EQA – Environmental quality/Qualité de l'Environnement/Qualità ambientale, 2 (2009) 47-57

PRELIMINARY RESULTS ON THE DISTRIBUTION AND SOLUBILITY OF HEAVY METALS IN URBAN AND SUBURBAN SOILS OF RAVENNA

RESULTATS PRELIMINAIRES SUR LA DISTRIBUTION ET SOLUBILITE DES MÉTAUX LOURDS DANS DES SOLS URBAINS ET SUBURBAINS DE RAVENNE

RISULTATI PRELIMINARI SULLA DISTRIBUZIONE E SOLUBILITÀ DI METALLI PESANTI IN TERRENI URBANI E SUBURBANI DI RAVENNA

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Abstract

Three location types with of different environmental impacts were considered in the district of Ravenna, a city park, a suburban pinewood and arable fields. In this paper we report the preliminary results about the relationship between land use and soil management with chemical fractionation of heavy metals. The distribution and solubility of Cr, Ni, Cu, Zn, Cd and Pb was determined by water and LMWOAs extraction procedures in horizons A1 and A2 of 13 soils. In general the maximum potentially toxic element concentrations were associated with soil collected from the pinewood, and they tended to decrease with depth. The upper layer enrichment of the pinewood soils clearly revealed an anthropogenic origin of pollution. Under the pinewood, the extraction power by the single extraction procedures showed a pattern quite similar in terms of ranking of metals extracted, except that Zn and Ni were more dissolved than Cu by the use of LMWOAs. Under the pinewood, the metal levels presented a rather similar distribution pattern in terms of ranking of extractive power by the single extraction procedures, with Zn and Ni being more dissolved than Cu by the use of LMWOAs extractant. However, both readily available pools were demonstrated to be more enriched in Ni, Zn, Cd and Pb compared those of city park and arable soils. City park and arable soils had high contents of Cu. The highest concentrations were particularly shown by the arable soil under orchard, due to frequent fungicide applications. Single extractions were compared to metals dissoved in *aqua regia* by bivariate correlations. By comparison, pinewood soils showed higher positive relationships between pseudo-total contents determined by *aqua regia* and metal concentrations from single extraction procedures than city park and arable soils. The highest correlation coefficients were found for Zn and Cd by water extraction, and for Cu and Pb by LMWOAs extraction. Both water and LMWOAs pools exhibited poor correlation with pseudo-total contents of Cr and Ni.

Keywords: heavy metals; extraction unique; urban soil; pinewood soil; pollution.

DOI: 10.6092/issn.2281-4485/3816

Résumé

Trois sites dans différentes incidences sur l'environnement ont été identifiés dans le district de Ravenne, un parc de la ville, une banlieue de forêt de pins et des champs cultivés. Dans cette contribution, nous avons rapporté des résultats préliminaires sur la relation entre l'utilisation et la gestion des sols et la chimie de fractionnement des métaux lourds. La distribution et la solubilité du Cr, Ni, Cu, Zn, Cd et Pb ont été déterminées en utilisant les procédures d'extraction dans l'eau et les acides organiques à faible poids moléculaire (LMWOAs) dans les horizons A1 et A2 de 13 sols. En général, la plus forte concentration d'éléments potentiellement toxiques était associée à des sols de la forêt de pins, en montrant une tendance à la baisse avec la profondeur. L'enrichissement de la couche supérieure du sol de la forêt de pins montre clairement une origine anthropique. Dans la forêt de pins, le contenu en métaux présentait un modèle de distribution assez similaire en termes de pouvoir d'extraction par la procédure simple, sauf que Zn et Ni étaient sont plus solubles que le Cu avec LMWOAs. Toutefois, les deux groupes se sont montrés plus riches en Ni, Zn, Cd et Pb que le sol du parc de la ville et les terres agricoles. Aussi bien les deux terrains du parc de la ville que ceux qui ont été cultivés étaient riches en Cu. Les concentrations les plus élevées ont été particulièrement remarquées dans le sol d'un verger, en raison des fréquentes applications de fongicides. Des extractions individuelles ont été comparés à celles de certains métaux dans l'eau régale au moyen de corrélations bivariées. Les sols de la forêt de pins montrent des relations positives plus élevées entre les pseudo-contenus et les concentrations totales obtenues à partir des procédures d'extraction que les sols de la ville, du parc et des terres agricoles. Les coefficients de corrélation significativement les plus élevés ont été trouvés pour le Zn et le Cd extraits dans l'eau, et pour le cuivre et le plomb extraits dans LMWOAs. Les extraction tant dans l'eau que dans LMWOAs montrent peu de corrélation avec la pseudo-totalité du contenu en Cr et Ni.

