible phase in the northern and southern sectors of the lagoon, suggesting association with Fe-Mn mineral structures. An outlier in the south-eastern sector is also evident, with a total concentration of 187 mg/kg mainly partitioned between the reducible fraction and the oxidizable one (96 and 76 mg/kg, respectively), further proving the anomaly of this sample, which is likely related to anthropogenic inputs. Copper can be mobilized from sediments by changes in redox conditions in the Pialassa Piomboni lagoon; as high as 39 mg/kg and 27 mg/kg could be released due to organic matter oxidation, or reduction of Fe-Mn oxy/hydroxides. Lead shows a great affinity with Fe-Mn oxy/hydroxides (reducible fraction), especially in the northern and eastern sectors, and with organic matter and sulfide (oxidizable fraction) in the middle-southern sector of the lagoon. A high Pb anomaly is evident in the southern sector of the lagoon, where this metal is predominantly bound to the reducible fraction, accounting for over 80% of the total Pb content (257 mg/kg). Zinc displays a homogenous spatial pattern, resulting equally partitioned between the reducible and the residual phases (from 11 to 163 mg/kg and from 42 and 168 mg/kg, respectively), with a slight predominance into oxides and hydroxides in the northern and eastern sectors of the lagoon. Conversely, it occurs mainly associated with the residual fraction in the central and southern sectors. An increase of Zn weakly bound to the sediment occurs within the eastern sector, thus suggesting exchanges with carbonates.

Mercury partitioning was not estimated into the different SEP phases, as its sequential extraction follows a selective and specific protocol employing different extracting solutions, due to the unique physical and chemical properties of the element (Bloom et al., 2003). Previous studies on Hg fractionation in the surrounding Pialassa Baiona lagoon showed that elemental Hg is the predominant fraction in the sediment, accounting for ~90% of total Hg, and negligible contributions from organo-chelated Hg and mercuric sulfide Hg (~6%) (Covelli et al., 2011). Considering that elemental Hg is often studied as a good estimation of the free Hg(0) present in the sediment, and that the source of Hg pollution in the Ravenna coastal lagoons is related to its past use as a catalyzer in a chemical plant, potential sources of HgS as cinnabar can be excluded. The sulfide-bound mercury fraction should be therefore considered mainly as metacinnabar, that is Hg sulfide formed as a consequence of the strong sulfate reduction in the lagoon sediments (Fabbri et al., 2001), and not Hg bound to a stable crystalline mineral phase.

3.4. Sediment quality assessment

The regional geochemical background for Cr, Cu, Ni, Pb and Zn was computed as the 95th percentile of the dataset reported in Table S3 (Supplementary Material) and is shown in Table 4. Since no data were available for Hg, a background value of 0.12 mg/kg measured in deep core sediments from lagoon environments in the proximity of the northern Adriatic Sea (Guerzoni et al., 1984), associated to a background content of Al₂O₃ of 14.6 wt% (Donnini et al., 2007), has been chosen as

Table 4
Regional background value (mg/kg) and its corresponding value normalized to Al; EF classification and percentage of samples (%) falling into each class of enrichment for Cr, Cu, Ni, Pb, Zn, and Hg.

	Cr	Cu	Ni	Pb	Zn	Hg
Regional background value (mg/kg)	163	48	100	27	127	0.12
Al-normalized background value	20.1	6.8	13.1	3.6	16.1	0.01
EF classification	Sample percentage (%)					
EF value	Interpretation					
<1.5	98	94	100	74	56	10
1.5–3	2	4	–	20	36	16
3–5	–	2	–	4	8	2
5–10	–	–	–	–	–	28
10–25	–	–	–	2	–	22
25–50	–	–	–	–	–	16
>50	–	–	–	–	–	6

reference value. Chromium and Ni do not show anthropogenic enrichment over the study area with respect to the regional background levels of 163 mg/kg and 100 mg/kg, respectively, indicating that the high concentrations detected are due to the lithogenic composition of sediments (Amorosi, 2012; Amorosi and Sammartino, 2007; Amorosi et al., 2013; Curzi et al., 2006; Dinelli et al., 2013), as previously highlighted by their predominance in the residual and less mobile phase of the sediment. Conversely, Cu, Pb and Zn, show anomalous levels, with 22%, 36% and 68% of samples far exceeding their background levels, respectively. Mercury registers concentration values consistently higher than the regional background within the Pialassa Piomboni lagoon (>90% of samples).

