



CASE STUDY ON THE RELATIONSHIPS BETWEEN SOIL CONTENTS OF SOME HARMFUL CHEMICAL ELEMENTS DETERMINED BY DIFFERENT EQUIPMENT

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Abstract. Comparison of total contents of Ba, Cr, Cu, Mn, Mo, Ni, Sn, Pb, V, Zn, Al, Ca, Fe, Mg determined in topsoil of central part of Vilnius by optical atomic emission spectrophotometry (OAES) with respective contents determined by energy-dispersive x-ray fluorescence (EDXRF), analysis of their correlation and linear relationship with and without outliers are the tasks of research. For most elements, except Ca, Sn, Ba, the contents determined by EDXRF are significantly lower and less variable. They can be predicted according to OAES-contents using linear equations. After elimination of outliers for all elements the correlation is significant at $p < 0.05$.

Keywords: optical atomic emission spectrophotometry, energy-dispersive x-ray fluorescence, urban soil, chemical elements.

Introduction

Until 2007 all geochemical investigations at the Institute of Geology and Geography (IGG) were based on the total contents of trace elements determined by optical atomic emission spectrophotometry (OAES) using DFS-13 equipment. This equipment was used both for determination of soil background values [1-4] and for urban geochemical mapping [5-8]. So the results obtained in IGG before 2007 can be compared. In urban topsoil investigations the following potentially toxic trace elements were usually determined: Ag, B, Ba, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sn, V, Zn. Since 1997 the laboratory has been participating with OAES in "International Soil-analytical exchange" (ISE) program organised by Wageningen University. In 2007 new energy-dispersive x-ray fluorescence (EDXRF) equipment SPECTRO XEPOS was purchased and IGG started to participate in ISE with EDXRF. Using TURBOQUANT calibration method for pressed pellets the total contents of chemical elements from Na to U can be determined.

Aiming to compare the results obtained by EDXRF and OAES equipment, it is necessary to re-analyse old samples by EDXRF. Case study of the relationships between urban soil contents of Ba, Cr, Cu, Mn, Mo, Ni, Pb, Sn, V, Zn, determined by OAES (OAES-contents) and EDXRF (EDXRF contents) is the object of this research. The relationships between OAES-contents and EDXRF-contents of major elements Al, Fe, Ca, Mg are also analysed.

Materials and methods

Composite topsoil samples were taken in 2006 from 141 site in central part of Vilnius. Each sample was gathered by collecting 20-25 similar mass increments, homogenised and reduced to 1 kg. Then the samples were sieved through 1 mm sieve, ashed at 300-350⁰C and milled. OAES-contents of 13 trace and 4 major elements (Al, Ca, Fe and Mg) were determined by vaporization of 0.5 g of fine-milled soil at 5000-6000⁰C in the electric arc between three graphite nails; determination was done by optical spectrophotometer DFS 13. The results obtained by this type of analysis have been already discussed analysing the distribution of harmful trace elements both in the oldest part of Vilnius [9] and in younger districts [10].

In 2010 real total contents of large group of major or trace elements were determined in the same samples by EDXRF [11]. Sample preparation for this analysis was as follows: the sieved samples were milled with MM 400, homogenised with Licowax (4 g of sample and 0.9 g of wax) and pressed with PP15 press into 32 mm pellets. The primary content of chemical elements in each pellet was determined using SPECTRO XEPOS equipment and TURBOQUANT for pressed pellets calibration method. Total number of measurements was 282, as for each sample two pellets were prepared. The contents of almost all the elements, which are the object of this research, were above their DL in all pellets, the only exception was Mo: in 74.4% of pellets its content was below DL. Great part of undefined measurements of Mo was a serious obstacle for comparison of its results obtained by two methods. In order to have database without missing values, the value 0.1 ppm was inserted for primary measurements of those pressed pellets where Mo content was below DL. Median content of each element in each sample was calculated according to measurements of two pellets. The primary median measurement values in each sample were recalibrated using 44 ISE reference samples, CRM 2709 and CRM 2711. In all cases, except Al, linear regression was used for this aim with coefficient of determination higher than 0.9.

