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Total and potentially phytotoxic trace metals in southeastern Italian soils

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Abstract

A number of soils from Southeastern Italy have been characterized for their principal physico-chemical properties and total and available contents of trace metals in order to evaluate their possible phytotoxic effects on locally-grown crops. Trace metal toxicity was evaluated by measuring their content in the shoots of different crops (olive, orchards, vineyards and vegetables) grown on these soils, and by using phytotoxicity tests based on seed germination and seedling growth. The total contents measured for trace metals are generally within the usual range found in Italian soils. Only total Pb and Cd contents were close to the upper limits of environmental hazardous concentration. Trace metal contents in plant shoots and results of phytotoxicity tests confirmed the presence in these soils of metal concentrations not harmful to plants.

Key words: Italian soils, trace metals, bioavailability, phytotoxicity, *Avena sativa* L., *Lepidium sativum* L.

Introduction

In recent decades several anthropogenic activities have caused a remarkable release of trace metals into agricultural soils. The most relevant of these include the application of fertilizers, liming materials, agrochemicals, sewage sludges and other wastes used as soil amendments, the use of irrigation waters, and atmospheric deposition from industrial, urban and road emissions[1-2]. Although some trace elements are important plant micronutrients, an excessive concentration may result in soil contamination and plant uptake, which in turn may affect negatively the yield and quality of agricultural crops. Further, toxic trace elements may enter the food chain and/or leach down to groundwater, thus contaminating drinking water resources, with obvious negative consequences for the environment and human and animal health[2]. The total content of a trace metal in soil is generally of limited use for evaluating the amount of metal that can be absorbed by plants. An increase in the total metal content does not necessarily correspond to an increase in plant uptake. Bioavailability of trace metals in soil and their phytotoxicity are related to the specific forms of metals in soil, and to several soil properties, such as pH, clay, silt and organic matter content and quality, redox potential, and cation exchange capacity[3-5]. Further, the amount of trace metals absorbed by plants is a critical aspect in evaluating the risk of phytotoxicity in a particular site[6]. Several chemical methods using various extractants have been applied to assess metal speciation and availability in soils[5,7-8]. Chemical analysis of soil metals are, however, not completely reliable for the purpose of evaluating their actual phytotoxicity in field conditions[9-10]. Plant toxicity tests, including seed germination, root elongation and early seedling-growth tests, are simple, rapid, reliable and reproducible methods that can be used to study metal phytotoxicity[11-13]. The evaluation of metal uptake by selected metal-sensitive plant species (bio-indicators), such as cress (*Lepidium sativum* L.) and oat (*Avena sativa* L.), which promptly react to soil contamination by metals, resulted more informative than results obtained by the use chemical methods[14], and more advantageous than tests using animals, algae and bacteria, in assessing the phytotoxicity of metals and other chemicals in soil[15]. The main purpose of this work was to determine the total and available concentrations of trace metals in various Southeastern italian soils by chemical methods and phytotoxicity tests, and to evaluate their correlations with various physico-chemical soil parameters. Another purpose of the work was to investigate the influence of soil depth and agricultural practices related to crop species on trace metal concentrations in the soil. Further, the uptake of two representative trace metals, Cu and Pb, by cress and oat plants grown on soils containing the largest amount of total and available metals was evaluated.

Materials and Methods

Soil samples: Soil samples were collected from 42 rural sites (including some greenhouses) in Southeastern Italy (Apulia region) cropped to olive, vineyard, orchard and vegetables. The location and number of sites sampled in each location are indicated in Figure 1. Soils in each field site were sampled at two depths, 0-10 cm and 10-30 cm, whereas greenhouse soil samples were collected at a depth of 0-10 cm. A total number of 75 soil samples was analyzed. Before analysis each soil sample was spread on trays and air-dried, then thoroughly mixed and rolled in a mortar to break up clods, and finally passed through a 2-mm sieve.

