EQA – *Environmental quality/Qualité de l'Environnement/Qualità ambientale, 2 (2009) 1-14*

POTENTIALLY TOXIC ELEMENTS ALONG SOIL PROFILES IN AN URBAN PARK, AN AGRICULTURAL FARM, AND THE SAN VITALE PINEWOOD (RAVENNA, ITALY)

ELEMENTS POTENTIELLEMENT TOXIQUES LE LONG DES PROFILS DU SOL DANS UN PARC URBAIN, UNE EXPLOITATION AGRICOLE ET DANS LA PINEDE DE SAN VITALE (RAVENNE, ITALIE)

ELEMENTI POTENZIALMENTE TOSSICI LUNGO PROFILI DEL SUOLO IN UN PARCO CITTADINO, IN UN'AZIENDA AGRICOLA E NELLA PINETA DI SAN VITALE (RAVENNA, ITALIA)

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Abstract

Potentially toxic elements (PTEs) abundances in top soil and along the soil profiles from areas affected by different anthropogenic inputs were investigated.. The study area is located within the Ravenna Municipality, a complex territorial system highly affected by industrial (a large petrolchemical complex) agricultural activities. Three zones with distinct environmental features were identified: the San Vitale Pinewood affected by atmospheric deposition pollutans from the industrial complex (PW1, PW4, PW6 and PW8 soil profiles); a public garden within the Ravenna city center, mainly affected by traffic pollution (GP1 soil profile); the "Luigi Perdisa" farm located immediately northwards Ravenna was selected due to the use of fertilizers as well as atmospheric deposition (PER2 soil profile). The total concentration of PTEs (Ba, Cr, Cu, Cr, Ni, Pb, Zn) was determined by X ray fluorescence spectrometry (XRF), and the pseudo-total concentration with aqua regia digestion (AR) and ICP-OES quantification in order to evaluate the extractability of the elements. Results showed a significant increase of some PTEs (Cu, Pb, Zn) in the top soil compared to the pedological substrate. In the Ravenna urban park (GP1 station), Pb and Zn concentrations exceeded the threshold values established by current Italian laws for soils from "public, residential and private areas" (D. Lgs 152/2006). The correlation between top soil and the subsoil highlighted that some PTEs, such as Cu, Pb and Zn, are anthropogenic and they are mainly associated to the deposition of airborne pollutants, whereas other elements (Cr and Ni) are lithologenic.

DOI: 10.6092/issn.2281-4485/3822

Key-words: *heavy metals; enrichment factor; soil profiles; Pinewood San Vitale; ICP-OES;XRF*

Résumé

Le but de cette étude est d'évaluer le taux de concentration d'éléments potentiellement toxiques (EPT) dans les horizons supérieurs et le long du profil de sols intéressés par les différents impacts anthropiques. Les études ont été conduites dans la zone qui englobe la commune de Ravenne, caractérisée par un système territorial complexe en raison de la présence d'un pôle pétrochimique mais aussi d'une agriculture très productive. Trois zones avec des impacts différents pour l'environnement ont été identifiées : la Pinède de San Vitale touchée par des dépôts atmosphériques dérivant de l'activité de l'industrie pétrolochimique (profils pédologiques PW1, PW4, PW6 et PW8) ; un jardin public qui se trouve dans le centre historique de la ville de Ravenne et qui subit une pollution due à la circulation automobile (profil pédagogique GP1). Pour finir, l'entreprise agricole "Luigi Perdisa" située immédiatement au nord-est de Ravenne a été choisie aussi bien à cause de la contamination possible par des produits chimiques utilisés en agriculture que pour les différents types de dépôts atmosphériques (profil pédologique PER2). Les études ont permis de déterminer les concentrations totales en spectrométrie de fluorescence aux rayons X (XRF) mais aussi pseudo-totales avec solubilisation dans l'eau régale (AR) de certains métaux lourds (Ba, Cr, Cu, Cr, Ni, Pb, Zn), à la suite de quoi a eu lieu la lecture en ICP-OES dans le but d'évaluer dans quelle mesure ces éléments peuvent être extraits.

Les déterminations effectuées démontrent un enrichissement significatif de certains EPT (Cu, Pb, Zn) dans les horizons de surface par rapport au substrat pédologique. Dans le parc urbain de Ravenne (GP1), les concentrations de Pb et Zn sont supérieures aux limites prévues par la législation italienne (Décret Législatif 152/2006) dans les zones résidentielles et les espaces verts. La corrélation entre les valeurs de concentration de certains EPT comme CU, Pb et Zn rencontrés dans les horizons en surface et en profondeur met clairement en évidence leur origine anthropique due en majeure partie à des dépôts d'agents polluants présents dans l'atmosphère tandis que l'origine d'autres éléments (Cr et Ni) résulte de type lithologique.