As the Enrichment Factor (EF) is an useful index to determine the degree of contamination of trace metals pollution, EFs were calculated to evaluate anthropogenic influences on trace metals in sediments of the Pialassa Piomboni. A summary of EFs values is provided in Table S4, and the percentage of samples in each EF class is reported in Table 4. Nickel does not show any sample above the 1.5 threshold, and Chromium displays similar results, with only one sample slightly above the 1.5 threshold. These results reinforce the hypothesis that Cr and Ni concentrations are dependent on the geochemical provenance of sediments rather than on anthropic contributions. The only Cr anomaly in the western sector of the Pialassa Piomboni is likely related to the predominance of sandy material. This is consistent with the occurrence of Cr-bearing heavy minerals (e.g. garnet, pyroxene) in the sedimentary deposits of the coastal plain (Rizzini, 1974; Marchesini et al., 2000). A minor-to-moderate Cu enrichment is reported for ~5% of samples, with one outlier displaying a 4-fold enrichment (EF of 4.3), thus suggesting a local anthropogenic input. Lead exceeds the regional background value of 27 mg/kg with a minor enrichment in 20% of the samples, and one outlier reaching a 10-fold enrichment (EF = 11). This punctual severe enrichment is restricted within the southern sector of the study area, and clearly reflects an anomaly in contamination related to the surrounding industrial activities, as well as hunting practices (Migani et al., 2015). A minor-to-moderate enrichment of Cu and Pb is detected in the eastern sector of the Pialassa Piomboni, in accordance with the spatial distribution of Cu and Pb total and extracted content (see Figs. 2 and 5). As far as Zn is concerned, 44% of samples exceed the EF baseline of 1.5, with 8% showing a moderate enrichment, and reaching an EF of 3.9 in the eastern sector of the study area. Mercury values are consistently higher than the regional background value in >90% of samples, with ~50% of samples showing moderate-to-very severe enrichment, and ~5% displaying an extremely severe enrichment (EF > 50). Samples with the highest Hg content and EFs values (up to 88) are all constrained in the northern sector of the study area. Overall, EFs values evidence a widespread contamination of Hg all over the study area, and this fact is supported by the anomalous behavior of the element as highlighted by factor analysis, in which Hg did not show any correlation with geochemical features except of a weak correlation with sulfur, thus indicating a prevalent anthropic origin (see Table 2 and previous comments).

The calculation of the Enrichment Factor is an useful tool to identify situations of metals contamination; nevertheless, it does not give information about metals availability and their subsequent potential ecological risk for biota. Therefore, in addition to the EF evaluation, RAC and SEM-AVS approaches were used as indicators of metals bioavailability and the related risk for benthic organisms.

Fig. 6a shows calculated RAC values for the analyzed metals (Co, Cr, Cu, Ni, Pb, Zn), representative of the percentage of total metal content detected in the exchangeable and carbonate fraction of sediments (fraction A), which is the most easily leachable and thus potentially bioavailable fraction. In general, Cr, Cu, and Pb show RAC values lower than 1, indicating that these metals are not bioavailable and remain preferentially bound to the solid phase of the sediment, and thus fall into the “no risk” category. Only few outliers are registered for Cu and Pb, with RAC values of 1–10% (low risk), including samples which also show a