Soil analysis: Standard methods have been used for soil analysis[16]. In particular, pH was measured by a glass electrode in water and in 1M KCl suspension (pH_{H2O} and pH_{KCl}, respectively) at a 1:2.5 soil to liquid phase ratio. Electrical conductivity (EC) and soluble salt content ($salts_{sol}$) were determined by a conductimeter on soil suspensions at a 1:2 soil to water ratio. Particle size distribution was determined by the hydrometer method after dispersion of the sample in sodium hexametaphosphate solution. Total organic carbon (C_{org}) was measured by the Walkley-Black method, and organic matter (OM) was calculated by multiplying C_{org} by 1.724. Total nitrogen (N_t) was determined by the Kjeldahl method, and available phosphorus (P_2O_5) by the Olsen method. Cation exchange capacity (CEC) and exchangeable bases (Ca, Mg, Na and K) were determined on $BaCl_2$-triethanolamine (TEA) soil extracts by means of an inductively coupled plasma spectrometer (ICPS, Tracescan Thermo Jarrel Instrument). Total $CaCO_3$ content was measured by the gas-volumetric method using the Dietrich-Fruehling calcimeter. Exchangeable sodium percentage (ESP) was calculated as the ratio Na to CEC. Total trace metal concentrations in soils were determined by using the U.S.-EPA Method n. 3052[17]. Briefly, a solution of $HCl\text{-}HNO_3$ (3:1, v/v) was added to 3 g of soil in closed pressure boxes which were then placed in a microwave oven (Milestone, model Ethos 900). Mixtures were heated by using an energy program consisting of 4 steps, 250 W, 400 W, 600 W and 250 W, at 6 min each. The samples were then cooled and added with distilled water up to 25 mL, stored in plastic containers, and finally measured for their metal contents by ICPS. Optical lines were chosen so that to ensure the lowest interaction between emissions of the various elements present in the extracted solutions. The available trace metal contents were determined by extracting the soil samples by diethylenetriamine pentaacetic acid (DTPA)[7], and analyzing the extracts by ICPS[18]. All reagents used were Fluka analytical grade.

Phytotoxicity tests: Metal phytotoxicity of 33 soil samples (all from the upper soil layer), which were selected from the total 75 samples on the basis of the higher trace metal (one or more) contents, was evaluated by seed germination and short-term plant growth indexes which are widely utilized to test phytotoxicity of various substrates including composts, sludges, organic chemicals and wastewaters[13,15,19-22]. Two plant species, oat (*Avena sativa* L.) and cress (*Lepidium sativum* L.) were used in these two tests.

Seed germination: The experiment was conducted in quadruplicate on sets of 25 oat or cress seeds placed on a 5-mm moistened layer of each soil sample and covered with a moistened filter paper in 8-cm diameter petri dishes[23]. A metal-unpolluted soil sample mixed with 30% of perlite was used as the control. All dishes were sealed to avoid water evaporation and left in the dark in a Phytotron growth chamber at 21 ± 1 °C. Seed germination and primary-root lengths were evaluated after 2 and 3 days, respectively for cress and oat. The percentage of seed germination (SG) and the germination index (GI) were calculated according to Zucconi et al.[19]:

where Gs and Gc are, respectively, the percentages of seed germination in the sample and in the control, and Ls and Lc are the primary-root lengths of the sample and the control, respectively.

$$SG = \frac{\text{No. of seeds germinated}}{\text{No. of total seeds}} \times 100 \qquad (1)$$

$$GI = \frac{Gs \times Ls}{Gc \times Lc} \times 100 \qquad (2)$$

Short-term growth: The experiment was conducted by transplanting 10 oat and cress seedlings into small plastic pots filled with 200 mL of soil sample, and irrigating with tap water every 3 days for 21 days. Growth was determined by measuring the fresh and dry weights of shoots at the end of the growing period. The relative growth index (RGI) was obtained by the following equation[13]:

where Ws and Wc are, respectively, the shoot weights of the sample and the control. This index was calculated both on fresh and dry shoot weights.

$$RGI = \frac{Ws}{Wc} \times 100 \qquad (3)$$

Trace metal contents in the shoots: The content of Pb and Cu was determined in the shoots of plants grown on 9 soil samples that presented a potential risk of phytotoxicity on the basis of the bioavailable amounts of Pb and Cu in these soils and the previously obtained SG, GI and RGI indexes. Shoots were cut with a blade and then oven-dried at 80°C until a constant weight was achieved. Each oven-dried sample was ground in an agata mortar and then stored in a plastic container until analysis.

The extraction of Cu and Pb from the shoots was performed by digesting in a microwave oven 100 and 150 mg, respectively, of cress and oat dry material in a mixture of 0.5 mL of 30% H_2O_2 and 3 mL of 65% HNO_3[17]. The resulting mixtures were collected with distilled water, filtered through a 0.45-µm syringe sieve, and then analyzed for Pb and Cu content by ICPS.

In order to assess the influence of soil properties on Cu and Pb uptake by plants, the soil-to-plant transfer ratio[5] were evaluated by calculating the biological absorption coefficients (BAC), i.e., the ratio of Cu and Pb concentrations in the plant shoots (Me_{plant}) to either the total or the available corresponding metal concentrations in soils (Me_{tot} and Me_{ava}, respectively) according to Chen et al.[14]:

$$BAC_T = Me_{plant}/Me_{tot} \qquad (4)$$

$$BAC_A = Me_{plant}/Me_{ava} \qquad (5)$$

Statistical analysis: Correlations between soil properties data and total and available trace metal contents were statistically evaluated by calculating the correlation coefficients (r) at $P < 0.001$. Regression equations and determination coefficients (R^2) between total and available contents of some metals were also calculated. The values of SG, GI and RGI have been statistically analyzed by one-way analysis of variance (ANOVA) at both 95% and 99% confidence levels. The mean values were separated by using the least significance difference (LSD) test. Data obtained for all treatments were statistically compared to the control treatment data.

