

A field screening test for the assessment of concentrations and mobility of potentially toxic elements in soils: a case study on urban soils from Rome and Novi Sad

Maria Rita Montereali · Valentina Pinto · Francesca Schiavella · Giovanna Armiento · Massimo Angelone · Cinzia Crovato · Maja Manojlović · Ranko Čabilovski · Carlo Cremisini

Received: 28 March 2017 / Accepted: 1 August 2017 / Published online: 23 August 2017
© Springer International Publishing AG 2017

Abstract The increasing demand for environmental pollution control results in the development and use of new procedures for the determination of dangerous chemicals. Simple screening methods, which can be used directly in the field for a preliminary assessment of soil contamination, seem to be extremely advantageous. In our laboratory, we developed and optimized a rapid test for a preliminary evaluation of both the concentration and the mobility of some potentially toxic metals in soils. This screening test consists of a single extraction of the soil sample with a buffer solution, followed by the titration of the extracted solution with dithizone to determine the contents of bi-valent heavy metals (such as Pb, Cu, Zn, and Cd). This screening method was then directly applied in the field during the sampling campaign in the framework of an Italian–

Serbian collaborative project, finalized in the study of metal availability in soils. The results obtained in the field with the rapid test were compared with those obtained in the laboratory following the conventional procedure commonly used to evaluate metal bioavailability (diethylenetriaminepentaacetic extraction). Moreover, selected samples were analyzed sequentially in the laboratory using the standardized BCR three-step sequential extraction procedure. The screening test gave results conceptually in good agreement with those obtained via the BCR procedure. These preliminary data show that the proposed screening test is a reliable method for the preliminary rapid evaluation of metal total concentrations and of potential metal mobility in soils, supporting sampling activities directly in the field.

M. R. Montereali (✉) · F. Schiavella · G. Armiento · M. Angelone · C. Crovato · C. Cremisini
ENEA - Italian National Agency for New Technologies, Energy and Sustainable Economic Development – Department SSPT-PROTER-BIOGEOC, Casaccia Research Centre, Via Anguillarese 301, 00123 Rome, Italy
e-mail: mariarita.montereali@enea.it

V. Pinto
ENEA–Italian National Agency for New Technologies, Energy and Sustainable Economic Development, Frascati Research Centre, Via Enrico Fermi 45, Frascati, 00044 Rome, Italy

M. Manojlović · R. Čabilovski
Faculty of Agriculture, University of Novi Sad, Novi Sad, Trg Dositeja Obradovića 8, Novi Sad 21 000, Serbia

Keywords Metal availability in urban soils · Total metal contents · Extraction procedures · In-field screening test · Dithizone

Introduction

The need for a constant monitoring of environmental pollution and the increasing number of polluting substances has resulted in extensive research aimed at developing new technologies and screening methodologies. Nowadays, the necessary analytical information must be supplied as fast as possible and often the gathered data exceed the current demands for effective decision-

making. For these reasons, it is increasingly important to develop simple methods that can be used directly in the field on different environmental matrices. In general, these screening methods should be characterized both by the capability of a low-cost continuous on-site monitoring and the possibility to obtain quick responses. Fast responses have the advantage to enable “guided” sampling activities, increasing the representativeness of the collected samples while limiting their numbers; samples can then be successively analyzed in the laboratory using standardized analytical procedures/techniques. Devices for environmental diagnosis are usually simple “tools” that can be used directly in the field, avoiding problems related to sample preservation and transport. They involve little or no sample treatment and therefore, the preliminary operations of conventional analytical procedures can be avoided or minimized; this represents a clear advantage since sample treatments are often time-consuming and expensive. Moreover, elaborated sample treatments are sources of major random and systematic errors and often imply the use of hazardous chemicals (Rubio and Ure 1999). The “semi quantitative” response provided by screening methods represents a reliable indication and can be used for immediate decision-making (Valcarcel et al. 1999; Munoz-Olivas 2004; Jozic et al. 2009). In regard to the assessment of soil contamination by heavy metals and soil remediation studies, the availability of in-field screening tests allows producing/elaborating a timely contaminant distribution map, which is extremely useful in the design of a successful sampling strategy.

Urban environments are considered of great interest for the study and comprehension of the accumulative effects of pollution due to the presence of concentrated anthropogenic activities. Vehicular traffic, emissions of the heating systems, industrial, agricultural, and commercial activities (Ajmone-Marsan and Biasioli 2010) can be considered the most relevant pollution sources. As a consequence, the population can be heavily exposed to potentially toxic chemicals from these different sources, and serious health hazards may result from the combined effects of pollutants (Poggio et al. 2009; Madrid et al. 2004). Although most of the environmental directives of different countries set strict limits on the levels of the total concentrations of toxic elements, in recent years, many studies have demonstrated that the total metal content of a soil does not provide adequate information to assess the associated environmental risk. Suitable information can be obtained by evaluating the environmental mobility and

bioavailability of the potentially toxic elements (Peralta-Videa et al. 2009). Bioavailability has been defined as “the degree to which chemicals present in the soil may be absorbed or metabolized by humans or ecological receptors or are available for interaction with biological systems” (Report ISO 11074: 2005). The bioavailability of metals in soils is related to several factors, such as their physical and chemical soil properties, the metal speciation, the plant species, and, especially, the soil-plant interactions (Kabata-Pendias 2004; Ehlers and Luthy 2003). Many studies on the mobilization of metals, particularly heavy metals, from soils are based on the fractionation of metals from samples, step by step, using different reagents or extractants (Ure and Munthau 1993; Mester et al. 1998; Filgueiras et al. 2002; Bacon and Davidson 2008). Among the one-step extraction methods most frequently used for bioavailability evaluation, especially for the simplicity and ease of operation, is the diethylenetriaminepentaacetic acid (DTPA) extraction method that has been largely used due to its capacity to form stable complexes with metal cations (Lindsay and Norvell 1978). In addition, the extraction with DTPA is the Italian official method for the measurement of plant-available fractions (D.M. 13/09/99 http://ctntes.arpa.piemonte.it/Bonifiche/Documenti/Norme/13_Set_99.pdf).

At the same time, several sequential extraction schemes, which differ for the reagents used and for the number of extractions performed, have been developed in order to evaluate the metal fractions available to plants and the environmentally accessible trace metals (Tessier et al. 1979; Sahuquillo et al. 2003). With the aim of harmonizing all the procedures, the European Commission, with the BCR Program and its successor (Standards, Measurements and Testing Programme - SMT), through a series of inter-laboratory studies, optimized a three-step sequential extraction method and produced a certified reference material (CRM 601), successively optimized and distributed as certified reference material BCR 701 (Quevauviller et al. 1997; Rauret et al. 1999). According to this extraction protocol, metals can be divided into acid soluble/exchangeable, reducible, and oxidizable fractions. However, sequential extraction procedures are time-consuming and costly; as a consequence, they can be used only on a limited number of samples selected from a large set. Contaminated sites are usually extended over wide and heterogeneous areas, and a representative study requires a huge number of samples.

For this reason, it is particularly interesting to use a rapid, effective, and simple screening method, which reliably identifies the most significant sampling points to collect samples for more accurate measurement through complex standard laboratory procedures (Brunori et al. 2005; Pacifico et al. 2007).

In this paper, we describe a case study on the in-field application of a rapid screening method, developed in our laboratory at ENEA (Italian National Agency for New Technologies, Energy and Sustainable Economic Development) and then optimized in the field for the preliminary evaluation of the total concentration and mobility of some potentially toxic metals in soils.