The estimates of relative standard measurement uncertainties for the mean contents of 10 trace elements U_m (%) determined by different equipment are given below. For EDXRF, these values ($U_{m-EDXRF}$) were estimated according to 56 (for Mo 46) repeated measurements of CRM 2709 during the first quarter of 2010. $U_{m-EDXRF}$ values of 14 trace and 10 major elements did not exceed 5%, though respective uncertainties for individual measurements ($U_{ind-EDXRF}$) were higher and for V, Sn, Mo exceeded 5% [11]. As concerns trace elements of this research, $U_{m-EDXRF}$ values were the following: Zn(0.09), Mn(0.11), Ni(0.15), Pb(0.28), Ba(0.31), Cu(0.50), Cr(0.5), V(0.81), Mo(4.96), Sn(1.66). For OAES, the U_{m-OAES} values (%) were estimated in 2004 according to 22 repeated measurements of another sample (ISE No.921). All these values were also below 5%. Though element contents in CRM 2709 and ISE No.921 differ and this can influence repeatability, preliminary comparison of U_m values was done. It showed that for most trace elements U_{m-OAES} values were higher than $U_{m-EDXRF}$: Zn (11 times), Mn(7.28 times), Ni(6.97 times), Pb(3.69 times), Ba(2.48 times), Cu(2.09 times), Cr(2.01 times), V(1.05 times). Only for 2 elements from 10 they were lower than the values of $U_{m-EDXRF}$: Mo(4.65 times), Sn(1.63 times). Though in regression models usually more precise variables are taken as independent, namely OAES-content was chosen as independent variable because the number of soil samples in Lithuania analysed by EDXRF is still low, besides, for Mo and Sn the U_{m-OAES} are lower. The latter 2 elements as well as Cr and V are characterised also by the highest joint uncertainty from trace elements of this research (arising during EDXRF measurement and sample preparation), this uncertainty exceeds 5% [11]. According to increasing joint uncertainty the elements are arranged as follows: Al(0.95) < Fe(1.13) < Zn(1.79) < Mn(1.90) < Mg(2.03) < Ba(2.26) < Ca(2.50) < Ni(3.29) < Cu(3.86) < Pb(4.10) < Sn(6.14) < Cr(10.3) < V(15.0) < Mo(66.7).

To reveal for each chemical element the differences between 2 variables measured in the same samples (OAES-content and EDXRF-content), two non-parametric tests were used: Sign test and Wilcoxon matched pair test. Pearson correlation coefficients were determined between OAES-content and EDXRF-content. Linear regression model (a – coefficient before independent variable, i.e. slope, b – intercept) was used to find out the relationships between these contents. The suitability of this model was checked according to p-value of F-test in ANOVA table. To test the null-hypothesis that regression parameters do not differ from zero, p-values of t-test were checked. The level of significance in all tests was 0.05. If p-values of F-test and t-test are lower than 0.05, the linear equations can be used for prediction of EDXRF-contents according to OAES-contents. When analysing the relationships between different contents, the outliers were revealed and eliminated. There were two consecutive stages of elimination of outliers. The first one was elimination of considerable outliers. The

sample measurement (case) was supposed to be considerable outlier, when at least one of 3 criteria was fulfilled: 1) absolute value of standard residual of this case was higher than 3 [12]; 2) Cook's distance exceeded the critical value (as the number of cases was always higher than 120, the $F_{0.5}(2, \infty)=0.693$ was chosen [12]); 3) there was noticeable deviation of this case from the line $y=x$ in the graph "residual versus deleted residual". The second stage (realised after the first stage) was elimination of inconsiderable outliers, i.e. the cases for which the value of standard residual was in the interval [2-3] or which were characterized by less noticeable deviation from the line $y=x$ in the graph "residual versus deleted residual". Higher standard residuals indicate cases with the deviation from regression line. Both Cook's distance and deleted residual are measures of impact of the respective case on the regression equation. Cook's distance indicates the difference between the computed values of slope and the values one would have obtained, had the respective case been excluded. If it exceeds critical value [12], there is reason to believe that the respective case biased the estimation of the regression coefficients. If the deleted residual differs greatly from the respective residual value (this can be seen from the graph), then this case is possibly an outlier because its exclusion changed the regression equation. The minimum and maximum values of OAES-content and EDXRF-content were determined according to all data, according to data after the first stage and after the second stage of elimination.