Results and Discussion

Table 1 shows the average values of physical and chemical parameters of the 75 soil samples examined, including the total and available contents of some trace metals together with the usual and extreme ranges of total trace metal contents in soil[2]. In general, soils examined can be classified as medium-fine-textured soils (30.6% are clay soils, 16% silty-clay soils and 24% silty loam soils). Some parameters markedly differ between the two layers, e.g., the EC of the 0-10 cm layer is almost twice than that of the 10-30 cm layer. The contents of organic matter (OM), P_2O_5, N_t, Na and ESP are also higher in the surface layer than in the bottom layer, whereas no significant difference is observed between the two layers for pH, texture and CEC. Figure 2 shows the distribution (in %) of the 75 soils examined for their range values of pH_{KCl} and C_{org}. The majority (92%) of soil samples shows pH values close to neutrality (6.5-7.5), 5.3% of samples show a pH > 7.5, and only two soils are acidic (pH 6.5-5). The amount of C_{org} can be considered adequate or good in most soils (97.3%), with only

Table1. Average values of some physical and chemical parameters, including total and available contents of some trace metals, of the 75 soil samples examined. The usual and extreme range values of total trace metal contents in soil are also reported (from Senesi et al.[2]).

Depth (cm)	Sand	Silt	Clay	$CaCO_3$	pH_{H2O}	pH_{KCl}	EC
	(g kg^{-1})						(dS m^{-1}
0 – 10	333.2	389.0	277.9	96.0	7.9	7.1	0.9
10 –30	330.3	397.3	272.4	112.9	8.0	7.2	0.5
	$Salts_{sol}$ (g kg^{-1})	CEC (cmol kg^{-1})	C_{org}	OM	N_t	C/N	P_2O_5 (mg kg^{-1})
			(g kg^{-1})				
0 –10	1.2	32.4	17.0	29.3	1.7	9.8	143.7
10 –30	0.7	32.2	15.8	27.3	1.5	10.6	110.6
	Na	K	Ca	Mg	ESP (%)	Ca/Mg	K/Mg
	(cmol kg^{-1})						
0 – 10	1.0	1.9	25.4	3.7	3.3	10.2	0.8
10 –30	0.6	1.8	26.8	2.8	1.7	12.5	0.8
	As_{tot}	Cd_{tot}	Cr_{tot}	Cu_{tot}	Ni_{tot}	Pb_{tot}	Zn_{tot}
	(mg kg^{-1})						
0–10	39.0	1.8	84.9	61.2	39.3	99.9	132.1
10–30	39.2	1.9	82.1	62.1	37.5	103.6	136.7
Usual range	1-50	0.01-0.70	5-1,000	2-100	5-500	2-200	10-300
Extreme range	0.1-1,000	0.01-7.0	0.1-35,800	10-14,000	0.5-6,200	0.1-10,000	6-30,000
	As_{ava}	Cd_{ava}	Cr_{ava}	Cu_{ava}	Ni_{ava}	Pb_{ava}	Zn_{ava}
	(mg kg^{-1})						
	0.08						
0–10	0.09	0.11	0.06	7.33	0.44	3.33	7.10
10–30		0.09	0.03	6.89	0.30	3.16	6.31

