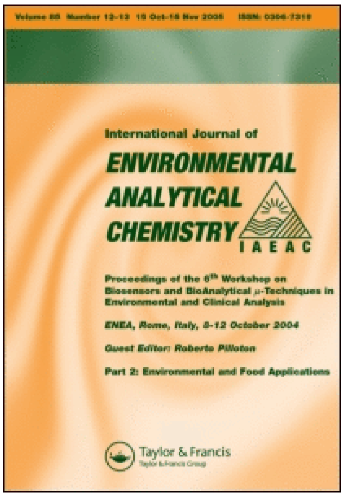

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Quality and comparability of measurement of potentially toxic elements in urban soils by a group of European laboratories

Christine M. Davidson[a]; Alison Nordon[a]; Graham J. Urquhart[a]; Franco Ajmone-Marsan[b]; Mattia Biasioli[b]; Armando C. Duarte[c]; Encarnation Diaz-Barrientos[d]; Helena Grcman[e]; Andreja Hodnik[e]; Iain Hossack[f]; Andrew S. Hursthouse[f]; Karin Ljung[g]; Fernando Madrid[d]; Erasmus Otabbong[g]; Sonia Rodrigues[c]
[a] WestCHEM, Department of Pure & Applied Chemistry, University of Strathclyde, Glasgow, UK [b] DI.VA.P.R.A., Chimica Agraria, Università di Torino, Torino, Italy [c] Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal [d] Instituto de Recursos Naturales y Agrobiología de Sevilla (CSIC), Sevilla, Spain [e] Univerza v Ljubljani, 1000 Ljubljana, Slovenia [f] School of Engineering & Science, University of Paisley, Paisley, UK [g] Department of Soil Sciences, Swedish University of Agricultural Sciences, Uppsala, SE-750 07, Sweden

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Quality and comparability of measurement of potentially toxic elements in urban soils by a group of European laboratories

CHRISTINE M. DAVIDSON*†, ALISON NORDON†, GRAHAM J. URQUHART†, FRANCO AJMONE-MARSAN‡, MATTIA BIASIOLI‡, ARMANDO C. DUARTE§, ENCARNATION DIAZ-BARRIENTOS¶, HELENA GRCMAN‖, ANDREJA HODNIK‖, IAIN HOSSACK⊥, ANDREW S. HURSTHOUSE⊥, KARIN LJUNG$, FERNANDO MADRID¶, ERASMUS OTABBONG$ and SONIA RODRIGUES§

†WestCHEM, Department of Pure & Applied Chemistry,
University of Strathclyde, 295 Cathedral St, Glasgow G1 1XL, UK
‡DI.VA.P.R.A., Chimica Agraria, Università di Torino,
Via Leonardo da Vinci, 44, 10095 Grugliasco, Torino, Italy
§Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal
¶Instituto de Recursos Naturales y Agrobiología de Sevilla (CSIC),
Apartado 1052, 41080 Sevilla, Spain
‖Univerza v Ljubljani, Biotehniska fakulteta, 1000 Ljubljana, Slovenia
⊥School of Engineering & Science, University of Paisley, High Street, Paisley PA1 2BE, UK
$Department of Soil Sciences, Swedish University of Agricultural Sciences,
PO Box 7014, SE-750 07 Uppsala, Sweden

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A study has been conducted to assess the quality and comparability of measurement of aqua-regia-soluble cadmium, chromium, copper, iron, manganese, nickel, lead, and zinc in urban soils within a small cohort of European research laboratories specializing in soil science or environmental analytical chemistry. An initial survey indicated that highly variable levels of analytical quality control (e.g. use of certified reference materials) were routinely implemented in participant laboratories. When a set of soil samples—differing in metal contents and in characteristics such as pH and organic-matter content—were exchanged and analysed, approximately 20% of results differed from target values by more than 25%. A principal-component analysis was applied to data for chromium, copper, nickel, lead, and zinc, and proved successful in assessing overall laboratory performance. The study indicates that greater prominence needs to be given to quality assurance and control if comparable data are to be generated in international, collaborative research projects.

Keywords: Urban soil; Potentially toxic elements; Principal-component analysis

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*Corresponding author. Fax: +44-141-548-4212. Email: c.m.davidson@strath.ac.uk

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1. Introduction

There is growing interest in soil in Europe, as demonstrated by current efforts to develop a 'Thematic Strategy on Soil Protection' under the 6th Environment Action Programme [1]. Large amounts of soil quality data are already available. However, there is concern that the value of much of these data, in terms of their usefulness for policy-making, may be limited due to a lack of comparability between measurements performed in different laboratories and countries [2].