Results and discussion

The contents of 11 chemical elements determined by EDXRF are lower than respective contents obtained by OAES. For Al, Fe, Mn and Ni this regularity is observed in all samples (Table 1). For other 7 chemical elements the percentage of samples where the content determined by EDXRF is lower than the content determined by OAES exceeds 50%, according to this percentage the latter elements are arranged as follows: $V(99.3)>Mg(95.7)>Cr(95.0)>Pb(91.5)>Cu(90.1)>Mo(88.7)>Zn(85.1)$. These 11 chemical elements are characterized by higher median OAES-content than median EDXRF-content, all of them, except Pb and Cu, have also higher maximum AOES-content than maximum EDXRF-content.

Only Ca, Sn and Ba are distinguished by the opposite regularity, i.e. higher percentage of samples where OAES-content is lower than EDXRF-content. The opposite tendency is especially characteristic of Ca, which has lower median OAES-content than median EDXRF-content and lower maximum OAES-content than maximum EDXRF-content. For almost all chemical elements there are significant ($p<0.05$) differences between OAES-content and EDXRF-content both according to Sign test and according to Wilcoxon matched-pairs test. For Ba the differences according to both tests are insignificant, for Sn they are insignificant according to Sign test.

For most chemical elements (except Cu, Pb and V) the variation coefficients of OAES-contents are higher than of EDXRF-contents.

For all trace elements Pearson correlation coefficients R between OAES-contents and EDXRF-contents are significant ($p<0.05$) both before and after elimination of outliers though not all coefficients of determination R^2 are higher than 0.25 (Table 2). For example, Mn has low R^2 both before and after elimination of outliers, Ba and V – after elimination of outliers. Trace elements in Table 2 are arranged according to decreasing R^2 (and R) values of linear regression obtained according to data without elimination of outliers.

Linear regression analysis performed according to primary data of trace elements (without any elimination of outliers) as well as after elimination of outliers showed significant p-values of ANOVA F-test (the same as p-values of t-test for slope), also significant p-values for intercept.

In most cases the elimination of outliers according to deviations from line in the graph “residual versus deleted residual” is realised in the first stage, but for Mo, Pb and Cu also in the second stage.

Table 1.

Comparison of chemical element contents obtained by OAES and EDXRF

El.	Md1 (ppm)	Md2 (ppm)	Mx1 (ppm)	Mx2 (ppm)	VK1 (%)	VK2 (%)	Md1/ Md2	Mx1/ Mx2	VK1/ VK2	PL (%)	S	W
Ca	19600	20600	46800	52000	34.3	32.6	0.95	0.90	1.05	36.2	*	*
Mg	7370	4900	114000	10100	115	25.3	1.50	11.29	4.54	95.7	*	*
Al	38000	20100	52300	27300	13.4	11.5	1.89	1.92	1.16	100.0	*	*
Fe	16000	8790	32800	23800	21.4	20.9	1.82	1.37	1.03	100.0	*	*
Ba	320	316	908	653	30.3	15.3	1.01	1.39	1.98	49.6	ns	ns
Cr	30.9	19.6	204	95.7	60.6	50.6	1.58	2.13	1.20	95.0	*	*
Cu	32.6	20.9	232	273	72.6	107	1.56	0.85	0.68	90.1	*	*
Mn	509	300	977	495	24.1	16.8	1.70	1.98	1.44	100.0	*	*
Mo	1.06	0.61	178	58.5	516	385	1.75	3.04	1.34	88.7	*	*
Ni	15.9	8.30	47.6	27.8	32.9	31.6	1.91	1.71	1.04	100.0	*	*
Pb	60.0	43.8	914	13100	108	770	1.37	0.07	0.14	91.5	*	*
Sn	5.09	6.14	49.9	38.0	81.7	58.7	0.83	1.31	1.39	41.8	ns	*
V	35.6	14.4	137	59.7	42.7	58.0	2.48	2.30	0.74	99.3	*	*
Zn	228	133	1000	530	66.7	59.3	1.71	1.90	1.13	85.1	*	*

