Electronic Supplementary Information

Simultaneous determination of Cd, Pb, Cu and Zn as total and labile fractions in soil using a small-sized electrothermal vaporization capacitively coupled plasma microtorch optical emission spectrometer after diffusive gradients in thin-film passive accumulation

Simion Bogdan Angyus, [a,b,c] Marin Senila,[a] Eniko Covaci,[b,c] Michaela Ponta,[b,c] Maria Frentiu[a] and Tiberiu Frentiu [*b,c]

[a] National Institute for Research and Development of Optoelectronics INOE 2000 INCD Bucharest, Research Institute for Analytical Instrumentation, Donath 67, 400293 Cluj-Napoca, Romania.
[b] Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, Arany Janos 11, 400028 Cluj-Napoca, Romania. E-mail: tiberiu.frentiu@ubbcluj.ro.
[c] Babes-Bolyai University, Research Center for Advanced Analysis, Instrumentation and Chemometrics, Arany Janos 11, 400028 Cluj-Napoca, Romania

This online resource contains the following data:

1. Working conditions in SSETV-µCCP-OES method for simultaneous determination of Cd, Cu, Pb and Zn as total and labile fraction in soil after DGT passive accumulation on Chelex-100

2. Calculation of the total concentration and DGT-based labile fraction of metals in soil

3. Matrix composition of CRMs and real samples of soil analyzed for total content and DGT-based labile fraction determination of Cd, Pb, Cu and Zn in soil

4. Results for the quantification of total content of Cd, Pb, Cu and Zn in CRM soils by SSETV-µCCP-OES and GFAAS without DGT passive accumulation

5. Relative individual uncertainties and relative combined uncertainty of sample preparation protocol and analysis for the determination of total Cd, Pb, Cu and Zn in soil by SSETV-µCCP-OES and GFAAS after DGT passive accumulation

6. Bland–Altman plots for the comparison of total concentration and labile fractions of Cd, Pb, Cu and Zn in soil obtained by DGT-SSETV-µCCP-OES and DGT-GFAAS

7. The indicator evaluation of the ability of the solid phase of soil to resupply Cd, Pb, Cu and Zn into soil solution

1. Working conditions in SSETV-µCCP-OES method for simultaneous determination of Cd, Cu, Pb and Zn as total and labile fraction in soil after DGT passive accumulation on Chelex-100

Table S1. Optimal operating conditions for the SSETV-µCCP-OES equipment used for the simultaneous determination of Cd, Pb, Cu and Zn in soil (total and labile fraction) after DGT passive accumulation

Parameter	Setting
Plasma power	15 W
Ar flow rate for microsample transport and plasma sustaining	150 mL min^{-1}
Observation height in plasma	0.8 mm above the Mo tip microelectrode
Volume of microsample	10 µL
Microsample drying	80 °C for 180 s in air
Microsample vaporization	1500 °C for 10 s
3D spectra recording	100 episodic spectra; 100 ms integration time per episode
Wavelengths	Cd 228.802 nm; Pb 261.418 nm; Cu 249.215 nm; Zn 213.856 nm
Signal measurement	Time-integrated (Area signal)
Calibration	External (0-100 µg L^{-1} Cd and 0-1000 µg L^{-1} Pb, Cu and Zn; n = 7 calibration standards in 2% (v/v) HNO$_3$ medium)

2. Calculation of the total concentration and DGT-based labile fraction of metals in soil

The principle is based on the algorithm described by Davison.[37,38] The mass of analyte (M) retained by binding resin gel from the uptake solution prepared for the total metal content determination in soil, and that retained from smooth soil paste for the determination of DGT-based labile fraction was calculated using eq. (1), considering the concentration (c) determined by SSETV-µCCP-OES and GFAAS in eluate:

$$M = \frac{c(V_{acid} + V_{gel})}{f_e}$$

(1)

where V_{acid} is the volume of 1 mol L^{-1} HNO$_3$ solution used for elution (1 mL); V_{gel} is the volume of the binding gel provided by the manufacturer (0.15 mL) and f_e is the elution factor of analytes from the binding gel in the HNO$_3$ solution.

The M was then used to calculate the time-averaged mean concentration in uptake solution or soil solution (c_{DGT}) using eq. (2), according to the first Fick's law of diffusion.[37,38]

$$c_{DGT} = \frac{M \times \Delta g}{D \times A \times t}$$

(2)

where Δg is the thickness of the effective diffusion layer (cm) given by the manufacturer of the DGT sampler (Δg = 0.094 cm = 0.080 cm thickness of the diffusive gel + 0.014 cm thickness of the filter membrane of polyethersulphone); A is the physical exposure area of the diffusion surface (3.14 cm^2); t is the deployment time for accumulation (s) and D is the diffusion coefficient of the analyte ion through the diffusion layer gel (cm^2 s^{-1}).

The c_{DGT} values were then used to calculate the total concentration and DGT-based labile fraction of analytes in soil according to the sample preparation protocol.

In calculus of M we used the f_e values experimentally determined (n = 3) under laboratory conditions based on the mass balance of analyte in CRM sample as difference between the mass in the uptake solution before and after removing the DGT device and mass in eluate, as well as the values recommended by the manufacturer (0.80).[37,38] Therefore, it was necessary to determine the analyte concentrations in the uptake solution before and after removing the DGT. Also, for the calculation of c_{DGT} we used both the diffusion coefficients experimentally determined in laboratory based on the uptake kinetics of the analytes from the CRM samples (Analyte accumulated mass/Analyte mass in uptake solution ratio-M/M_{soln}), versus deployment time), and the diffusion coefficients provided by the manufacturer for experiments in liquid samples (DGT Research Ltd., Lancaster, UK, https://www.dgtresearch.com/).