The test is based on a single leaching step of the soil sample, performed using trisodium citrate and hydroxylamine hydrochloride buffer as extracting solution at pH 9.3. This solution was chosen for the possibility of directly extracting both the “easily extractable” fraction and the fraction bound to iron and manganese oxides of metals. The concentration of bi-valent metals, such as Pb, Cu, and Zn (being among the most representative metals in contaminated soils, particularly in urban areas) and of other bi-valent elements, such as Cd, in the extracted solution is directly determined via titration with dithizone solubilized in an organic solvent (Pinto et al. 2010). The fraction bound to Fe-Mn oxides is often a quantitatively important component of the total metal content in soils and poses a risk in case of changes in the oxy-reductive *status* of the superficial soil layers. With the purpose of a direct “in-field” use, preliminary studies were carried out in our laboratory, aimed at optimizing the procedure and at selecting the best operational conditions for the rapid test. The method was then directly tested in the field to optimize the whole procedure. Successively, in the framework of a scientific collaborative project between Serbia and Italy, (Urbesoil project—see details in the acknowledgements), our rapid test was employed during the sampling activity to evaluate the environmental availability of Pb, Cu, Zn, and Cd. Soils samples were collected in two green central areas of Novi Sad (Limansky Park and Železnički Park—the railway station park) and in the Villa Borghese in Rome, and metal mobility was studied performing a direct evaluation in the field using the rapid screening test. Subsequently, the results obtained with the rapid test were compared with those obtained by using a conventional procedure: the Italian official method for the measurement of the plant-available fraction with diethylenetriaminepentaacetic acid (DTPA).

The samples providing the most interesting results on metal mobility, according to the screening test, were then analyzed in the laboratory applying the standardized BCR three-step sequential extraction in order to evaluate the reliability of the field test.

Materials and methods

Sampling

To optimize the use of the screening test in the field, two different sampling sites were selected: one representative of soils with low metal concentrations and the second site of soils with a higher metal content. One soil sample (S) was collected inside the rural area of our research center (Enea Casaccia, Roma). A sampling campaign was then carried out in the second site, the metal basin (sphalerite and galena: ZnS, PbS with significant presence of Cu, Cd, As, Sb, and Ag) of the Tolfa Hills, an area located about 70 km north of Rome exploited for lead and iron from the Bronze age until recent times. In this mining area, three soil samples were collected: sample 1T close to the area where lead-extractive processes were active; sample 2T collected downstream along a water course, and sample 3T collected just outside the mining area.

For the Italian–Serbian bilateral Urbesoil research project, sampling sites (Fig. 1a–c) were selected in the main central public parks in Rome (Villa Borghese garden) and in Novi Sad (Limanski and Zeleznicki parks). Villa Borghese covers an area of 80 ha in the heart of Rome, between the ancient Aurelian Walls and two new blocks built in the early twentieth century. Among the Roman parks, it is one of the richest in artistic masterpieces and landscapes. It encloses buildings, monuments, sculptures, and fountains belonging to different artistic periods, surrounded by ancient trees, lakes, Italian gardens, and lawns. It includes a large number of evergreen species, such as oaks, plane trees, stone pines, cedars, and firs. The largest green area in the city of Novi Sad is Limanski Park, covering an area of 12.9 ha. Originally, poplar and willows were the main trees in the park, but later, it was enriched with linden trees, birches, cedars, oaks, spruces, and decorative bushes. Zeleznicki Park occupies an area between the railway embankment and a main road of Novi Sad. It abounds with lawns and trees and hosts a children playground area.



Fig. 1 Sampling sites: **a** Villa Borghese park, Rome; **b** Limanski and **c** Zeleznicki Parks, Novi Sad

In each site, ten top (0–5 cm) and ten bottom (40–50 cm) soil samples were taken. This work concerns only the top soil samples, as the upper layer is more influenced by anthropogenic activities. Soil samples were air-dried at 40 °C and sieved to 2 mm. We

measured pH and some pedological parameters (organic content (%) and soil texture) according to international procedures; values are shown in Table 1. For the determination of heavy metal contents, the samples were ground to 100 µm to ensure sample homogeneity.

Reagents, solutions, and materials

We used 69% nitric acid HNO₃ Normapur (BDH), 40% hydrofluoric acid HF Aristar (BDH), 37% hydrochloric acid Aristar (BDH), and 30% hydrogen peroxide H₂O₂ Suprapur (Merck) for the total dissolution of the soil samples.

For the leaching experiments, a buffer solution of trisodium citrate and hydroxylamine hydrochloride at pH 9.3 was prepared, as described in Pinto et al. (2010), dissolving trisodium citrate Na₃C₆H₅O₇·2H₂O RPE (MERCK) and hydroxylammonium hydrochloride NH₂OH·HCl RPE (FLUKA) in ultrapure water (18.2 MΩ cm⁻¹ at 25 °C) obtained from a MilliQ Element System (Millipore); the pH was adjusted to 9.3 with NH₃ (Aristar®, BDH). For titration analysis, ≈ 2 × 10⁻⁵ M dithizone (1,5-diphenylthiocarbazone C₁₃H₁₂N₄S, FW: 256.33 g/mol, FLUKA) solution was prepared daily by dissolving the appropriate amount of the corresponding chemical in toluene (BDH). Diethylenetriaminepentaacetic acid, 98% C₁₄H₂₃N₃O₁₀

(AlfaAesar), calcium chloride dihydrate CaCl₂·2H₂O, RG Merck, 32% ammonium hydroxide, NH₄OH RG (Rudi Pont), and 98% triethanolamine (HOCH₂CH₂)₃N (Sigma) were used to prepare the DTPA extracting solution according to the procedure described in Lindsay and Norvell (1978).

Glacial acetic acid CH₃COOH RG (Rudi Pont), hydroxylammonium hydrochloride NH₂OH·HCl RPE (Fluka), 69% nitric acid HNO₃ NormaPur (BDH), 30% hydrogen peroxide H₂O₂ Suprapur (Merck), ammonium acetate CH₃COONH₄, and analytical reagent (Riedel-de Haën) were used for the sequential extractions and prepared according to the procedure described in Rauret et al. (1999). All laboratory glassware was soaked in a 1:3 69% nitric acid and ultrapure water mixture overnight and then repeatedly rinsed with ultrapure water before use to eliminate any contamination. Ultrapure water (18.2 MΩ cm⁻¹ at 25 °C) with 1% nitric acid was used for the calibrating solutions and for all the dilutions. Polypropylene Falcon tubes (BD Falcon™), 0.45-μm filter membranes HA Millex, MF Millipore,

Table 1 Pedological data for Rome and Novi Sad urban soils (T indicates top soil)

	pH (H ₂ O)	Organic content (%)	Sand (%)	Silt (%)	Clay (%)	USDA—textural soil classification
Rome						
VB1T	7.7	15	50	43	7	Loam—sandy loam
VB2T	7.9	7.6	54	39	7	Sandy loam
VB3T	7.8	1.6	63	32	5	Sandy loam
VB4T	7.7	7.2	32	55	13	Silt loam
VB5T	8.0	2.2	41	46	13	Loam
VB6T	7.7	10	60	36	4	Sandy loam
VB7T	7.4	10	32	51	17	Silt loam
VB8T	7.7	11	33	54	13	Silt loam
VB9T	7.7	9.4	50	43	7	Loam—sandy loam
VB10T	8.0	11	43	47	10	Loam
Novi Sad						
NSL1T	7.9	5.1	95	3	2	Loamy coarse—sand
NSL2T	7.9	4.6	57	13	30	Loam
NSL3T	7.8	4.7	60	14	26	Loam
NSL4T	8.1	3.3	96	2	2	Loamy coarse—sand
NSL5T	8.3	2.6	50	17	33	Loamy clay
NSZ1T	7.9	4.9	96	2	2	Loamy coarse—sand
NSZ2T	7.8	5.1	79	6	15	Fine sand loam
NSZ3T	7.8	9.8	87	4	9	Loamy coarse—sand
NSZ4T	7.8	4.9	68	11	21	Fine sand loam
NSZ5T	7.8	5.4	72	9	19	Fine sand loam

and syringes BD Plasticpack™ were used for the extraction experiments.