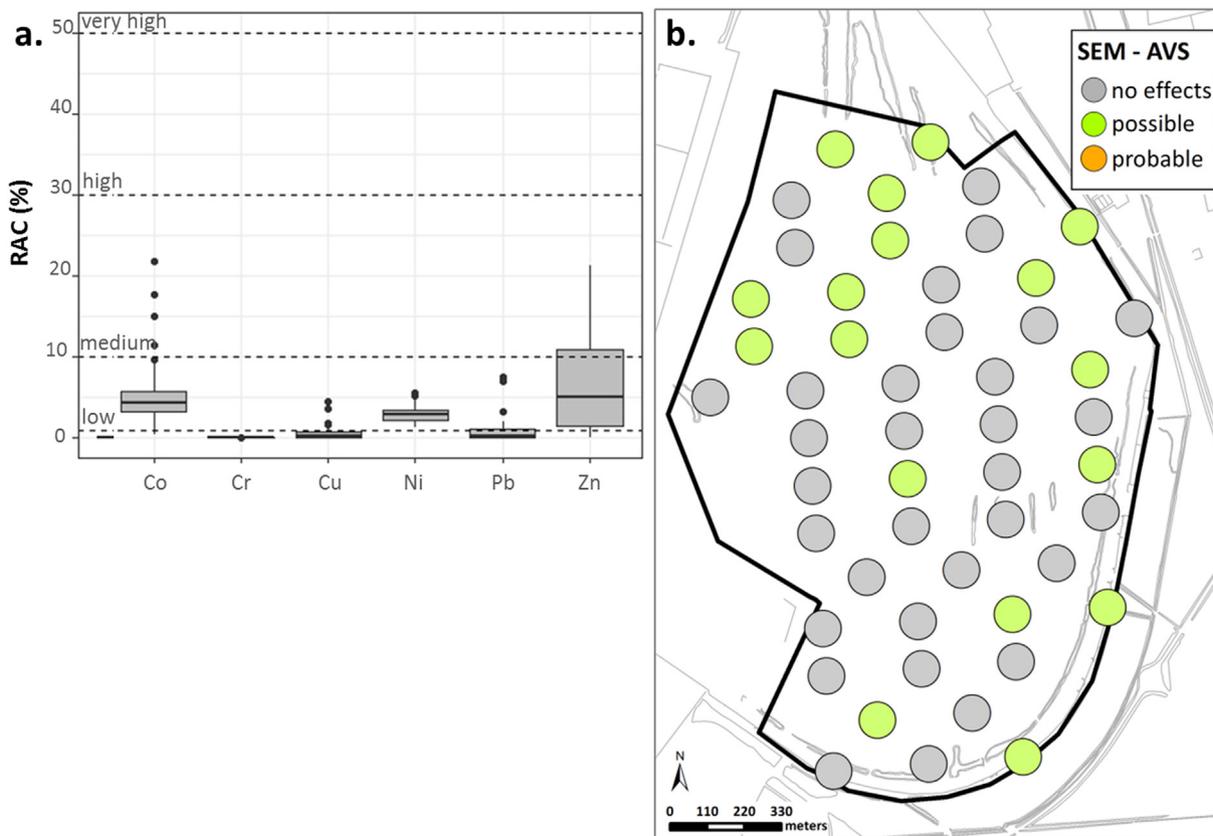


Fig. 6. Assessment of heavy metals bioavailability: (a) RAC classification of percentage of metal content within fraction A; (b) $\sum \text{SEM-AVS}$ classification into “no effects” ($\sum \text{SEM-AVS} < 0$), “possible effects” ($0 < \sum \text{SEM-AVS} < 5$), and “probable effects” ($\sum \text{SEM-AVS} > 5$).

moderate-to-severe enrichment ($EF > 3$), confirming the hypothesis of an anthropogenic input. However, these RAC outliers suggest only a low bioavailability for Cu and Pb, which regards few well-defined samples. Nickel RAC values fall in the range of 1.3–5.6% (low risk); however, Ni concentrations associated with this weakly-bound fraction could be the result of a small weathering from bulk sediment and subsequent re-association with the exchangeable fraction. RAC values > 1 , thus, are not of concern as regards Ni. Cobalt RAC values can be classified as “low risk”, with the exception of some outliers scored as “medium risk”. Cobalt is a mobile element and commonly occurs in the fine-grained fractions of sediment, varying with Fe- and Mn content and following the behavior of Ni; relatively high concentrations of this element found in the weakly-bound phase could be indicative of a bulk provenance as for Ni. Yet, Co total concentrations are not of concern from an environmental and ecological point of view (see Table 1 for range of values). RAC values for Zn are indicative of “low” risk in the majority of samples ($\text{RAC} > 1\%$); however, few RAC values suggest medium risk ($\text{RAC} > 10\%$). The Zn content bound with this labile fraction is mainly associated with carbonates, as highlighted in Fig. 5e, thus suggesting a low mobility and bioavailability in the alkaline waters of the Pialassa Piomboni.