two samples presenting a small C_{org} content. These results may suggest a scarce mobility of trace metals in most soils which are expected to be adsorbed and/or immobilized by OM. The total content of each trace metal generally falls in the usual range reported in the literature[2], and is similar between the two layers, whereas the contents of available metals are slightly higher in the surface layer than in the deeper layer. The values of the ratio Me_{tot}/Me_{ava} follows the order Cu > Ni > Cd > Zn > Pb >> As > Cr. Only the total content of Cd is above the upper limit of the usual range, probably because of Cd impurities added to soil by phosphate fertilizers[24-26]. The lowest concentrations of total and available trace metals are found in sandy soils, while the highest ones are measured in soils rich in OM. These effects can be ascribed, respectively, to the limited weathering and/or great metal mobility in the former soils and the high metal adsorption by OM in the latter soils[1,26]. Relevant differences can be observed between some soil parameters as a function of the crop species grown (Table 2). The largest contents of OM, As_{tot}, Cd_{tot}, As_{ava} and Cd_{ava} are measured in soils cropped to olive, whereas exchangeable cations, CEC and ESP show the highest values in soils cropped to vegetables. Vineyard soils show the highest values of EC, $salts_{sol}$, $CaCO_3$, P_2O_5, Cr_{tot}, Zn_{tot}, Cu_{ava} and Zn_{ava}. These differences are probably related to the different agricultural practices used for the various crops, such as types and doses of fertilizers and pesticides applied and irrigation water quality. The correlation coefficients calculated between some soil parameters are shown in Table 3. Silt is positively correlated to the contents of OM, Ca, K, N_t and to CEC. The pH_{H2O} is negatively correlated to EC, P_2O_5 and N_t. As expected, CEC is correlated positively to OM content and negatively to $CaCO_3$ and sand contents. The Ca content is correlated negatively to Na and Mg contents and positively to K content. The ESP is correlated negatively to both silt and OM contents, and positively to clay content. When the correlation coefficients are calculated separately for the two soil layers (data not shown), almost all the physico-chemical parameters appear to be highly ($P < 0.001$) correlated to both silt and clay in the 0-10 cm layer, whereas these correlations do not hold in the 10-30 cm layer. Further, in the 0-10 cm layer, the OM content is highly correlated to N_t and exchangeable cation contents. The regression equations and statistical parameters shown in Table 4 indicate that the available contents of Cd, Cu, Pb and Zn in the soils examined are highly significantly correlated to their total contents, whereas no correlation is found for As, Cr and Ni. Further, trace metal contents are all intercorrelated positively (data not shown), which can be ascribed to their general increased concentration due to various inputs including atmospheric deposition, anthropogenic activities and application of fertilizers and amendments to soil. In Table 5 only the highly significant ($P < 0.001$) correlations found between the total and available trace metal contents and soil parameters are shown distinguished for different crops. Few correlations are held for orchard soils, whereas particularly relevant positive correlations of several total and/or available trace metal contents are obtained with: (a) CEC, especially for olive-cropped soils; (b) OM content, especially for vineyard soils; (c) total N content, especially for vegetable-cropped soils; and (d) available P_2O_5 content for vineyard, olive-cropped and vegetable-cropped soils. Sand is the only relevant soil property holding a negative correlation with some

Table 2. Dependence of some average soil properties on the crop species grown.

	$CaCO_3$	EC	$Salt_{sol}$	CEC	OM	P_2O_5	Na	K	Ca	Mg	ESP	As_{tot}	Cd_{tot}	Cr_{tot}	Zn_{tot}	As_{ava}	Cd_{ava}	Cu_{ava}	Zn_{ava}
Olive	81.4	0.4	0.6	33.2	33.8	94.8	0.3	1.7	28.0	2.5	1.0	42.7	2.0	80.9	130.0	0.11	0.12	4.76	6.46
Vineyard	134.8	1.5	1.9	33.0	27.1	241.8	0.8	2.0	27.0	3.0	2.3	38.4	1.9	99.7	188.9	0.10	0.10	11.43	13.32
Orchard	115.5	0.5	0.7	32.3	25.5	111.0	0.6	1.9	26.6	3.0	1.9	39.6	2.0	83.7	140.9	0.08	0.09	10.24	5.29
Vegetables	92.4	0.7	0.9	34.3	27.6	119.6	1.0	2.5	27.1	3.6	2.8	34.1	1.6	86.6	137.4	0.07	0.12	7.39	6.58

Table 3. Coefficients (r) for significant correlations ($P < 0.001$) found between some soil characteristics.

	Sand	Silt	Clay	$CaCO_3$	pH_{H2O}	pH_{KCl}	EC	CEC	OM	N_t	C/N	P_2O_5	Na	K	Ca	Mg	ESP	Ca/Mg
Sand				0.543		0.492												
Silt	-0.611						-0.410											
Clay		-0.519																
$CaCO_3$						0.520												
pH_{H2O}																		
pH_{KCl}					0.795													
EC					-0.440													
CEC	-0.50	0.499		-0.708		-0.459			0.543	0.467				0.528	0.816			
OM		0.562																
N_t		0.450			-0.413				0.834									
Cs/N			-0.378				-0.400		0.519									
P_2O_5					-0.535		0.392			0.435								
Na		-0.546					0.563		-0.465						-0.517	0.692		
K		0.411							0.383						0.419			
Ca	-0.436	0.672		-0.445					0.619	0.464	0.455							
Mg		-0.453	0.485				0.575				-0.421				-0.561			
ESP		-0.630	0.387				0.551		-0.518		-0.530		0.982		-0.621	0.696		
Ca/Mg		0.471	-0.554				-0.462				0.477		-0.620		0.534	-0.891	-0.630	
K/Mg		0.412	-0.488								0.472		-0.435	0.714		-0.648	-0.458	0.747

Table 4. Regression equations and statistical parameters relating DTPA-available Cu, Cd, Pb and Zn to their corresponding total contents.