3. Matrix composition of CRMs and real samples of soil analyzed for total content and DGT-based labile fraction determination of Cd, Pb, Cu and Zn in soil

Table S2. Composition of the analyzed agricultural soil samples

Samples	Sampling site	Soil type	Soil texture	Sand (%)	Silt (%)	Clay (%)
1–3	1	Luvisol	Clay loam	25	43	32
4–6	2	Luvisol	Clay loam	33	40	27
7–10	3	Luvisol	Clay loam	27	43	30

Table S3. Matrix composition in uptake solution obtained from soil CRMs analyzed for total content determination of Cd, Pb, Cu and Zn by SSETV-µCCP-OES after DGT passive accumulation

CRM	Element concentrations by ICP-OES (mg L^{-1})										GFAAS (mg L^{-1})[b]
	Fe	Ni	Cr	Co	Mn	Ca	Mg	Na	K	Sr	As
SQC001 Metals in soil	1.00	0.02	0.03	0.01	0.09	0.39	0.19	0.17	0.65	0.04	0.004
CRM048 Trace metals – Sand 1	0.93	0.01	0.02	0.02	0.11	0.56	0.49	0.70	1.04	0.02	0.010
Metranal 34 Loam	1.98	0.01	0.01	0.01	0.10	1.24	0.79	0.03	0.59	0.02	0.004
CRM025–050 Metals in soil	0.92	<LOD[a]	0.03	<LOD	<LOD	2.82	0.49	0.11	14.1	0.05	0.036
Min.	0.92	0.01	0.01	0.01	0.09	0.39	0.19	0.03	0.59	0.02	0.004
Max.	1.98	0.02	0.03	0.02	0.11	2.82	0.79	0.70	14.1	0.05	0.036
Mean	1.21	0.01	0.02	0.01	0.10	1.25	0.49	0.25	4.10	0.03	0.014
Median	0.97	0.01	0.02	0.01	0.10	0.90	0.49	0.14	0.84	0.03	0.007
Standard deviation	0.49	0.004	0.01	0.004	0.01	1.05	0.24	0.29	6.34	0.01	0.015

[a] LODs (3σ criterion) obtained by ICP-OES (mg L^{-1}): Na 0.001; K 0.001; Mg 0.001; Ca 0.007; Fe 0.009; Cr 0.003; Mn 0.001; Co 0.004; Ni 0.004; Sr 0.005. [b]LOD obtained by GFAAS for As 0.001 mg L^{-1}.

Table S4. Matrix characterization of the uptake solution for the determination of total concentration of Cd, Pb, Cu and Zn in soil

Sample	Element concentrations by ICP-OES (mg L^{-1})[a]										GFAAS (mg L^{-1})[c]	Soil pH
	Fe	Ni	Cr	Co	Mn	Ca	Mg	Na	K	Sr	As	
S1	1.25	<LOD[b]	<LOD	<LOD	0.08	0.89	0.25	0.01	0.32	0.03	0.004	7.2
S2	1.27	<LOD	<LOD	<LOD	0.09	0.65	0.29	0.02	0.21	0.02	< LOQ[d]	7.1
S3	2.15	<LOD	<LOD	<LOD	0.15	0.59	0.32	0.03	0.20	0.02	0.033	7.0
S4	1.05	<LOD	<LOD	<LOD	0.05	0.49	0.23	0.02	0.17	0.02	0.003	7.2
S5	1.66	<LOD	<LOD	<LOD	0.14	0.64	0.22	0.02	0.15	0.05	0.012	7.3
S6	1.56	<LOD	<LOD	<LOD	0.10	0.74	0.40	0.02	0.19	0.02	0.011	6.9
S7	1.42	<LOD	<LOD	<LOD	0.08	0.56	0.21	0.03	0.17	0.03	0.004	7.2
S8	1.64	<LOD	<LOD	<LOD	0.11	0.38	0.22	0.03	0.13	0.02	0.022	6.5
S9	1.84	<LOD	<LOD	<LOD	0.13	0.24	0.17	0.02	0.11	0.01	0.017	7.2
S10	1.38	<LOD	<LOD	<LOD	0.05	0.49	0.19	0.01	0.12	0.01	0.010	7.1
Min.	1.05	-	-	-	0.05	0.24	0.17	0.01	0.11	0.01	< LOQ	6.5
Max.	2.15	-	-	-	0.15	0.89	0.40	0.03	0.32	0.05	0.033	7.3
Mean	1.52	-	-	-	0.10	0.57	0.25	0.02	0.18	0.02	0.013	7.1
Median	1.49	-	-	-	0.10	0.58	0.23	0.02	0.17	0.02	0.011	7.1
St. dev.	0.32	-	-	-	0.03	0.18	0.07	0.01	0.06	0.01	0.010	0.2

[a] Element concentrations in uptake solution resulted by 0.1 g soil sample digestion in 100 mL and 1:10 dilution, in which the DGT devices were immersed;