The $\sum \text{SEM-AVS}$ approach was also applied to surface sediments of the Pialassa Piomboni, as an additional indicator of metals (Cd, Cu, Ni, Pb, and Zn) bioavailability and their potential adverse biological effects. As shown in Fig. 6b, the majority of sediment samples ($> 60\%$) report $\sum \text{SEM-AVS} < 0$, with no indication of adverse effects on the aquatic biota, whereas $\sim 30\%$ of samples display $0 < \sum \text{SEM-AVS} < 5$, indicating that adverse effects are possible. Nonetheless, it should be taken into consideration that not all sediments with $\sum \text{SEM-AVS} > 0$ can cause toxicity on biota, as there are many other binding phases in sediments which could trap metals, decreasing their bioavailability (Burton et al., 2005; Di Toro et al., 2005). No sediment samples show $\sum \text{SEM-AVS}$

> 5 , confirming that concentrations of divalent metals in sediments are not of high concern in terms of adverse effects on the resident biota. Sediments associated with possible adverse effects are located in the northern sector of the Pialassa Piomboni, in close connection with the harbor area through the Candiano Channel, where sediments are mainly composed by clay minerals; other samples are located in the eastern area and are characterized by a high organic matter content (Figs. 3 and 6b). In the southern area, where sediments are dominated by clay minerals, only 2 samples are also classified with possible adverse effects on aquatic biota and correspond to the highest concentrations of total Pb and Cu detected in this study. In general, the spatial distribution of sediments falling into the category of $0 < \sum \text{SEM-AVS} < 5$ mostly reflects the spatial distribution of bioavailable Zn content (Zn in fraction A, Fig. 5e), which is consistent with RAC results, and thus confirming that Zn is likely the most bioavailable metal in sediments of the Pialassa Piomboni. It is noteworthy, though, that this fraction of Zn is mainly associated with carbonates in sediments and thus not readily bioavailable, but it can be re-mobilized with changes in pH. The amount of bioavailable Zn that can be released from sediments is not so high, though, ranging from not detectable to 60 mg/kg, with a median value of 6 mg/kg (Table S2), which are far below the regional background value of the study area (127 mg/kg), and the Limit of Chemical Level (LCL) of 170 mg/kg proposed by the Italian Environmental Ministry as the concentration level above which adverse toxic effects on organisms can be expected (APAT-ICRAM, 2007).

4. Conclusions

The geochemical characterization of the Pialassa Piomboni identified different patterns of sediment composition, with northern and southern areas dominated by clay minerals, a central sector characterized by carbonates, an eastern sector enriched in organic matter, and a sandy zone

on the western and eastern borders of the lagoon. Sediment quality assessment highlighted a contribution from natural sources for Cr and Ni, as their concentrations were below their regional geochemical background. Copper, lead and zinc showed a minor-to-moderate enrichment mainly confined in the eastern part of the lagoon, indicative of anthropogenic inputs. Zinc also displayed a localized low to medium risk according to RAC classification, thus suggesting an increased mobility and bioavailability. Mercury showed a remarkable spread contamination with moderate-to-very severe enrichment all over the study area, clearly evidencing that contribution of past industrial activities in the surrounding areas are still impacting sediment quality within the Pialassa Piomboni lagoon. In general, the Σ SEM-AVS approach highlighted no great concern in terms of metals bioavailability and associated biological effects for resident organisms; however, adverse effects would be somewhat possible in the northern and eastern sectors of the lagoon. Further biological research aimed at assessing the real risk of Hg posed on aquatic organisms in the Pialassa Piomboni should be addressed in order to find out the best management options of such contaminated sediments.

Acknowledgements

The authors are grateful to Autorità Portuale di Ravenna for funding the work and allowing sediment sampling within the Pialassa Piomboni lagoon. The authors wish to thank all the group members for their constant field and laboratory assistance, helpful advice and in-depth discussion, and in particular Juan Pablo Pozo Hernández for the setup and assistance in SEM-AVS analysis.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.04.093>.