	Regression equation	Multiple R^2 value	R^2	F value	Significance of F
Copper	$Cu_{ava} = -2.305 + 0.153Cu_{tot}$	0.81	0.65	137.94	< 0.0001
Cadmium	$Cd_{ava} = -0.018 + 0.066Cd_{tot}$	0.43	0.19	16.75	< 0.0005
Lead	$Pb_{ava} = -2.258 + 0.054Pb_{tot}$	0.68	0.46	63.03	< 0.0001
Zinc	$Zn_{ava} = -5.544 + 0.091Zn_{tot}$	0.77	0.60	108.34	< 0.0001

Table 5. Coefficients (r) for highly significant correlation (P < 0.001) between total or available metal contents and some soil characteristics distinguished for different crops.

	Soil characteristics												
	Sand	Clay	$CaCO_3$	pH_{H2O}	CEC	OM	N_t	P_2O_5	Na	K	Ca	Mg	ESP
As_{tot}	-0.614$^{(a)}$				0.785$^{(a)}$						0.678$^{(a)}$	0.795$^{(d)}$	
	-0.840$^{(c)}$												
Cd_{tot}					0.573$^{(a)}$							0.750$^{(d)}$	
Cr_{tot}	-0.797$^{(a)}$				0.597$^{(a)}$		0.899$^{(d)}$	0.918$^{(d)}$		0.826$^{(c)}$			
			-0.782$^{(a)}$										
Cu_{tot}					0.946$^{(b)}$	0.944$^{(b)}$	0.860$^{(d)}$	0.670$^{(a)}$					
								0.939$^{(b)}$					
Ni_{tot}	-0.580$^{(a)}$												
	-0.825$^{(c)}$												
Pb_{tot}	-0.926$^{(b)}$					0.785$^{(d)}$	0.863$^{(d)}$	0.750$^{(d)}$			0.934$^{(b)}$		
		-0.822$^{(d)}$											
Zn_{tot}						0.951$^{(b)}$	0.858$^{(d)}$	0.930$^{(b)}$					
As_{ava}													
Cd_{ava}									0.690$^{(a)}$				0.609$^{(a)}$
Cr_{ava}									0.761$^{(d)}$			0.581$^{(a)}$	0.761$^{(d)}$
Cu_{ava}			0.695$^{(a)}$			0.982$^{(b)}$	0.937$^{(b)}$	0.648$^{(a)}$					
					-0.652$^{(a)}$		0.871$^{(d)}$	0.940$^{(b)}$			-0.581$^{(a)}$		
								0.773$^{(d)}$					
Ni_{ava}								0.693$^{(a)}$		0.620$^{(a)}$			
				-0.723$^{(a)}$									
Pb_{ava}						0.956$^{(b)}$	0.783$^{(d)}$	0.942$^{(b)}$					
Zn_{ava}						0.980$^{(b)}$	0.890$^{(d)}$						

(a) olive, (b) vineyard, (c) orchard, (d) vegetables crop.

Table 6. Seed germination (SG), germination index (GI) and relative growth index (RGI) related to fresh weight (f. w.) and dry weight (d. w.) of *A. sativa* (oat) and *L. sativum* (cress) for some representative soil samples (depth 0-10 cm).

	OAT				CRESS			
Soil Sample	SG (%)	GI (%)	RGI (f. w.)	RGI (d. w.)	SG (%)	GI (%)	RGI (f. w.)	RGI (d. w.)
I 7							66**	
I 17					73*			
I 31		74*						
I 72		65*						
I 74								
I 75		64**			72**	53*		
I 76			73*					
I 79		44**			28**	17**		
I 84					61**			
I 85		61**			44**	23**	71*	75**
I 87	76*							
I 98		71*			53**	53*		
I 102					56**	54*		
I 103					52**	58*		
I 105	71**	38**			38**	23**	42**	
S1	68**							
S2	61**							
S4	66**							
S6	75*							
Control	**90**	**100**			**86**	**100**	**100**	**100**

The symbols ** and * refer, respectively, to a difference significant at 0.01P and 0.05P, according to LSD test. Only values statistically lower than the control values are shown.

Table 7. Contents of Cu and Pb mg kg^{-1}in shoots of *A. sativa* (oat) and *L. sativum* (cress) grown on some soils examined (depth 0-10 cm).