Mots-clés: métaux lourds; extraction simple; sol urbain; sol de pinède; pollution.

Riassunto

Tre siti di diverso impatto ambientale sono stati individuati nel distretto di Ravenna, un parco cittadino, una pineta suburbana e un'area agricola. In questo contributo vengono riportati i risultati preliminari sulla relazione tra l'uso e gestione del suolo e il frazionamento chimico di metalli pesanti. La distribuzione e la solubilità di Cr, Ni, Cu, Zn, Cd e Pb sono state determinate utilizzando procedure di estrazione in acqua e acidi organici a basso peso molecolare (LMWOAs) negli orizzonti A1 e A2 di 13 suoli.

In generale, la massima concentrazione di elementi potenzialmente tossici era associata ai suoli della pineta, manifestando una tendenza a diminuire con la profondità. L'arricchimento dell'orizzonte più superficiale dei suoli della pineta evidenzia chiaramente un inquinamento di origine antropica. In pineta, il potere estrattivo delle singole procedure determinava una sequenza di estrazione dei metalli abbastanza simile, con la differenza che Zn e Ni erano maggiormente solubilizzati del Cu con l'impiego di LMWOAs. Comunque, entrambi i pools prontamente disponibili sono

risultati più arricchiti in Ni, Zn, Cd e Pb rispetto a quelli dei suoli del parco cittadino e dell'area agricola. Sia i terreni del parco cittadino che quelli coltivati sono risultati molto dotati di Cu. Le concentrazioni più elevate sono state particolarmente riscontrate nel suolo sotto frutteto, a causa di frequenti applicazioni di fungicidi.
Le singole procedure di estrazione sono state confrontate con i metalli dissolti in *acqua regia* attraverso correlazioni bivariate. Rispetto ai suoli del parco cittadino e dell'area agricola, i suoli della pineta mostrano relazioni positive superiori tra i contenuti pseudo-totali determinati in *acqua regia* e quelli ottenuti dalle estrazioni in acqua e LMWOAs. I coefficienti di correlazione significativamente più elevati sono stati trovati per Zn e Cd estratti in acqua, e per Cu e Pb estratti in LMWOAs. Sia l'estrazione in acqua che in LMWOAs indicano una scarsa correlazione con i contenuti pseudo- totali di Cr e Ni.
Parole chiave: metalli pesanti, Estrazione singola, Suoli urbani, Suoli di pineta, Inquinamento

Introduction

Urban areas are particularly vulnerable to pressure from human activities which result in release of potentially toxic elements into the environment. Soil pollution may result from widespread emissions of industrial plants, thermal power stations as well as vehicular traffic (Chen et al., 1997; Imperato et al., 2003). The city of Ravenna is particularly suitable for the systematic study of the enrichment and bioavailability of potentially toxic elements, because of the existence of many industrial activities such as steelworks, petrol refineries and chemical industries in the western district of the city near the sea. Rural soils may also be affected by increasing levels of heavy metals due to intensive agriculture in the in the suburban areas of the city. Cr, Cu, Zn and Cd are common anthropogenic elements in the cultivated soils. The eco-toxicological significance of heavy metals in soil is mostly dependent on their soluble and exchangeable existing forms and on the soil's ability to release ions from the soil solid phase to replenish those removed from solutions by plants. The evaluation of metal contamination based on total or "pseudo total" soil content is solely one of the aspect to be considered, although at the moment an *aqua regia* extraction procedure (ISO 11466) is often required by regulations to estimate contamination of soils. It is of great concern in the scientific community to define single or sequential extraction procedures for identification of metals pools, which differ in mobility and thus in capability to interact with plant roots. Potentially toxic metals and micronutrients occur within the soil matrix as free ions and soluble complexes, exchangeable ions, associated with soil organic matter, occluded or co-precipitated with metal oxides, carbonates or phosphates and other secondary minerals, ions in crystal lattices of primary minerals (Adriano, 2001).
Water soluble metals can easily be mobilized and may considered as highly available (Seguin et al., 2004). Extraction of pore water, leaching test and DGT are selected methods for assessment of bioavailability of heavy metals in soil solution (ISO, 2008). In addition the National Institutes for environmental protection (ISPRA, Istituto Superiore per la Protezione e la Ricerca Ambientale) and health (ISS, Istituto Superiore