Mots-clés: *EPT ; facteur d'enrichissement ; profils du sol ; Pinède de San Vitale ; ICP-OES ; XRF.*

Riassunto

Scopo di questo studio è la valutazione del grado di anomalia di elementi potenzialmente tossici (EPT) negli orizzonti superficiali e subsuperficiali di suoli soggetti a differenti iuput antropogenici. L'area di studio ha interessato il comune di Ravenna, caratterizzata da un sistema territoriale complesso per la presenza di un polo petrolchimico, ma anche soggetta ad un'attività agricola intensa ed altamente produttiva. Sono state identificate tre zone potenzialmente impattate da differenti attività antropiche: la Pineta di San Vitale interessata da deposizioni atmosferiche derivanti dall'attività dell'industria petrolchimica (profili pedologici PW1, PW4, PW6 e PW8); un giardino pubblico presente nel centro storico della città di Ravenna, interessato da inquinamento da traffico veicolare (profilo pedologico GP1); l'azienda agricola "Luigi Perdisa" collocata immediatamente a nord-est di Ravenna scelta sia per la possibile contaminazione da prodotti chimici usati in agricoltura sia per i diversi tipi di deposizioni atmosferiche (profilo pedologico PER2). Di alcuni metalli pesanti (Ba, Cr, Cu, Cr, Ni, Pb, Zn) sono state determinate sia le concentrazioni totali in spettrometria di fluorescenza a raggi X (XRF), sia quelle pseudo totali con solubilizzazione in *aqua regia* (AR) e successiva lettura in ICP-OES con lo scopo di valutare il livello di estraibilità di tali elementi.

Le determinazioni effettuate mostrano un significativo arricchimento di alcuni EPT (Cu, Pb, Zn) negli orizzonti di suolo superficiale rispetto al substrato pedologico; nel parco urbano di Ravenna (GP1), le concentrazioni di Pb e Zn sono superiori ai limiti previsti dalla legislazione italiana (D. Lgs 152/2006) per le aree residenziali e di verde pubblico. La correlazione tra i valori di concentrazione di alcuni EPT, quali Cu, Pb e Zn, riscontrati negli orizzonti superficiali e di profondità evidenzia chiaramente la loro origine antropica per lo più dovuta a deposizioni di contaminanti presenti in atmosfera, mentre per altri elementi (Cr e Ni) la loro provenienza risulta litologenica.

Parole chiave: *EPT; fattore di arricchimento; profili del suolo; Pineta di San Vitale; ICP-OES; XRF.*

Introduction

The environmental quality of urban soil is closely related to human health (De Miguel et al, 1998; Madrid et al., 2002) so that monitoring potenzially toxic elements (PTEs) environmental compartments has gained considerable importance nowadays. Their increase due to anthropic activities, has very often reached critical thresholds of toxicity (Alloway et al., 1990; Adriano et al., 1992). The vehicular traffic is one of the main and more significant sources, wich has increased the fluxes of atmospheric pollutants. For a sound evaluation of the impact of anthropogenic activities on heavy metals distribution it is essential to know the natural (background) level in an undisturbed situation geologically similar to the study setting (Plant et al., 2001). Only knowing that, it is possible to evaluate the bias compared to natural conditions (Reimann & Garrett, 2005) and to, quantify the alteration using different approaches such as a Geoaccumulation Index (Igeo, Müller, 1979; Förstner & Müller, 1981) or an Enrichment Factor (Rubio et al., 2000) calculation.

These approaches have been applied to several sites within the Ravenna city centre and its close surroundings which have been extenaively affected by all the potential sources of contamination (urban, agricultural, industrial). Soil samples were collected from some profiles excavated in a urban garden located in the city centre, in a agricultural field just north of the city. In addition, several profiles were

DOI: 10.6092/issn.2281-4485/3822

"opened" and subsampled in the San Vitale Pinewood, a protected area close to a large industrial complex.

Among all the investgated profiles, six of them were selected to compar total (XRF) and pseudo-total (*aqua regia*) (Alloway, 1990) metal concentrations. Total element concentrations are more relevant if a geochemical interpretation of data is requited as in this specific study. Besides, direct comparison with available geochemical data on sedimentary deposits in the area is also possible. Following the pseudo-total approach, result describe the maximum concentration of an PTE that can be released from a parent materials in natural environment. The *aqua regia* leach or digestion procedure is normally used for simulating this characteristic in the laboratory. It is potentially extremely interesting, althoug it can be affected by many uncertainties regarding the operating procedures. In any case, the comparison of the two results ìs a useful approach to discuss and to gain an insight into metal stability in the soil environment.

Materials and methods

Sites description and soil profiles sampling. The study area belongs to the Ravenna Municipality (Emilia Romagna region), a complex territorial system chatacterized by the development of petrolchemical industrial complex and,, also, by an intensive agricultural activity. The monitoring sites selected in Ravenna city were: the Central Urban Park (GP) located in the historical city, the ITAS "L. Perdisa" extra-urban farm (PER*)*, and the San Vitale Pinewood (PW), an importance community site (ICS).