Explanation: El. – chemical elements, Md1, Mx1, VK1 – median, maximum and coefficient of variation of OAES-content, respectively; Md2, Mx2, VK1 – median, maximum and coefficient of variation of EDXRF-content, respectively; Md1/Md2, Mx1/Mx2, VK1/VK2 – ratios of respective characteristics; PL – percentage of samples where EDXRF-content is lower than OAES-content; S, W – characterization of p values obtained by Sign test or Wilcoxon test (* – significant, i.e. $p < 0.05$, ns – not significant). High contents are rounded.

Only for Cu, Sn and Mn consecutive elimination of considerable and inconsiderable outliers increases correlation between their OAES-contents and EDXRF-contents. For most trace elements (Mo, Zn, Pb, Cr, Ni, Ba, V) elimination of outliers leads to the opposite tendency.

This might be explained by fact that single outliers characterized by extremely high OAES-contents or EDXRF-contents can artificially increase the correlation. Obvious decrease of maximum values of both OAES-contents and EDXRF-contents after elimination of considerable outliers confirms this. For Pb, Mo, V, Cr this decrease is especially pronounced. Elimination of inconsiderable outliers either does not change maximum values of OAES-contents and EDXRF-contents or changes them to a lower extent.

However, the second stage of elimination often leads to some increase of R^2 (and R) values, e.g. for Zn, Cr, Ni, Ba, V.

The question arises which linear regression equations should be used. On our opinion, though the correlation between OAES-contents or EDXRF-contents is supposed to exist also at high concentrations of trace elements, there is insufficient data to use the respective linear regression for prediction. Therefore regression equations after elimination of anomalies seem to be more based.

The necessity to eliminate outliers with high contents is confirmed by the fact that for some elements, e.g. Pb, Cu, linear regression parameters without any elimination are greatly different from respective parameters after elimination of outliers (Table 2). On the whole, the estimates of linear regression parameters on different stages are rather similar.

After the elimination of outliers the arrangement of trace elements according to decreasing R^2 (and R) values is as follows: Cu>Zn>Pb>Sn>Cr>Ni>Mo>Ba>Mn>V (Fig 1).

Table 2.