Single ICP-MS standard solutions, 1000 mg L⁻¹, of lead, copper, cadmium, and zinc, in nitric acid, were used for the preparation of the multi-standard calibration solution. Rhodium ICP-MS standard solution, 1000 mg L⁻¹, in nitric acid Aristar (BDH), was used as internal standard with the appropriate concentration.

Instrumentations

The pH measurements were performed using a portable 250A Orion pH Instrument (Thermo Electronic Corp.) equipped with an Orion gel-filled combination pH-electrode (Thermo Electronic corp.). A microwave system (Milestone 1200 Mega) was used for the total dissolution of the soil samples. A vertical rotary shaker, Rotator Drive STR4 (Stuart Scientific), a thermostatic bath with stirring (Kottermann Labortechnik), and a PK 110 ALC centrifuge (Thermo) were used for both DTPA soil extractions and sequential extractions. All the measurements of the metal contents were made with a Perkin-Elmer Elan 6100 ICP-MS spectrometer (USA) equipped with a cross-flow nebulizer and with a Perkin-Elmer Optima 2000 DV ICP-OES spectrometer equipped with a Scott-type spray chamber.

Determination of the total metal content

Approximately 0.5 g of soil, accurately weighted, were digested with a mixture of 7 mL 69% HNO₃, 2 mL 40% HF, 2 mL 30% H₂O₂, and 0.5 mL 37% HCl in TFM vessels with the microwave system. The working program used for microwave digestion was set as follows: 5 min at 250 W power, 10 min at 400 W, 10 min at 600 W, and 5 min at 250 W. Microwave digestion was followed by an open-vessel procedure. The samples were first evaporated smoothly nearly to dryness, in PFA vessels, and the residues were subsequently dissolved in 1 mL HNO₃ and the solutions again evaporated nearly to dryness. The residues were then submitted twice to analogous treatment with 1 mL of HNO₃ each time. Finally, 1 mL of HNO₃ was added to each sample and the resulting solution was completely transferred to a 50-mL volumetric flask and diluted to volume with ultrapure water (18.2 MΩ cm⁻¹ at 25 °C). Each sample was analyzed in triplicate and the mean values were considered. Procedural blanks were always evaluated. Adequate quality assurance was guaranteed by

analyzing, using the same procedure used for the soil samples, ISE 973 Reference Material (WEPAL).

Optimization of the sampling procedure for the “in-field” rapid test

Previous studies (Pinto et al. 2010) have demonstrated that the kinetic extraction of the screening procedure reaches the steady state in 60 min and that the leaching experiments can be performed for 5 and 60 min, as it is interesting to investigate metal leachability at the beginning and at a pseudo-equilibrium state. For this reason, the soil extractions in-field were carried out for 5 min. Preliminary experiments were performed in order to investigate the feasibility of performing measurements directly in-field with the proposed screening test and to optimize the soil sampling procedure. For these purposes, the number of replicates of both the extractions of soils and titration of the extracts, the level of contamination of soils and the operational procedures to be performed, were examined in detail. The three soils sampled in the mining area (high concentration of heavy metals) and the one sampled in the rural area inside the Enea Casaccia Research Center (relatively low content of potentially toxic metals) were studied as representatives of different environmental contexts. Each sample, sieved at 2 mm, was divided into three portions: two of these were analyzed directly in-field with the rapid test and the third one was measured in the laboratory using the screening test after the usual procedure followed for the soil sample preparation (air drying at 40 °C of the soil and sieving at 2 mm). Of the two aliquots tested in the field, one was dried with a camp stove and the other analyzed in order to clarify the influence of sample humidity on the screening test results. The procedure used, extensively described in Pinto et al. (2010), was as follows: 0.5 g of soil sample, sieved at 2 mm, were extracted with 30 mL of trisodium citrate, and hydroxylamine hydrochloride buffer solution at pH 9.3. Polyethylene tubes containing the sample and the extracting solution were stirred manually for 5 min, and the extract was then separated from the solid residue by filtration through 0.45-μm syringe membrane filters. The aqueous solution was titrated with DZ in toluene [$\approx 2 \times 10^{-5}$ M] until the color of the organic phase changed from pink to gray.

Field screening test

Seven top soil samples collected in Rome and five top soils samples of Novi Sad were firstly analyzed directly in the field for the evaluation of metal availability with the rapid screening test, using the procedure described in the previous paragraph. The field tests were performed in triplicate on each soil extract. The contents of Pb, Cu, Zn, and Cd (the latter present at a significantly lower concentration), expressed as their Σ in mol L⁻¹ without distinguishing between elements, was calculated using a calibration curve obtained from the titration of a multi-element standard solution.

DTPA soil extractions

The same soil samples analyzed with the rapid screening test were also extracted with DTPA in the laboratory, according to the following procedure: 10 g of soil, air-dried at 40 °C and sieved at 2 mm, were placed in polypropylene Falcon tubes and shaken for 2 h at 60 rpm with 20 mL of the DTPA extracting solution on a vertical shaker. Subsequently, the suspensions were centrifuged at 4000 rpm for 10 min and the solutions were separated and filtered through 0.45- μ m syringe membrane filters into volumetric flasks. Afterwards, the filtrates were analyzed for Pb, Cu, Cd, and Zn using the ICP-OES spectrometer. All extraction experiments, including the blanks, were performed in triplicate and the mean values were considered. For the final analytical determination of the elements of interest, the extracted samples were diluted 1:10 in 1% nitric acid and, to ensure matrix matching, standard solutions for daily calibrations were prepared in a DTPA solution diluted 1:10 in 1% nitric acid.

Sequential extractions

The BCR three-step sequential extraction procedure, summarized in Table 2, was applied to some selected urban topsoil samples of each city, according to the method described in Rauret et al. (1999). The residues from step 3 were solubilized using the same acidic dissolution method used for the determination of the total trace element contents of the soil samples. The BCR 701 CRM was analyzed to check the analytical performance of the laboratory tests in the sequential

Table 2 BCR standardized three-step sequential extraction procedure

Step	Extracting solution
1: exchangeable and weakly adsorbed fraction	A: CH ₃ COOH, 0.11 mol L ⁻¹
2: reducible fraction (bound to Fe and Mn oxides)	B: NH ₂ OH - HCl, 0.5 mol L ⁻¹
3: oxidizable fraction (organically bound and sulfide-bound)	C: H ₂ O ₂ , 8.8 mol L ⁻¹ , then, D: CH ₃ COONH ₄ , 1.0 mol L ⁻¹ at pH 2

extraction procedure. Table 3 shows the results obtained in our laboratory compared with the certified reference values for BCR 701 CRM.