Geographical location. Three zones of different anthropogenic impact were identified: the San Vitale Pinewood probably affected by atmospheric deposition that could be derived from the petrolchemical industry or from vehicle exhaust (soil profiles PW1, PW4, PW6, and PW8); a public garden within Ravenna city, mainly affected by traffic pollution (soil profile GP1); the farm "Luigi Perdisa" located immediately northwards of Ravenna was selected because of the use of fertilizers and also subject to various types of atmospheric deposition (soil profile PER2). All the sites were georeferenced (UTM33-WGS'84 reference systems) using a GPS system (Fig.1).

Pedological survey. The San Vitale Pinewood is located along the 118 pedological delineation of the Emilia Romagna region (www.regione.emilia-romagna.it). CER3/SAV1/PIR1 soils were present. The San Vitale Pinewood is characterized by sand and calcareous soils forming upon deposits of sand bar consolidated by old reforestation. Cerba (CER3), and Aquic Ustipsamments (USDA, 2006) are the most commonly represented soils; in those areas which are morphologically higher, San Vitale soils, Typic Ustipsamments (SAV1) are present whereas in those lower areas, between the dunes, Pirottolo soils are recognized (PIR1,Typic Psammaquents). The extra urban farm ITAS "L. Perdisa" is placed along the 996 pedological delineation and the SMB1 soils (www.regione.emilia-romagna.it). The pedological substrate of both farm (PER2) and urban park (GP1) is plane flooded deposits and the soil is Udifluventic Haplustepts (USDA, 2006). The soil of Ravenna urban park is classified Udifluventic Haplustepts (USDA, 2006) and this belongs to the 94 pedological delineation introducing the soil complex VIL1/SMB1, characterized by canal deposits.

Soil sampling. At each site (Fig. 1), a soil profile was open down to 150 cm depth, and each horizon was sampled . Moreover, at each site also the soil material between 0-20 and 80-100 cm was collected and prepared for analysis. Among the all the investigated sites reported in Figure 1, PW 1, 4, 6, 8; PER2 and GP1 were selected for the detailed analytical work**.**

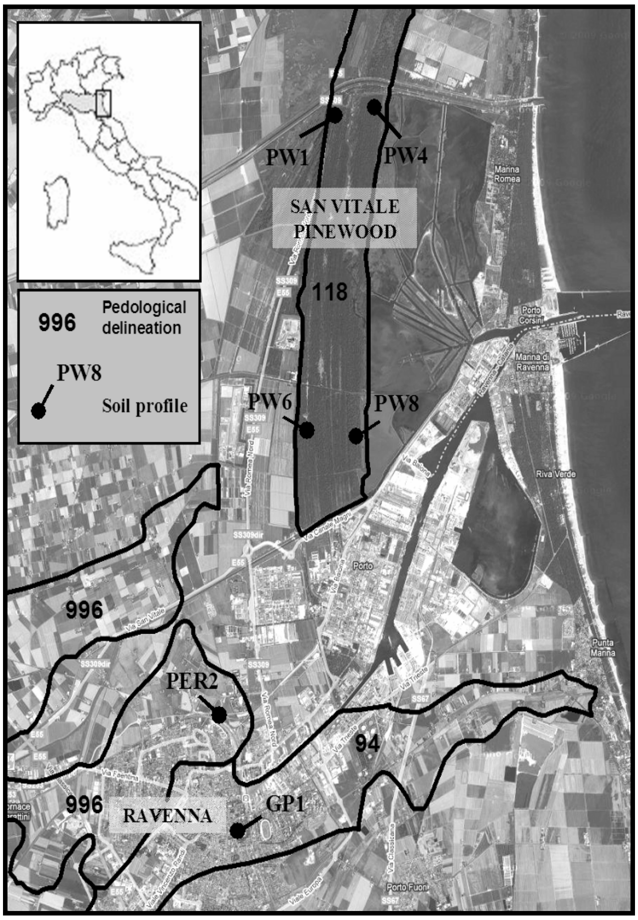


Figure 1

Geographical location of sampling sites on pedogical delineations of Emilia-Romagna soil map (http://gias.regione.emilia-romagna.it/suoli.asp)

Pedogical delineations:
94 *Udifluventic Haplustepts*

118 *Aquic, Typic Ustipsamments/Typic Psammaquents complex*

996 *Udifluventic Haplustepts*

Soil profiles:
PER2
in ITAS "L. Perdisa" farm.
GP1
in Central Urban Park..
PW1 and **PW4**
in San Vitale Pinewood North transect.
PW6 and **PW8**
in San Vitale Pinewood South transect.