[b] LODs (3σ criterion) obtained by ICP-OES (mg L^{-1}): Na 0.001; K 0.001; Mg 0.001; Ca 0.007; Fe 0.009; Cr 0.003; Mn 0.001; Co 0.004; Ni 0.004; Sr 0.005. [c] LOD (3σ criterion) obtained by GFAAS for As 0.001 mg L^{-1}.[d] LOQ is the limit of quantification (LOQ = 3 x LOD)

Table S5. Matrix characterization of the soil solution for the determination of DGT-based labile fraction of Cd, Pb, Cu and Zn in soil

Sample	Element concentrations by ICP-OES (mg L^{-1})[a]										GFAAS (mg L^{-1})[d]	Anion concentrations (mg L^{-1})[a]				Carbon fraction concentrations (mg L^{-1})[a]			pH
	Fe	Ni	Cr	Co	Mn	Ca	Mg	Na	K	Sr	As	F$^-$	Cl$^-$	NO$_3^-$	SO$_4^{2-}$	DOC[c]	DIC[c]	TDC[c]	
S1	3.10	<LOD[b]	<LOD	<LOD	0.04	26.91	7.93	1.36	34.56	0.06	0.020	0.12	1.01	6.72	5.96	31.77	54.65	86.42	7.4
S2	0.48	<LOD	<LOD	<LOD	0.09	24.17	3.78	0.77	11.26	0.05	0.020	0.15	0.71	2.23	4.40	38.08	16.52	54.60	7.1
S3	1.42	<LOD	<LOD	<LOD	0.69	21.06	3.02	0.59	8.49	0.04	0.005	0.19	0.87	0.82	10.80	51.53	10.69	62.04	7.0
S4	0.49	<LOD	<LOD	<LOD	0.25	26.73	5.24	0.53	2.59	0.06	0.010	0.26	0.80	1.23	4.46	39.07	15.63	57.70	7.1
S5	0.63	<LOD	<LOD	<LOD	0.10	29.05	4.29	0.73	7.68	0.15	0.075	0.37	0.75	6.69	4.65	43.61	13.92	57.53	7.2
S6	0.31	<LOD	<LOD	<LOD	0.01	31.15	4.61	0.44	10.66	0.08	0.045	0.24	0.65	8.60	5.98	35.08	32.09	67.17	6.8
S7	1.58	<LOD	<LOD	<LOD	0.17	22.44	2.64	1.36	5.43	0.06	0.034	0.14	0.74	3.06	5.16	38.21	10.03	48.24	7.2
S8	2.57	<LOD	<LOD	<LOD	1.96	18.70	1.88	0.98	2.36	0.04	0.044	0.24	0.78	0.45	13.20	130.10	6.37	136.50	6.3
S9	21.53	<LOD	<LOD	<LOD	1.46	10.60	3.49	1.90	6.46	0.03	0.046	0.13	0.87	0.58	7.40	55.94	9.37	65.31	7.2
S10	0.71	<LOD	<LOD	<LOD	0.34	43.82	1.54	0.73	1.90	0.07	0.021	0.35	0.73	1.06	7.75	33.10	21.75	54.85	7.1
Min.	0.31	-	-	-	0.01	10.60	1.54	0.44	1.90	0.03	0.005	0.12	0.65	0.45	4.40	31.77	6.37	48.24	6.3
Max.	21.53	-	-	-	1.96	43.82	7.93	1.90	34.56	0.15	0.075	0.37	1.01	8.60	13.20	130.10	54.65	136.50	7.4
Mean	3.28	-	-	-	0.51	25.46	3.84	0.94	9.14	0.06	0.032	0.22	0.79	3.14	6.98	49.65	19.10	69.04	7.0
Median	1.06	-	-	-	0.21	25.45	3.63	0.75	7.07	0.06	0.028	0.22	0.77	1.73	5.97	38.64	14.78	59.87	7.1
St. dev.	6.48	-	-	-	0.67	8.71	1.85	0.47	9.53	0.03	0.021	0.09	0.10	3.04	2.94	29.32	14.51	25.87	0.3

[a] Concentration in bulk soil solution separated from soil paste by centrifugation and determined by ICP-OES for elements, As by GFAAS, ion chromatography for anions and multi N/C analysis for DOC and DIC;

[b] LODs (3σ criterion) obtained by ICP-OES (mg L^{-1}): Na 0.001; K 0.001; Mg 0.001; Ca 0.007; Fe 0.009; Cr 0.003; Mn 0.001; Co 0.004; Ni 0.004; Sr 0.005.

[c] DOC – dissolved organic carbon; DIC – dissolved inorganic carbon and TDC – total dissolved carbon.