Correlation and linear relationship of two different contents of trace elements

El _i	R ²	R	N	Mx(S)\Mx(X); outliers eliminated	a	b
Mo ₁	0.9870	0.9935	141	178\58.5;	0.3464	0.4014
Mo ₂	0.4455	0.6675	135	4.32\3.44; N21(RDC), N22(RDC), N23(RD), N24(RD), N04(D), Sn13(D)	0.3869	0.2877
Mo ₃	0.4331	0.6581	136	4.32\2.40; N26(D)	0.3083	0.3683
Zn ₁	0.7777	0.8819	141	1000\530;	0.4933	33.549
Zn ₂	0.7271	0.8527	138	720\408; N11(RD), N17(D), Se02(D)	0.4688	37.961
Zn ₃	0.7511	0.8667	135	720\408; Zr26, Zr28, A09a	0.4712	35.237
Pb ₁	0.7751	0.8804	141	914\13100;	11.859	-751.48
Pb ₂	0.6961	0.8343	139	189\171; Se04(RDC), Se21(RDC)	0.6520	5.1306
Pb ₃	0.6666	0.8165	135	165\155; Se05(D), A09(D), Sn17(D), Zv03(D)	0.6392	5.8739
Cu ₁	0.6986	0.8358	141	232\273;	0.8147	-6.1007
Cu ₂	0.7326	0.8559	139	128\111; A09(RDC), Sn08(RDC)	0.4971	4.6179
Cu ₃	0.7810	0.8837	136	128\111; Se29, Zr08, A10(D)	0.5432	3.3337
Cr ₁	0.7713	0.8782	141	204\95.7;	0.4532	5.7101
Cr ₂	0.4238	0.6510	138	70.1\47.3; N21(D), N22(D), Zr12(R)	0.4663	5.1915
Cr ₃	0.4920	0.7014	133	70.1\47.3; N09, Se04, Se17, Zr27, A11	0.4749	4.4621
Ni ₁	0.5309	0.7286	141	47.6\27.8;	0.3709	2.6565
Ni ₂	0.4450	0.6671	138	39.1\16.7; Se04(R), Se09(R), Zr12(RDC)	0.3013	3.6589
Ni ₃	0.4744	0.6888	135	39.1\16.7; N28, Se07, Sn05	0.2849	3.8154
Ba ₁	0.4701	0.6856	141	908\653;	0.3418	211.2
Ba ₂	0.2330	0.4827	139	624\462; N11(RDC), Zv10(D)	0.2198	248.78
Ba ₃	0.2464	0.4964	134	624\413; N10, N22, Sn2	0.2080	251.51
V ₁	0.3352	0.5790	141	137\597;	0.3125	3.2083
V ₂	0.0785	0.2802	138	60.6\33.3; N21(DC), N22(DC), A10(RDC)	0.2427	5.6373
V ₃	0.0788	0.2807	136	60.6\31.2; Zr06, Zr16	0.2321	5.7675
Sn ₁	0.2926	0.5409	141	49.9\38.0;	0.3983	4.1225
Sn ₂	0.4068	0.6378	138	23.2\17.0; N28(RDC), Se28(RC), A20(R)	0.4642	3.5344
Sn ₃	0.5233	0.7234	135	23.2\12.3; Se03, Se26, Zv03	0.4473	3.4330
Mn ₁	0.1630	0.4037	141	977\495;	0.1599	216.48
Mn ₂	0.1731	0.4161	140	977\435; Se09(R)	0.1559	217.28
Mn ₃	0.2132	0.4617	134	977\397; Se02, Se04, Se19, A02, Sn10, Zv02	0.1544	215.15

Note. El_i – element and information about elimination of outliers: index 1 – without elimination of outliers, index 2 – after elimination of considerable outliers, index 3 – after elimination of inconsiderable outliers; R² – coefficient of determination; R – Pearson correlation coefficient; N – number of observations in linear regression; Mx(S)\Mx(X) – maximum OAES-content and maximum EDXRF-content; estimated values of linear regression parameters: a – coefficient before independent variable, i.e. slope, b – intercept. The outliers are indicated by sample identification numbers with the following additional information given in parentheses: R – absolute value of standard residual exceeds 3; C – Cook's distance exceeds critical value (0.693) [12], D – deleted residual differs from residual.