DOI: 10.6092/issn.2281-4485/3816

di Sanità) recommended a soil water extraction as a method to determine the solid-liquid partition coefficient of soil contaminants for healthy-environmental risk assessment (APAT-ISS, 2007).

Adsorption-desorption processes are important controls on the concentration of metals in the soil solution. From this point of view, study on sorption-desorption reactions of heavy metals showed that low-molecular-weight-organic-acids (LMWOAs) are involved in many interactions with the physicochemical properties of soils influencing desorption of metal cations by complexation (Harter, 1983; Bruemmer et al., 1988; Pohlman and McColl, 1988; Fox, 1995; Drever and Stilligs, 1997; Qin et al., 2004). Soil solution LMWOAs, mainly aliphatic mono-, di- and tricarboxylic acids, originate from several biotic sources (Strobel, 2001). Major sources are from decomposition of soil organic matter in the upper soil horizons (Christ and David, 1996; Evans, 1998), microbial metabolites and plant roots exudates (Jones, 1998; Ma and Miyasaka, 1998). Root exudation of chelating aliphatic LMWOAs improves weathering and release of cations from soil minerals and increase the availability of nutrient cations in the rhizosphere of plants and fungi (Leyval and Berthelin, 1991; Marschner and Römheld, 1994). In order to mimic soil solution levels of heavy metals a single extraction procedure with LMWOAs was investigated to estimate metal phytoavailability (Shan et al, 2003; Wang et al., 2003; Feng et al., 2005). The authors observed better correlations between plant uptake and extractable levels by LMWOAs extractant in comparison with other one-step extraction methods and attributed to LMWOAs the extraction of the labile fractions in soil solution which are responsible for the short-term available pool.

The main objectives of this study were to assess spatial changes of metals in surface soils in the urban environment of Ravenna and to correlate them with soil physico-chemical properties and metal content in plant leaves simultaneously sampled. Specifically in this paper we reported the preliminary results about the relationship between land use and management and chemical fractionation of metals in the topsoil using single extractions. Further, single extractions were compared to *aqua regia* digestion by bivariate correlation.