Harmonization of chemical analysis has been a goal of EU research for many years, and a variety of major, environment-related projects have been conducted in this area under the Community Bureau of Reference, or Standards, Measurement and Testing Program (for example, QUASIMEME [3] and CEEM [4]). There remains, however, a tendency for different laboratories, in different countries, to use different, preferred methods. This can be due to country-specific legislation prescribing a particular analytical approach or may simply relate to analyst preference or equipment availability.

Inter-laboratory comparison exercises are often used to assess variability between laboratories measuring the same analyte. Intercomparisons focused on the determination of potentially toxic elements (PTEs) have been conducted for soils [5–7] and various related materials, including peat bog [8], fly ash [9], airborne particles [10], humus and moss [11]. In general, participants in such exercises are laboratories with a strong appreciation of analytical quality issues. However, seldom reported are comparisons between workers who are primarily 'end-users' of analytical techniques and thus do not regularly participate in external proficiency testing. Such researchers are frequently experts in their own disciplines (e.g. soil or environmental science) but may have variable levels of expertise in chemical analysis. Because considerable discrepancies can occur, even in data produced by expert analytical facilities [12], there is a need to improve knowledge of the likely magnitudes (and, where possible, the sources) of variability between results produced by such 'non-expert' laboratories.

The URBSOIL project was conducted under the EU Energy, Environment and Sustainable Development Programme. Urban soils are less well characterized than their agricultural equivalents [13] but are an increasing focus of attention [14] because of their high spatial variability and the wide variety of different components and contaminants they contain [15]. A major part of the URBSOIL study involved the measurement of a suite of soil quality indicators in samples from public-access areas, such as urban parks, within six European cities: Aveiro (Portugal), Glasgow (UK), Ljubljana (Slovenia), Seville (Spain), Torino (Italy), and Uppsala (Sweden). Project partners included two environmental analytical-chemistry research groups (one of which spanned two neighbouring institutes) and four specialist soil-science laboratories. Some analytes, e.g. polycyclic aromatic hydrocarbon content, were measured by only one or two laboratories for all cities' soils. Others, including PTEs, were measured by each partner, for their own samples. It was therefore necessary to investigate whether comparable data could be obtained by different laboratories. This was achieved by means of a small comparative study, the results of which are presented here. The aims of this exercise were (1) to obtain a realistic assessment of levels of analytical expertise, and comparability between results obtained, within a small cohort of atomic spectrometry users in six European countries and (2) to investigate the usefulness of principal-component analysis (PCA) for assessing inter-laboratory performance.

2. Experimental

An urban soil sample (approximately 15–30 kg wet weight) was collected by each project partner from a single location (typically an urban park) in their own city. The samples (referred to within the project as URBSOIL Reference Materials, URMs) were pre-treated (e.g. air-dried, crushed, sieved, homogenized) then digested and analysed to establish 'target values'. Samples were then exchanged and all partners invited to measure the pseudototal metal contents in other cities' URMs. In contrast to conventional intercomparison exercises, only very general guidelines were issued to laboratories (e.g. use of aqua regia for digestion), but each was otherwise allowed to employ their own preferred methodology. Information on the analytical procedures used was collected by means of a questionnaire circulated to partners. Details of these procedures, and results obtained, were collated at the University of Strathclyde. Data analysis was performed on selected PTE concentrations by means of Matlab version 7.04 (Mathworks Inc., Natick, MA) using the PLS_Toolbox version 3.5 (Eigenvector Research, Manson, WA).

3. Results and discussion

3.1 *Procedures used for preparation and characterization of URMs*

Examination of questionnaire responses indicated some variations in the analytical methodologies used by project participants (see table 1). Three laboratories (partners B, C, and D) heat-stabilized their samples, as is common in the preparation of certified reference materials, and then stored them under refrigeration prior to distribution. Other partners did not. All partners analysed the <2 mm soil fraction, but only four ground the test portion to <150 µm before digestion. Four partners (A, B, E, and F) reported use of the ISO aqua regia digestion procedure [16]. However, each based their digestion on a different samples mass, and one modified the recommended soil: solution ratio slightly. Microwave-assisted digestion was favoured by two laboratories, one of which used a soil: solution ratio close to that recommended by ISO, while the other (partner D) used a large excess of aqua regia.