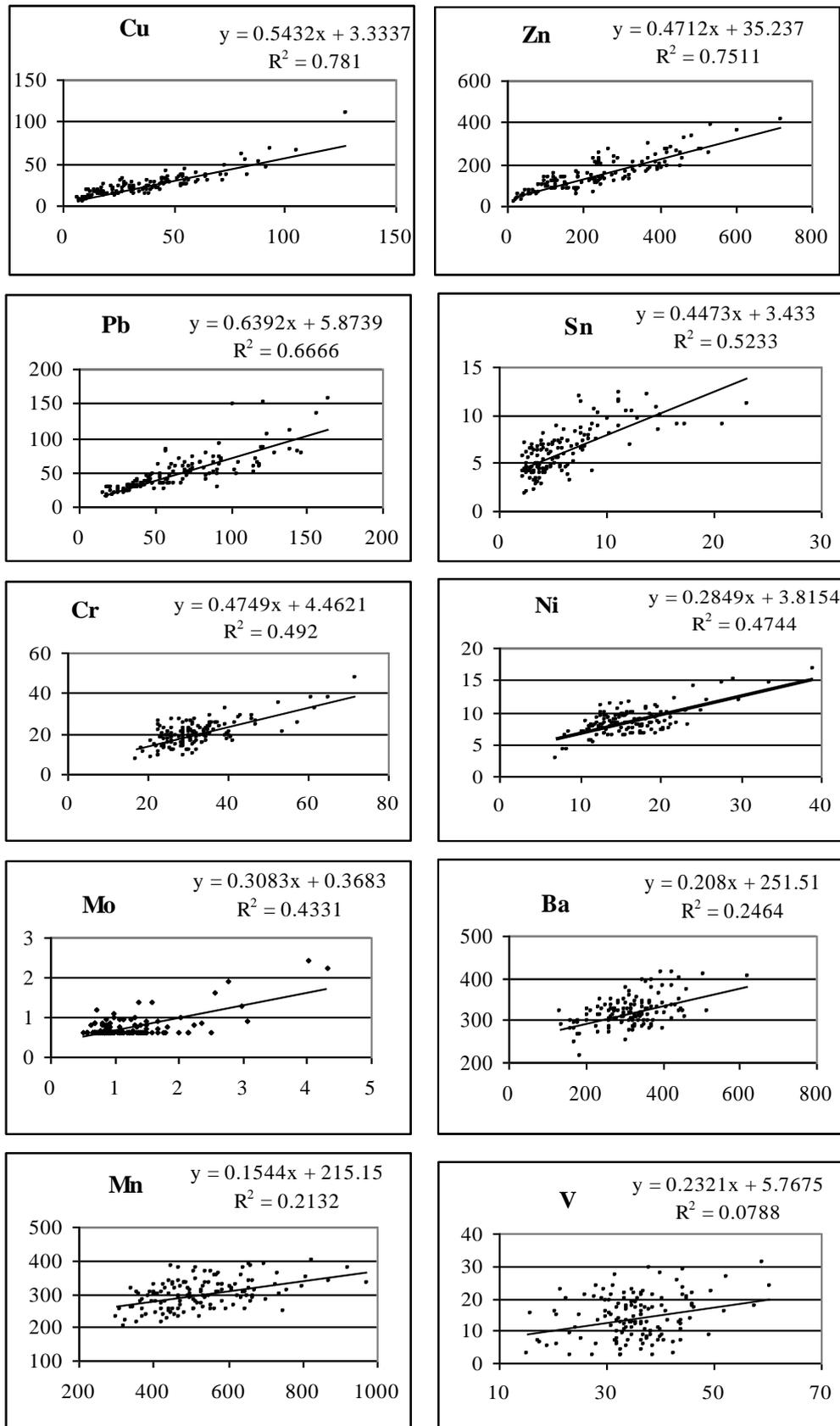


Fig.1. Correlation between trace element contents determined by different equipment

It is obvious that for chalcophiles (Cu, Zn, Pb, Sn) the correlation between OAES-contents and EDXRF-contents is higher than for siderophiles or lithophiles. The highest slope of linear regression is characteristic of Pb(0.639). It is followed by Cu(0.543), other trace elements are arranged as follows: Cr(0.475), Zn(0.471), Sn(0.447), Mo(0.308), Ni(0.285), V(0.232), Mn(0.213), Ba(0.208). For most siderophile or lithophile trace elements (except Cr) the slope is lower.

As concerns major elements, the coefficients of determination are not always sufficiently high and Pearson correlation coefficients are not always significant, especially for Al, also for Mg before elimination of anomalies (Table 3). Most probably, there were rough mistakes of Mg determination by OAES in 2 samples. Linear regression performed according to primary data of major elements (without any elimination of outliers) showed significant ($p < 0.05$) values of ANOVA F-test for Ca, Mg and Fe, both parameters (slope and intercept) being also significant ($p < 0.05$). For Al, F-test of ANOVA and t-test for slope being equal to zero resulted in insignificant p-values ($p > 0.05$). Elimination of anomalies slightly improved the correlation between OAES-contents and EDXRF-contents of Al and it became significant ($p < 0.05$). Still it is hardly possible to predict EDXRF-contents of Al according to its OAES-contents or additional data are necessary. As for most trace elements, for Fe the elimination of outliers lead to decrease of R^2 (and R) values as well as considerable decrease of its maximum OAES-contents and EDXRF-contents. For other 3 major elements the tendency was the opposite. According to decreasing values of R^2 (and R) after the second stage of elimination of outliers, the major elements are arranged as follows: Ca>Mg>Fe>Al. The same arrangement of major elements is according to regression slope values after the second stage of elimination of outliers.