Materials and methods

Three location types of different environmental impact were identified in the district of Ravenna, Italy: a city park mainly exposed to vehicular traffic; a suburban pinewood of naturalistic importance at 10 km north of the city surrounded by industrial infrastructures and rural arable fields to the east of Ravenna city. In October 2008 nine pinewood, two city park, and two arable soil profiles were selected and sampled accordingly to pedogenetic horizons. Developed on the same parent material, the thirteen soil profiles vary with respect to textural classes of the top soil layer: pinewood soils were predominantly sandy, city park soils were sandy loam and arable soils were silty loam. Pedological survey and physico-chemical composition of soil profiles are reported in Vittori Antisari et al., this conference. Surface soil samples referred as A1 (0-5 cm depth) and A2 (5 cm-variable depth) horizons, previously air dried and sieved to 2 mm, were further ground with a planetary mill bowls in agate at 700 rpm min^{-1} and sieved to 0.2 mm in order to achieve better homogenization and then minimize the errors related to sub-sampling. The single extraction procedures were carried out in triplicate, including the blanks. Water soluble heavy metals were determined accordingly to the method APAT-ISS, 2007. Briefly, 50 g soil was shaken in 100 mL of MilliQ (resistivity 18.2 MΩ cm) water for 24h. The soil suspension was then centrifuged and filtered. LMWOAc soluble heavy metals were extracted by mixing 5.5 g soil with 25 mL of acetic, formic, citric and malic acids at a total concentration of 10 mM and at a molar concentration ratio of 2:2:1:1 (Shan et al., 2003). The soil suspension was shaken for 12h, centrifuged and filtered. Soil moisture was determined on 10 g samples by oven drying at 105 °C to constant weight. After filtration, the concentrations of Cr, Ni, Cu, Zn, Cd and Pb in the extracts were immediately determined by ICP-MS (Agilent mod. 7500ce) equipped with collision cell. At the beginning of the measurement session the instrument was accurately calibrated using multi-element standard solutions. The detection limits of the method (MDL) were calculated multiplying 3.3 * SD of the blanks by the dilution factor. In the absence of certified reference materials accuracy was evaluated including several "matrix-matched" solutions in the analysis run. The average recovery of the "spike" was within -3% and +9% and -4% and +19% for water and LMWOA extraction, respectively. Basic statistics and Spearman correlation coefficients were performed using SPSS 15.0 for Windows (SPSS Inc., USA). Normality of data was analyzed using the Shapiro-Wilk test.

Results and discussion

The descriptive statistics concerning the content of Cr, Ni, Cu, Zn, Cd and Pb in the water and LMWOAs extracts of the nine pinewood top soil layers are shown in table 1. The data indicate remarkable differences between the extractive ability of the two single procedures. Although the variety of extractants and extraction procedures in previous studies make it difficult to compare the results obtained by different workers, as expected, LMWOAs solubilised more soil metals than water. With the exception of LMWOAs soluble Cd in the A2 horizon, concentration sets were not normally distributed almost all being rather right-skewed, i.e., the *mass* of the metal data were concentrated at low values. It was reported that pollutants released into the soil from point sources are apt to experience successive random dilutions giving rise to concentration distributions that are right-skewed (Wayne, 1995).

Left-skewed distributions were only observed for Cd and Ni in one of the two horizons under study. Therefore medians instead of means would best describe such distributions.

A1 horizon of the pinewood soils showed a decreasing order of water solubility as follows: Cu, Zn, Ni, Pb, Cr, and Cd. A2 horizon partially reflected the previous ranking order due to a greater enrichment of Ni with respect to Zn. Compared with water soluble metals LMWOAs dissolved more Zn and Ni, thus mobility of the six metals declined in the following order: Zn, Ni, Cu, Pb, Cr, and Cd. A2 horizon was enriched in Cr compared with A1 horizon, producing a reverse order between Pb and Cr.

DOI: 10.6092/issn.2281-4485/3816

Table 1 - *Water and LMWOAs extractable metals in the 9 soil pinewood samples for each horizon under investigation (µg kg^{-1})*.*

Extractant	Horizon		Cr	Ni	Cu	Zn	Cd	Pb
Water	A1	Range	3.0-71	31-132	24-223	19-252	0.14–1.2	3.3-60
		Median	7.1	50	86	81	0.67	16
		Mean ± SD	15±22	61 ±32	94 ±62	94±72	0.59±0.39	21±19
	A2	Range	3.2-76	15-260	15-296	7.7-121	<0.09-1.1	<0.6-116
		Median	7.8	53	61	15	0.24	11
		Mean± SD	15±23	68±74	90±85	41±40	0.35±0.30	28±41
LMWOAs	A1	Range	21-289	86-297	42-270	228-2559	1.2 - 3.5	15-284
		Median	33	191	112	661	2.0	41
		Mean ± SD	63±86	181 ±69	139 ±80	723±467	2.2 ±0.82	70 ±84
	A2	Range	11-210	127-385	14-226	29-1988	0.78-3.9	<1.9-707
		Median	46	186	87	290	2.3	13
		Mean± SD	63±59	239±101	109 ±71	419 ±603	2.4 ±0.95	123±234

* Mean values in triplicate determinations

For both water and LMWOAs extracts Zn concentrations decreased with depth: water soluble zinc, ranging from 19 to 252 µg kg^{-1}, median of 81 µg kg^{-1}, lowered in the range of 7.7 - 121 µg kg^{-1}, median of 15 µg kg^{-1}; LMWOAs soluble zinc ranging from 228 to 1559 µg kg^{-1}, median of 661 µg kg^{-1}, declined to the range of 29 - 1988 µg kg^{-1}, median of 290 µg kg^{-1}. A more gentle decreasing trend was shown by Cu and Pb.