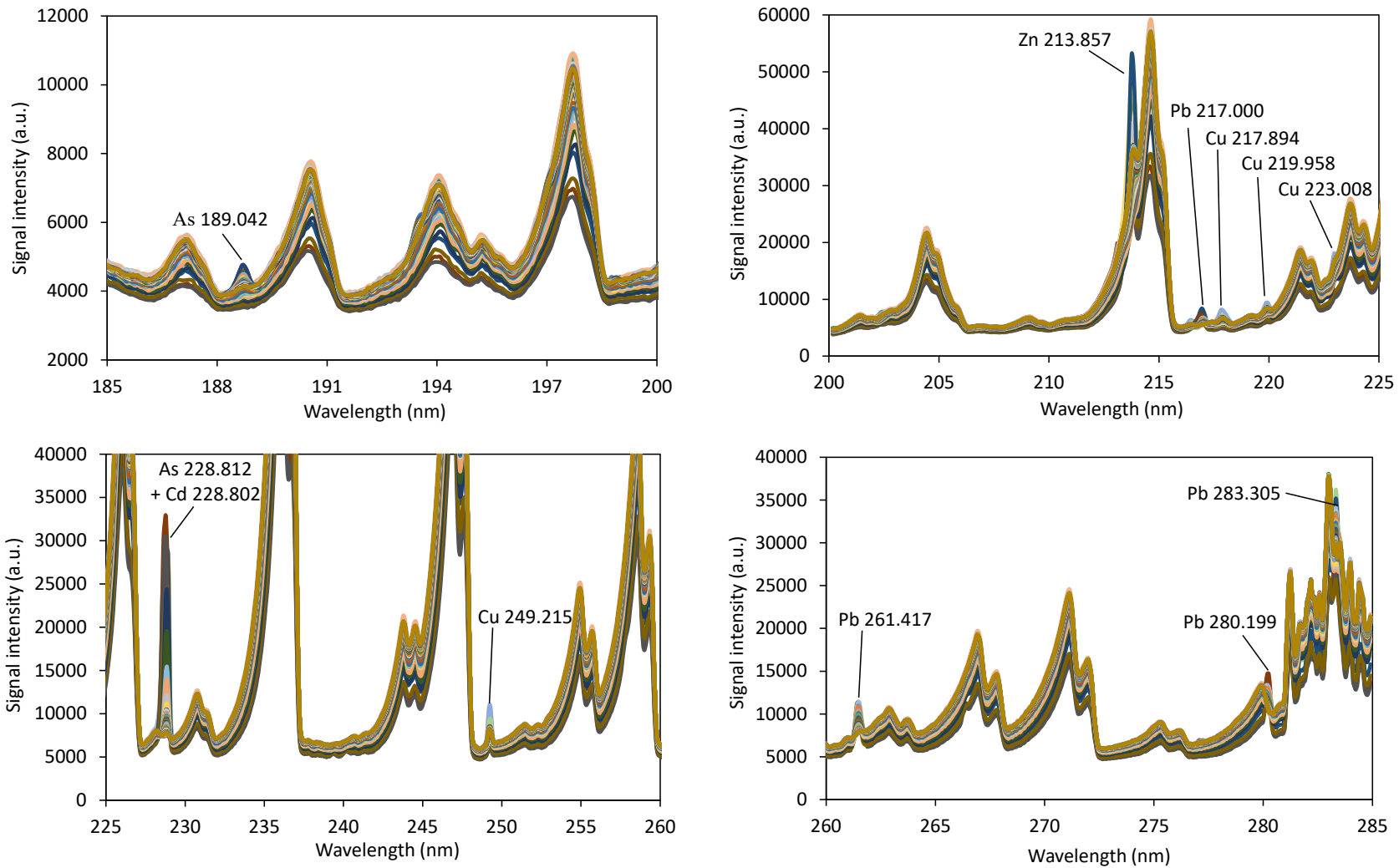[d] LOD (3σ criterion) obtained by GFAAS for As 0.001 mg L^{-1}

