Spatial distribution of elements in near surface sediments as a consequence of sediment origin and anthropogenic activities in a coastal area in northern Italy

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Abstract

The study reports the results of a geochemical survey in a coastal area of northern Italy with focus on the distribution of chemical elements in near surface sediments as result of both sediment origin and anthropogenic activities. In addition to emphasizing the source-to-sink element dynamics in the area, the main purpose of this paper is to ascertain if anthropic presence could have altered the composition of near surface sediments in urban and industrial areas. We considered 173 sampling sites, and collected soil material from a depth of 90–110 cm. Major and trace elements assessment on milled 2 mm fraction was conducted using WDXRF for Al, As, Ba, Ca, Ce, Co, Cr, Cu, Fe, K, La, Mg, Mn, Na, Nb, Ni, P, Pb, Rb, Si, Sr, Th, Ti, V, Y, Zn and Zr. In addition, Loss On Ignition (LOI) was determined. Principal component analysis (PCA) and cluster analysis (CA) were performed for data interpretation.The distribution of element concentration is heavily related to sediment origin. The major presence of Al, Fe, K, LOI, Mg, Nb, Rb and V characterizes alluvial plain sediments. These materials of Apenninic origin have a finer texture and a major presence of carbonates in respect to the other sediments of the area. Coastal sediments display a general wider range of variation in element concentrations (i.e. Al, Ca, Cr, K, Mg, Mn, P, Si, Ti and Zr) due to a dual origin. In particular, the greater Cr, Mn and Zr content is related to sediments enriched by heavy minerals (e.g. garnet, chromite, zircon) of Alpine origin, while the lesser concentrations trace back to Apenninic origin.Near surface sediments of urban and industrial areas always contain higher Cu, Pb and Zn concentrations with respect to the same sediments not impacted by urban and industrial settlements. This is likely a consequence of the movement of materials made by men over the last 2000 years.

These results suggest that the adopted depth of sampling for the calculation of background values might need to be increased in urban and industrial areas to reach unaltered near surface sediments.

1 Introduction

The Po Plain (north of Italy) is the surface expression of a thick sedimentary basin, bounded by the Alps to the north and the Apennines to the south. It records a complex depositional history and tectonic evolution (Amorosi and Sammartino, 2007). Moreover, its eastern part around the city of Ravenna, in addition to being interested by sediments of different origin, has a history of human settlement of >2000 years (Andraghetti, 2007). Natural evolution and anthropic modifications of the drainage system, coastline evolution and reclamation activities combined with progressive urbanization profoundly influenced and remodeled this territory over time.

Numerous stratigraphic investigations (Amorosi, 2012; Amorosi et al., 1999; Bondesan et al., 1995) corroborated by historical research (Veggiani, 1974) have shown that the near surface sediment is partly the result of these profound transformations mostly carried out by man.

The assessment of element content in near surface sediments related to their origin is particularly important because it could help to distinguish between contamination phenomena and natural concentration.

In this study, with the term near surface sediment, we intend the soil parent material i.e. in this environment, the C horizon, not or slightly affected by pedogenic processes (Soil Survey Staff, 2014) and human interferences.

Surveys on the content of some trace elements in near surface sediments have already been conducted in the southern part of the Po Valley (Amorosi et al., 2014; Marchi et al., 2016) leading to the identification of the natural background values.

Several studies (Amorosi et al., 2002; Amorosi, 2012; Curzi et al., 2006; Greggio et al., 2018) on the geochemistry of sediments of this area identified some significant tracers of sediment provenance, in particular Cr and Ni.

On the one hand, relatively high Cr and Ni concentrations in alluvial and coastal plain sediments have been inferred to reflect the abundance of ultramafic detritus supplied by the Po River and its tributaries that drain the ophiolitic complexes of the western Alps and north-western Apennines (Amorosi, 2012; Amorosi et al., 2014). It is worth mentioning that until 1152 A.D. the present-day course of the Reno river was instead the southernmost branch (*Po di Primaro*) of an old Po delta system (Amorosi, 2012). On the other hand, sediments transported from the NE Apennines have lower concentrations of Cr and Ni and, originally, a greater presence of carbonates due to the abundance of marl and sandstone in their river catchments (Amorosi and Sammartino, 2007).

Conversely, less studied is the influence of human activities on the characteristics of near surface sediments, and the consequent presence and distribution of its elements in urban and industrial areas.

In urban areas, extensive excavation and movement of materials made during centuries of human settlement affected not only the soil but likely also the near surface sediments. The characteristics of these materials might not be representative of the local geogenic background. The above mentioned geochemical studies (Amorosi and Sammartino, 2007; Amorosi, 2012; Amorosi et al., 2014) have been conducted over large areas with a low

density of sampling, unsuitable for recognizing localized phenomena and far from areas clearly affected by anthropic activities.

The goals of this study are: (i) to assess the distribution of element concentrations in relation to sediment facies associations; (ii) to identify different groups of chemical elements with the same geochemical pattern; (iii) to recognize the sediment origin on the basis of typical element fingerprints; (iv) to identify the presence of different element as a function of the distribution of urban and industrial areas.

2 Study area

This study was carried out in the city of Ravenna and its surroundings, located in the NE of Italy (Fig. 1a). The investigated territory extends over approximately 33,200 ha and is delimited to the north by the Reno River, to the east by the Adriatic Sea, to the south by the Bevano creek and to the west by both the Senio River and the SS16 *Adriatica* highway.

Fig. 1
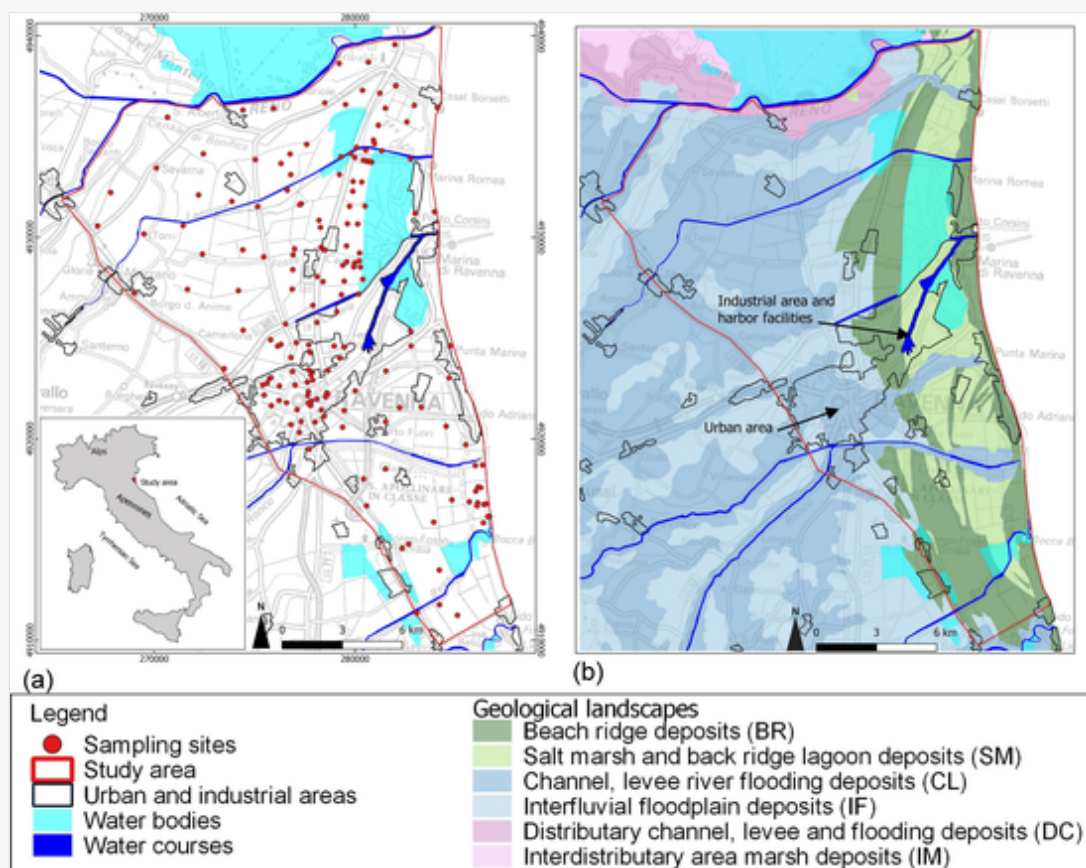
(a) Localization of the 173 sampling sites in the studied area (Datum WGS84-UTM 33); (b) Geological landscape of the studied area (from: http://geo.regione.emilia-romagna.it/geocatalogo). Background image modified from Emilia-Romagna Region topographic map, original scale 1:250,000).

The area includes one of the largest industrial districts in Italy with a petrochemical complex for the production of fertilizers and chemicals and plants for plastic treatment and other industrial activities.

The area was formed by recent sedimentary deposits. On the basis of this depositional environment, six facies associations were identified (Amorosi and Sammartino, 2007) (Fig. 1b).