Results and discussion

Optimization of the sampling procedure for the “in-field” rapid test

Total concentrations of Pb, Cu, Zn, and Cd, measured in the soil sample (S) from the rural area within the Enea Casaccia Research Center, after acid digestion in the microwave system, according to the procedure previously described, were Pb: 121 ± 3 mg kg⁻¹, Cu: 43 ± 1 mg kg⁻¹, Cd: 0.2 ± 0.1 mg kg⁻¹, and Zn: 127 ± 13 mg kg⁻¹.

The concentrations of these metals measured in 1T, 2T, and 3T sample soils, sampled in the mining area of Tolfa, were Pb: 2714 ± 434 mg kg⁻¹, Cu: 788 ± 80 mg kg⁻¹, Cd: 106 ± 5 mg kg⁻¹, and Zn: 38,706 ± 1551 mg kg⁻¹ for 1T; Pb: 1090 ± 26 mg kg⁻¹, Cu: 101 ± 1 mg kg⁻¹, Cd: 2.8 ± 0.1 mg kg⁻¹, and Zn: 808 ± 29 mg kg⁻¹ for 2T and Pb: 54 ± 1 mg kg⁻¹, Cu: 152 ± 7 mg kg⁻¹, Cd: 3.1 ± 0.1 mg kg⁻¹, and Zn: 780 ± 10 mg kg⁻¹ for 3T. The relevant differences in the measured concentrations of these soils can be explained by their different origin. The sample 1T showed the highest metal contents because it was collected within the mining site; soil 2T, characterized by lower metal concentrations, was collected farther along a creek, whose water could have contributed to metal depletion. In contrast, soil 3T was sampled in an area outside the mine where no mineralization occurred.

The results of the preliminary tests carried out in the field (A and B experiments) and in the laboratory (C experiment) with the dithizone method on the rural soil

Table 3 Comparison of the results of the BCR sequential extraction procedure on BCR 701 Reference Material determined in our laboratory and the certified values of this CRM

BCR 701	Pb (mg kg ⁻¹)	Cu	Cd	Zn
Step 1—measured	2.87 ± 0.14	48.7 ± 0.5	7.2 ± 0.1	203 ± 2
Certified reference values	3.18 ± 0.21	49.3 ± 1.7	7.3 ± 0.4	205 ± 6
Step 2—measured	122 ± 1	114 ± 1	3.61 ± 0.03	107 ± 1
Certified reference values	126 ± 3	124 ± 3	3.77 ± 0.28	114 ± 5
Step 3—measured	10.0 ± 0.2	59 ± 1	0.29 ± 0.01	49 ± 1
Certified reference values	9.3 ± 2.0	55 ± 4	0.27 ± 0.06	46 ± 4

sample (S) and on the three mining soils (1T, 2T, and 3T) for the optimization of the sampling soil procedure are reported in Table 4.

In the field experiments A, wet sample soils were directly analyzed without any preliminary drying, while in the field experiments B, before performing the screening tests, soils were dried using a camp stove. In the laboratory (C), soils were air-dried at 40 °C in an oven and the metals were successively extracted and measured according to the screening test procedure previously described.

The concentrations of the extracted metals, shown in tables, are the average value of nine titrations, since three aliquots of each soil sample were separately extracted and every extraction solution was analyzed by titration three times.

As shown in the tables, the metal concentrations measured in the solution obtained extracting the wet soil and those obtained extracting the dried samples were comparable. It can be only evidenced that the standard deviation values associated to the concentrations measured in the

soil samples dried using the camp stove, were in two cases, higher values than those of the concentration values were measured for the wet soils. As a consequence, to obtain preliminary information about metal mobility directly in the field, it is not strictly necessary to dry the soil samples (except in the case of extremely wet soils, also because in this case, it is impossible to obtain the granulometric fraction < 2 mm by sieving). Then, it can be noticed that the concentrations of the metals from different soil samples measured with the screening test in the field follow trends comparable to those obtained using the rapid test in the laboratory, and the concordance between the results is observed for a wide range of metal concentrations. Therefore, these data demonstrate that the proposed rapid test is not significantly influenced by the operational conditions used, such as agitation and/or grinding or by ambient factors such as light.

In addition, one further point to mention is that the screening test provides interesting information about different potential mobility/bioavailability of metals in

Table 4 Results of the field (A and B) and laboratory (C) experiments for rural (S) and mining (T series) soils with the rapid screening test

	Rural soil S		Mining area soil 1T		Mining area soil 2T		Mining area soil 3T	
	M^{++} average value ± SD (mmol kg ⁻¹)	RSD %	M^{++} average value ± SD (mmol kg ⁻¹)	RSD %	M^{++} average value ± SD (mmol kg ⁻¹)	RSD %	M^{++} average value ± SD (mmol kg ⁻¹)	RSD %
A (wet soil)	0.13 ± 0.01	10	126 ± 32	25	2.0 ± 0.1	6	0.25 ± 0.02	9
B (dried soil)	0.11 ± 0.01	2	138 ± 52	38	1.7 ± 0.1	5	0.31 ± 0.05	16
C (air-dried at 40 °C)	0.13 ± 0.01	8	135 ± 10	8	1.2 ± 0.1	9	0.39 ± 0.02	4

soil samples collected at short distance. This evidence supports the use of the rapid test during the sampling in order to obtain a quick response on metal availability of the soil samples and to select those samples that need further analyses with standardized procedures.

Total metal contents

For the Urbesoil project, analysis of a great number of soil samples (both top and bottom) and the determination of a large number of chemical elements were planned. For these reasons, it was decided to charge an external laboratory, already used in previous occasions and tested for its reliability in performing large numbers of determinations. At the same time, we analyzed some selected soil samples in terms of total metal concentrations, obtaining results in total agreement with the data provided by the private laboratory.

The Pb, Cu, Cd, and Zn concentrations (mean ± SD, expressed in mg kg⁻¹) measured in the top soils (depth 0–5 cm) sampled in Villa Borghese in Rome and in the top soils collected in the two parks (Limanski and Železnički Parks) in Novi Sad are shown in Tables 5 and 6.

Table 5 Pb, Cu, Cd, and Zn mean concentration values and concentration ranges (expressed in mg kg⁻¹) in Villa Borghese in Rome. In the last line, the limit values based on the Italian Legislative decrees 152/06 for residential and park soil use

Rome	Pb	Cu	Cd	Zn
VB1T	1160 ± 16	132 ± 1	1.11 ± 0.02	365 ± 1
VB2T	236 ± 39	83 ± 4	< 0.5	150 ± 7
VB3T	88 ± 1	66 ± 3	< 0.5	141 ± 2
VB4T	176 ± 29	97 ± 4	< 0.5	112 ± 5
VB5T	288 ± 47	100 ± 4	< 0.5	132 ± 6
VB6T	595 ± 97	149 ± 7	< 0.5	140 ± 7
VB7T	728 ± 119	145 ± 6	< 0.5	142 ± 7
VB8T	200 ± 33	76 ± 3	< 0.5	100 ± 5
VB9T	384 ± 63	141 ± 6	< 0.5	157 ± 7
VB10T	462 ± 76	121 ± 5	< 0.5	161 ± 8
Mean	432	111		160
Min.	88	66	< 0.5	100
Max.	1160	149	1.11	365
Limit values Italian Legislative decrees 152/06 for residential and park soil use	100	120	2	150