The further discussion about the spatial distribution of the six heavy metals in the pinewood soils will be limited to the concentrations determined in the water extract (table 2). PIN 9 is mostly responsible for the maximum value of the ranges shown in table 1.

Assuming that the pinewood soils were undisturbed, the highest levels of easily soluble Cr, Ni, Cu, Cd and Pb in the lower horizon make PIN-9 the soil with the highest mobility of anthropogenic metals with depth. This soil is located in the south-eastern part of the pinewood, at the border of a wet-land which became the collector of industrial waste during the period 1950-1973 (Fabbri et al., 1998). PIN-8 and PIN-3 also resulted highly enriched in soluble metals, in particular Zn. The proximity to PIN-9 of PIN-8 justifies this result, more difficult is to interpret the content of water extractable metals of PIN-3, being located to the north of the pinewood, along with PIN-1, -2, -4 and -5, not so much enriched in water extractable metals.

There were significant differences between city park and arable soils in extractable contents of potentially toxic elements. Average concentrations are displayed in table 3.

As far as concerned the upper horizon, water soluble Cr and Zn were significantly higher in city park than in arable soils ($p<0.05$). In the arable soils Pb was below the detection limit of the method (MDL), thus no comparison was done. In water, MDL were 5.8 μg kg^{-1} Zn, 0.09 μg kg^{-1} Cd and 0.60 μg kg^{-1} Pb. Water soluble Ni and Cd showed no significant differences between city park and arable soils.

Table 2 - *Mean concentrations and standard deviations of water extractable metals of pine-wood surface soils (μg kg^{-1})*

Soil	water-Cr		water-Ni		water-Cu		water-Zn		water-Cd		water-Pb	
	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
Horizon A1												
PIN-1	3.0	0.09	50	0.95	60	1.3	58	3.9	0.24	0.03	3.9	0.2
PIN-2	10	0.47	39	0.31	43	3.8	62	5.8	0.17	0.12	20	1.6
PIN-3	11	0.96	83	1.39	160	5.4	130	3.3	0.70	0.06	36	2.3
PIN-4	4.0	0.04	31	0.03	24	1.1	19	1.8	0.14	0.01	3.3	0.2
PIN-5	4.4	0.05	35	1.73	86	9.9	19	0.03	0.39	0.33	16	1.9
PIN-6	4.2	0.57	39	1.46	71	1.5	98	3.8	0.67	0.00	4.3	0.8
PIN-7	7.1	0.20	65	5.01	94	4.5	81	7.1	1.2	0.15	12	1.4
PIN-8	19	2.36	69	1.28	87	3.5	252	23	0.68	0.28	33	9.8
PIN-9	71	1.03	132	3.28	223	5.2	127	26	1.1	0.27	60	5.6
Horizon A2												
PIN-1	3.8	0.40	27	0.40	29	7.1	7.7	2.7	0.15	0.09	3.9	0.2
PIN-2	4.9	2.26	15	2.70	15	1.7	9.9	3.0	0.13	0.07	11	3.8
PIN-3	13	1.67	63	3.00	112	9.0	121	12	0.56	0.07	81	7.5
PIN-4	3.2	0.03	26	0.01	39	1.1	14	0.1	0.22	0.02	<0.6	---
PIN-5	3.9	0.11	47	1.23	100	4.7	14	0.6	<0.09	---	7.7	1.2
PIN-6	8.0	0.14	53	2.67	52	2.7	44	10	0.39	0.10	12	0.8
PIN-7	7.8	0.88	57	1.64	109	6.6	15	0.7	0.24	0.04	8.9	2.1
PIN-8	12	0.04	69	0.61	61	0.9	65	10	0.33	0.05	11	0.2
PIN-9	76	1.77	260	6.27	296	4.1	80	16	1.1	0.11	116	10