The coastal area is characterized by beach ridge deposits (BR) (medium and fine sand) (Regione Emilia-Romagna, 1999) and by salt marsh and back ridge lagoon deposits (SM) (silt, sand and fine sand). The alluvial plain is characterized by channel, levee and river flooding deposits (CL) (fine and very fine silty sand) and by interfluvial floodplain deposits (IF) (silty clay, clay and laminated clayey silt). In the northern sector of the study area, which is part of the Po delta plain, distributary channel, levee and flooding deposits (DC) (medium to fine sands) and marsh deposits in interdistributary area (IM) (silty clay, silt and very fine sand) are present.

On the basis of regional pedological data (https://ambiente.regione.emilia-romagna.it/) and previous research in the area (Buscaroli et al., 2009; Buscaroli and Zannoni, 2010; Vittori Antisari et al., 2009), it is possible to assess the range of organic matter content in the different geological deposits as follow: BR = 0.1–0.5%; SM = 0.6–0.9%; CL = 0.3–0.8%; IF = 0.7–1%; DC = 0.7–0.8%.

3 Materials and methods

3.1 Sampling and sample preparation

Soil samples were collected at 173 sites (Fig. 1a), distributed in the study area to comprehend all sedimentary facies (the number of soil samples per geological landscape unit is BR = 68, SM = 15, CL = 55, IF = 31, DC = 4), excluding IM and DC deposits north of the Reno river. Sampling was performed by means of an auger and samples were collected at a depth of 90–110 cm from the soil surface. As reported by Amorosi and Sammartino (2007) and Huisman et al. (1997), at this depth it is expected that sediments have accumulated under pre-industrial conditions and are, therefore, considered useful for the assessment of the natural content of elements.

In agricultural areas, soil samples were collected adopting an ideal almost regular grid, whereas, in natural, urban and industrial areas, the sampling density was greatly conditioned by accessibility. The 173 soil samples were put into properly labelled plastic bags and conserved for analysis.

3.2 Analysis

Samples were air-dried at room temperature for two weeks, crushed and sieved through a 2 mm screen and the <2 mm fraction was conserved for analysis. Approximately 30 g of each sample was finely ground using an agate swing mill. The total concentration of major and trace elements (Al, As, Ba, Ca, Ce, Co, Cr, Cu, Fe, K, La, Mg, Mn, Na, Nb, Ni, P, Pb, Rb, Si, Sr, Th, Ti, V, Y, Zn, Zr) was determined by Wavelength Dispersive X-Ray Fluorescence (WDXRF) on pressed powder pellets using a Panalytical Axios 4000 spectrometer, following the methods proposed by Franzini et al. (1972); 1975) and Leoni and Saitta (1976) for matrix correction. Volatile content was determined by Loss of weight On Ignition (LOI) after overnight heating at 950 °C (Heiri et al., 2001).

Certified reference materials were used to ensure accuracy and precision in element analysis. The accuracy for determining trace elements was generally within 5% except for elements with concentrations of 10 ppm or lower, where the accuracy was between 10 and 15%.

3.3 Data analysis and mapping

For statistical computation, the concentration of elements below the instrumental detection limit (DL) was assigned a value corresponding to 50% of the detection limit.

Multivariate statistical tools, principal component analysis (PCA) and cluster analysis (CA), were applied to the geochemical data in order to assist the interpretation of data (Jöreskog et al., 1976). PCA was used to investigate the complex multivariate relationships among the variables, which are not normally clear using simple correlation analysis. PCA basically served to identify different groups of chemical elements with approximately the same geochemical pattern. The different components obtained were studied and interpreted in accordance with sediment origin and eventual anthropogenic influence. A CA based on the distance among sites was performed to evaluate the similarities between sites, based on the geochemical composition. All the analyzed elements and the LOI were considered in the analysis and z-transformation was applied taking into account the Euclidian distance.

Statistical analysis was performed with PAST (https://folk.uio.no/ohammer/past/) and R software. Output maps were realized by means of the Qgis software ver. 3.6.0 - Noosa (https://qgis.org/it/site/).

For each selected principal component, a score dot density map was produced. Some concentration dot density maps of the most correlated elements were also realized and reported in the Supplementary materials.

4 Results and discussion

4.1 Sediment geochemical characterization

The main statistical parameters for analyzed elements are displayed in Table. 1.

Table 1

(i) The table layout displayed in this section is not how it will appear in the final version. The representation below is solely purposed for providing corrections to the table. To preview the actual presentation of the table, please view the Proof.

Statistical parameters calculated for the analyzed elements: minimum, first quartile (Q1), median, third quartile (Q3) and maximum value for major elements, LOI and trace elements expressed in $mg \cdot kg^{-1}$ (n = 173).

Elements	Min	Q1	Median	Q3	Max
Al	32,653	51,811	59,009	63,825	77,214
As	2	2	4	7	26
Ba	23	275	318	347	1264
Ca	15,938	83,047	108,276	117,639	223,056
Ce	2	26	40	52	107
Co	2	4	7	10	18
Cr	35	84	104	127	380
Cu	5	13	23	32	427
Fe	13,219	23,921	29,236	33,923	54,976
K	10,211	15,358	17,267	18,180	21,335
La	2	18	25	36	73

LOI	27,700	100,800	155,100	184,400	266,700
Mg	10,071	18,756	20,927	22,977	26,294
Mn	697	1007	1007	1084	1626
Na	3487	8309	11,128	15,208	163,949
Nb	2	6	8	10	17
Ni	22	54	63	73	99
P	44	436	524	698	3491
Pb	2	14	18	24	1093
Rb	34	59	76	101	143
Si	121,354	190,726	207,835	263,323	340,736
Sr	156	271	326	370	475
Th	2	8	12	19	59
Ti	1379	2577	3117	3416	7612
V	25	49	67	81	124
Y	6	17	21	24	53
Zn	14	43	63	82	1037
Zr	18	83	102	127	317

The abundance of elements and LOI on the basis of median concentrations is as follows: [Instruction: There is a problem at page 3, Section 4.1, in the list of elements' abundance
]Si > LOI > Ca > Al > Fe > Mg > K > Na > Ti > Mn > P > Sr > Ba > Cr > Zr > Rb > V > Ni = Zn > Ce > La > Cu > Y > Pb > Th > Nb > Co > As. Among major elements, Si and Ca display the highest concentration while the trace elements Sr and Ba are the most represented in the samples. Several elements have a range of concentration covering one order of magnitude (As, Ca, Cr, La, Na, Th, Zr), others cover two orders of magnitude (Ba, Ce, Cu, Zn) and Pb covers three orders of magnitude. This, in addition to confirming the high variability of the natural substrate, suggests further research into whether the high punctual concentration of some elements may be due to anthropogenic activities.

Fig. 2 displays the box plot of the elements arranged on the basis of the geological facies associations sampled. For certain elements (i.e. As, Cr, Cu, Pb, V and Zn) the concentration exceeds the threshold limits set by Italian environmental law (Gazzetta Ufficiale, 2006). However, it is important to remind that the analysis technique recommended by the Italian legislation (*aqua regia* extraction) was different from the one we adopted in this study (WDXRF).