Fig. S1. Episodic emission spectrum obtained by SSETV-μCCP-OES for CRM048-50G after digestion in *aqua regia*. Plasma power: 15 W; Ar flow rate: 150 mL min^{-1}; observation height: 0.8 mm above the tip of Mo electrode. Analyte concentrations (μg L^{-1}): 90(Cd), 320(Pb), 80(Cu), 420(Zn) and 100(As) as concomitant.
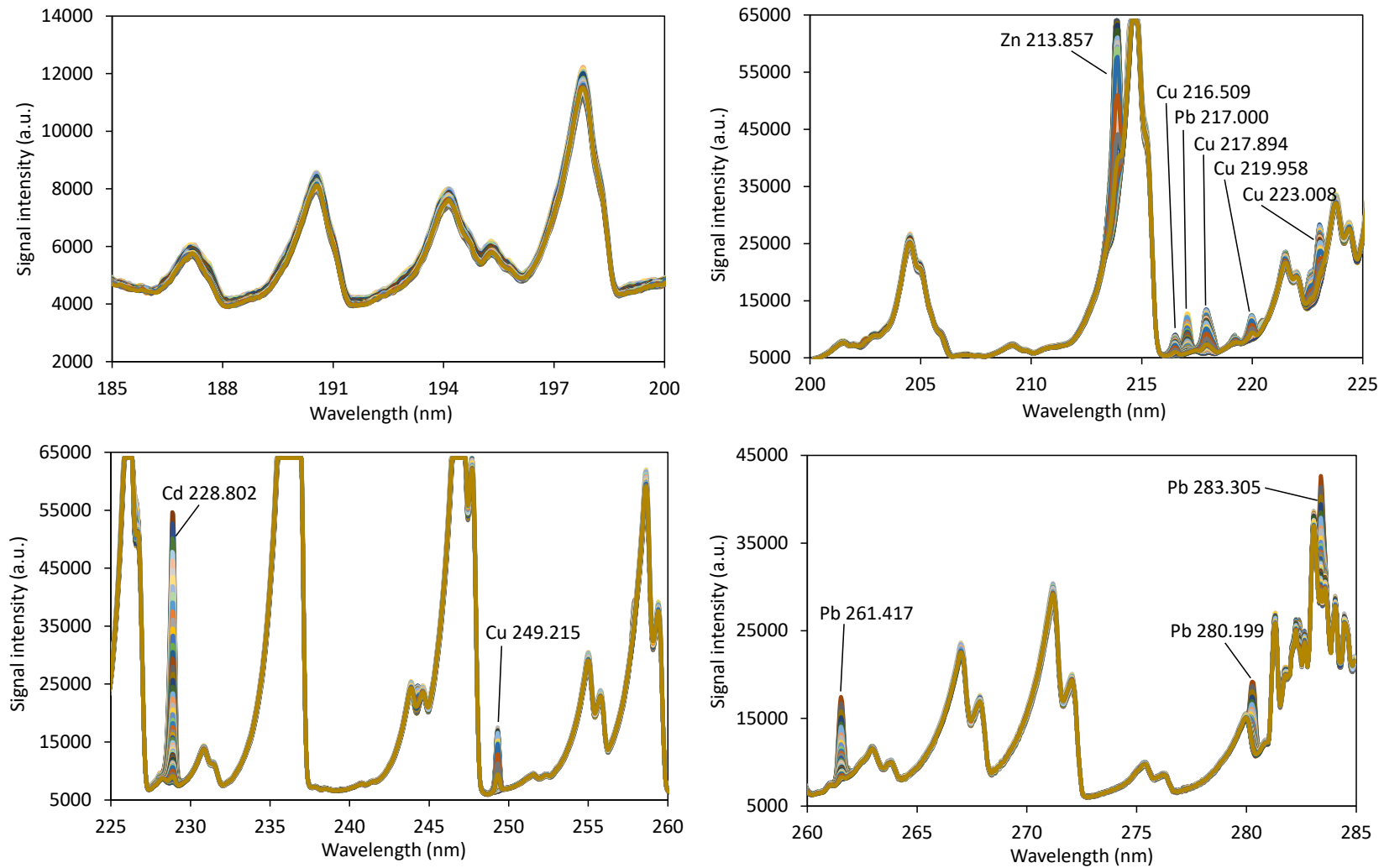
Fig. S2. Episodic emission spectrum obtained by SSETV-µCCP-OES in eluate after accumulation from an uptake solution prepared from CRM048-50G after digestion in *aqua regia,* 10-fold dilution. Plasma power: 15 W; Ar flow rate: 150 mL min^{-1}; observation height: 0.8 mm above the tip of Mo electrode; accumulation time: 24 h at 21 ± 1 °C and pH of 4.0 ± 0.1.

4. Results for the quantification of total content of Cd, Pb, Cu and Zn in CRM soils by SSETV-µCCP-OES and GFAAS without DGT passive accumulation

Table S6. Results for the quantification of total content of Cd, Pb, Cu and Zn in CRM soils by SSETV-µCCP-OES and GFAAS without DGT passive accumulation

CRM/Analyte	Certified concentration Mean ± U_{CRM} (mg kg^{-1})[a]	Found concentration without DGT accumulation Mean ± U_{lab} (mg kg^{-1})[b]		Accuracy Recovery ± U_{lab} (%)[b]	
		SSETV-µCCP-OES	GFAAS	SSETV-µCCP-OES	GFAAS
SQC001-30G					
Cd	118 ± 2	73 ± 14	137 ± 23	62 ± 19	116 ± 17
Pb	144 ± 2	94 ± 28	124 ± 17	65 ± 30	86 ± 14
Cu	330 ± 4	246 ± 47	287 ± 41	75 ± 19	87 ± 14
Zn	874 ± 11	546 ± 199	902 ± 148	62 ± 37	103 ± 16
CRM048-50G					
Cd	92.8 ± 1.55	69.1 ± 12.03	80.6 ± 17.82	74 ± 17	87 ± 22
Pb	320 ± 6.27	233 ± 76.22	268 ± 44.56	73 ± 33	84 ± 17
Cu	84.3 ± 1.45	70.3 ± 16.83	71.5 ± 12.33	83 ± 24	85 ± 17
Zn	425 ± 9.14	304 ± 36.80	403 ± 52.39	72 ± 12	95 ± 13
Metranal 34					
Cd	1.44 ± 0.07	0.99 ± 0.26	1.53 ± 0.26	69 ± 26	106 ± 17
Pb	83.1 ± 2.3	54.2 ± 12.1	75.1 ± 13.8	65 ± 22	90 ± 18
Cu	167 ± 1	115 ± 30	153 ± 23	69 ± 26	92 ± 15
Zn	198 ± 6	148 ± 39	215 ± 38	75 ± 26	108 ± 18
CRM025–050					
Cd	369 ± 19	276 ± 45	325 ± 52	75 ± 16	88 ± 16
Pb	1447 ± 88	841 ± 225	1596 ± 198	58 ± 27	110 ± 12
Cu	7.76 ± 0.73	5.79 ± 1.34	8.63 ± 1.27	75 ± 23	111 ± 15
Zn	51.8 ± 3.35	33.5 ± 4.32	42.3 ± 6.42	65 ± 13	82 ± 15

[a] – U_{CRM} is absolute expanded uncertainty for certified concentration (k = 2; 95% confidence level).