Table 6 Pb, Cu, Cd and Zn mean concentration values and concentration ranges (expressed in mg kg⁻¹) in Limanski and Zeleznicki Parks in Novi Sad. In the last line, the limit values and the intervention values based on Dutch target (VROM, 2000) for soils not intended for agricultural use in the Serbian legislation

Novi Sad	Pb	Cu	Cd	Zn
NSL1T	35 ± 6	28 ± 1	< 0.5	108 ± 5
NSL2T	33 ± 5	25 ± 1	< 0.5	80 ± 4
NSL3T	27 ± 2	25 ± 3	< 0.5	114 ± 5
NSL4T	45 ± 7	47 ± 2	< 0.5	101 ± 5
NSL5T	31 ± 5	31 ± 1	< 0.5	87 ± 4
NSZ1T	56 ± 5	54 ± 1	< 0.5	199 ± 22
NSZ2T	31 ± 5	42 ± 2	< 0.5	94 ± 4
NSZ3T	40 ± 7	42 ± 2	< 0.5	151 ± 7
NSZ4T	39 ± 6	51 ± 2	< 0.5	111 ± 5
NSZ5T	76 ± 12	45 ± 2	< 0.5	126 ± 6
Mean	41	39	–	117
Min.	27	25	< 0.5	80
Max.	76	54	–	199
Limit values Dutch target and intervention values	85/530	36/190	0.8/12	140/720

The tables report data of the total concentrations measured by the external laboratory. For the aims of this work, the limit of detection given for Cd was sufficient, since the contribution of this element to the metal availability, expressed as sum of the total amounts of the extracted metals (mainly Pb, Cu, and Zn, especially in urban soils) can be considered negligible. As a matter of fact, the purpose of the proposed screening test is that of providing reliable information on the soils elements and on their potential availability as a whole, rather than giving information on each single potentially toxic metal.

As expected, determination of the total concentrations of some potentially toxic elements (such as Pb, Cu, Zn, and Cd) of the urban soil samples confirmed great differences between the nature of the soil of these two cities, mainly related to the different geological settings, as shown by the pedological data in Table 1. In Tables 5 and 6, the Rome soil samples show a wider variability of the metal concentration values and higher metal contents than those from Novi Sad. These evidences can be explained considering the different nature of the mineral phases present in the soil parent material and the different anthropogenic influences of the two towns. In Rome,

soils mainly originate from volcanic rocks characterized by high natural metal contents, while in Novi Sad, soils derive from river sediments characterized by low contents of metals. In many of the soil samples from Villa Borghese in Rome, the measured concentrations of Pb and, in some cases, also of Cu and Zn exceeded the threshold values established by the D. Lgs 152/06 Italian Directive for these metals in public parks (as shown in Table 5). However, particularly in Rome, vehicular traffic represents the major source of metals: with an estimated traffic of 2.5 million vehicles, more than 800 vehicles for every 1000 inhabitants, Pb, Cu, Cd, and Zn mainly derive from the corrosion of vehicle chassis and from tires and brakes wear rather than from the combustion of oils and fuel (Sternbeck et al. 2002; Grigoratos and Martini 2015). Moreover, although lead was removed from gasoline, its long use and persistence in the environment has concentrated this element in urban areas, and higher lead concentration values were measured in soils collected near roads with high traffic volume (Ajmone-Marsan and Biasioli 2010; Massadeh and Snook 2002). From the results shown in Table 5, VB1T soil, sampled along the NE border of Villa Borghese near a main road of Rome, where stop and

go traffic occurs, is characterized by extremely high metal contents. On the other hand, lower metal concentrations were measured in soils sampled in the inner parts of the park (for example, VB3T sample); in fact, as expected and also reported in previous papers (Cinti et al. 2002; Calace et al. 2012), the metal content of soils generally decreases with the distance from traffic roads. In regard to the results obtained for the soils sampled in the two parks of Novi Sad, the studied elements (Pb, Cu, Cd, and Zn) do not exceeded the limit values for uncontaminated soils and only in the case of Zn, for two soil samples (NSZ1T and NSZ3T, Table 6), the measured concentrations exceeded the target value of 140 mg kg^{-1} . Moreover, although unleaded fuels have been introduced recently, Pb levels in soils are lower than in Rome and, as expected, this is an evidence of both a lower contribution due to the vehicular traffic and a different nature of the soil. Comparing the soil metal concentrations in both Novi Sad parks, we noticed slightly higher metal contents in Zeleznicki Park soils, which can be justified considering the park location in an area between the railway, a traffic main road, and a bus station.

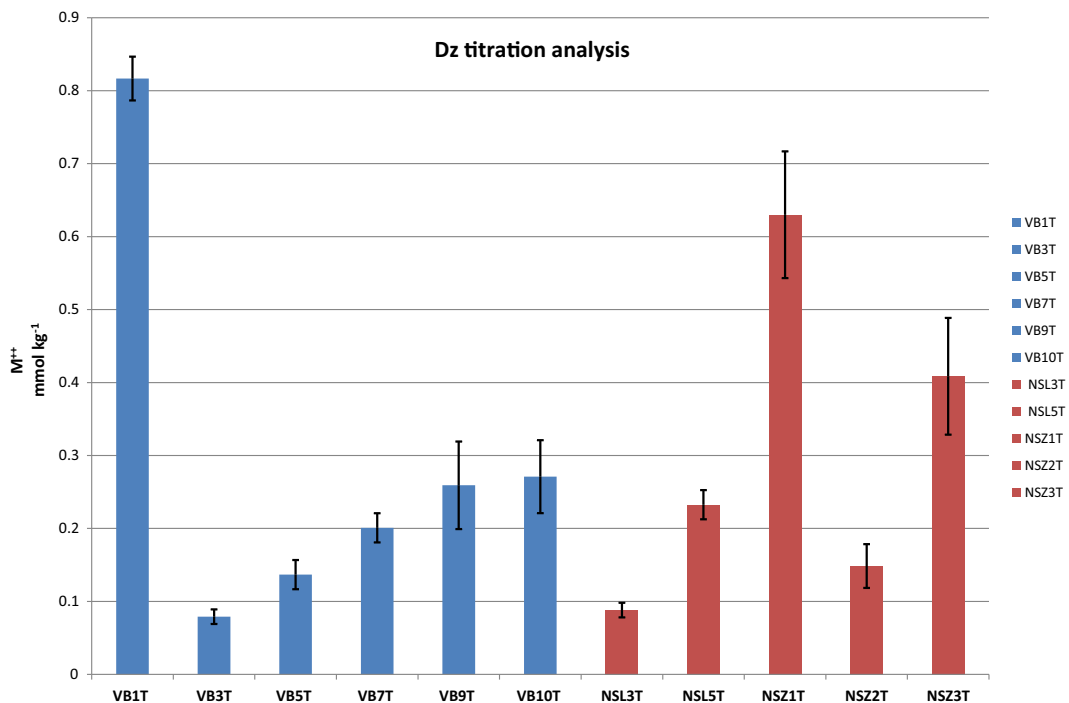
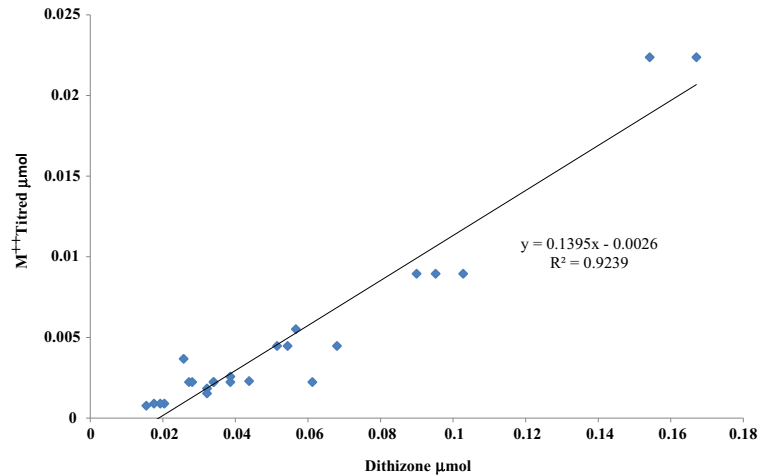