Fig. 2
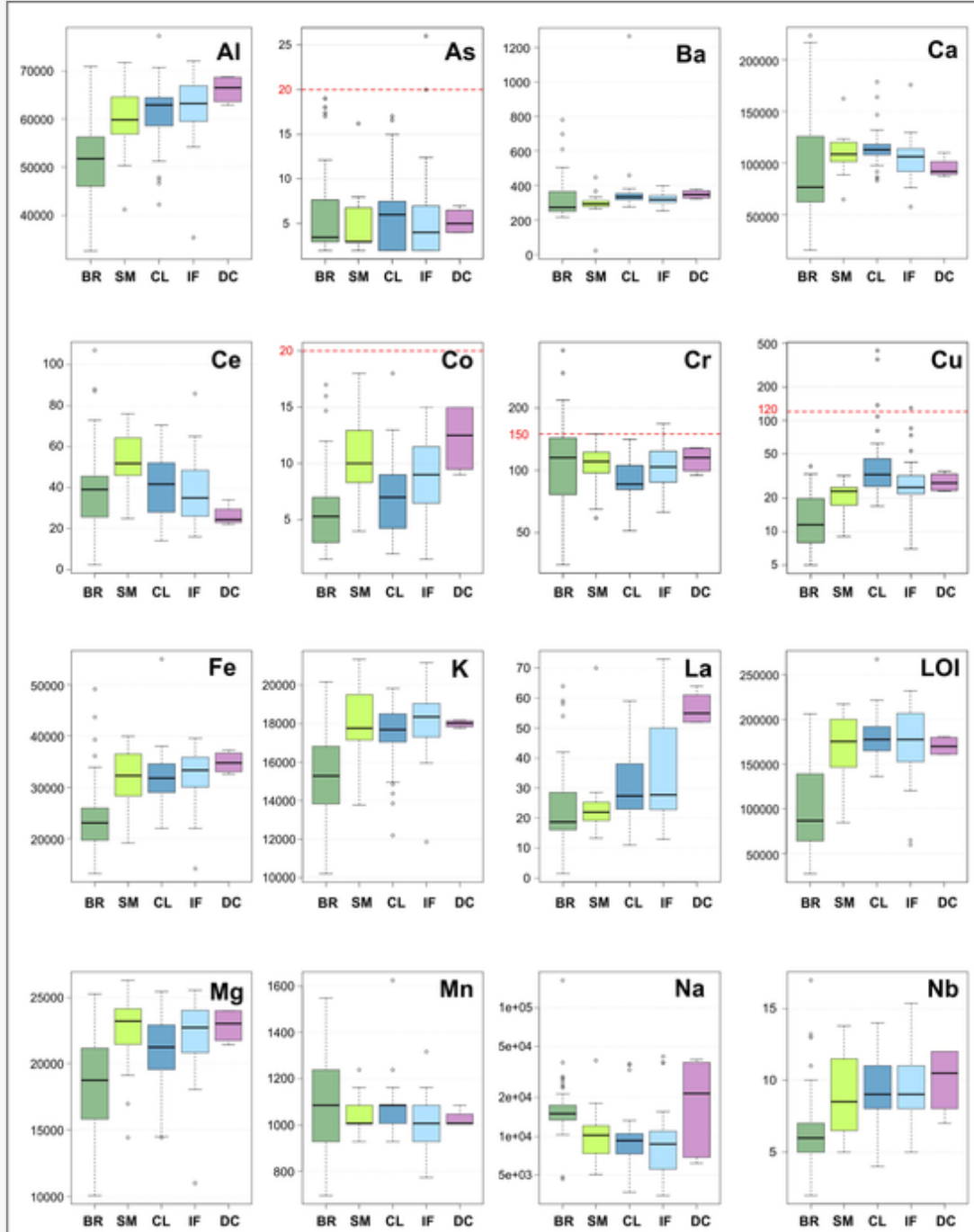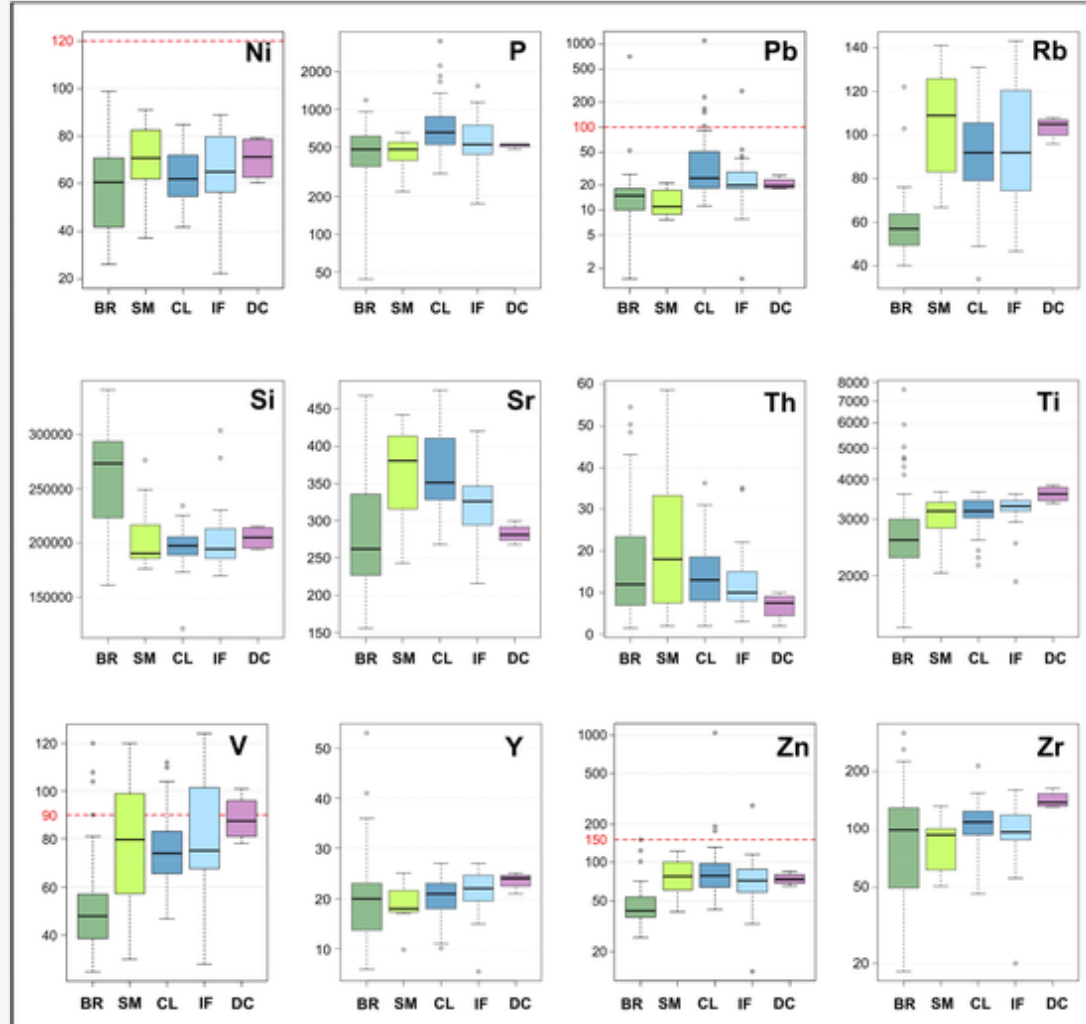
Box plot of elements arranged on the basis of the surficial geological facies associations mapped in the area. BR = beach ridge deposits; SM = salt marsh and back ridge lagoon deposits; CL = channel, levee and river flooding deposits; IF = interfluvial floodplain deposits; DC = distributary channel, levee and flooding deposits. Red dashed line: threshold limits from the Italian environmental law (Gazzetta Ufficiale, 2006). Values in $\text{mg} \cdot \text{kg}^{-1}$.

When studying the box plots (Fig. 2) we observed the specular behavior of Al, Fe and Nb with respect to that of Si, particularly present in BR deposits. In these deposits, most of the elements have the greatest variability. This is due to the particular heterogeneity of sediments as stated by Amorosi and Sammartino (2007), Amorosi (2012) and Amorosi et al. (2014). Cobalt, Fe, K, Mg, Rb and V have significantly higher median values in SM, CL, IF

and DC deposits, highlighting the affinities of these elements with the finer grain size of geological facies, as already observed by Dinelli et al. (2007) in these depositional environment. Copper, P, Pb and Zn reach the highest concentration in CL deposits and the lowest concentration in BR deposits.

Compared to the data reported by Amorosi et al. (2014), Cr shows a greater difference in variability and median concentration in the BR deposits. Copper, Pb and Zn show greater variability in the CL and IF deposits, while Ni values are quite similar.

4.2 Principal component analysis

In order to investigate the multivariate relationship between the studied variables, a PCA was performed. Table 2 reports the factor loadings obtained for each variable and statistical parameters suitable to better evaluate the goodness-of-fit. The selected factors, based on eigenvalues >1, explain 85.5% of the total variance. The high communalities suggest that factors do well represent all analyzed elements.

Table 2

ⓘ The table layout displayed in this section is not how it will appear in the final version. The representation below is solely purposed for providing corrections to the table. To preview the actual presentation of the table, please view the Proof.

Factor loadings and communalities of each variable; eigenvalues, explained % of variance and cumulative % of variance for each selected factor (F1-F7), for 173 soil samples. **F1** = V, Fe, Al, Mg, Ti, Ni, Co, Rb, Y, Nb, K, La, Cr, Zr, LOI; **F2** = Sr, LOI, Ca, Ba, Cu, Zn, Pb, *Y, Cr, Zr, Si*; **F3** = Pb, P, Zn, Cu, Cr, Mn, Zr, *Rb*; **F4** = Th, Ce, Mn, *Pb*; **F5** = La, Na, *Ce*; **F6** = As; **F7** = Na, *As*. In the caption italic entries = negative factor loadings (<−0.4). In the table, normal bold entries = positive factor loadings (>0.4); italic bold entries = negative factor loadings (<−0.4).