Chemical analysis

X-Ray Fluorescence – total PTEs concentration. Total metal concentration and major element composition were obtained by X-Ray fluorescence spectrometry (XRF). All samples were homogenized in an agate mortar. Chemical determinations were obtained by X-ray fluorescence spectrometry (Philips PW

DOI: 10.6092/issn.2281-4485/3822

1480) on pressed powder pellets, following the matrix correction methods of Franzini et al. (1972; 1975), Leoni & Saitta (1976) and Leoni et al. (1986). The estimated precision and accuracy for trace-element determinations are better than 5%, except for those elements <10 ppm (10-15%). LOI (Loss on Ignition) was evaluated after overnight heating at 950°C. International reference material were used in the calibration and as analytical monitor. Among the PTEs only the results for Ba, Cr, Cu, Ni, Pb, V e Zn will be discussed.

Aqua regia digestion (AR) – pseudo-total PTEs concentration. The soil samples were dried at room temperature, then ground in an agate mill and passed through a 2 mm mesh sieve and then fine pulverized. A 250 mg aliquot from each homogenized and powdered sample was mineralized with Aqua Regia (HCl/HNO_3 3:1) in a micro-wave oven (Milestone 1200) in a Teflon vessel and the specific digestion program consisted of four steps: 1) heating at 250 Watt for 3 min; 2) heating at 400 Watt for 2 min; 3) resting at 0 Watt for 2 min; 4) heating at 700 Watt for 2 min. After digestion and cooling, digested soil solutions were transferred at a dilution of 20 mL. Solutions were analysed for heavy metals and microelements using a Spectro Inductively Coupled Plasma Optical Emission Spectrometer (Circular Optical System CIR.O.S.^{CCD}). For the construction of calibration lines, certified multi elements standard solutions were used (CPI International - Amsterdam). The accuracy of the analytical method and of the results obtained were verified by analyzing certified standard specimens of soil (BCR-CRM 141R, 142R, 143R).

Among the 36 elements analyzed, only the results for Ba, Cr, Cu, Ni, Pb, V e Zn which are the most significant and allow direct comparison with total concentration are discussed.

Statistics. One-factor analysis (ANOVA) was performed to evaluate the main effects of PTEs concentrations in the top soil and the 80-100 cm horizons (background) . The significance of these variables was determined by using Tukey's test at a significance level (a) of 0.05.

Results and discussion

Variation of total metal concentration(XRF). The total concentrations of Ba, Cr, Cu, Ni, Pb, V e Zn obtained by XRF analisis, as well as some useful data for comparison (Amorosi et al. 2002; Curzi et al., 2006) are reported in table 1.

The Pb and Zn concentrations showed maximum values at the topsoil of all profiles, whereas the other PTEs tended to remain constant or showed slightly higher values in the deeper horizons. The difference in Cu concentrations between the top soil and the background material was more marked in the agricultural site PER2, where, on the contrary, Pb contents are relatively constant. All the PTEs displayed strong grain-size dependence, as reported by the detailed discussion referring to samples from the area by Dinelli et al. (2007).

Table 1 - *PTEs concentrations determined by fluorescence X ray along some soil profiles. The Pinewood transect-North was represented by PW1 and PW4 soil profiles, the Pinewood transect-South was represented by PW6 and PW8 soil profiles, the urban park transect was represented by GP1 soil profile, while the farm transect was represented by PER2 soil profile. Concentration ranges from Late Pleistocene-Holocene samples from boreholes in the area are provided as reference values (Amorosi et al., 2002; Curzi et al., 2006).*

Transect	Soil profile	Depth (cm)	Heavy metal concentrations (mg/kg)						
			Ba	Cr	Cu	Ni	Pb	V	Zn
PW-North	PW1	0-5	251	101	5	47	54	50	60
		5-20	285	115	7	47	47	47	37
		20-80	254	112	3	60	9	45	33
		80-100	247	121	2	71	9	47	28
	PW4	0-5	265	117	4	62	33	51	51
		5-20	294	124	12	76	22	48	49
		20-60	279	120	6	66	24	49	45
		60-80	265	95	bdl	61	10	40	26
		80-100	244	208	8	69	15	71	48
PW-South	PW6	0-3/4	255	68	8	44	19	42	103
		3/4-20	262	91	2	50	26	46	46
		20-80	353	113	bdl	55	21	41	26
		80-100	251	86	3	46	15	41	31
	PW8	0-5	258	68	10	58	48	61	93
		5-20	263	89	5	64	37	58	70
		20-80	255	96	4	60	17	42	30
		80-100	258	80	10	59	8	41	37
GP	GP1	0-3	332	75	41	61	86	72	142
		3-7	413	78	53	65	86	73	149
		7-25	431	91	53	65	105	77	159
		25-57	333	100	23	72	20	85	68
		57-80	351	97	33	71	32	85	80
		80-100	366	103	36	66	24	84	82
PER	PER2	0-28	361	99	65	76	25	89	84
		28-53	326	87	26	70	22	82	72
		53-83	336	90	28	69	24	84	74
		83-120	349	95	23	74	20	89	69
		120-153	356	89	22	62	30	72	62
		153-194	446	99	32	60	21	71	63
		194-210	391	90	22	66	21	75	59
Borehole data	(Amorosi *et a*l., 2002)		285-535	96-210	4-19	61-130	4-27	87-169	52-124
	(Curzi *et al*.., 2006)		206-381	66-268	13-45	30-148	6-29	54-117	43-99