Two laboratories used atomic absorption spectrometry (AAS) and three inductively coupled plasma optical emission spectrometry (ICPOES). However, only one of the ICP-users (laboratory D) measured each analyte at two separate wavelengths to cross-check results obtained. Partner F carried out no in-house analysis, and was unable to provide details on analytical techniques, quality assurance, or quality-control procedures used in the laboratory that performed the work.

The majority of partners elected to analyse one or more certified reference material (CRM), in parallel with their URM. Laboratory A did not routinely use CRMs, and hence none were included in their analyses. Partner F reported no knowledge concerning CRMs, although it is possible that these were used by the contract analytical laboratory that performed the measurements.

Results of CRM analysis are shown in table 2, together with certified values. Analyte recoveries were generally acceptable. Most mean values were within two standard deviations of the certified result, and all were within three standard deviations except

Table 1. Information on project partners and procedures used for pre-treatment, digestion, and analysis of urban soil secondary reference materials (URMs).

Lab	Principle expertise	Heat stabilization	Storage	Sieving (<)	Grinding (<)	Digestion procedure	Instrumental technique(s)	Analytical wavelengths (nm)	Reference soils analysed
A	Soil science	None	Room temperature, dark	2 mm	150 µm	Reflux 1 g: 10 mL	FAAS (PerkinElmer 3030)	Cu (324.8); Cr (357.9); Ni (232.0); Pb (217.0); Zn (213.9)	None
B	Analytical chemistry	105°C, 48 h	4°C, dark	2 mm	150 µm	Reflux 3 g: 28 mL	ICPOES (Jobin Yvon JY70 plus)	Cd (214.4); Cr (267.7); Cu (324.8); Fe (274.0); Mn (257.6); Ni (231.6); Pb (220.4); Zn (213.9)	BCR CRM 142R
C	Soil science	105°C, to constant mass	4°C, dark	2 mm	150 µm	Microwave 0.4 g: 4 mL (Milestone Ethos 900)	ICPOES (Thermo Jarrell Ash IRIS Advantage)	Cd (214.4); Cr (267.7); Cu (324.7); Fe (271.4); Mn (257.6, 260.5); Ni (231.6); Pb (230.2); Zn (213.8)	BCR CRM 141R
D	Analytical chemistry	120°C, 2 h	4°C, dark	2 mm	None	Microwave 1 g: 20 mL (CEM MDS 2000)	ICPOES (PerkinElmer Optima 3000)	Cd (214.4, 228.8); Cr (205.6, 267.7); Cu (224.7,324.8); Fe (238.2, 239.6); Mn (257.6, 260.6); Ni (221.6,232.0); Pb (217.0, 220.4); Zn (206.2, 213.9)	BCR CRM 143R
E	Soil science	None	Room temperature	2 mm	150 µm	Reflux 3 g: 28 mL	FAAS (PerkinElmer 1100B) ETAAS (PerkinElmer Zeeman 5100)	Cr (357.9); Cu (324.8); Mn (279.5); Ni (232.0); Pb (283.3); Zn (213.9) Cd (228.8)	WEPAL samples
F	Soil science	None	Room temperature	2 mm	None	Reflux 1.5 g: 14 mL	ICPMS	Not applicable	None

Table 2. Results obtained for analysis of certified and other reference materials ($mg\,kg^{-1}$).[a]

		n	Cd	Cr	Cu	Mn	Ni	Pb	Zn
BCR 141R	Certified		14.0 ± 0.5	138 ± 6	46.9 ± 2.3	653 ± 20	93.9 ± 5.8	51.3 ± 2.6	270 ± 11
	Laboratory C	12	12.5 ± 0.9	144 ± 11	50.6 ± 1.0	555 ± 35	90.1 ± 7.0	58.0 ± 3.9	244 ± 9
BCR 142R	Certified		0.249 ± 0.006	86.2 ± 7.4[b]	69.8 ± 1.0[b]	802 ± 50[b]	61.1 ± 1.9	25.7 ± 1.7	93.3 ± 3.4
	Laboratory B	3	0.320 ± 0.026	83.7 ± 2.1	66.7 ± 1.4	793 ± 26	60.1 ± 1.5	25.5 ± 0.9	88.2 ± 2.4
BCR 143R	Certified		72.0 ± 1.6	426 ± 13	128 ± 7[b]	858 ± 13	296 ± 4	174 ± 5	1060 ± 20
	Laboratory D	4	72.2 ± 0.9	405 ± 8	127 ± 1	857 ± 15	296 ± 8	174 ± 4	1100 ± 2
WEPAL ISE2001-4 samp 1	Reference		2.35 ± 0.09	77.9 ± 4.3	91.1 ± 2.8	1120 ± 41	37.2 ± 1.2	158 ± 5	502 ± 12
	Laboratory E	4	2.34 ± 0.02	72.0 ± 3.6	90.3 ± 3.2	1200 ± 65	36.1 ± 1.0	160 ± 7	508 ± 17
WEPAL ISE2002-2 samp 1	Reference		2.35 ± 0.11	78.2 ± 3.3	90.8 ± 2.2	1120 ± 40	37.5 ± 1.4	157 ± 6	499 ± 15
	Laboratory E	3	2.20 ± 0.11	71.5 ± 1.0	94.7 ± 2.7	1120 ± 10	38.7 ± 1.6	166 ± 1	505 ± 14
WEPAL ISE2002-2 samp 2	Reference		6.92 ± 0.28	160 ± 8	125 ± 4	954 ± 36	45 ± 2	235 ± 10	862 ± 27
	Laboratory E	5	6.66 ± 1.04	155 ± 8	131 ± 9	881 ± 82	43.1 ± 2.0	238 ± 15	861 ± 73