Fig. 2 Results of metal availability of the soils sampled in the parks of Rome and Novi Sad using the screening test in-field; the extracted metals (sum of Pb, Cu, Cd, and Zn) are expressed as mmol kg^{-1}

Fig. 3 Calibration curve obtained from the titration of multi-element standard solutions used to calculate the content of Pb, Cu, Cd, and Zn with the rapid test



Evaluation of bioavailability by one-step extraction

Metal mobility in some soil samples, measured with the rapid screening test directly in the field during the sampling campaign, is shown in Fig. 2. The concentrations expressed as mmol kg^{-1} , without distinguishing among the elements, were calculated using the calibration curve

(Fig. 3) obtained by the titration of multi-element standard solutions (prepared considering the most usual ratio in urban soil samples). Figure 4 compares the results of the rapid screening method with those of metal availability of the same soil samples obtained using DTPA and performing the extractions in the laboratory.

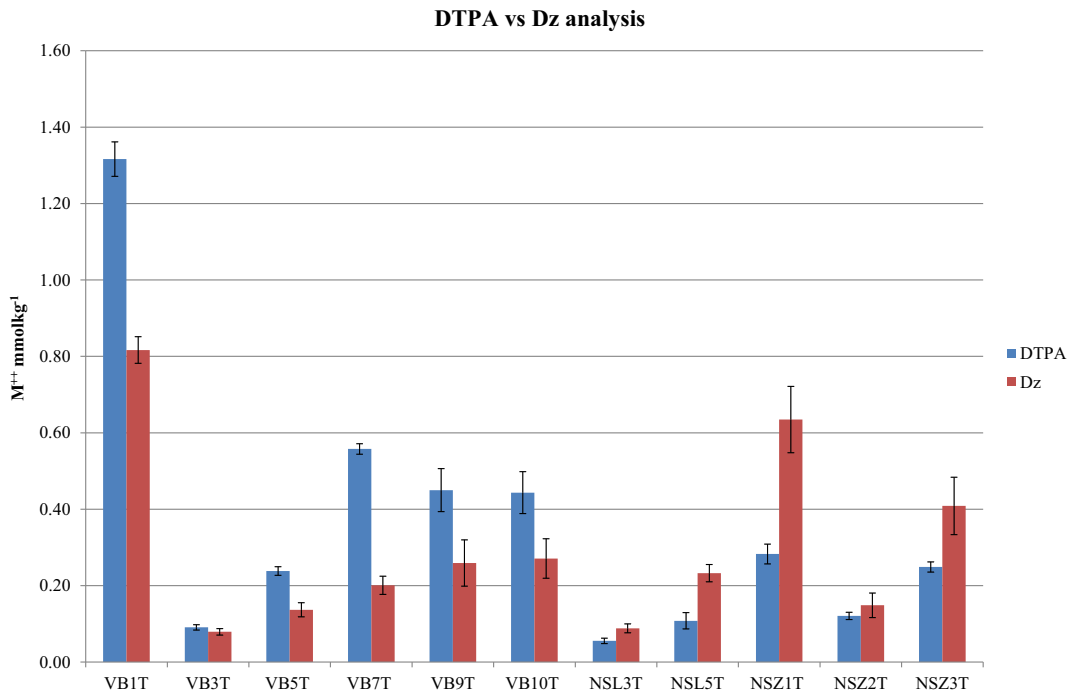
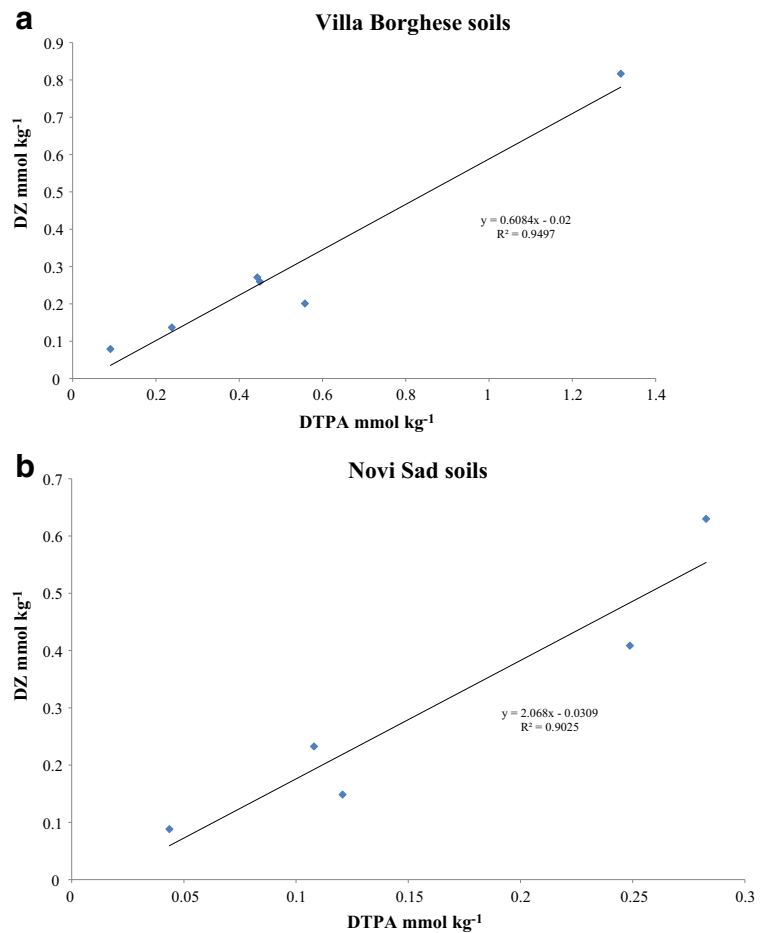


Fig. 4 Comparison of the metal concentrations, expressed as mmol kg^{-1} , measured performing the extractions on the same soil samples using the DTPA procedure in the laboratory and the rapid test in-field

Fig. 5 Metal concentrations, in mmol kg^{-1} , obtained with the rapid screening test (DZ) plotted versus results of the metal concentrations extracted using DTPA, respectively, for the soils sampled in Villa Borghese in Rome (a) and in the two parks in Novi Sad (b)



To facilitate a comparison between the two procedures, the concentrations of the extracted metals using the DTPA conventional method of the studied soil samples were expressed in mmol kg^{-1} .