Elements	Factor loadings							Communality
	F1	F2	F3	F4	F5	F6	F7	
Al	**0.903**	−0.023	−0.165	−0.142	−0.226	−0.095	−0.001	0.92
As	0.002	−0.021	0.116	0.020	−0.233	**0.649**	***−0.486***	0.73
Ba	−0.288	**0.723**	0.333	0.040	0.255	0.083	0.027	0.79
Ca	−0.344	**0.786**	−0.180	0.306	0.197	0.014	−0.213	0.95
Ce	0.252	0.182	0.316	**0.589**	***−0.510***	−0.029	0.255	0.87
Co	**0.790**	0.117	0.023	0.027	0.233	0.356	0.209	0.86
Cr	**0.506**	***−0.492***	**0.490**	0.301	0.114	0.252	0.115	0.92
Cu	0.085	**0.656**	**0.542**	−0.329	−0.101	−0.072	−0.063	0.86
Fe	**0.928**	0.266	0.187	0.017	0.063	0.027	0.031	0.97
K	**0.658**	0.113	−0.383	−0.303	−0.341	−0.082	−0.165	0.83
La	**0.631**	−0.121	−0.031	−0.111	**0.572**	0.022	−0.277	0.83
LOI	**0.411**	**0.788**	−0.371	−0.078	0.095	−0.060	−0.007	0.95
Mg	**0.865**	−0.080	−0.109	0.031	−0.054	0.076	−0.049	0.78

Mn	−0.345	0.382	**0.432**	**0.569**	0.177	0.052	−0.168	0.84
Na	−0.226	−0.235	−0.041	−0.219	**0.422**	−0.046	**0.505**	0.59
Nb	**0.684**	0.273	−0.064	0.396	−0.066	−0.242	0.128	0.78
Ni	**0.795**	−0.129	0.095	−0.213	−0.145	0.278	0.221	0.85
P	0.133	0.370	**0.638**	−0.293	−0.226	−0.344	−0.133	0.83
Pb	0.010	**0.455**	**0.655**	**−0.417**	−0.039	0.086	0.115	0.83
Rb	**0.765**	0.294	**−0.488**	−0.094	−0.008	0.046	0.030	0.92
Si	−0.348	**−0.827**	0.327	−0.046	−0.165	0.057	0.028	0.95
Sr	0.016	**0.812**	−0.250	0.209	0.015	−0.059	−0.049	0.77
Th	−0.312	0.394	−0.133	**0.592**	−0.148	0.139	0.242	0.72
Ti	**0.817**	−0.188	0.273	0.388	0.083	−0.131	−0.083	0.96
V	**0.948**	0.184	−0.127	0.004	0.046	0.064	0.049	0.96
Y	**0.725**	**−0.406**	0.279	0.262	0.152	−0.142	−0.073	0.89
Zn	0.176	**0.646**	**0.587**	−0.306	0.059	0.106	0.142	0.92
Zr	**0.488**	**−0.509**	**0.400**	0.159	0.148	−0.308	−0.254	0.86
Eigenvalue	9.03	5.72	3.29	2.35	1.40	1.09	1.06	
Explained % variance	32.3	20.4	11.7	8.4	5.0	3.9	3.8	
Cumulative % variance	32.3	52.7	64.4	72.8	77.8	81.7	85.5	

Table 2 lists the seven accepted associations of the elements (F1-F7) along with their respective loading. Elements with loading values >0.4 or <−0.4 are considered representative members of each association.

4.2.1 Element association F1

The element association F1 (V, Fe, Al, Mg, Ti, Ni, Co, Rb, Y, Nb, K, La, Cr, Zr, LOI) explains 32.3% of the total variance (Table. 2). It was observed that some of these elements (V, Zn, Rb, Fe, La, Co, K and Al) have positive correlations with fine particle size (very fine silty sand, silty clay and clay) and negative correlations with sands and coarse silt as already observed by Dinelli et al. (2007). The higher positive scores are in the inland plain deposits (CL and IF) and in the coastal areas in correspondence with salt marsh and back ridge lagoon deposits (SM) (Fig. 3) also characterized by silty, sandy and fine sandy sediments.

Fig. 3
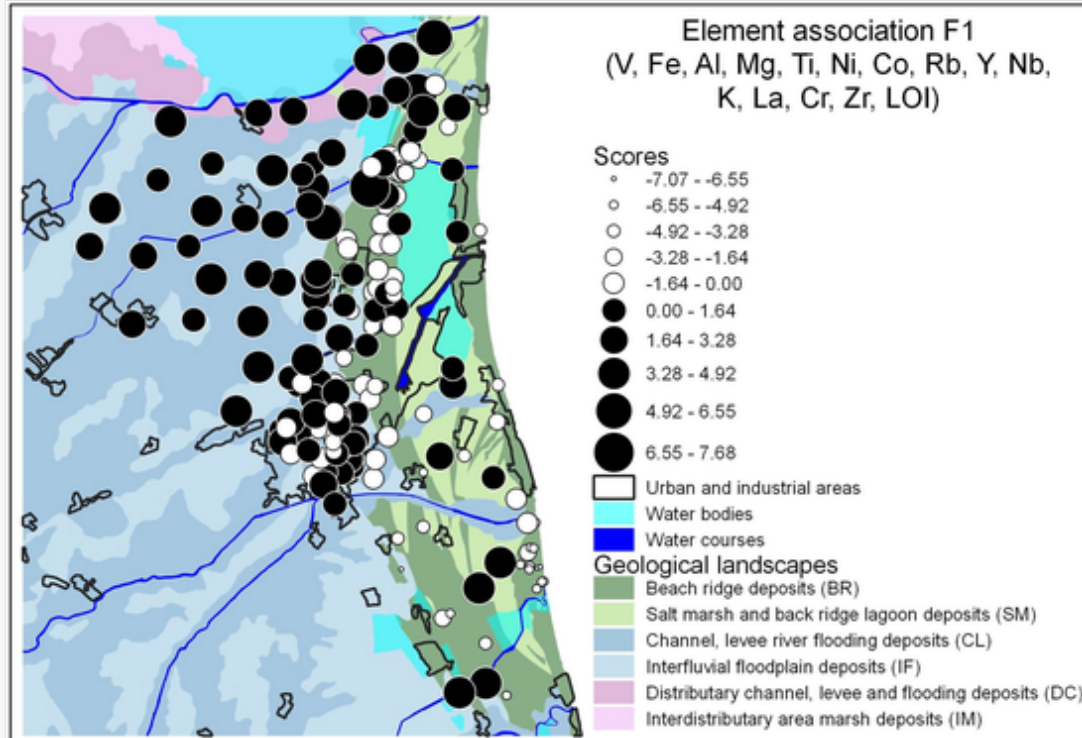
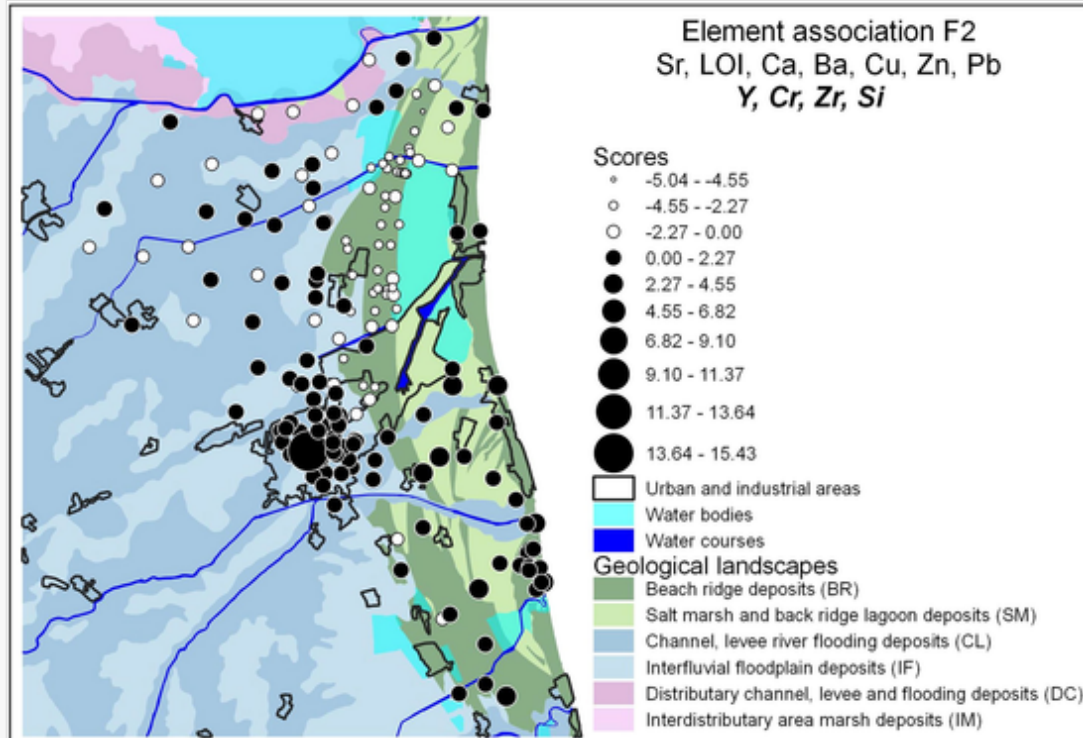Scores distribution of element association F1 (V, Fe, Al, Mg, Ti, Ni, Co, Rb, Y, Nb, K, La, Cr, Zr, LOI).

On the contrary, negative scores are present in the coastal areas at sites along the sandy beach ridge deposits (BR) characterized by elevated Si concentrations (Fig. 2) and in scattered sites in the urban areas.