[a] Results presented are mean values ±1 SD except for the reference values for the WEPAL reference soil which are median values ± median of absolute deviation obtained by participants in the International Soil Analytical Exchange programme.

[b] Indicative value.

for copper measured by laboratory C and zinc by laboratory D. In both these cases, however, the mean measured value was within 10% of the certified value. Laboratory E did not analyse a CRM. However (unusually among the URBSOIL participants), they are regular participants in inter-laboratory proficiency testing through the International Soil Analytical Exchange program organized under the auspices of the Wageningen Evaluation Program for Analytical Laboratories (WEPAL). Results obtained for some WEPAL reference soils, during the period of the current study, are also shown in table 2. The comparison between found and target values was excellent, except for chromium and lead in soil WEPAL ISE2002-2 sample 1.

The results obtained for preliminary analysis, by each laboratory, of their own URM are shown in table 3, together with several general soil characteristics. Reported concentrations varied markedly between cities for some elements, e.g. the soil from city A contained greater levels of nickel than the other soils, while the URM from city D was relatively rich in the so-called 'urban metals' (copper, lead, and zinc) [17]. Some of these variations may have geochemical origins [18], but the majority of differences are most probably due to the variable degree of 'urbanization' within the cities and sampling sites. All results were below the maximum acceptable limit values for soils of residential/recreational use applicable in the particular country from which the sample originated, although it should be noted that these limits differ markedly between EU countries and regions [19].

Almost all measurements showed an RSD value $<9\%$, for the numbers of replicate specimens of their own URM that each laboratory elected to analyse (table 3). Cadmium in URMs B and D was found to be below laboratory B and D's respective detection limits. Laboratory C obtained a poor precision (39% RSD) for measurement of cadmium in URM C, despite analysing a large number of replicate specimens ($n=36$). This may reflect proximity to the ICPOES detection limit. Laboratory F also obtained a rather high uncertainty (17% RSD, $n=9$) when measuring cadmium. This is unlikely to arise from measurement close to detection limits since ICPMS was used but may indicate inhomogeneity in URM F. Laboratory E, which measured cadmium by means of ETAAS, reported good precision ($\mathrm{RSD}=2.1\%$, $n=4$).

3.2 *Comparative study*

URMs prepared in all cities were distributed to all project partners for analysis. Participation in the comparison was generally good, i.e. most partners analysed all the URMs (although the analytes quantified and number of replicate specimens varied between laboratories). Laboratory F, however, analysed only URMs A and F.

The concentrations of cadmium were too low in the URMs for quantification by partner A (the FAAS-user), and although signals were obtained for some samples, they were considered to be too low for reliable quantification in laboratory D when compared with the procedural detection limit of 0.74 mg/kg (calculated on the basis of $3\sigma_{\mathrm{BLANK}}$ ($n=10$)). Laboratories B, C, E, and F all reported results for cadmium, but these varied markedly (figure 1) with partner C systematically overestimating the concentration of this element with respect to the other partners. Laboratory C was aware of the potential inaccuracy in their cadmium measurements, reporting that data should be considered as indicative only. The discrepancies between the other partners are probably due to measurements being performed close to the effective detection

Table 3. General characteristics of the urban soil secondary reference materials (URMs) and target values established for concentrations of PTE (mg kg^{-1}).[a]