References

- Airolidi, L., Ponti, M., Abbiati, M., 2016. Conservation challenges in human dominated landscapes: the harbour and coast of Ravenna. *Reg. Stud. Mar. Sci.* 8, 308–318.
- Allen, H.E., Fu, G., Deng, B., 1993. Analysis of acid-volatile sulphide and simultaneous extracted metals for the estimation of potential toxicity in aquatic sediments. *Environ. Toxicol. Chem.* 12, 1441–1453.
- Alloway, B.J., 2013. Heavy Metals in Soils. *Trace Metals in Soils and Their Bioavailability*. Springer.
- Amorosi, A., 2012. Chromium and nickel as indicators of source-to-sink sediment transfer in a Holocene alluvial and coastal system (Po Plain, Italy). *Sediment. Geol.* 280, 260–269.
- Amorosi, A., Sammartino, L., 2007. Influence of sediment provenance on background values of potentially toxic metals from near-surface sediments of Po coastal plain (Italy). *Int. J. Earth Sci.* 96, 389–396.
- Amorosi, A., Centineo, M.C., Dinelli, E., Lucchini, F., Tateo, F., 2002. Geochemical and mineralogical variations as indicators of provenance changes in Late Quaternary deposits of SE Po Plain. *Sediment. Geol.* 151, 273–292.
- Amorosi, A., Colalongo, M.L., Dinelli, E., Lucchini, F., Vaiani, S.C., 2013. Cyclic variations in sediment provenance from late Pleistocene deposits of the eastern Po Plain, Italy. *Geol. Soc. Am. Spec. Pap.* 420, 13–24.
- APAT, 2006. Protocollo operativo per la determinazione dei valori di fondo di metalli/metalloidi nei suoli dei siti d'interesse nazionale.
- APAT-ICRAM, 2007. Manuale per la movimentazione di sedimenti marini. Agenzia per la Protezione dell'Ambiente e per i Servizi Tecnici (APAT) – Istituto Centrale per la Ricerca Applicata sul Mare (ICRAM), p. 67.
- Arfaeini, H., Nabipour, I., Ostovar, A., Asadgol, Z., Abuee, E., Keshtkar, M., Dobaradan, S., 2016. Assessment of sediment quality based on acid-volatile sulfide and simultaneously extracted metals in heavily industrialized area of Asaluyeh, Persian Gulf: concentrations, spatial distributions, and sediment bioavailability/toxicity. *Environ. Sci. Pollut. Res.* 23, 9871–9890.
- Azzoni, R., Giordani, G., Viaroli, P., 2005. Iron-sulphur-phosphorous interactions: implication for sediment buffering capacity in a Mediterranean eutrophic lagoon (Sacca di Goro, Italy). *Hydrobiologia* 550, 131–148.
- Bandini, R., 1996. Caratterizzazione ambientale della Pialassa Piombone. *Bollettino economico: pubblicazione mensile della Camera di Commercio, Industria e Agricoltura*, 1996.3, pp. 53–62.
- Baran, A., Tarnawski, M., 2015. Assessment of heavy metals mobility and toxicity in contaminated sediments by sequential extraction and a battery of bioassays. *Ecotoxicol. Polut. Res.* 24, 1279–1293.
- Birch, G.F., Olmos, M.A., 2008. Sediment-bound heavy metals as indicators of human influence and biological risk in coastal water bodies. *ICES J. Mar. Sci.* 65 (8), 1407–1413.
- Bloom, N.S., Preus, E., Katon, J., Hiltner, M., 2003. Selective extractions to assess biogeochemically relevant fraction of inorganic mercury in sediments and soils. *Anal. Chim. Acta* 479, 233–248.