4.2.2 Element association F2

The element association F2 (Sr, LOI, Ca, Ba, Cu, Zn, Pb, *Y, Cr, Zr, Si*) accounts for 20.4% of the total variance (Table. 2) with a marked bipartition. On the one hand elements with positive factor loadings (Sr, LOI, Ca, Ba, Cu, Zn, Pb) can be related to higher levels of carbonates, hydrates and labile hydroxy-compounds. In fact, Sr as well as other elements such as Ba, Cu, Pb and Zn, has a well-known affinity with carbonates (Bayon et al., 2007; Brand et al., 1999; Stehli and Hower, 1961; Šurija and Branica, 1995). On the other hand, elements with negative scores (Y, Cr, Zr and Si) can be associated with the origin (Alps) of sandy deposits enriched in heavy minerals (e.g. garnet, chromite, zircon) as stated by Marchesini et al. (2000).

The highest scores are in the urban and industrial areas and particularly in the center of Ravenna (Fig. 4), characterized by higher Pb, Cu and Zn concentrations (Fig. S4, S5 and S6 in the supplementary materials). Elevated scores arise in the southern and coastal BR deposits and in the low areas corresponding to SM deposits. The lowest negative factor scores are located in the northern BR area, confirming a sediment provenance from the Alpine region (see Fig. 5).

Fig. 4

Scores distribution of element association F2 (Sr, LOI, Ca, Ba, Cu, Zn, Pb, *Y*, *Cr*, *Zr*, *Si*). Italic bold entries = negative factor loadings (<−0.4).

Fig. 5
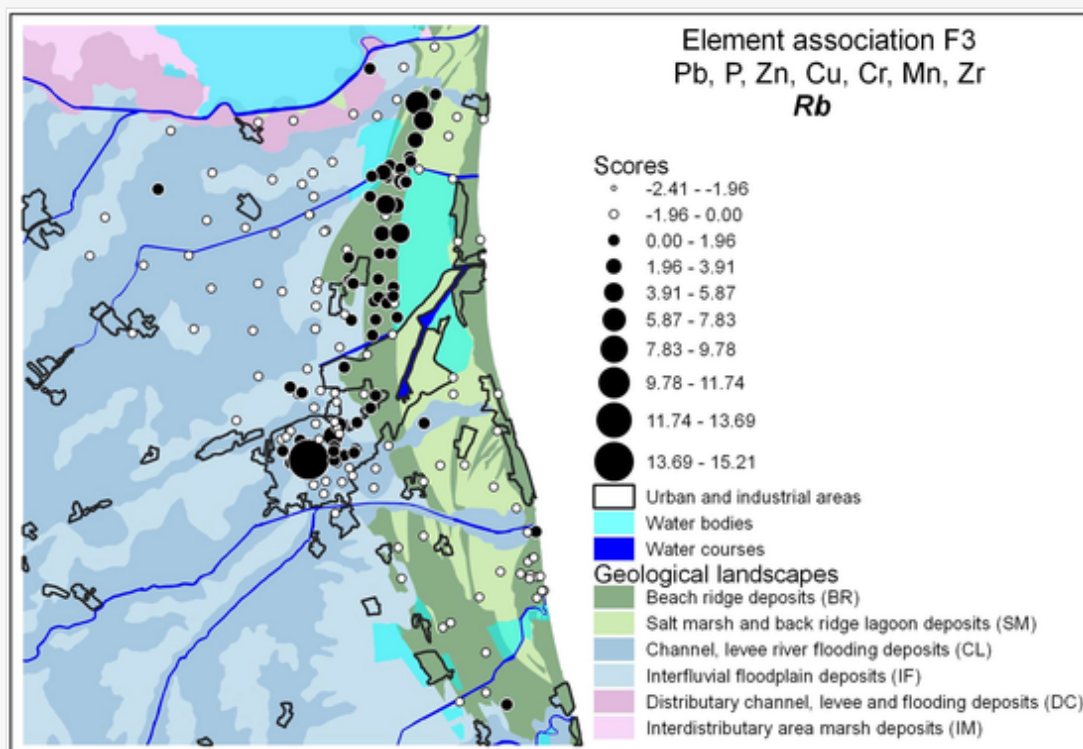
Scores distribution of element association F3 (Pb, P, Zn, Cu, Cr, Mn, Zr, *Rb*). Italic bold entries = negative factor loadings (<−0.4).

4.2.3 Element association F3

The element association F3 (Pb, P, Zn, Cu, Cr, Mn, Zr, *Rb*) accounts for 11.7% of the total variance (Table. 2). The high scores in the northern part of the o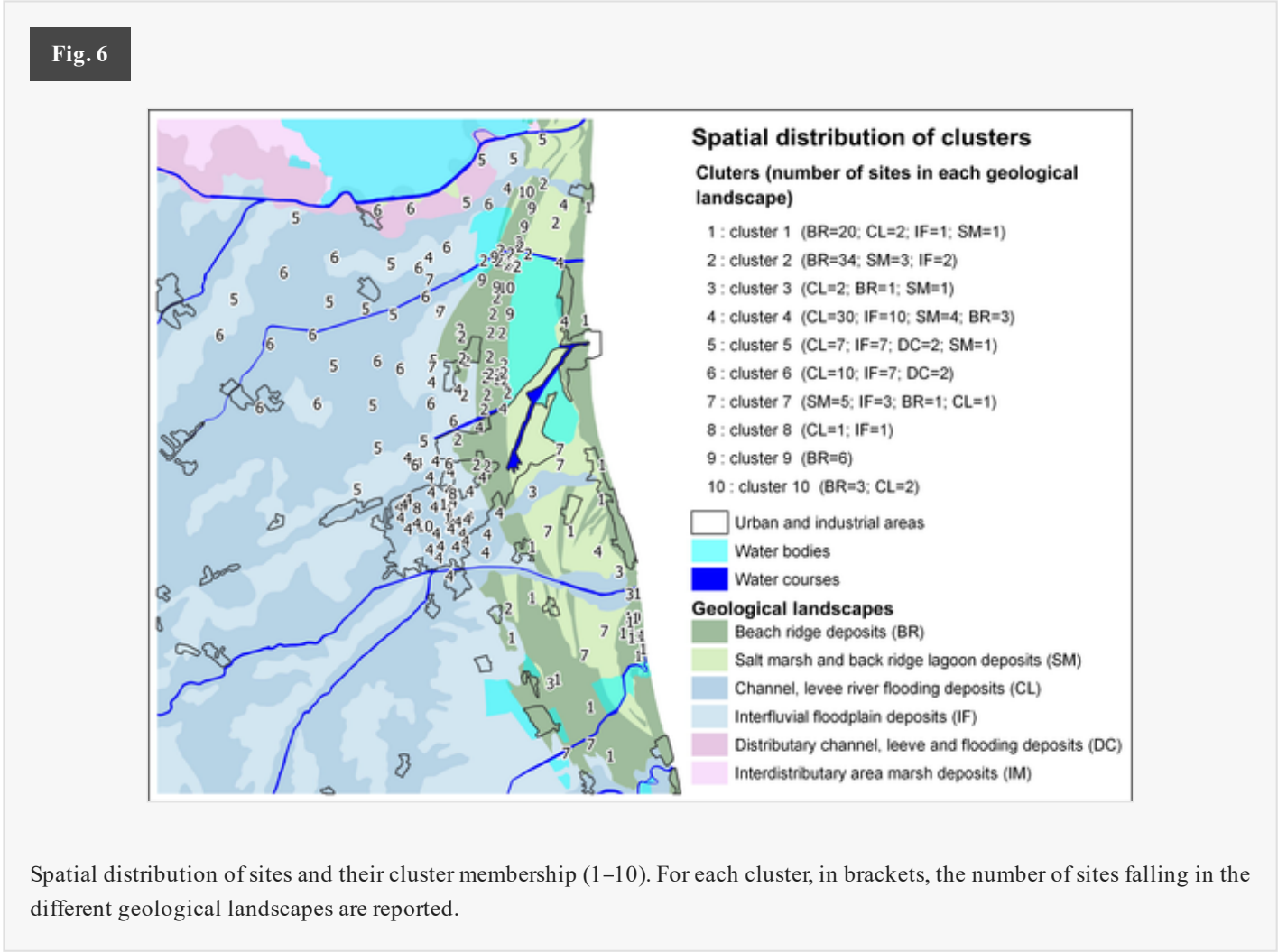ldest BR deposits are justified by the major concentration of some elements, like Cr and Zr, related to sand deposits of Alpine origin (Figs. S2 and S3 in the supplementary materials). Lead, Cu and Zn influenced the scores mainly in the urban area, while P and Mn influenced the scores of the component in these two areas. Rubidium, which is frequently associated with clay, and a likely major presence of carbonate, contribute to negative scores in the SM, CL, IF and DC deposits (Fig. 5).

The first three element associations (F1-F3) explain 64.4% of data variability, while the remaining four element associations (F4-F7) explain only 21.1% of data variability and do not contribute substantial additional information. Therefore, they will not be discussed hereafter.

4.3 Cluster analysis

A cluster analysis was performed to investigate linkages between samples and possible additional subdivisions among sites other than the one based on the geological landscape. The results of this analysis are displayed in the dendrogram of Fig. S7 in the supplementary materials, while the spatial distribution of clusters is reported in Fig. 6.