Source of soil	pH ($CaCl_2$)	CEC (meq/100 g)	Organic matter (%)	*n*	Cd	Cr	Cu	Fe (%)	Mn	Ni	Pb	Zn
City A	6.3	4.59	1.30	10	NA	49.3 ± 2.4	44.3 ± 1.9	3.70 ± 0.19	NA	79.6 ± 3.5	55.1 ± 1.4	101 ± 8.8
City B	4.6	9.12	4.02	5	<0.2	13.4 ± 0.3	35.0 ± 0.4	1.16 ± 0.02	99.2 ± 1.6	8.35 ± 0.50	27.5 ± 0.8	44.3 ± 0.8
City C	7.3	11.8	1.82	36	0.501 ± 0.194	29.3 ± 2.6	17.7 ± 1.0	1.11 ± 0.01	233 ± 13	18.7 ± 1.1	36.6 ± 5.2	54.8 ± 4.6
City D	4.2	17.3	11.7	34	<0.74	43.2 ± 3.0	111 ± 5	3.06 ± 0.12	442 ± 18	48.8 ± 7.0	389 ± 25	177 ± 11
City E	6.8	15.9	9.38	4	0.480 ± 0.008	42.0 ± 0.5	30.6 ± 0.4	NA	481 ± 10	26.4 ± 0.5	74.3 ± 2.1	129 ± 6
City F	6.6	22.0	5.38	9	0.180 ± 0.030	49.3 ± 1.4	29.4 ± 1.9	3.91 ± 0.35	446 ± 37	31.6 ± 1.4	25.3 ± 1.9	114 ± 5.1

[a] Results presented are mean values ± 1SD obtained by each partner for analysis of their own soil, except for pH and CEC, which were measured for all soils by laboratory C, and organic matter, which was measured for all soils by laboratory E; *n* = number of replicate specimens of soil analysed for PTE content; < denotes a value below detection limit; NA: not analysed.