	OAT		CRESS	
Soil Sample	Cu	Pb	Cu	Pb
I 17	1.65	0.20	1.99	0.78
I 31	2.77	0.17	2.07	0.61
I 75	1.50	0.19	2.73	1.10
I 79	1.45	0.09	1.87	0.13
I 84	1.53	0.23	2.14	0.53
I 85	1.60	0.58	3.31	1.02
I 102	1.98	0.22	1.84	0.88
I 103	1.71	0.31	1.69	0.71
I 105	1.53	0.16	1.74	1.26
Mean values	1.75	0.24	2.16	0.78
Control	1.38	0.19	3.09	0.72
Permissible levels in vegetables[29]	40	5.0	40	5.0
Maximum normal and unharmful values to plants[30]	20-30	10-30	20-30	10-30

Table 8. Biological absorption coefficients (BAC_T and BAC_A) of total and available contents of Cu and Pb in soil for shoots of *A. sativa* (oat) and *L. sativum* (cress).

	OAT				CRESS			
Sample	$^aCu_{tot}$	$^bCu_{ava}$	$^aPb_{tot}$	$^bPb_{ava}$	$^aCu_{tot}$	$^bCu_{ava}$	$^aPb_{tot}$	$^bPb_{ava}$
I 17	0.01	0.07	0.00	0.01	0.02	0.09	0.00	0.06
I 31	0.01	0.27	0.00	0.03	0.01	0.20	0.00	0.12
I 75	0.02	0.15	0.00	0.02	0.03	0.27	0.01	0.11
I 79	0.03	0.21	0.00	0.02	0.04	0.27	0.00	0.03
I 84	0.01	0.08	0.00	0.02	0.02	0.11	0.00	0,05
I 85	0.02	0.09	0.01	0.08	0.03	0.18	0.01	0.14
I 102	0.03	0.16	0.00	0.14	0.03	0.15	0.01	0.58
I 103	0.03	0.21	0.00	0.25	0.03	0.21	0.01	0.58
I 105	0.01	0.08	0.00	0.03	0.02	0.09	0.01	0.27
Mean values	*0.02*	*0.15*	*0.00*	*0.07*	*0.02*	*0.17*	*0.01*	*0.21*

Superscripts a and b refer, respectively, to BAC_T and BAC_A

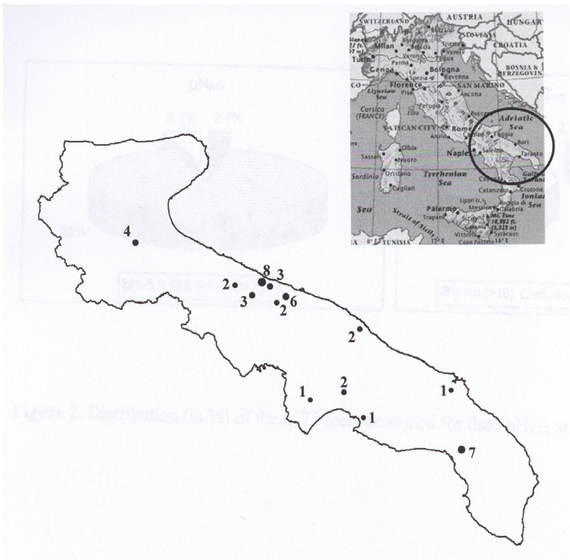

Figure 1. Location and number of sampling sites in each lo cation in the Apulia.

trace metal total contents, especially in olive and orchard soils. These results confirm that metal contents in soils are strongly influenced especially by the OM content, CEC, and sand content[3]. An important role is also played by agricultural practices related to the crop type grown on the soil[27]. The values of the toxicity indexes SG, GI and RGI used to evaluate the potential phytotoxicity of representative soils on oat and cress are shown in Table 6. In general, the response to these indexes is different for the two species tested on dependence on the soil type and the index considered. In particular, with respect to the control values, the parameter SG is significantly reduced when oat or cress are grown on different groups of soils, whereas RGI is affected only in very few cases. Some soils appear to affect negatively only oat seed germination (SG), whereas other soils influence mostly oat primary-root length (GI), and only one soil reduces oat shoot weight (RGI). Also in the case of cress the RGI parameter, i.e., cress shoot weight, is generally not affected with the exception of three soils. On the other hand, the same group of soils reduce both the SG and the GI indexes, i.e., seed germination and primary-root length of cress. In general, cress appears to be more sensitive than oat to these tests. According to Cheung et al.[9], leafy plants such as cress react more than cereals such as oat to the toxicity of the substrate. This effect is ascribed to the larger food reserves of seeds of cereals, legumes and root crops with respect to leafy plants[9]. Only two of the soil samples examined appear to affect most of the indexes in both species.The contents of Pb and Cu in cress and oat shoots grown on some of the soils examined (Table 7) are in agreement with values reported in the literature[28]. Although the contents measured are slightly higher than those in the control, they are always far below the levels permissible for vegetables fixed by FAO and WHO[29] and the limits reported as harmful to plants[30]. The values in Table 7 indicate that cress tend to accumulate metals more than oat, which confirms that metal accumulation in leafy crops are higher than in grain and fruit crops[31]. Analysis of correlation coefficients does not show relevant relationships between metal contents in plant shoots and analytical soil parameters examined (data not shown). The only exceptions are the positive correlations ($P < 0.01$) of the Pb content to $CaCO_3$ and sand contents in oat. Pb content is also correlated negatively to CEC and As, Cr and Ni contents, probably on dependence of antagonistic effects in the plant uptake. Statistical analysis does not show any correlation between Pb or Cu contents in the two plants and soil Pb_{ava} or Cu_{ava}. The BAC values of total and available Cu and Pb contents in some soils are shown in Table 8 for cress and oat shoots. In cress the BAC values for Cu_{ava} and Pb_{ava} contents (0.17 and 0.21, respectively) are much higher than those for Cu_{tot} and Pb_{tot} contents[5]. The BAC values of Cu and Pb are lower for plants grown on soils richer in available Cu and Pb, and this is in agreement with findings of Chen et al.[14]. Probably, when the concentration of trace metals in soil is high, plants can adjust their physiological activities by decreasing biomass and growth rate so that to reduce metal uptake and related toxic mechanisms[14]. Both BAC values for Cu and Pb are smaller for cress than for oat, thus indicating that a leafy plant such as cress tends to uptake trace elements from soil to a greater degree than a cereal crop such as oat[32].