This fact explains the different ranges observed in the Pinewood of San Vitale and the other two sites. The former are sandy samples whereas the latter have a larger proportion of clayey material, as reported by Buscaroli et al. (2009). Compared to other data available from the area, referred to deeper and older sediments that include either fine or coarse grained sediments (Amorosi et al., 2002; Curzi et al. 2006), Pb and Zn display wider ranges and highest maxima suggesting anthropogenic contribution for these elements. In the GP1 profile, the higher concentrations occur down to 25 cm depth, thus suggesting a diffuse migration of

DOI: 10.6092/issn.2281-4485/3822

Pb and Zn elements to deeper horizon. All other elements, except for only one sample having high Cu concentration in PER2 profile, are within the ranges observed for reference borehole data.
Geoaccumulation index (Igeo) has been calculated for each metal (Table 2) in order to evaluate metals contamination in soil samples from the Ravenna area. Geoaccumulation index was originally defined by Müller (Müller, 1979; Forstner and Müller, 1981) as a quantitative tool to determine metals contamination in sediments and is based on the comparison of current concentrations with pre-industrial levels. Geoaccumulation index (Igeo) can be calculated by the equation:

$$Igeo = \log_2 [Cn/(1.5 \cdot Bn)] \quad [1]$$

where C_n = metal concentration in the the topmost sample; B_n = metal concentration in the 80-100 cm sample. In this way each site has a different background values but it helps because of the difference in grain size that affects EPT abundance. In any case the concentration in the deep samples are comparable with those of boreholes of analogous grain size as already pointed out.
Müller has distinguished seven classes of sediments: unpolluted (Igeo ≤ 0), from unpolluted to moderately polluted ($0 < I_{geo} < 1$), moderately polluted ($1 < I_{geo} < 2$), from moderately to strongly polluted ($2 < I_{geo} < 3$), strongly polluted ($3 < I_{geo} < 4$), from strongly to extremely polluted ($4 < I_{geo} < 5$), extremely polluted ($I_{geo} > 5$). According to these scheme the Pb is most critical element suggesting moderately polluted conditions in the san Vitale pinewood in both transects with the soil profiles near to industrial settlement (PW1 and PW8) and for the Ravenna urban park. The most likely origin is related to emissions from vehicle exhaust that have been concentrated in these sites characterized by limited or absent reworking. There appears to be moderate pollution for copper in the PER2 site, for the reasons already outlined.

Table 2 – *Values of the Igeo calculated according to Müller (1979). Only positive values were reported.*

Transect	Soil profile	Geoaccumulation index I_{geo}						
		Ba	**Cr**	**Cu**	**Ni**	**Pb**	**V**	**Zn**
PW-North	**PW1**			**0.6**		**1.9**		**0.5**
	PW4					**0.6**		
PW-South	**PW6**			**0.7**				**1.1**
	PW8					**2.0**	**0**	**0.7**
GP	**GP1**					**1.3**		**0.2**
PER	**PER2**			**1.4**				

Comparison between total and pseudo-total data (AR). The comparison of total (XRF) versus pseudo total concentration (AR) provided some useful suggestions about PTEs behaviour in the soil environment. In general, as one might expect, the PTEs total concentrations both top sand depth soil were higher than pseudo-total s in almost all cases, as one can verify by the results on selected samples reported in

table 3. A better picture could be obtained by the visual comparison of the results presented in figure 2, that included the analysed samples.
Barium was the elements with the minor amount extracted by AR; the very low (<20%) concentration was found in the Pinewood samples wherethe abundance of K-feldspars suggests a strong bind of the element to crystal lattice and slightly higher (20-40%) in the other two sites, where the finer grain-size and the presence of clay minerals and secondary oxides affects its stability.