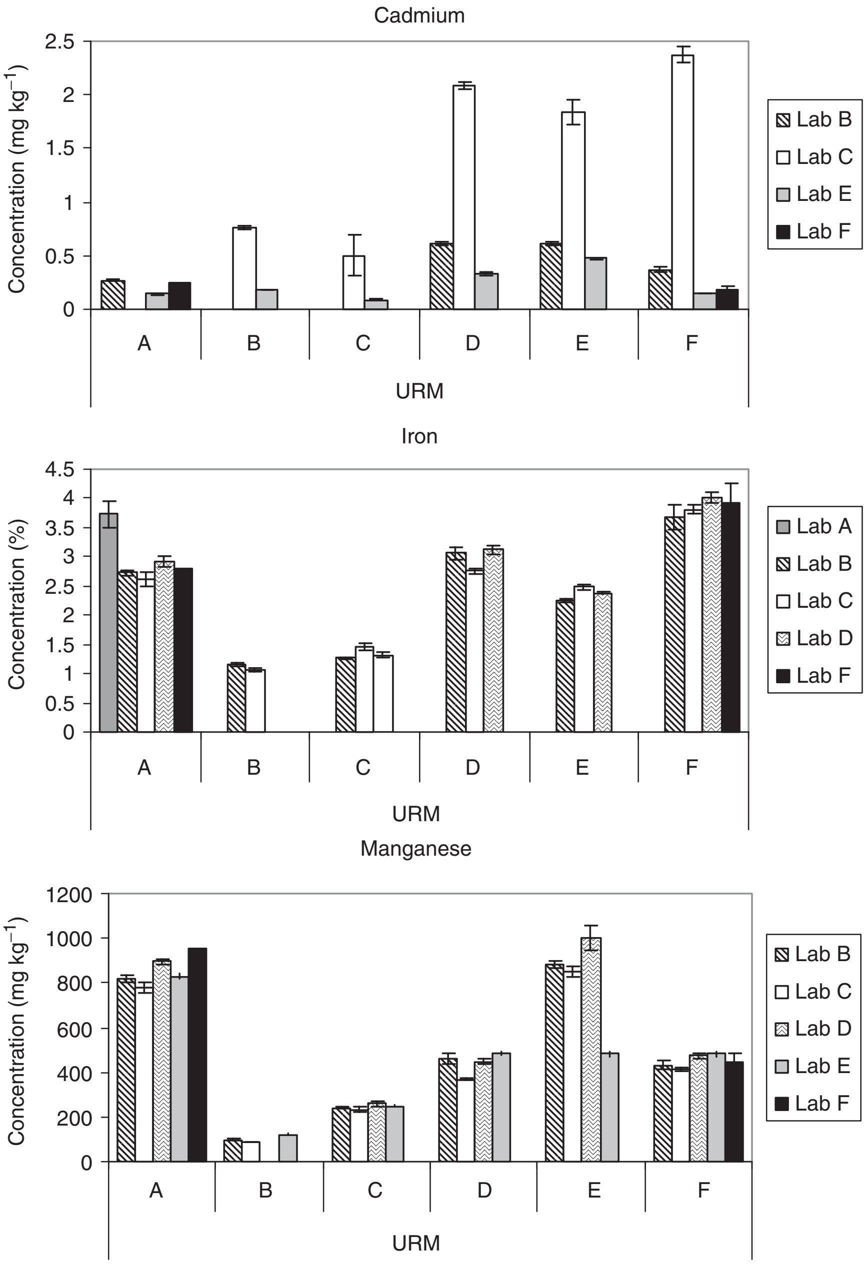

Figure 1. Reported concentrations of cadmium, iron, and manganese in the urban soil reference materials (mg kg^{-1}). Error bars represent one standard deviation: Lab A, $n = 3$ (except URM A where $n = 10$); Lab B, $n = 5$; Lab C, $n = 6$ (except URM C where $n = 36$); Lab D, $n = 3$ (except URM D where $n = 34$); Lab E, $n = 5$ (except URM A and URM E where $n = 4$); Lab F, $n = 2$ for URM A and $n = 9$ for URM F.

limits for this element (quoted as $0.2\,\mathrm{mg\,kg^{-1}}$ in laboratory B, $0.11\,\mathrm{mg\,kg^{-1}}$ in laboratory E, and $0.012\,\mathrm{mg\,kg^{-1}}$ in laboratory F).

All laboratories that measured iron obtained results within approximately 10% of each other, for each URM (figure 1). The exception was laboratory A, which appeared to overestimate the concentration of this element in their soil (recovery = 135% with respect to mean value obtained by other partners). Unfortunately, this laboratory did not measure iron in the other soils, so it is not clear whether the error was systematic. For manganese (figure 1), the inter-laboratory agreement was reasonable except for the analysis of URM E by one partner, laboratory E (recovery = 53% relative to mean of other partners). Re-analysis of the sample revealed the discrepancy to be due to gross error; an incorrect dilution factor was used in the calculation of the manganese concentration originally reported. This would not have been detected under normal circumstances, and an erroneous result would have been reported.

Five elements were measured by all laboratories: chromium, copper, nickel, lead, and zinc. Rather than considering each element individually, results for these analytes were subjected to PCA to obtain an overall assessment of the laboratories' performances. Data for each of the six soils were autoscaled individually, so that the mean and variance of the metal concentrations obtained by all laboratories for each soil was 0 and 1, respectively. The autoscaled data for each soil were then vertically concatenated, and the entire dataset was assessed using principal-component analysis. The first two principal-components, which captured 72% of the variance in the data, were rotated orthogonally using the varimax method. The autoscaled data were then projected onto the rotated axes to compute the scores.

PC1 was associated with measured concentrations of chromium and nickel (loadings of 0.60 and 0.58, respectively, see table 4), copper (loading 0.42), and zinc (loading 0.35). PC2 was highly correlated with reported lead levels (loading 0.86) but also with copper and zinc results (loadings of 0.32 in both cases).

Score plots, indicating the relative performance of each laboratory for measurement of all five analytes in the URMs, are shown in figures 2 and 3. PCA scores for laboratory A were unevenly distributed about the origin. Almost all the data obtained for URM A had negative PC1 and positive PC2 score values, while data for other URMs generally had positive PC1 score values and were widely scattered. The differences in PC1 score may occur because this laboratory underestimated chromium concentration in their own URM, but overestimated nickel concentrations in URMs C, D, E, and F, relative to the other partners. Variable chromium data could arise from difficulty in atomizing this element in an air–acetylene flame (nitrous oxide–acetylene was not available), while nickel contamination is a potential concern in City A because the rocks in this part of Europe are naturally rich in this element [18].

Table 4. Correlation coefficients between variables and principal components.