- Bonanni, G.M., 2010. Caratterizzazione geochimica dell'acquifero freatico costiero di Ravenna (area Nord). Università degli Studi di Bologna (Master thesis (supervisor: Dinelli E.)).
- Botwe, B., Alfonso, L., Nyarko, E., Lens, P.L., 2017. Metal distribution and fractionation in surface sediments of coastal Tema Harbour (Ghana) and its ecological implications. *Environ. Earth Sci.* 76, 514.
- Burton, G.A., Nguyen, L.T.H., Janssen, C., Baudo, R., McWilliam, R., Bossuyt, B., Beltrami, M., Green, A., 2005. Field validation of sediment zinc toxicity. *Environ. Toxicol.* 24 (3), 541–553.
- Celis-Hernandez, O., Rosales-Hoz, L., Cundy, A.B., Caarranza-Edwards, A., 2017. Sedimentary heavy metal(loids) contamination in the Veracruz shelf, Gulf of Mexico: a baseline survey from a rapidly developing tropical coast. *Mar. Pollut. Bull.* 204, 213.
- Covelli, S., Emili, A., Acquavita, A., Koron, N., Faganeli, J., 2011. Benthic biogeochemical cycling of mercury in two contaminated northern Adriatic coastal lagoons. *Cont. Shelf Res.* 31, 1777–1789.
- Curzi, P.V., Dinelli, E., Ricci Lucchi, M., Vaiani, S.C., 2006. Palaeoenvironmental control on sediment composition and provenance in the late Quaternary deltaic successions: a case study from the Po delta area (northern Italy). *Geol. J.* 41, 591–612.
- De Vivo, B., Lima, A., Siegel, F.R., 2004. *Geochimica ambientale. Metalli potenzialmente tossici*. Liguori editore.
- Di Toro, D.M., McGrath, J.A., Hansen, D.J., Berry, W.J., Paquin, P.R., Matthew, R., Wu, K.B., Santore, R.C., 2005. Predicting sediment metal toxicity using a sediment biotic ligand model: methodology and initial application. *Environ. Toxicol. Chem.* 24 (10), 2410–2427.
- Dinelli, E., Ghosh, A., Rossi, V., Vaiani, S.C., 2012. Multiproxy reconstruction of late pleistocene-holocene environmental changes in coastal successions: microfossil and geochemical evidences from the Po Plain (Northern Italy). *Stratigraphy* 9 (2), 153–167.
- Dinelli, E., Tateo, F., Summa, V., 2013. Geochemical and mineralogical proxies for grain size in mudstones and siltstones from the Pleistocene and Holocene of the Po River alluvial plain, Italy. *Geol. Soc. Am. Spec. Pap.* 420, 25–36.
- Donnini, F., Dinelli, E., Sangiorgi, F., Fabbri, E., 2007. Integration of biological and geochemical analysis to assess the environmental quality of a coastal lagoon, the Pialassa Baiona (Ravenna, Italy). *Environ. Int.* 33, 919–928.
- Dung, T.T.T., Cappuyens, V., Swennen, R., Phung, N.K., 2013. From geochemical background determination to pollution assessment of heavy metals in sediments and soils. *Rev. Environ. Sci. Biotechnol.* 12, 335–353.
- Durán, I., Sánchez-Marín, P., Beiras, R., 2012. Dependence of Cu, Pb and Zn remobilization on physicochemical properties of marine sediments. *Mar. Environ. Res.* 77, 43–49.
- Dypvik, H., Harris, N.B., 2001. Geochemical facies analysis of fine-grained siliciclastics using Th/U, Zr/Rb and (Zr + Rb)/Sr ratios. *Chem. Geol.* 181 (1–4), 131–146.