Table 3 - *Total (XRF) and pseudo-total (acqua-regia AR) PTEs concentrations in topsoil (0-20 cm) and subsoil (80-100 cm) and Enrichment Factor (EF) between the concentration mean value obtained by different depths. (EF: positive values were reported in bold = the enrichment in topsoil was higher than in background - Negative values was reported in bold and italics = the subsoil concentrations was higher then topsoil). The Pinewood transect-North was represented by PW1 and PW4 soil profiles, the Pinewood transect-South was represented by PW6 and PW8 soil profiles, the urban park transect was represented by GP1 soil profile, while the farm transect was represented by PER2 soil profile.*

Tran sect	Soil pro file	Depth (cm)	Potentially Toxic Elements concentrations (mg/kg)													
			Ba		Cr		Cu		Ni		Pb		V		Zn	
			XRF	AR	XRF	AR	XRF	AR	XRF	AR	XRF	AR	XRF	AR	XRF	AR
PW-North	PW1	0-20	268	53	108	64	6	17	47	34	51	59	49	27	49	55
		80-100	247	22	121	70	2	6	71	59	9	10	47	28	28	30
		EF	0.08	**0.58**	-0.12	-0.09	**0.67**	**0.63**	***-0.51***	***-0.74***	**0.82**	**0.83**	0.04	-0.03	**0.43**	**0.44**
	PW4	0-20	280	40	121	72	8	10	69	56	28	35	50	31	50	47
		80-100	244	22	208	107	8	6	69	57	15	11	71	34	48	33
		EF	0.13	**0.46**	***-0.72***	***-0.48***	0.0	**0.40**	*0.0*	*-0.01*	**0.46**	**0.70**	***-0.42***	*-0.07*	0.04	**0.30**
PW-South	PW6	0-20	259	43	80	44	5	18	47	32	23	24	45	26	75	101
		80-100	251	15	86	54	3	6	46	38	15	6	41	21	31	32
		EF	0.03	**0.65**	-0.08	***-0.22***	**0.40**	**0.69**	0.02	***-0.19***	**0.35**	**0.74**	0.09	**0.20**	**0.59**	**0.68**
	PW8	0-20	261	67	79	55	8	29	61	43	43	58	60	52	82	97
		80-100	258	26	80	44	10	9	59	45	8	8	41	21	37	36
		EF	0.01	**0.62**	-0.01	**0.20**	-0.25	**0.70**	0.03	-0.03	**0.81**	**0.87**	**0.32**	**0.59**	**0.55**	**0.63**
GP	GP1	0-20	392	146	81	52	49	54	64	49	92	75	74	51	150	118
		80-100	366	116	103	60	36	27	66	57	24	28	84	57	82	72
		EF	0.07	**0.20**	***-0.27***	***-0.15***	**0.27**	**0.49**	-0.03	-0.16	**0.74**	**0.63**	-0.14	-0.12	**0.45**	**0.39**
PER	PER2	0-20	361	99	99	67	65	104	76	62	25	34	89	61	84	78
		80-100	349	110	95	67	23	24	74	60	20	24	89	63	69	64
		EF	0.03	***-0.11***	0.04	-0.01	**0.65**	**0.77**	0.03	0.02	**0.20**	**0.30**	0.0	-0.03	**0.18**	**0.18**

Chromium extracted in AR ranges from 50 to 70 % of the total concentration, suggesting that this elements is bound to relatively stable position in crystal lattice deeper horizons could indicate limited contribution from other sources, but it has to be verified with further work.
Copper showed good agreement among the two methods suggesting that all copper is extracted by AR. This point to high mobility and sensitivity particularly to organic matter which is particularly concentrated in the topsoil samples (Buscaroli et al., 2009).
Nickel generally displays high levels of extractability, usually > 75%, that does not change among different horizons.
Lead, in almost all cases provided comparable results, which means that a large portion of the elements is extractable and it suggests association with different exchangeable sites of clays, Mn Fe and Al oxides, organic matter and all components dissolved by AR reaction. An important source related to

DOI: 10.6092/issn.2281-4485/3822

contamination is likely to be present, as already pointed out. Some samples from deep horizon in the Pinewood area display low extractability (<50%) which is coherent to the occurrence of Pb in association with K-feldspars where the element is more strongly bound and less susceptible of release.
Vanadium presented from low to intermediate extractability (50-70% of total concentration) with highest fraction observed in the samples with fine grain-size. Although the element is known for its strong association with organic matter there not seem to be a dependence of extractability with organic matter abundance. Other soil components which should affect V distribution should be clay minerals and iron oxides but these should be sensitive to AR digestion. An other possibility, particularly valid for the pinewood samples, was the occurrence of heavy minerals in sandy deposits such as pyroxene, amphiboles, garnet, Fe-Cr-Ti spinels (Marchesini et al., 2000). In such conditions the elements should be strongly bonded to lattice position and less affected by the AR digestion.
Zinc generally shows a significant mobility in the soil environment (Kabata Pendias and Pendias, 1992). This is confirmed by our results that report a good correspondence between the two different extraction methods suggesting that the element is easily extractable, likely for a non natural source.
For both data sets we have been calculated the Enrichment Factor (EF) as proposed by Rubio et al (2000) defined as [2]

$$EF = (C_n - B_n)/C_n \qquad [2]$$

where Cn = PTEs concentration in the sample between 0 - 20 cm; Bn = PTEs concentration in the sample at 80-100 cm (background). The EF values are reported in Table 3. The EF were particularly significant for Pb and Zn and their values decreased from the topsoil to deeper horizons and further testify for non natural contribution to the soil environment in all the top soil samples.
To better constrain these considerations a statistical treatment of the two population of data using the Kolnogorov-Smirnov method has been performed. The results indicate statistically significant differences for Ba, Cr, Ni e V, whereas they are not significant for Cu, Pb e Zn (Fig. 2a,b).