Variable	PC 1	PC 2
Cr	0.59626	−0.1244
Cu	0.42018	0.32359
Ni	0.58429	−0.18751
Pb	−0.074011	0.86134
Zn	0.34792	0.32053

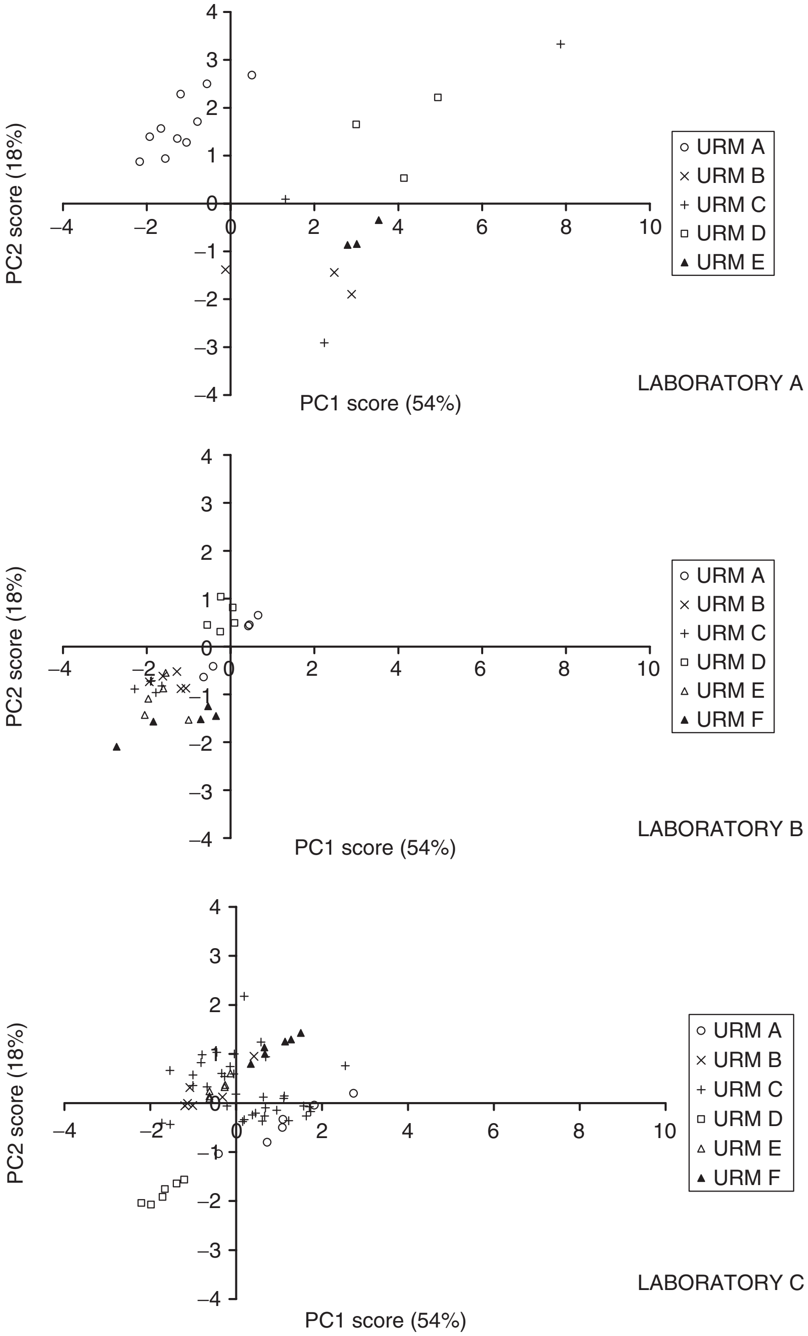

Figure 2. Varimax score plots illustrating the relative performance of laboratories A, B, and C when measuring five analytes (chromium, copper, nickel, lead, and zinc) in the urban soil reference materials.