- Fabbri, D., Felisatti, O., Lombardo, M., Trombini, C., Vassura, I., 1998. The Lagoon of Ravenna (Italy): characterisation of mercury-contaminated sediments. *Sci. Total Environ.* 213 (1–3), 121–128.
- Fabbri, D., Locatelli, C., Snape, C.E., Tarabusi, S., 2001. Sulfur speciation in mercury-contaminated sediments of a coastal lagoon: the role of elemental sulfur. *J. Environ. Monit.* 3 (5), 483–486.
- Farina, D., Soprani, S., Ricci, C., Tarroni, C., Zanetti, S., 1994. *Geografia attuale del sistema*. In: Soprani, S., Ricci, C. (Eds.), *Analisi dello stato ambientale e sanitario nelle valli ravennati*. La Pialassa Baiona. Azienda U.S.L., Dipartimento dei Servizi di Prevenzione, Ravenna, pp. 53–65.
- Franzini, M., Leoni, L., Saitta, M., 1972. A simple method to evacuate the matrix effects in X-ray fluorescence analysis. *X-Ray Spectrom.* 1, 151–154.
- Franzini, M., Leoni, L., Saitta, M., 1975. Revisione di una metodologia analitica per fluorescenza-X basata sulla correzione completa degli effetti di matrice. *Rend. Soc. Ital. Mineral. Petrol.* 31, 365–378.
- Garcia, D., Ravenne, C., Maréchal, B., Moutte, J., 2004. Geochemical variability induced by entrainment sorting: quantified signals for provenance analysis. *Sediment. Geol.* 171 (1–4), 113–128.
- Guerra, R., Pasteris, A., Ponti, M., 2009. Impacts of maintenance channel dredging in a northern Adriatic coastal lagoon. I: effects on sediment properties, contamination and toxicity. *Estuar. Coast. Shelf Sci.* 85, 134–142.
- Guerra, R., Pasteris, A., Lee, S.H., Park, N.J., Ok, G., 2014. Spatial patterns of metals, PCDDs/Fs, PCBs, PBDEs and chemical status of sediments from a coastal lagoon (Pialassa Baiona, NW Adriatic, Italy). *Mar. Pollut. Bull.* 89, 407–416.
- Guerzoni, S., Frignani, M., Giordani, P., Frascari, F., 1984. Heavy metals in sediments from different environments of a Northern Adriatic Sea Area, Italy. *Environ. Geol. Water Sci.* 6 (2), 111–119.
- Hansen, D.J., Berry, W.J., Mahony, J.D., Boothman, W.S., Di Toro, D.M., Robson, D.L., Ankley, G.T., Ma, D., Yan, Q., Pesch, C.E., 1996. Predicting the toxicity of metal-contaminated field sediments using interstitial concentration of metals and acid-volatile sulfide normalizations. *Environ. Toxicol. Chem.* 15 (12), 2080–2094.
- Huisman, D.J., Vermeulen, F.J.H., Baker, J., Veldkamp, A., Kroonenberg, S.B., Klaver, G.Th., 1997. A geological interpretation of heavy metal concentrations in soils and sediments in the southern Netherlands. *J. Geochem. Explor.* 59, 163–174.
- Jain, C.K., 2004. Metal fractionation study on bed sediments of River Yamuna, India. *Water Res.* 38 (3), 569–578.
- Jonathan, M.P., Roy, P.D., Thangadurai, N., Srinivasalu, S., Rodriguez-Espinosa, P.F., Sarkar, S.K., Lakshumanan, C., Navarrete-Lopez, M., Munoz-Sevilla, N.P., 2011. Metal concentrations in water and sediments from tourist beaches of Acapulco, Mexico. *Mar. Pollut. Bull.* 62 (4), 845–850.