The metal availability results obtained with the two methods show a similar trend, demonstrating that our rapid screening test is consistent with the reference method based on DTPA soil extractions used for the evaluation of metal phytoavailability. Moreover, it is interesting to observe that, although the behavior of the screening test versus DTPA extractions in the two set of soils sampled in Rome and Novi Sad, respectively, was different (in VB, $DZ < DTPA$, in NS $Dz > DTPA$), trends were similar in the same soil subgroup. The lower concentrations of extracted metals obtained with the rapid test in all samples from Villa Borghese is the evidence of a lower presence, in these soils, of the reducible fraction (bound to Fe and Mn oxides) with respect to the soil samples of Novi Sad. Data agreement

is clear, as illustrated in Fig. 5a, b, where the metal concentrations extracted and measured using our method are plotted versus those obtained via the DTPA method, respectively, for the soils sampled in Villa Borghese in Rome and for those sampled in the two parks of Novi Sad.

BCR three-step sequential extraction procedure

Considering the results obtained with our rapid test used directly in the field during the sampling activities in the parks of Rome and Novi Sad, we investigated two samples using a conventional procedure usually applied in metal mobility studies. The selected top soils were VB3T for Villa Borghese and NSZ1T, collected in the park of Novi Sad. The two samples were selected because the concentrations of the studied elements were quite similar.

Table 7 Percentage distribution of Pb, Cu, and Zn between the BCR fractions (step 1, step 2, step 3, and residue) in the two selected sample soils VB3T, collected in Villa Borghese, and NSZ1T, collected in Zeleznicki Park

	Pb		Cu		Zn	
	VB3T	NSZ1T	VB3T	NSZ1T	VB3T	NSZ1T
% Step 1	0.54	1.2	0.5	1.2	0.9	7.3
% Step 2	22	61	1.2	61	7.0	30
% Step 3	7.2	12	7.6	12	< LOQ ^a	16
% Residue	66	25	88	25	98	47

^a LOQ, limit of quantification for Zn, expressed as percentage, was 0.1%

The operationally standardized BCR three-step sequential extraction procedure was chosen to extract these two samples.

Due to the fact that both the DTPA extraction procedure and the field test cannot extract the residual fraction, this fraction is not considered in the discussion. Moreover, also the fraction of step 1 was relatively insignificant, as shown in Table 7. Figure 6 summarizes in

graphs the distribution, expressed in mg kg⁻¹, of the different fractions (only step 1, step 2, and step 3) for the amounts of Pb, Cu, and Zn sequentially extracted from the studied samples.

As shown in Table 7, the VB3T sample showed 66% of residual fraction and about 22% of reducible (step 2) fraction for Pb, while NSZ1T for this element showed 25% of residual fraction and about 61% of fraction

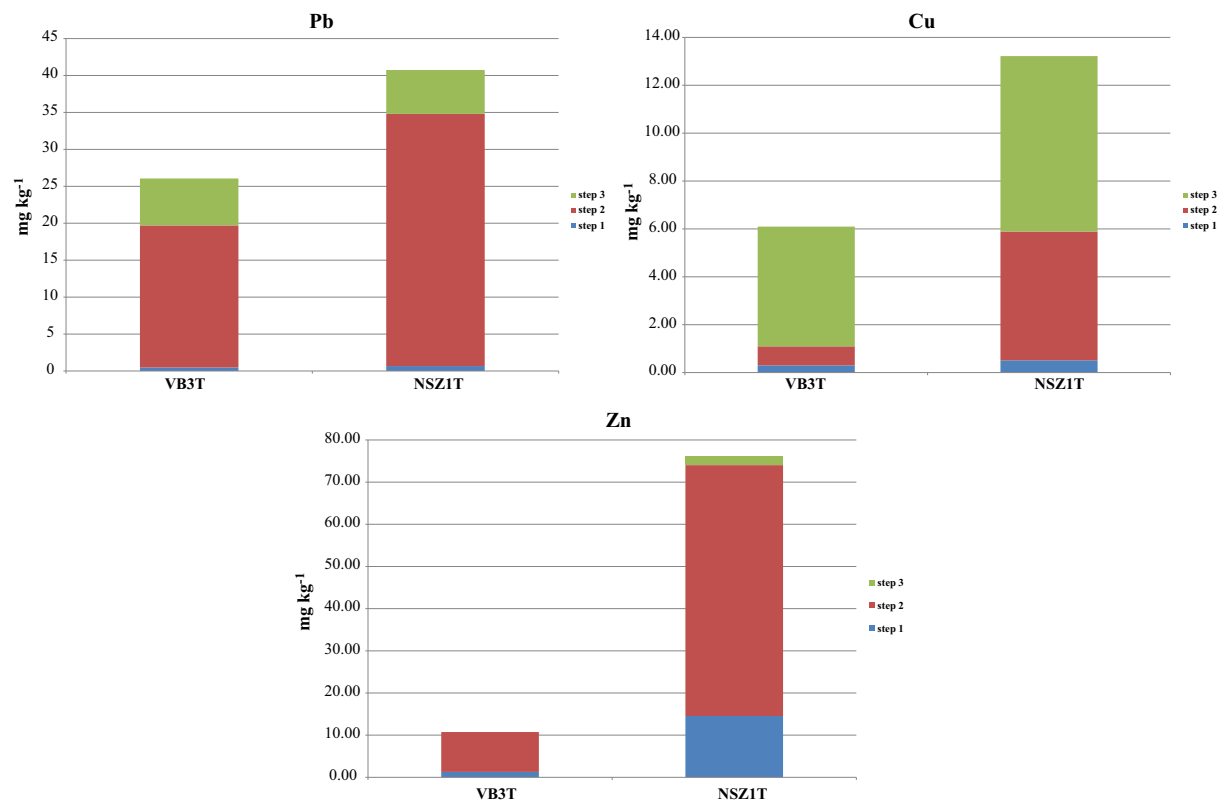


Fig. 6 Results of the BCR sequential extraction procedure for Pb, Cu, and Zn, expressed as mg kg⁻¹, (only fractions of step 1, step 2, and step 3) performed on top soils sampled in Villa Borghese (VB3T) in Rome and in Zeleznicki Park (NSZ1T) in Novi Sad in Novi Sad

related to step 2. The same behavior was observed for the two soils by the distributions between residual and reducible fractions of Cu (which, as expected, revealed particularly high (bio)availability) and Zn levels.

These results are in good agreement with those of the screening test and the DTPA extraction results previously discussed.

The VB3T soil sample was collected from the inner area of the park, far from possible sources of traffic contamination; in fact, the total concentrations of the metals analyzed in this soil sample were lower than those measured for the other collected soils. The amounts of Pb, Cu, and Zn, sequentially extracted from the sample NSZ1T, collected in Zeleznicki Park, were appreciably high, although the total content of metals measured for this sample was rather low; therefore, metal availability, shown by this soil sample, could be explained taking into account vehicular traffic as source of pollution as well as the large additional contribution to the anthropogenic contamination related to former industrial activities in this Serbian town.

Simplifying, the urban soils collected in Villa Borghese Park in Rome are characterized by relatively high natural metal concentrations due to the presence of a volcanic parent material naturally enriched with some heavy metals (Salzano et al. 2008) and, in some case, enhanced by anthropogenic pollution mainly associated to vehicular traffic. In Novi Sad, soils mostly derive from alluvial and aeolian sediments (loess) with very low metal contents, so that their presence in the soils of this town, even if relatively lower compared to Rome, could be also related to previous industrial activities absent in Rome. This different behavior of metals in the soils of these two cities can be explained by the different anthropogenic inputs, which are usually responsible for a higher mobility regardless of the total concentration of an element.