Table 3 - *Average water and LMWOAs extractable metals from city park (CP) and arable (AR) soils (μg kg^{-1}).*

Extractant	Soil	Horizon	Cr	Ni	Cu	Zn	Cd	Pb
Water	CP	A1	5.6 ±3.7	33 ±16	80 ±10	32 ±11	0.29 ± 0.06	3.7 ±0.23
		A2	7.0 ±4.6	23 ±9.4	73 ±6.6	17 ±2.3	0.13 ± 0.05	1.4* ±0.19
	AR	A1	1.9 ±0.11	21 ±2.9	118 ±86	10 ±4.5	0.26 ± 0.12	<0.60
		A2	1.5 ±0.48	9.0 ±0.69	48 ±21	7.3* ±2.2	0.12*±0.02	<0.60
LMWOAs	CP	A1	38 ±4.7	84 ±16	149 ±5.4	107 ±17	1.4 ± 0.67	9.8 ±5.3
		A2	55 ±8.3	198 ±89	224 ±23	118 ±43	2.6 ± 0.49	5.6* ±1.1
	AR	A1	44 ±8.7	124 ±7.4	436 ±344	<18	2.3 ± 1.7	2.7* ±0.5
		A2	39 ±1.5	120 ±5.8	227 ±143	<18	1.9 ± 0.55	<1.9

* mean of one in two soils: the second one <MDL

A different behaviour characterized the two arable soils under investigation as regards the content of copper, being one of them sampled under orchards. Since many years, treatments with fungicides based on copper salts have been widely applied, resulting in

DOI: 10.6092/issn.2281-4485/3816

a considerable build-up of water and LMWOAs extractable Cu. Therefore, largest standard deviations caused a lack of significance between copper means. In the lower horizon highest metal concentrations were observed in city park soils, except for Cd. LMWOAs extraction showed a different mobilization of metals compared to water extraction.

Relative larger amounts of Zn and Pb were extracted by LMWOAs procedure in the city park soils, being arable soils very poor in those metals. MDL were 18 and 1.9 μg kg^{-1} for Zn and Pb, respectively. In the upper horizon significantly higher concentrations of Ni and Cu and lower amounts of Pb were observed in the arable soils compared to city park soils. LMWOAs soluble Cr and Cd showed no significant differences between city park and arable soils. As it has been pointed out previously, with depth the majority of metals significantly declined in rural soil, with the exception of copper, for the reasons previously detailed. From another point of view the above results might be attributed to the relative increase of extractable metals with depth in city park soils and to the relative unchanging concentrations with depth in arable soils.

It is well established that there is no reliable single extractant to predict metal availability to plants. Besides metal chemical speciation, chemical properties of the soil, such as texture, organic matter content, cation exchange capacity, salinity, pH and redox potential are the main parameters controlling plant uptake of heavy metals (Sauerbeck and Hein, 1991, Davies, 1992). Significant effects of soil texture and particle-size distribution on mobility of heavy metals in soils have been reported (Qian et al., 1996; Meers et al., 2007).

In order to give an insight into the potentiality of the two single extraction procedures to reflect some measure of the pseudo-total soil content, data sets were divided into soils with sandy texture (pinewood soils) and sandy loam and silty loam texture (city park plus arable soils). In table 4 are displayed Spearman correlation coefficients (ρ) between the extracted metals by water and LMWOAs and pseudo-total soil content of heavy metals as determined by *aqua regia* (Vittori Antisari et al., 2009).