[b] – U_{lab} is absolute and relative expanded uncertainty in laboratory (k = 2, n = 3 parallel measurements and 95% confidence level)

5. Relative individual uncertainties and relative combined uncertainty of sample preparation protocol and analysis for the determination of total Cd, Pb, Cu and Zn in soil by SSETV-µCCP-OES and GFAAS after DGT passive accumulation
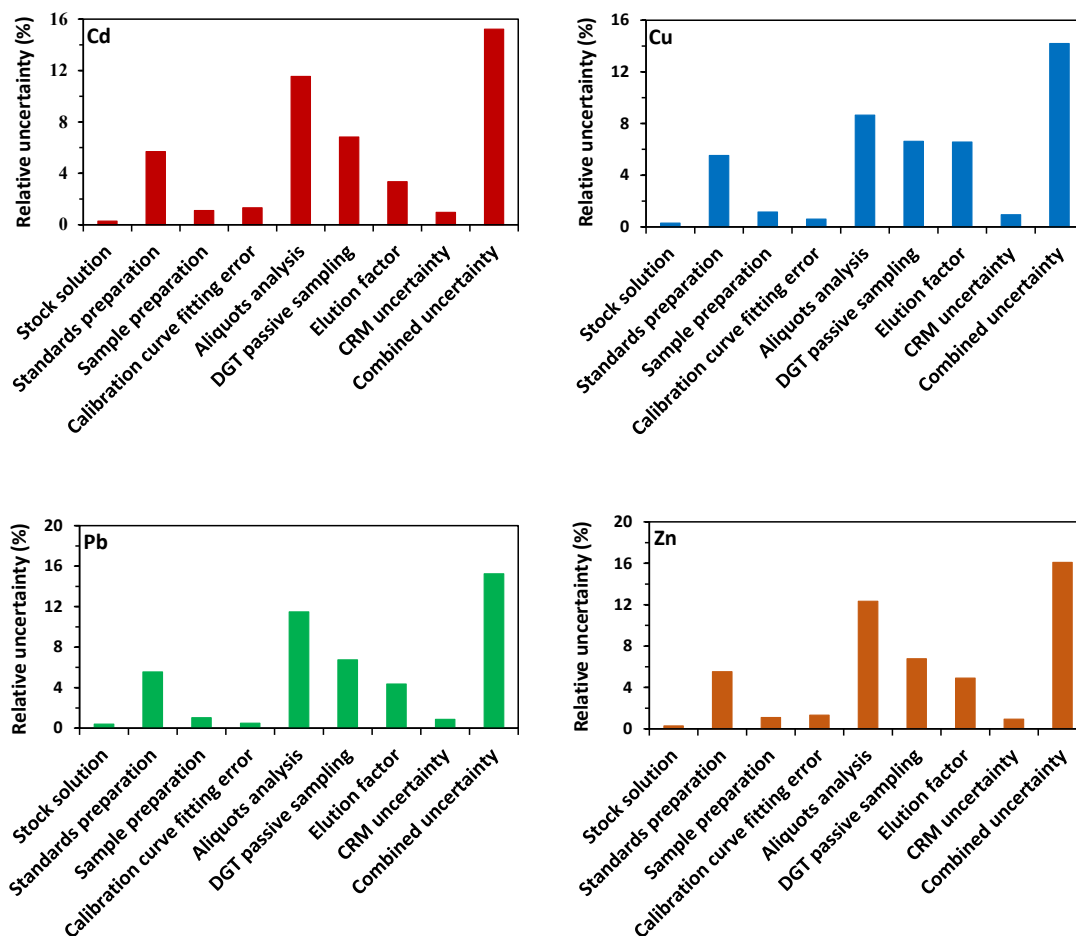