Conclusions

The reasonable concordance between the set of results obtained using standardized laboratory procedures and the proposed in-field screening method has been proved during the sampling of urban soils in Villa Borghese Park in Rome and in two parks of Novi Sad. The screening method provides sufficiently rapid and reliable information on the amount of potentially toxic metals that can be mobilized from the soil in natural

conditions and potentially generate risks to the environment. Fast and easy to use in-field methods, as the one proposed, allow a proper screening with reliable results, and only few samples were subjected to validation by more time-consuming and costly laboratory analyses. In this way, we reached our goal of matching the need, typical of the early stages of remediation, of reliable and rapid responses at socially and economically acceptable costs, balancing the requirements of risk assessment and risk management.

Acknowledgements This research was financially supported by the Italian Ministry of Foreign Affairs and International Cooperation (MAECI), in the framework of the scientific-technical cooperation program between Italy and the Republic of Serbia in the field of science and technology for the years 2013-2015, URBESOIL project.

The authors thank Mr. Maurizio De Cassan for his assistance during the sampling campaigns and Dr. Livia Della Seta for IT consultancy.

References

- Ajmoné-Marsan, F., & Biasioli, M. (2010). Trace elements in soils of urban areas. *Water Air Soil Pollution*. doi:10.1007/s11270-010-0372-6.
- Bacon, J. R., & Davidson, C. M. (2008). Is there a future for sequential chemical extraction? *Analyst*. doi:10.1039/b711896a.
- Brunori, C., Cremisini, C., D'Annibale, L., Massanisso, P., & Pinto, V. (2005). A kinetic study of trace element leachability from abandoned-mine-polluted soil treated with SS-MSW compost and red mud. Comparison with results from sequential extraction. *Analytical and Bioanalytical Chemistry*. doi:10.1007/s00216-005-3124-5.
- Calace, N., Calciandro, L., Petronio, B. M., Pietrantonio, M., Pietroletti, M., & Trancalini, V. (2012). Distribution of Pb, Cu, Ni and Zn in urban soils in Rome city (Italy): effect of vehicles. *Environmental Chemistry*. doi:10.1071/EN11066.
- Cinti, D., Angelone, M., Armiento, G., Somma, R., & Trocciola, A. (2002). Platinum and heavy metal concentration levels in urban soils of Naples (Italy). *Fresenius Environmental Bulletin*, 11(8), 432–436.
- Ehlers, L., & Luthy, R. G. (2003). Contaminant bioavailability in soils and sediments. *Environmental Science and Technology*, 37, 295A–302A.
- Filgueiras, A. V., Lavilla, I., & Bendicho, C. (2002). Chemical sequential extraction for metal partitioning in environmental solid samples. *Journal of Environmental Monitoring*, 4, 823–857.
- Grigoratos, T., & Martini, G. (2015). Brake wear particle emissions: a review. *Environmental Science and Pollution Research*. doi:10.1007/s11356-014-3696-8.
- ISO 11074. (2005). *Report 2005, soil quality vocabulary*. Geneva: International Standard Organization.

- Jozic, M., Peer, T., & Malissa, H. (2009). Rapid tests methods for the field screening of heavy metals in soil samples. *Water Air and Soil Pollution*. doi:10.1007/s11270-008-9878-6.
- Kabata-Pendias, A. (2004). Soil–plant transfer of trace elements—an environmental issue. *Geoderma*, 122, 143–149.
- Lindsay, W. L., & Norvell, W. A. (1978). Development of a DTPA soil test for zinc, iron, manganese and copper. *Soil Science of American Journal*, 42, 421–428.
- Madrid, L., Diaz-Barrientos, E., Reinoso, R., & Madrid, F. (2004). Metals in urban soils of Sevilla: seasonal changes and relations with other soil components and plant contents. *European Journal of Soil Science*. doi:10.1046/j.1365-2389.2004.00589.x.
- Massadeh, A., & Snook, R. D. (2002). Determination of Pb and Cd in road dusts over the period in which Pb was removed from petrol in the UK. *Journal of Environmental Monitoring*. doi:10.1039/b203905m.
- Mester, Z., Cremisini, C., Ghiara, E., & Morabito, R. (1998). Comparison of two sequential extraction procedures for metal fractionation in sediment samples. *Analytica Chimica Acta*, 359, 133–142.
- Munoz-Olivas, R. (2004). Screening analysis: an overview of methods applied to environmental, clinical and food analyses. *TRAC Trends in Analytical Chemistry*. doi:10.1016/S0165-9936(04)00318-8.
- Pacifico, R., Adamo, P., Cremisini, C., Spaziani, F., & Ferrara, L. (2007). A geochemical analytical approach for the evaluation of heavy metal distribution in lagoon sediments. *Journal of Soils and Sediments*. doi:10.1065/jss2007.06.231.
- Peralta-Videa, J. R., Lopez, M. L., Narayan, M., Saupe, G., & Gardea-Torresde, G. (2009). The biochemistry of environmental heavy metal uptake by plants: implications for the food chain. *International Journal of Biochemistry and Cell Biology*. doi:10.1016/j.biocel.2009.03.005.
- Pinto, V., Chiusolo, F., & Cremisini, C. (2010). Proposal of a simple screening method for a rapid preliminary evaluation of “heavy metals” mobility in soils of contaminated sites. *Journal of Soils and Sediments*. doi:10.1007/s11368-010-0208-4.
- Poggio, L., Vrscaj, B., Schulin, R., Hepperle, E., & Marsan, F. A. (2009). Metals pollution and human bioaccessibility of topsoils in Grugliasco (Italy). *Environmental Pollution*. doi:10.1016/j.envpol.2008.08.00957.
- Quevauviller, Ph., Rauret, G., Lopez-Sanchez, J. F., Rubio, R., Ure, A., & Muntau, H. (1997). Certification of trace metal extractable contents in a sediment reference material (CRM 601) following a three-step sequential extraction procedure. *Science of the Total Environment*. doi:10.1016/S0048-9697(97)00205-2.
- Rauret, G., Lopez-Sanchez, J. F., Sahuquillo, A., Rubio, R., Davidson, C., Ure, A., & Quevauviller, Ph. (1999). Improvement of the BCR three-step sequential extraction procedure prior to the certification of new sediment and soil reference materials. *Journal of Environmental Monitoring*. doi:10.1039/A807854H.
- Rubio, R., & Ure, A. M. (1999). Approaches to sampling and sample pretreatments for metal speciation in soils and sediments. *International Journal of Environmental Analytical Chemistry*. doi:10.1080/03067319308027626.
- Sahuquillo, A., Rigol, A., & Rauret, G. (2003). Overview of the use of leaching/extraction tests for risk assessment of trace metals in contaminated soils and sediments. *TRAC-Trends in Analytical Chemistry*. doi:10.1016/S0165-9936(03)00303-0.
- Salzano, R., Angelone, M., & Sprovieri, F. (2008). Caratterizzazione geochimica dei suoli dell'area romana. *Memoria descrittiva Carta Geologica d'Italia*, 80, 51–64.
- Stembeck, J., Sjödin, Å., & Andréasson, K. (2002). Metal emissions from road traffic and the influence of resuspension—results from two tunnel studies. *Atmospheric Environment*. doi:10.1016/S1352-2310(02)00561-7.
- Tessier, A., Campbell, P. G. C., & Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, 51(7), 844–851.
- Ure, A. M., & Munthau, H. (1993). Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. *International Journal of Environmental Analytical Chemistry*, 51(1–4), 135–151.
- Valcarcel, M., Cárdenas, S., & Gallego, M. (1999). Sample screening systems in analytical chemistry. *TRAC-Trends in Analytical Chemistry*, 18(11), 685–694.