Fig. 6

Spatial distribution of sites and their cluster membership (1–10). For each cluster, in brackets, the number of sites falling in the different geological landscapes are reported.

From Fig. 6 it is possible to observe that clusters 4–5–6 are mainly present in alluvial plain deposits while clusters 1–2–7–9 are mostly found in the coastal deposits. Clusters 3–8–10 include only few sites, respectively 4, 2 and 5, located in both alluvial plain and coastal deposits.

In Fig. 7 some boxplots useful for the interpretation of clusters distribution are displayed.

Fig. 7
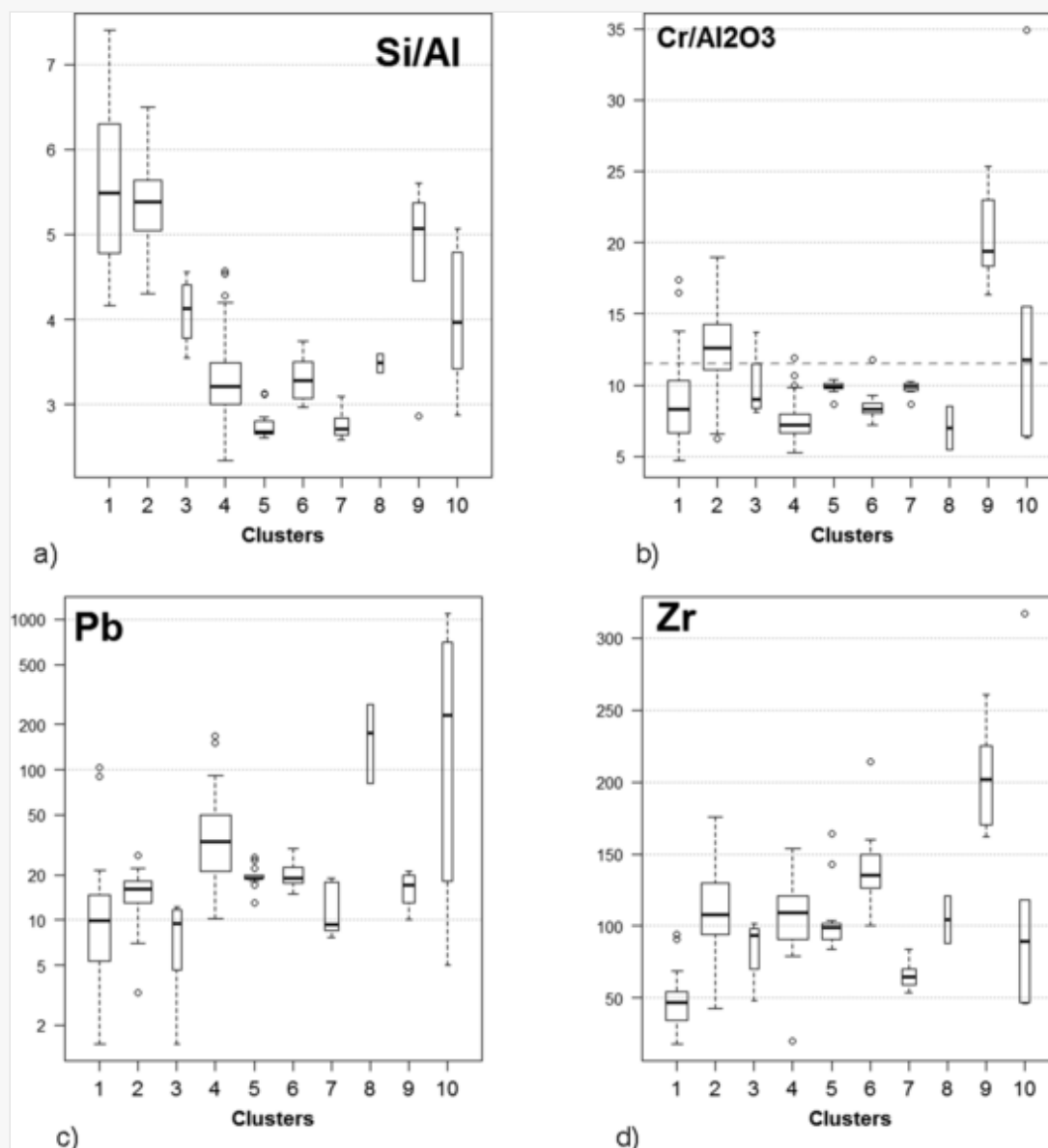
Boxplots of Si/Al (a), Cr/Al$_2$O$_3$ (b), Lead (c) and Zirconium (d) concentrations (mg·kg^{-1}). The dashed line in (b) indicates the ratio value of 11.5 assumed as threshold value to distinguish Alpine ($\geq$11.5) from Apenninic (<11.5) sediment provenance (Amorosi and Sammartino, 2007). The boxes are drawn with widths proportional to the square-roots of the number of sites.

The Si/Al ratio (Fig. 7a) highlights the presence of two distinct populations mostly reflecting different grain size distribution. On the one hand, clusters 4–5–6–7–8 are characterized by a lower Si/Al ratio and thus a finer texture, according to Dinelli et al. (2007). These clusters are in the alluvial plain deposits (CL, IF) and in the lower portions of the coastal deposits (SM).

On the other hand, clusters 1–2–9 are characterized by a larger Si/Al ratio, clue of a coarser texture. These clusters overlap the beach ridge deposits of the coastal area (BR). Cluster 3, represented by only 4 sites, likely depicts a mixing texture condition, while cluster 10 is composed by 5 sites located in geologically different positions of the area.

Fig. 7a further highlights the differences between the median values of clusters 4 and 6 and those of clusters 5 and 7 all characterized by a lower Si/Al ratio, suggesting additional details. Sites of clusters 4 and 6 have slightly coarser sediments than sites of clusters 5 and 7 and display a wider range of values. The Si/Al ratio median values of clusters 4 and 6 are similar, implying a common origin of sediments on the basis of textural characteristics. Anyway, a clearly higher Pb content, as well as Cu and Zn content (Fig. S8a–b, in the

supplementary materials) in cluster 4, in respect to cluster 6 emerges from Fig. 7c. Since sites of cluster 4 mostly fall within urban areas, it was decided to perform some further investigations to better comprehend elements distribution and the linkage to human activities (see Section 4.4.2).

Results of Fig. 7b highlight the different provenance among BR deposits. On the one hand, clusters 2 and 9 include sites of the northern part of the inland dune system, partially outlined also by element associations F2 and F3, characterized by a median value of Cr/Al_2O_3 ratio ≥ 11.5. This value was defined by Amorosi and Sammartino (2007) to identify the Alpine provenance of sediments in the area. As stated by Dinelli et al. (2007), Cr/Al_2O_3 does not appear to be controlled by grain size and thus Cr may serve efficiently as provenance indicator. Cluster 9 includes a small group of sites (n = 6) in the northernmost part of these inland dune deposits, characterized by a relatively higher Cr/Al_2O_3 ratio (Fig. 7a), and major concentrations of Zr (Fig. 7d), Y (Fig. S9a, in the supplementary materials) and Ti (Fig. S9b, in the supplementary materials) compared to that of cluster 2. These elements, likely associated with heavy minerals (e.g. Zircon, Garnet, Sphene, Rutile, Anatase, Brookite, Ilmenite, Xenotime), can be enriched in these samples as sorting effect (McLennan et al., 1990; Garcia et al., 2004; Dinelli et al., 2007; Garzanti et al., 2010) in a coastal high-energy environment close to a river mouth. The river mouth, active until 1152 AD, was the *Po di Primaro*, the southernmost branch of the old Po delta system (Amorosi, 2012). On the other hand, cluster 1 groups sites still located on BR deposits, but, as emerges from Fig. 7b, displaying a median value of Cr/Al_2O_3 ratio <=11.5 and thus an Apenninic provenance as stated by Amorosi and Sammartino (2007). In fact, as reported by Veggiani (1974), these sediments were deposited by rivers (i.e. Fiumi Uniti and Bevano) directly flowing from the Apenninic chain and characterized by a lower content in Zr (Fig. 7d) as well as in Y (Fig. S9a, in the supplementary materials) and Ti (Fig. S9b, in the supplementary materials) in respect to sediments of clusters 2 and 9.

4.4 Further insight on PCA and CA

Results of both multivariate techniques were further discussed with the aim of better comprehend the elements' distribution in the area. Specifically, the first analysis concerned the beach ridge deposits (BR). The second one, concerned the channel, levee and river flooding deposits (CL) interested, or not, by urbanization. The third one was devoted to elements' assessment in the town of Ravenna with respect to its development.