Fig. S3. Sources of the relative combined uncertainty in the determination of total Cd, Pb, Cu and Zn in soil CRMs by SSETV-µCCP-OES after DGT passive accumulation
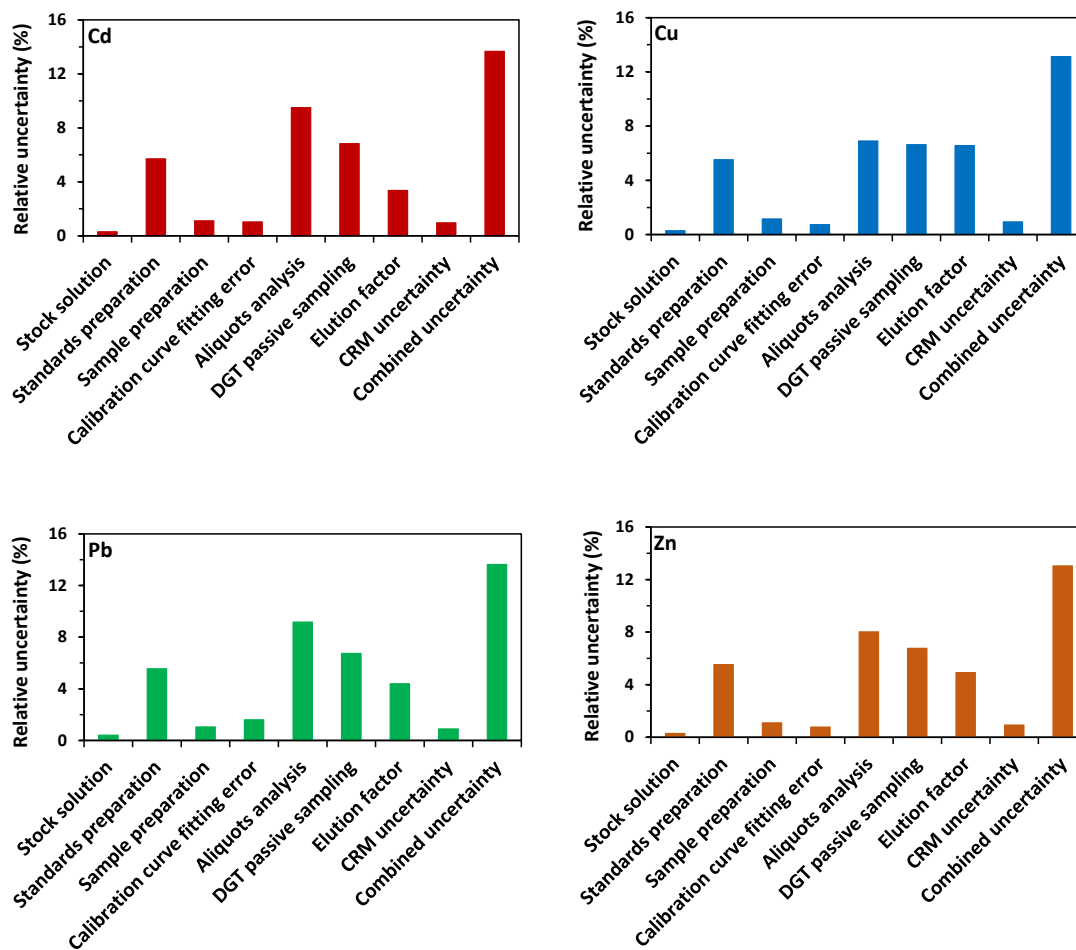
Fig. S4. Sources of the relative combined uncertainty in the determination of total Cd, Pb, Cu and Zn in soil CRMs by GFAAS after DGT passive accumulation

6. Bland–Altman plots for the comparison of total concentration and labile fractions of Cd, Pb, Cu and Zn in soil obtained by DGT-SSETV-µCCP-OES and DGT-GFAAS
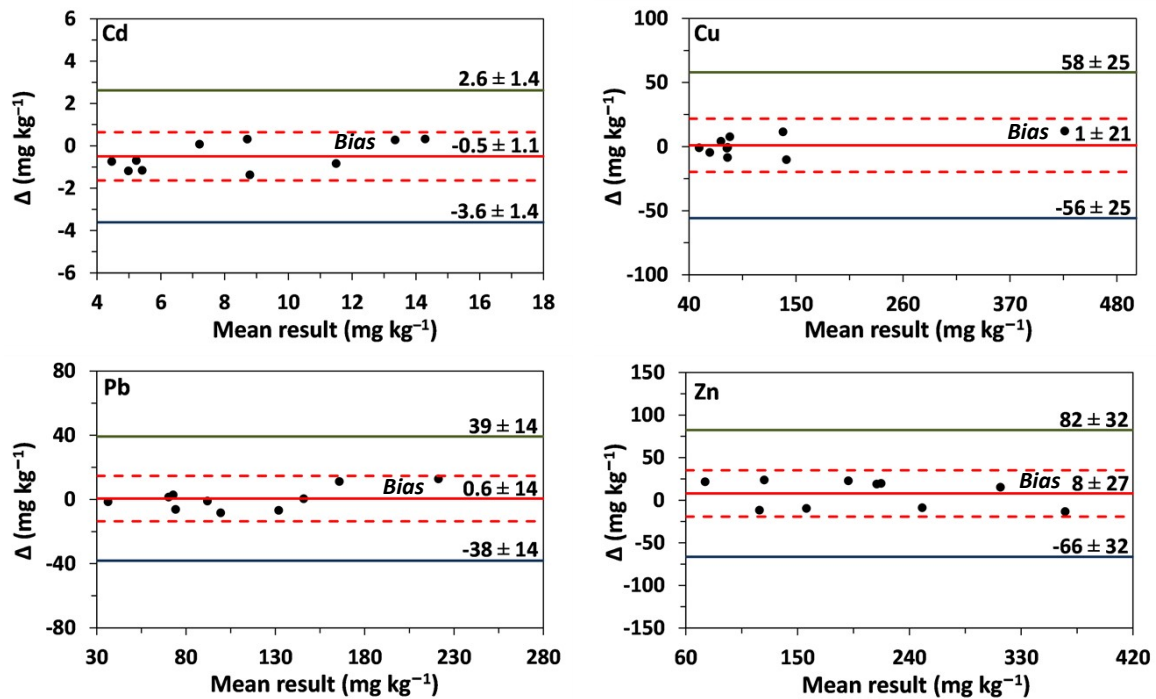