Conclusions

The results indicated significant topsoil enrichment for Pb and Zn in almost all the investigated sites, and less frequently, for Cu. According to the Igeo index, PW1 and PW8 can be defined as contaminated sites for lead. In this case, both sites are located in the San Vitale Pinewood and both close to main streets.

Figure 2a - *Comparison of total (XRF) vs. pseudo-total (AR) Ba, Cr, Cu, Ni concentrations for the studied samples. The 1:1 line is reported in the scatter diagram for comparison. On the right column the frequency histograms for the considered variables.*

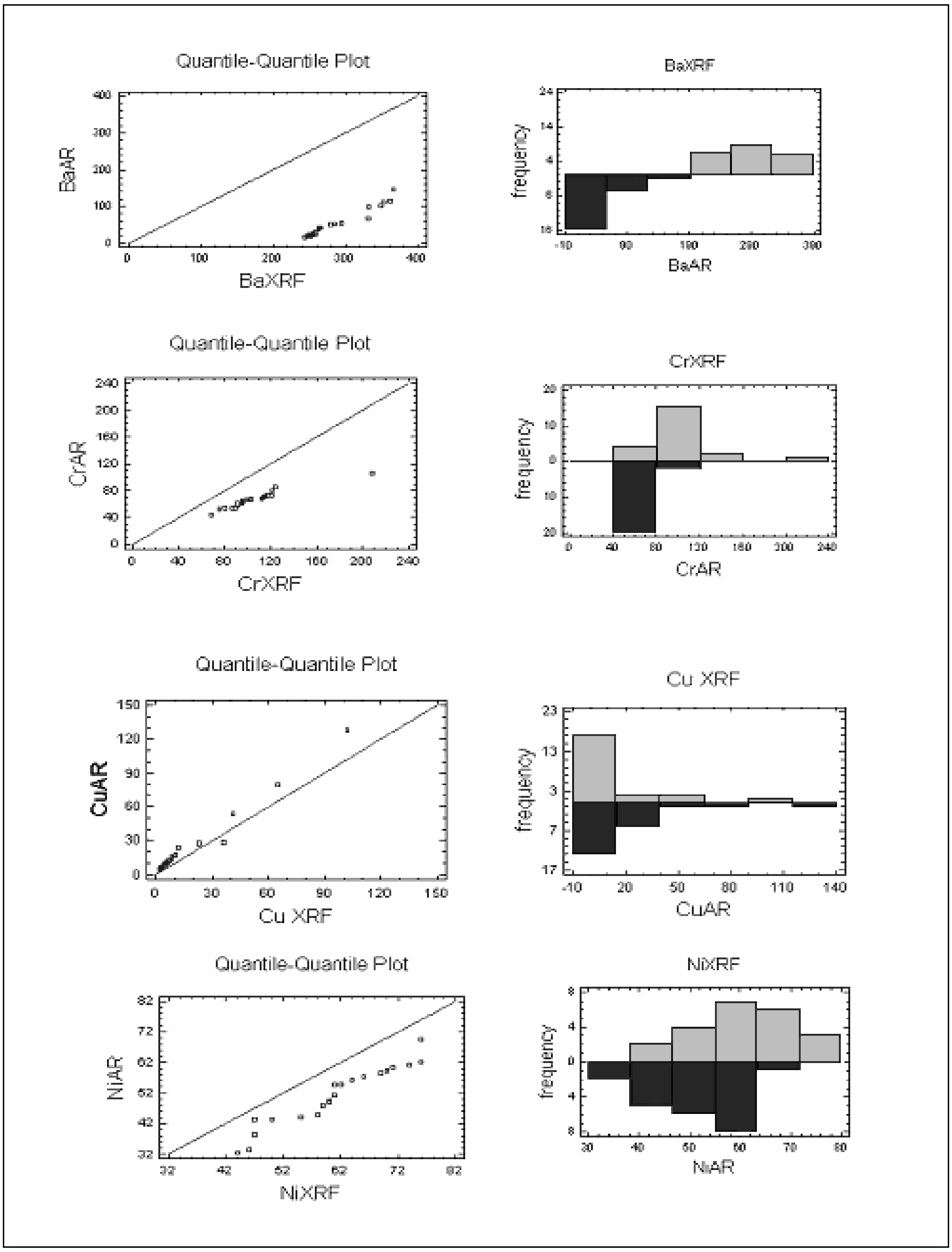
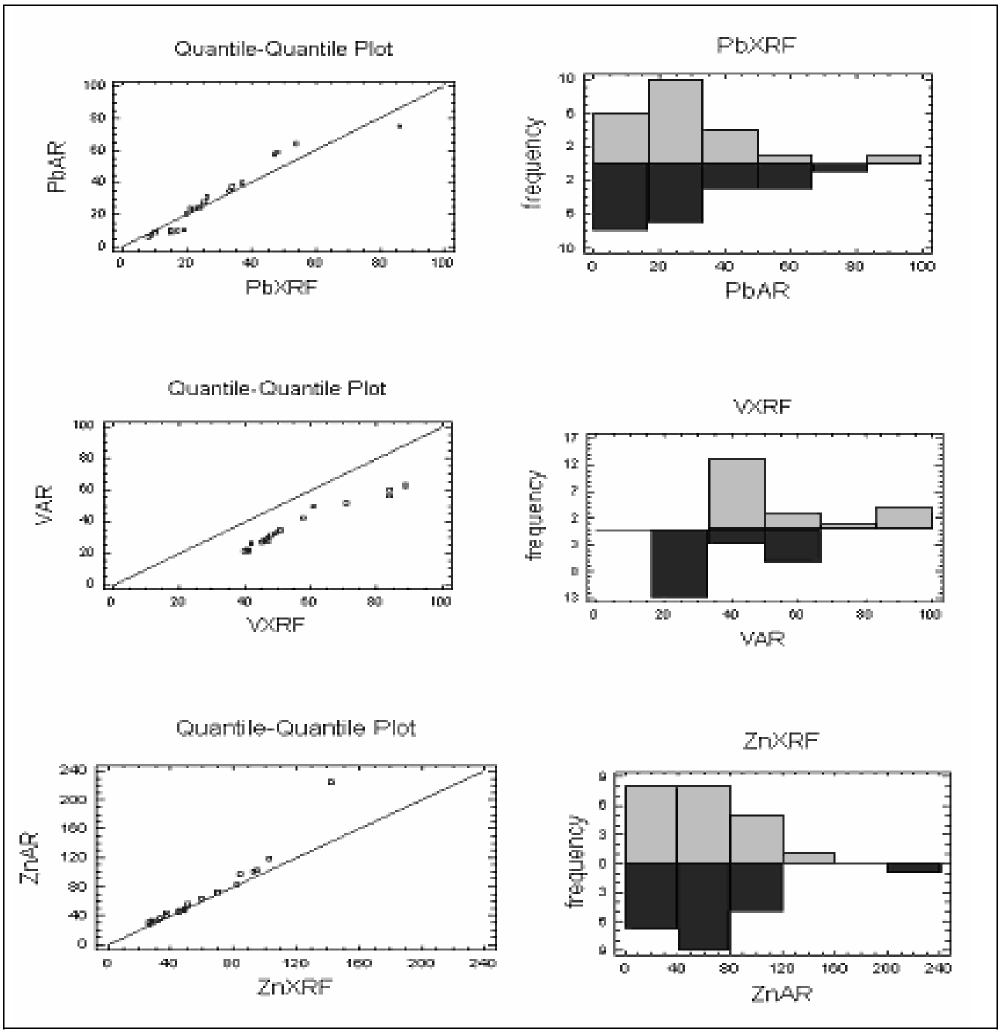