4.4.1 Comparison of sites within the beach ridge deposits (BR)

On the basis of the numerous available data on the periods of formation of the beach ridge (BR) deposits (Amorosi et al., 1999; Bondesan et al., 1995) and on the different origin of these sediments (Amorosi and Sammartino, 2007; Amorosi, 2012; Amorosi et al., 2014) the sites sampled within the BR deposits were subdivided into three groups with the aim of investigating in detail their geochemistry and finding clues for their provenance. The three groups are: 1) sites in Ancient Northern Beach Ridge deposits (ANBR); 2) sites in Ancient Southern Beach Ridge deposits (ASBR); 3) sites in Recent Beach Ridge deposits (RBR) (Fig. 8a). The ANBR and ASBR deposits are represented by the dune cords furthest from the coast, formed between the 10th to the early 18th century, to the north and to the south of the city of Ravenna (Bondesan et al., 1995). The RBR deposits are represented by the dune cords nearest to the coast, formed from the end of the 18th century to the early 20th century.

Fig. 8
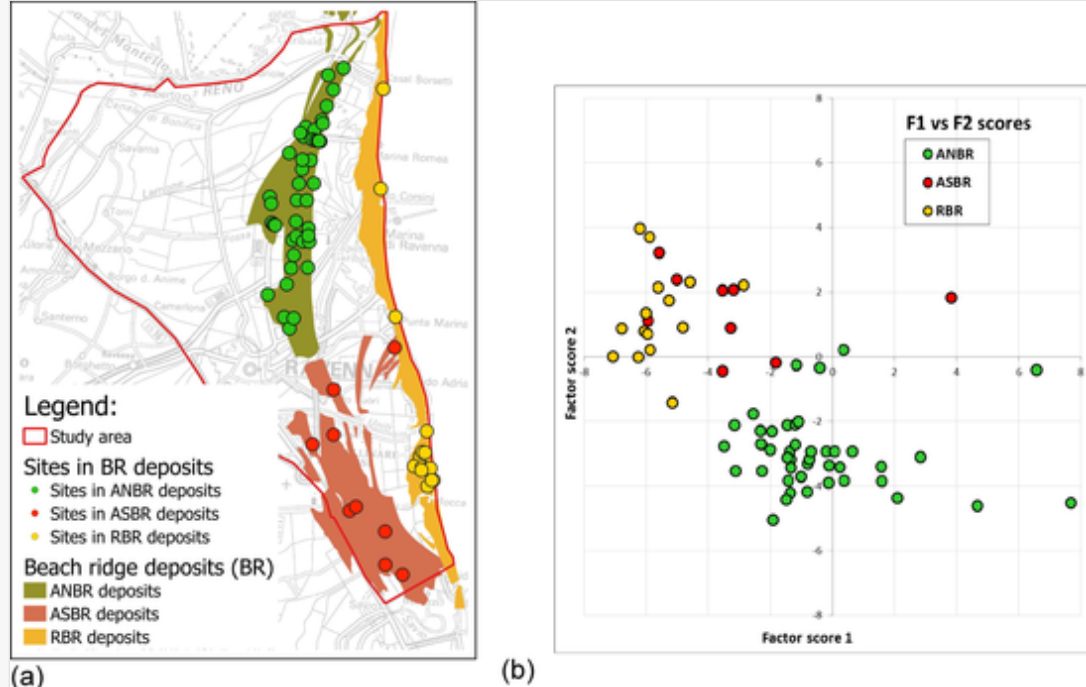
(a) Map of the distribution of sites in the ancient northern beach ridge deposits (ANBR), in the ancient southern beach ridge deposits (ASBR) and in the recent beach ridge deposits (RBR). (b) Scatterplot of Factor score 1 vs Factor score 2 of the three groups of sites.

From Fig. 2 it can be observed that 19 chemical parameters out of 28 considered have the greatest variability of concentration within BR deposits. This is evident for almost all major elements and LOI with the exception of P. For trace elements the greatest variability is observed for Ce, Co, Cr, La, Nb, Ni, Sr, Ti, Y and Zr.

Among the beach ridge deposits (BR) the most negative scores of F1 are observed in the RBR and ASBR deposits, while in the ANBR deposits the scores, although mostly negative, are closer to zero (Figs. 3 and 8b). In the latter, in fact, despite having a similar low content of V (Fig. S1 in the supplementary materials), clue of a coarse texture (Dinelli et al., 2007), there are much higher concentrations of Cr and Zr (Figs. S2 and S3 in supplementary materials), particularly evident in its northernmost part (cluster 9), evidence of an Alpine origin of the sediments (Marchesini et al., 2000).

With respect to F2, the scores of the sites in the ASBR and RBR deposits are almost all positive due to the higher presence of carbonates typical of Apenninic sediments, while those of the ANBR deposits are negative (Figs. 4 and 8b).

Within the ANBR deposit, Cr median concentration (137 mg·kg^{-1}) is similar to that described by Amorosi and Sammartino (2007) and Amorosi et al. (2014) but we found that some values (Cr concentrations over 200 up to 380 mg·kg^{-1}) (Fig. S2) are significantly higher than what was observed. Also in the other BR deposits the range of Cr values is slightly higher than that observed from the above authors in the same deposits (50– 82 mg·kg^{-1}). The combined results of PCA and CA thus confirm the different origin of the ANBR deposits compared to that of the other BR deposits, whose provenance is mainly Apenninic.

4.4.2 Comparison between sites on channel, levee, river flooding deposits (CL) outside and inside the urban and industrial areas

Sites of clusters 4 and 6 are largely localized on the channel, levee and river flooding deposits (CL), thus having a similar textural footprint characterized by a lower Si/Al ratio (Fig. 7a). However, while the former are mainly

localized in urban and industrial areas, the latter fall all outside them. Therefore, we investigated any potential difference in near surface sediment composition deriving from the different land use. In particular, the sites of cluster 4 on CL deposits within urban and industrial areas (4-CL-IN; n = 24) were compared to the sites of cluster 6 on CL deposits outside urban and industrial areas (6-CL-OUT; n = 10). Results are reported in Table 3.

Table 3

> (i) The table layout displayed in this section is not how it will appear in the final version. The representation below is solely purposed for providing corrections to the table. To preview the actual presentation of the table, please view the Proof.

Comparison of statistical parameters for major elements, LOI and trace elements between the sites of cluster 4 (4-CL-IN) and cluster 6 (6-CL-OUT), both on channel, levee, river flooding deposits (CL) and respectively inside (IN) and outside (OUT) the urban and industrial areas. In bold, elements that have significant different values (p-value < 0.05) between the two site groups, by Mann Whitney test. Values in $mg \cdot kg^{-1}$.

Elements	4-CL-IN			Significance	6-CL-OUT		
	Min	Median	Max		Min	Median	Max
Al	51,547	63,296	77,214	0.533	58,585	62,581	64,354
As	**2**	**2**	**15**	**0.045**	**2**	**7**	**9**
Ba	291	338	380	0.895	303	343	374
Ca	91,552	112,457	146,512	0.307	83,047	112,207	123,142
Ce	**32**	**50**	**67**	**0.000**	**14**	**24**	**42**
Co	**2**	**5**	**9**	**0.000**	**7**	**9**	**11**
Cr	**51**	**85**	**141**	**0.015**	**84**	**97**	**110**
Cu	**21**	**42**	**109**	**0.001**	**17**	**23**	**40**
Fe	23,921	30,670	36,301	0.299	29,236	32,559	34,412
K	16,022	17,433	19,342	0.058	16,022	18,429	18,927
La	**11**	**26**	**35**	**0.000**	**23**	**42**	**52**
LOI	145,100	175,400	200,700	0.089	139,900	161,950	196,900
Mg	**17,007**	**20,294**	**22,434**	**0.000**	**21,228**	**23,219**	**25,148**
Mn	1007	1084	1162	0.091	1007	1007	1084
Na	6009	9459	13,205	0.374	5416	8198	36,499
Nb	4	10	14	0.146	7	9	12
Ni	43	63	79	0.354	51	59	73
P	**393**	**785**	**1658**	**0.000**	**436**	**524**	**655**
Pb	**14**	**46**	**168**	**0.000**	**15**	**18**	**25**
Rb	49	91	111	0.130	82	99	109

Si	179,740	198,135	233,826	0.385	188,248	203,628	212,977
Sr	**320**	**381**	**448**	**0.000**	**268**	**305**	**330**
Th	**2**	**18**	**31**	**0.000**	**3**	**7**	**12**
Ti	**2577**	**3147**	**3536**	**0.002**	**3117**	**3446**	**3656**
V	49	75	93	0.264	67	76	92
Y	**12**	**20**	**24**	**0.002**	**19**	**23**	**25**
Zn	**43**	**85**	**191**	**0.003**	**54**	**63**	**72**
Zr	**79**	**106**	**154**	**0.000**	**120**	**135**	**214**

Table 3 highlights that 15 out of 28 elements show significant differences in element concentration between sites within the urban and industrial areas (4-CL-IN) and those outside (6-CL-OUT). Cerium, Cu, P, Pb, Sr, Th and Zn display higher median concentrations in 4-CL-IN sites than in 6-CL-OUT sites. On the contrary, As, Co, Cr, La, Mg, Ti, Y and Zr display higher median concentrations in 6-CL-OUT sites compared to 4-CL-IN sites.