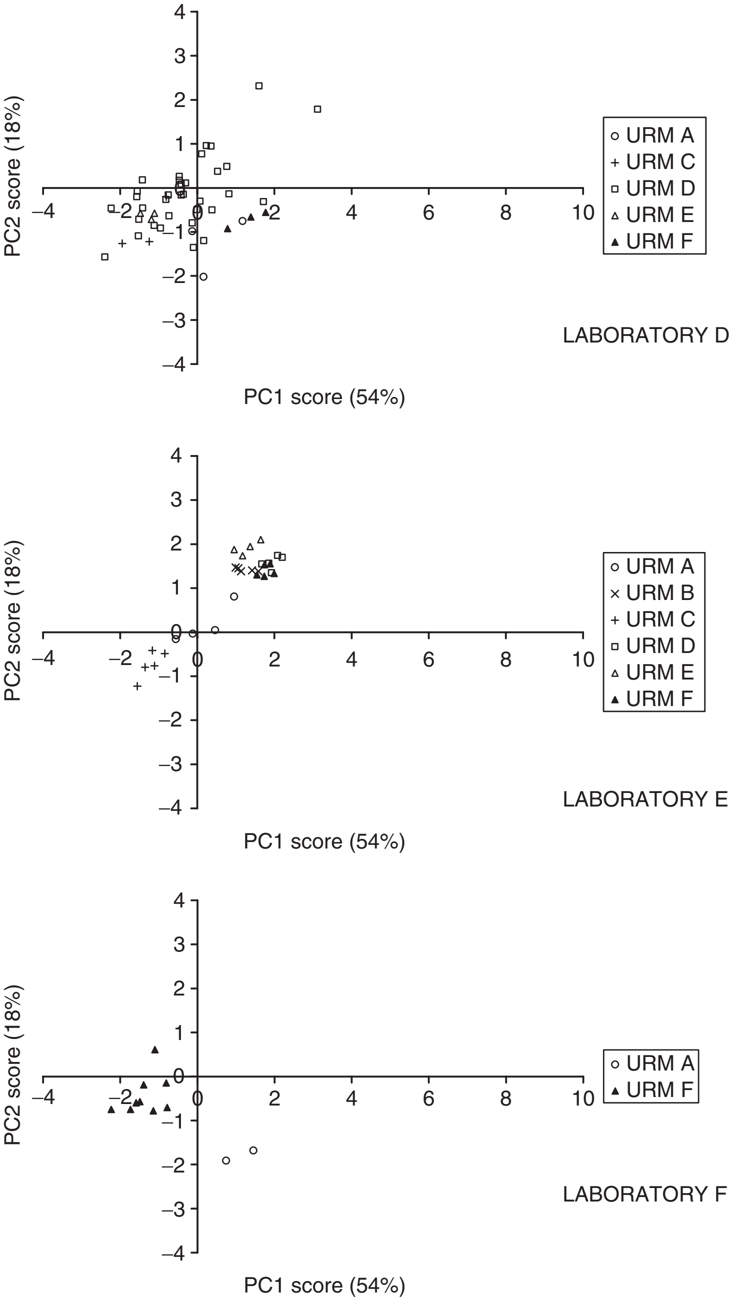

Figure 3. Varimax scores plots illustrating the relative performance of laboratories D, E, and F when measuring five analytes (chromium, copper, nickel, lead, and zinc) in the urban soil reference materials.

The variability in the PC2 score seems to arise from poor analytical repeatability. Widely different results were sometimes obtained when replicates of the same soil were digested and analysed (especially for URM C).

Scores obtained from the laboratory B results were closely grouped. The majority of data had negative score values for both principal components, indicating a slight tendency for this laboratory to underestimate analyte concentrations relative to the inter-laboratory mean values. Laboratory C's scores were relatively evenly scattered about the origin, although there is a suggestion of negative bias in analysis of URM D, results for which form a distinct cluster separate from those of the other soils. Laboratory D also produced data that was generally close to the origin (except for two analyses of URM D). The results from laboratory E showed a trend, with evidence of variable performance for the analysis of the different soils. Analyte concentrations in URM C were generally slightly lower than those obtained by the other partners, as shown by a negative score values for both principal-components. Results for URM A were close to, and centred about, the origin. Results for URMs B, D, E, and F were generally overestimated (positive scores values for both principal components). Possible reasons for this trend include variations in digestion efficiency for different types of soil, and soil-specific interference effects during measurement of analytes. Laboratory F analysed only two test portions of URM A, and it is therefore difficult to comment on the overall quality of data obtained. However, these results appear to fall in a different area of the score plot from the URM F results, perhaps, again, indicating an influence of general soil characteristics on analytical performance.

4. Conclusions

This small comparative study revealed significant inter-laboratory variability. Approximately 20% of results reported differed from target values by more than 25%, even though experienced researchers were conducting a relatively straightforward analysis. Reasons included quantification too close to detection limits, gross errors in calculation, and lack of adequate quality control in measurement. PCA indicated that the most reliable and consistent results originated in laboratories B and D, which is perhaps expected, given that these partners have research interests primarily in analytical science. Laboratory C also performed well, as did laboratory E, although here there was evidence that the nature of the soil influenced the results obtained. This effect was more pronounced in laboratory A, which also reported a high variability in replicate analysis. Unfortunately, laboratory F—the URBSOIL partner indicated to have the least prior experience in analytical chemistry quality issues—participated only to a very limited extent in the comparison, and so no assessment of overall performance can be made. The work clearly highlights the need for harmonization to be considered as an integral part of all international, environment-related, cooperative research projects involving chemical analysis, and supports the view that a lack of comparability may pose a serious impediment to the use of pre-existing soil quality data as the basis for development of effective, integrated, soil-protection strategies across the EU.

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