- Leoni, L., Saitta, M., 1976. X-ray fluorescence analysis of 29 trace elements in rock and mineral standard. *Rend. Soc. Ital. Mineral. Petrol.* 32, 497–510.
- Leoni, L., Menichini, M., Saitta, M., 1986. Determination of S, Cl, and F in silicate rocks by X-ray fluorescence analyses. *X-Ray Spectrom.* 11, 156–158.
- Li, F., Lin, J.Q., Liang, Y.Y., Gan, H.Y., Zeng, X.Y., Duan, Z.P., Liang, K., Liu, X., Huo, Z.H., Wu, C.H., 2014. Coastal surface sediment quality assessment in Leizhou Peninsula (South China Sea) based on SEM-AVS analysis. *Mar. Pollut. Bull.* 84, 424–436.
- Marchesini, L., Amorosi, A., Cibir, U., Zuffa, G.G., Spadafora, E., Preti, D., 2000. Sand composition and sedimentary evolution of a Late Quaternary depositional sequence, north-western Adriatic Coast, Italy. *J. Sediment. Res.* 70, 829–838.
- Matteucci, G., Rossini, P., Guerzoni, S., Arcangeli, A., Fonti, P., Langone, L., Miserocchi, S., 2005. Recent evolution of sedimentary heavy metals in a coastal lagoon contaminated by industrial wastewaters (Pialassa Baiona, Ravenna, Italy). *Hydrobiologia* 550, 167–173.
- Migani, F., Borghesi, F., Dinelli, E., 2015. Geochemical characterization of surface sediments from the northern Adriatic wetlands around the Po river delta. Part I: bulk composition and relation to local background. *J. Geochem. Explor.* 156, 72–88.
- Miserocchi, S., Langone, L., Guerzoni, S., Frascari, F., 1990. Inquinamento da mercurio ed altri metalli pesanti (Pb, Zn, Cu) nei sedimenti delle valli Ravennati (Pialassa della Baiona). *Acqua Aria* 4, 361–370.
- Müller, G., 1979. Schwermetalle in den Sedimenten des Rheins-Veränderungen seit. *Umschau* 79, 778–783.
- Pérez-Ruzafa, A., Marcos, C., Pérez-Ruzafa, I.M., Pérez-Marcos, M., 2013. Are coastal lagoons physically or biologically controlled ecosystems? Revisiting r vs k strategies in coastal lagoons and estuaries. *Estuar. Coast. Shelf Sci.* 132, 17–33.
- Perin, G., Craboleda, L., Lucchese, M., Cirillo, R., Dotta, L., Zanetta, M.L., Oro, A.A., 1985. Heavy metal speciation in the sediments of northern Adriatic Sea. A new approach for environmental toxicity determination. In: Lakkas, T.D. (Ed.), *Heavy Metals in the Environment*. CEP Consultants, Edinburgh.
- Preacher, K.J., MacCallum, R.C., 2002. Exploratory factor analysis in behavior genetics research: factor recovery with small sample sizes. *Behav. Genet.* 32 (2), 153–161.
- Prca, M., Dalmacija, B., Roncevic, S., Krcmar, D., Becelic, M., 2008. A comparison of sediment quality results with acid volatile sulfide (AVS) and simultaneously extracted metals (SEM) ratio in Vojvodina (Serbia) sediments. *Sci. Total Environ.* 389, 235–244.
- Rauret, G., López-Sánchez, J.F., Sahuquillo, A., Rubio, R., Davidson, C., Ure, A., Quevauviller, P., 1999. Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. *J. Environ. Monit.* 1, 57–61.
- Rizzini, A., 1974. Holocene sedimentary cycle and heavy-mineral distribution, Romagna-Marche coastal plain, Italy. *Sediment. Geol.* 11, 17–37.
- Roussiez, V., Ludwig, W., Radakovitch, O., Probst, J.L., Monaco, A., Charrière, B., Buscail, R., 2011. Fate of metals in coastal sediments of a Mediterranean flood-dominated system: an approach based on total and labile fractions. *Estuar. Coast. Shelf Sci.* 92, 486–495.
- Sahuquillo, A., López-Sánchez, J.F., Rubio, R., Rauret, G., Thomas, R.P., Davidson, C.M., Ure, A.M., 1999. Use of a certified reference material for extractable trace metals to assess sources of uncertainty in the BCR three-stage sequential extraction procedure. *Anal. Chim. Acta* 382 (3), 317–327.
- Soprani, S., Giaquinta, S., 1992. Studio e valutazioni sull'assetto ambientale della Pialassa Piombone. U.S.L. 35, Ravenna.
- Sorokin, Y.I., Zakuskina, O.Y., 2012. Acid-labile sulfides in shallow marine bottom sediments: a review of the impact on ecosystems in the Azov Sea, the NE Black Sea shelf and NW Adriatic lagoons. *Estuar. Coast. Shelf Sci.* 98, 42–48.
- US EPA, 2004. The Incidence and Severity of Sediment Contamination in Surface Waters of the United States, National Sediment Quality Survey. EPA 823-R-04-007. second ed. U.S. Environmental Protection Agency, Office of Water, Washington, DC.
- Vital, H., Statterger, K., 2000. Major and trace elements of stream sediments from the lowermost Amazon River. *Chem. Geol.* 168 (1–2), 151–168.
- Yu, K.C., Tsai, L.J., Chen, S.H., Ho, S.T., 2001. Chemical binding of heavy metals in anoxic river sediments. *Water Res.* 35 (17), 4086–4094.
- Zhang, J., Liu, C.L., 2002. Riverine composition and estuarine geochemistry of particulate metals in China-weathering features, anthropogenic impact and chemical fluxes. *Estuar. Coast. Shelf Sci.* 54, 1051–1070.
- Zhang, C., Yu, Z.G., Zeng, G.M., Jiang, M., Yang, Z.Z., Cui, F., Zhu, M.Y., Shen, L.Q., Hu, L., 2014. Effects of sediment geochemical properties on heavy metal bioavailability. *Environ. Int.* 73, 270–281.