Conclusions

The total and available contents of trace metals in soil samples examined generally fall within the range of the values reported in the literature. The contents of Pb_{tot} and Cd_{tot} are in most samples close to the limits reported as environmental hazardous concentrations. In particular, the content of Pb_{tot} is very high in soils close to major roads. In few cases the contents of Cu_{tot} and Zn_{tot} are above the normal range, probably as a consequence of the use of fertilizers and pesticides. The concentration of available trace metals is very low in all samples, probably because of soil pH values close to neutrality and adequate contents of OM and $CaCO_3$ that decrease trace metal availability. The response of both oat and cress to seed germination, plant short-term growth and metal contents in shoots indicates that trace metal concentrations are not harmful in all but two soils tested, even for a sensitive species such as cress. In conclusion, the soils examined can be considered not potentially phytotoxic for their trace metal contents.

References

[1] Adriano, D.C. 1986. Trace elements in the terrestrial environment. Springer-Verlag, New York.

[2] Senesi, G.S., G. Baldassarre, N. Senesi, and Radina, B. 1999. Trace element inputs into soils by anthropogenic activities and implications for human health. Chemosphere **39** (2): 343-377.

[3] McBride, M.B., S. Sauvé, and Hendershio, W. 1997: Solubility control of Cu, Zn, Cd and Pb in contaminated soils. Eur. J. Soil Sci. **48** (2): 337-346.

[4] van Duijvenbooden, W. 1998. Soil monitoring systems and their suitability for predicting delayed effects of diffuse pollutants. Agric. Ecosyst. Environ. **67:** 189-196.

[5] Planquart, P., G. Bonin, A. Prone, and Massiani, C. 1999. Distribution, movement and plant availability of trace metals in soils amended with sewage sludge composts: application to low metal loadings. Sci. Total Environ. **241:** 161-179.

[6] Luo, Y., and Rimmer, D.L. 1995. Zinc-copper interaction affecting plant growth on a metal-contaminated soil. Environ. Pollut. **88:** 79-83.

[7] Lindsay, W.L., and Norvell, W.A. 1978: Development of a DTPA soil test for zinc, iron, manganese, and copper. Soil Sci. Soc. Am. J. **42:** 421-428.

[8] Narwal, R.P., and Singh, B.R. 1998. Effect of organic materials on partioning, extractability and plant uptake of metals in an alum shale soil. Water, Air Soil Poll. **103:** 405-421.

[9] Cheung, Y.H., M.H. Wong, and Tam, N.F.Y. 1989. Root and shoot elongation as an assessment of heavy metal toxicity and 'Zn Equivalent Value' for edible crops. Hydrobiologia **188/189:** 377-383.

[10] Wang, W.H., M.H. Wong, S. Leharne, and Fisher, B. 1998: Fractionation and biotoxicity of heavy metals in urban dusts collected from Hong Kong and London. Environ. Geochem. Hlth. **20:** 185-198.

[11] Wong, M.H., and Bradshaw, A.D. 1982. A comparison of the toxicity of heavy metals, using root elongation of rye grass, *Lolium perenne*. New Phytol. **91:** 255-261.

[12] Wong, M.H., and Lau, W.M. 1985. Root growth of *Cynodon dactylon* and *Eleusine indica* collected from motorways at different concentration of lead. Environ. Res. **36:** 257-267.