Figure 2b - *Comparison of total (XRF) vs. pseudo-total (AR) Pb, V, Zn concentrations for the studied samples. The 1:1 line is reported in the scatter diagram for comparison. On the right column the frequency histograms for the considered variables.*

DOI: 10.6092/issn.2281-4485/3822



In fact, as said, PIN1 is located near the Romea street but also PIN8 is relatively close to an important pathway of the industrial area. This evidence can be explained as a diffuse contribution of airborne pollution accumulated in an undisturbed setting. As concern the urban park in Ravenna city (GP1), Pb and Zn concentrations exceeded the threshold values established by current Italian laws for soils of "public, residential and private areas" (D. Lgs 152/2006), as suggested by the pseudototal results (*aqua regia*). The comparison between total and pseudo-total concentrations for (Ba, Cr, Cu, Ni, Pb, V, Zn) indicated differences for Ba, Cr, Ni e V whereas Cu, Pb e Zn showed the same results for both extraction methods, which implies that the first group of elements are retained in stable lattice position and can be considered to have low mobility. Conversely, the latter are extractable almost completely which could suggest association to other phases in the soil environment (organic matter, Fe-Mn-Al oxides) more susceptible to instability and indicating the importance of non natural contribution.

Acknowledgment. Research co-financed of Ministry of University and Research, within the frame of the project 20077A9XJA_PRIN 2007 Subproject 003 (L. Vittori Antisari) of Bologna University, "Diffusion of PTE in the soil-plant system in environments characte-rized by different degrees of anthropic pressure: evaluation of concentrations and bioavai-lability"

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