Lead, Cu and Zn values in 4-CL-IN (Figs. S4–S6 in the supplementary materials) are markedly higher than those observed in the Emilia-Romagna Region by Amorosi et al. (2014) for this type of deposit (channel-levee, crevasse of Apennines' catchment without ophiolitic supply), while the concentrations of the three elements in 6-CL-OUT are in line with those values.

As known, Cu, Pb and Zn are part of the so-called "typical urban elements" (Tume et al., 2019), whose sources are usually linked to human activities (Acosta et al., 2011; Cheng et al., 2014; Wei and Yang, 2010). It is likely that the higher concentrations found in 4-CL-IN sites are a consequence of human presence and activities performed in these areas.

4.4.3 Metal concentration in Ravenna's urban area in relation to its development

Considering the long history of Ravenna, the metal presence in near surface sediment in relation to the city's development was investigated. Based on historical documents (Andraghetti, 2007) and other available database (https://geoportale.regione.emilia-romagna.it/it), we were able to reconstruct the development of the town from the 1st century BC until 2011, also highlighting the change of the city walls (Fig. 9).

Fig. 9
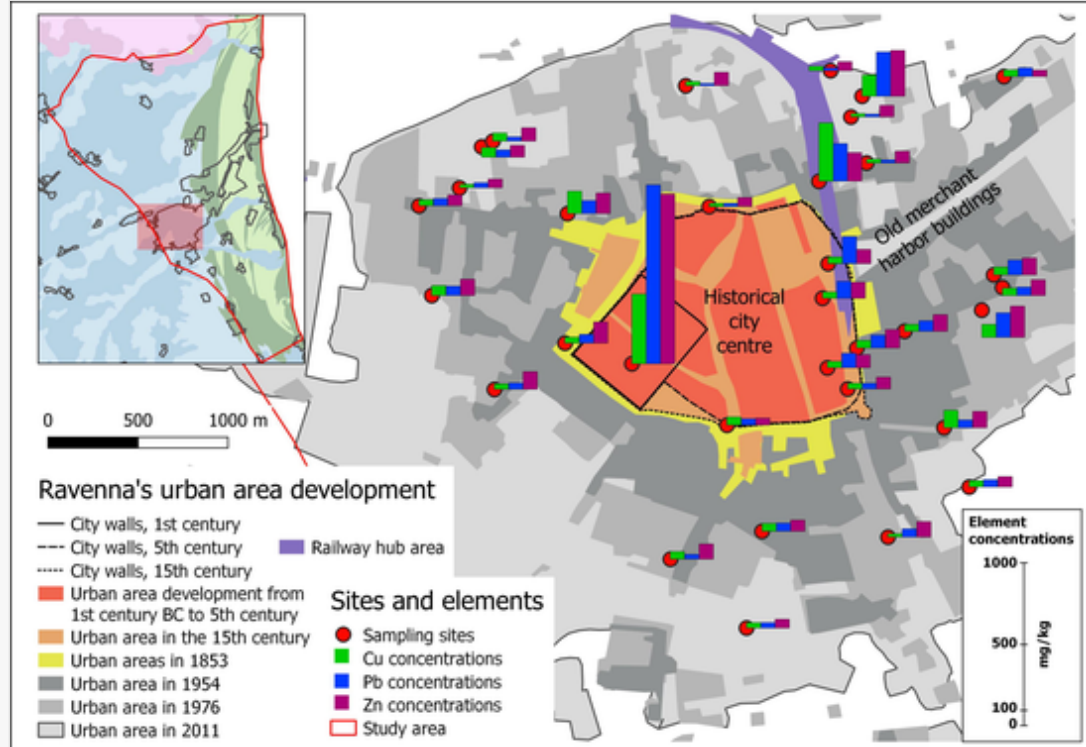
Ravenna's urban area development from the Roman empire age to 2011, with sampling sites and corresponding Cu, Pb and Zn concentrations. The lower right concentrations scale refers to the bar histograms next to the sampling dots.

Changes in near surface sediment characteristics could originate from a variety of sources: input of materials from other sites (e.g. earthworks for the construction of buildings and roads, watercourse modifications); mixing of soil with other materials (e.g. bricks, concrete and other building materials) and the subsequent alteration and homogenization of these materials. Furthermore, dredging or quarry sediments may have been used in the construction of more recent industrial areas.

Although it is difficult to establish a cause-effect relationship between the individual point values detected and the events linked to the evolution of the town, some general observations are possible.

The highest concentrations of Cu, Pb and Zn were found at a site in the oldest part of Ravenna within the 1st century walls (Fig. 9). Similar findings were also described by Gaberšek and Gosar (2018) in the old town area of Maribor (Slovenia) suggesting that the elevated concentrations have their sources in the past and related to the historical evolution of the town. In our study area, this first site dating from the Middle Ages to the end of the 19th century was earmarked for fields and gardens, and only later, in the early 20th century, for buildings. Thus, it is possible that the presence of elements in near surface sediments is likely attributable to this subsequent building activity.

With regards to the most recent part of the town, the highest concentrations of the three elements are observed in sites in the eastern part of the city, the one closest to the industrial area. These sites, located in small urban parks or gardens, are near the railway junction, and other sites are around the structures of the old merchant port, testifying the close relation between human activity and element presence in near surface sediments.

5 Conclusions

Geochemistry of near surface sediments can be useful to comprehend the origin and evolution of a territory especially when marked differences in sediment provenance are present. Furthermore, when urban settlements are considered, it can help emphasizing the influence of anthropogenic activities on the presence and distribution of some elements.

In the present study, both the PCA and the CA clearly contributed to the identification of the elements' distribution and main controlling factors.

Inland near surface sediments (CL and IF) and coastal salt marsh and back ridge lagoon deposits (SM) are characterized by finer particle size (lower Si/Al ratios) which is associated to a major presence of V, Zn, Rb, Fe, La, Co, K and Al.

Coastal beach ridge deposits (BR) all have a coarser texture (higher Si/Al ratio).

On the one hand, on the basis of the Cr/Al_2O_3 ratio, it was possible to confirm the Alpine origin of the ancient northern beach ridge deposits (ANBR) in respect to the Apenninic origin of the ancient southern beach ridge deposits (ASBR) and the recent beach ridge deposits (RBR). These last ones are characterized by a major presence of Sr, LOI, Ca, Ba, Cu, Zn and Pb which are related to higher levels of carbonates present in Apenninic sediments.

Furthermore, the CA indicated a particular enrichment in selected elements (Cr, Zr, Y and Ti) in the northernmost part of the ANBR deposits, interpreted as a deposit originated in an energetic morphological position close to the ancient, southern, Po river mouth (*Po di Primaro*).

Due to the millennial presence of humans, some original sedimentary footprints were probably altered and disturbed, and a separated analysis was performed in areas which are similar in respect to the origin and grain size distribution, but differ with regard to urbanization.

The analysis revealed significant differences in elements' content. In particular, the so-called "typical urban elements" Cu, Pb and Zn (among others), showed higher near surface sediments concentrations due to urban and industrial settlements.

A further study conducted on near surface sediments of downtown Ravenna revealed a major concentrations of these elements in the oldest part of the town and a significant presence especially where building activity was associated to the construction of main roads and rail networks, and the first industrial structures.

Since these elements are scarcely mobile, particularly at high pH, their major presence in urban and industrial near surface sediment could be linked to the movement of materials made by men over ca. 2000 years. This fact implies that the adopted depth of sampling in urban and industrial areas might be insufficient for the evaluation of natural background values. Ultimately, it is likely that the sampled material doesn't represent the unaltered near surface sediment but instead human transported material. This fact implies that, in urban and industrial

areas, the depth of sampling for the calculation of background values might be increased to reach unaltered near surface sediments.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Appendix A Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catena.2020.104842.

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> ⓘ The corrections made in this section will be reviewed and approved by a journal production editor. The newly added/removed references and its citations will be reordered and rearranged by the production team.

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Graphical abstract
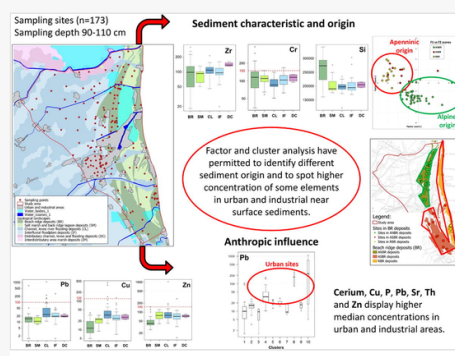
Highlights

- Elements' concentration in near surface sediments of a coastal area were analysed.
- Geochemical mapping allows to visualize element distribution in the area.
- Factor/cluster analysis have permitted to distinguish different sediment origin.
- Higher Cu, Pb and Zn cencentrations were detected in urban near surface sediments.
- Sampling depth should be likely increased in urban areas' investigations.

Appendix A Supplementary material

The following are the Supplementary data to this article:

Multimedia Component 1

Supplementary data 1

Multimedia Component 2

Supplementary data 2

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