[13] Collana Ambiente 1998. Metodi di analisi dei compost. Determinazioni chimiche, fisiche, biologiche e microbiologiche. Analisi merceologica dei rifiuti. A cura di: DIVAPRA, IPLA, ARPA. Torino, Italy.

[14] Chen, Y.X., G.W. Zhu, G.M. Tian, G.D. Zhou, Y.M. Luo, and Wu, S.C. 2002. Phytotoxicity of dredged sediment from urban canal as land application. Environ. Pollut. **117:** 233-241.

[15] Wang, X., C. Sun, S. Gao, L. Wang, and Shuokui, H. 2001. Validation of germination rate and root elongation as indicator to assess phytotoxicity with *Cucumis sativus*. Chemosphere **44:** 1711-1721.

[16] Sparks, D.L., A.L. Page, P.A. Helmke, R.H. Loeppert, P.N. Soltanpour, M.A. Tabatabai, C.T. Johnston, and Sumner, M.E. 1996. Methods of soil analysis. Part 3. Chemical methods. SSSA Book Ser. 5. SSSA and ASA, Madison, WI.

[17] U.S. Environmental Protection Agency 1995. Test Method 3052, Microwave assisted acid digestion of siliceous and organically based matrices. In: Test Methods for Evaluating Solid Waste, 3rd edition, 3rd update, Office of Solid Waste and Emergency Response. U.S. Environmental Protection Agency. Field Manual SW-846, Washington, DC.

[18] Baldwin, K.R., and Shelton, J.E. 1999. Availability of heavy metals in compost-amended soil. Bioresource Technol. **69:** 1-14.

[19] Zucconi, F., M. Forte, A. Monaco, and De Bertoldi, M. 1981. Biological evaluation of compost maturity. BioCycle **22:** 27-29.

[20] Bernal, M.P., C. Paredes, M.A. Sánchez-Monedero, and Cegarra, J. 1998. Maturity and stability parameters of composts prepared with a wide range of organic wastes. Bioresource Technol. **63:** 91-99.

[21] Helfrich, P., B. Chefetz, Y. Hadar, Y. Chen, and Schnabl, H. 1998. A novel method for determining phytotoxicity in composts. Compost Sci. Util. **6** (3): 6-13.

[22] Tiquia, S.M., and Tam, N.F.Y. 1998. Elimination of phytotoxicity during co-composting of spent pig-manure sawdust litter and pig sludge. Bioresource Technol. **65:** 43-49.

[23] Roh, Y., N.T. Edwards, S.Y. Lee, C.A. Stiles, S. Armes, and Foss, J.E. 2000. Heavy metals in the environment. J. Environ. Qual. **29:** 415-424.

[24] Senesi, N., and Polemio, M. 1981: Trace element addition to soil by application of NPK fertilizers. Fert. Res. **2:** 289-302.

[25] Senesi, N., and Polemio, M. 1983. Trace element content in inorganic fertilizers and relative supplies to soil. In: Golubev, G. (Ed.). Proc. Int. Conf. Environmental Management of Agricultural Watersheds, I.I.A.S.A., Laxemburg, Austria, p. 227-241.

[26] Bak, J., J. Jensen, M.M. Larsen, G. Pritzl, and Scott-Fordsmand, J. 1997. A heavy metal monitoring-programme in Denmark. Sci. Total Environ. **207:** 179-186.

[27] Kashem, M.A., and Singh, B.R. 2001: Metal availability in contaminated soils: I. Effects of flooding and organic matter on changes in Eh, pH and solubility of Cd, Ni and Cd. Nutr. Cycl. Agroecosys. **61:** 247-255.

[28] Kabata-Pendias, A., and Pendias, H. 1984. Trace Elements in Soils and Plants. CRC Press, Boca Raton, FL.

[29] Codex Alimentarius Commission 1984: Contaminants, Joint FAO/WHO Food Standards Program, Codex Alimentarius, Vol. XVII (1st edn.).

[30] Kabata-Pendias, A., and Piotrowska, M. 1984: Basic Conditions for Waste Material Using for Liming and Fertilising of Soils. In: Pollution of soils and crop plants with trace elements, CBR, Warszawa, p. 22 (in Polish).

[31] Jung, M.C., and Thornton, I. 1996. Heavy metal contamination of soils and plants in the vicinity of a lead-zinc mine, Korea. Appl. Geochem. **11**, 53-59.

[32] Lee, J.S., H.T. Chon, and Kim, K.W. 1998. Migration and dispersion of trace elements in the rock-soil-plant system in areas underlain by black shales and slates of the Okchon Zone, Korea. J. Geochem. Explor. **65:** 61-78.