Table 3.

Correlation and linear relationship of two different contents of major elements

El _i	R ²	R	N	Mx(S)\Mx(X); outliers eliminated	a	b
Ca ₁	0.7096	0.8424	141	46800\52000;	0.8414	4227.7
Ca ₂	0.7124	0.8440	139	36800\35600; Se03(RDC), Se09(RD)	0.8670	3775.3
Ca ₃	0.7378	0.8590	137	36800\35600; N22, Se01	0.8701	3578.7
Mg ₁	0.0522	0.2285	141	114000\10100;	0.0314	4779
Mg ₂	0.6278	0.7923	138	12300\8010; Se09(R), A02(R), A07(DC)	0.4435	1779.1
Mg ₃	0.5682	0.7538	133	12300\7510; A03, A04, A05, Se13, Se15	0.3857	2235.5
Fe ₁	0.3469	0.5890	141	32800\23800;	0.3145	3805.4
Fe ₂	0.2684	0.5181	139	24800\13000; Se09(RDC), A03(RD)	0.2188	5315.1
Fe ₃	0.2503	0.5003	138	24800\13000; A02	0.2031	5595.3
Al ₁	0.0267	0.1634	141	52300\27300;	0.0763	17574
Al ₂	0.0203	0.1425	139	50700\26800; N25(D), Se17(R)	0.0656	17899
Al ₃	0.0296	0.1720	132	50700\24700; N08, Se19, Zr05, Zr14, Zr25, Zv03, Zv09	0.0658	17602

Note: explanation is the same as in Table 3.

Conclusions

Most of chemical elements studied, except Ca, Sn and Ba, are characterised by significantly lower EDXRF-contents than OAES-contents. Unlike most elements, the EDXRF-content of Ca is significantly higher than OAES-content, Sn has also a tendency of higher EDXRF-content. Such differences can be explained by different standard reference materials used for re-calibration of measurements of total element contents obtained by different equipment. Continuous participation of IGG in WEPAL ISE program ensured increase of available ISE samples which can be used as standard reference materials for re-calibration of measurements

obtained by EDXRF. Preliminary comparison of relative standard measurement uncertainties of both methods for mean values of two reference materials has shown that most trace elements studied (Ba, Cr, Cu, Ni, Mn, Pb, V, Zn), except Sn and Mo, are characterised by lower uncertainty of EDXRF measurements. Due to these reasons EDXRF-contents are more reliable. However, huge problem of their application in practice arises, when it is necessary to estimate the danger category of contaminated urban soil, because all previous background values for soil were calculated on the basis of OAES measurements. According to the ratio of median EDXRF-content to median OAES-content the arrangement of potentially harmful elements is as follows: V(0.40) <Ni(0.52) <Mo(0.57) <Zn(0.58) <Mn(0.59) <Cr(0.63) <Cu(0.64) <Pb(0.73) <Ba(0.99) <Sn(1.21). It is obvious that the old background values of V, Ni, Mo, Zn, Mn, Cr, Cu, Pb estimated according OAES-content are absolutely unsuitable for calculation of concentration coefficients K_k and additive contamination index Z_d (which depends on K_k). If this fact is ignored, the underestimation of soil contamination categories according to Z_d threatens. Therefore the determination of background EDXRF-contents on uncontaminated territories is necessary. Since for all trace elements two contents determined by different equipment are significantly correlated, simple linear regression equations for prediction of EDXRF-content according to OAES-content might be useful. These equations differ before and after the elimination of outliers. The latter relationships indicate that for chalcophiles the correlation between OAES-contents and EDXRF-contents is higher than for siderophiles or lithophiles. Prediction of some major elements (Ca, Mg, Fe) is also possible according to linear regression equations. However, prediction of Al according to available data is problematic.

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