Table 4 - *Correlation coefficients (ρ) between soil pseudo-total contents of Cr, Ni, Cu, Zn, Cd and Pb and soluble metals by single extraction procedures.*

Element	Water		LMWOAs	
	Pine-wood soils (n=18)	City park and arable soils (n=8)	Pine-wood soils (n=18)	City park and arable soils (n=8)
Cr	– 0.106	– 0.429	0.304	0.167
Ni	– 0.084	– 0.143	– 0.040	– 0.024
Cu	0.558**	0.643*	0.779***	0.643*
Zn	0.792***	0.810**	0.498*	ND
Cd	0.806***	0.762*	0.040	– 0.310
Pb	0.470*	ND	0.695**	ND

*,** and *** significant at the probability level of $p<0.05$, $p<0.01$, $p< 0.001$, respectively. ND: not determined

Based on the weaker extraction procedure, a higher relative positive correlation of pseudo-total concentrations of Cu, Zn, and Cd of pinewood soils can be derived compared to the city park plus arable soils. For Pb, the correlation was found to be positive for pinewood soils but at a lesser probability level than for Cu, Zn and Cd. No Pb correlation was achieved for city park plus arable soils because over than 60% of the samples were below the detection limit of the method.

Pseudo-total Cu, Zn and Pb concentrations were positively correlated with metals released from the soil matrix by LMWOAs extraction. Correlation coefficients for Cu and Pb were better than those exhibited by water extraction for pinewood sandy soils. Compared with water pool, pseudo-total Cd correlated poorly with that of LMWOAs extraction. For Zn and Pb no correlations were performed for city park plus arable soils because samples were insufficient. Based on these results, water and LMWOAs extraction procedures seem to reflect some measure of soil pseudo-total content for some of the elements under study. The best relationships were found for Zn and Cd by water extraction, and for Cu and Pb by LMWOAs extraction. Several metals, particularly Cd, Zn and Ni, typically show a near-linear relationship of soluble or easily extractable concentration to total metal concentration in the soil after long term application of sewage sludge (McBride et all., 2000; Chaundri et all., 2001). These results suggest that soil metal enrichment from anthropogenic origin may render potentially toxic elements more available to organic receptors.

Both water and LMWOAs pools exhibited poor correlation with pseudo-total contents of Cr and Ni. Despite variable, and locally very high, background levels of Cr and Ni in the area under study, Sammartino et al. (2004) observed a very low degree of correlation between extracted Cr and Ni by weak acids and total metal excess in topsoil samples. By comparison, pinewood soils showed higher positive relationships between pseudo-total contents and extracted metals by single extraction procedures than city park plus arable soils. In the sandy soils of the pinewood mobility of Cu, Zn, Cd and Pb seems to be better controlled by the total content of such metals with more dangerous consequences from the environmental point of view.

Conclusions

Taking into account the fewer samples from city park and arable soils, in general the maximum potentially toxic element concentrations were associated with soil collected from the pinewood, and tended to decrease with depth. The upper layer enrichment of the pinewood soils clearly revealed an anthropogenic origin of pollution. Under the pinewood, the extraction power by the single extraction procedures showed a pattern quite similar in terms of ranking of metals extracted, except that Zn and Ni were more dissolved than Cu by the use of LMWOAs. Under the pinewood, the metal levels presented a rather similar distribution patter in terms of ranking of extractive power by the single extraction procedures, with Zn and Ni being more dissolved than Cu by the use of LMWOAs extractant. However, both readily available pools were demonstrated to be more enriched in Ni, Zn, Cd and Pb compared to city park and arable soils. City park and arable soils were highly endowed in Cu. The highest concentrations were particularly shown by the arable soil under orchard, due to frequent fungicide applications.

DOI: 10.6092/issn.2281-4485/3816

The data in this study indicate that neither of the extractant alone was good enough to reflect some measure of the pseudo-total contents of heavy-metal in soils. However, there were high positive correlations between water extractable Cu, Zn and Cd and between LMWOAs extractable Cu and Pb and respective pseudo-total contents under the pinewood, thus suggesting that the examined single extraction procedures might give an insight on soil pseudo-total contents of sandy soils. These preliminary results suggest further work on the effects of metals in such soils by testing the proposed methodologies on datasets acquired on the vegetation cover and soil parameters.

Acknowledgments. This research was partially supported by a grant from the Italian Ministry of University and Research (PRIN 2007-20077A9XJA-005), subproject "Determination of potentially toxic elements by ICP-MS in the water-soil-plant system in areas under different types of anthropogenic pressures".

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DOI: 10.6092/issn.2281-4485/3816