Fig. S5. Bland–Altman plots for the results obtained by DGT- SSETV-µCCP-OES and DGT-GFAAS for the total content of Cd, Pb, Cu and Zn in soil (n = 10 samples)
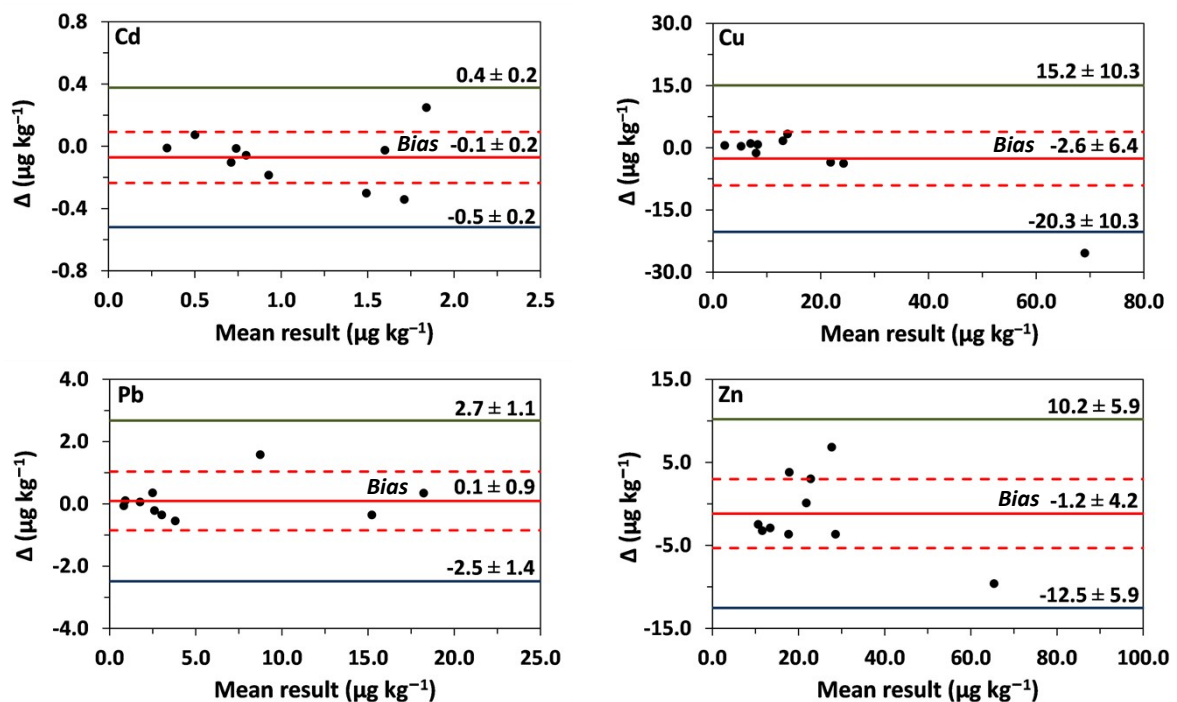

Fig. S6. Bland–Altman plots for the results obtained by DGT- SSETV-µCCP-OES and DGT-GFAAS for the labile fraction of Cd, Pb, Cu and Zn in soil (n = 10 samples)

7. The indicator evaluation of the ability of the solid phase of soil to resupply Cd, Pb, Cu and Zn into soil solution
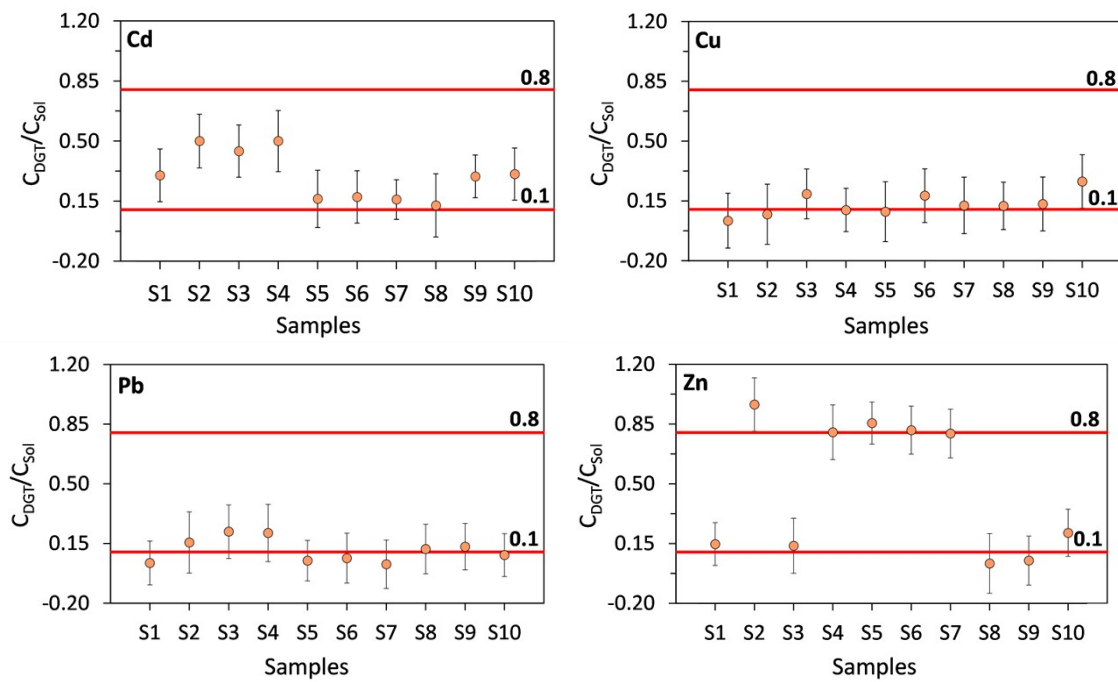

Fig. S7. Resupply (R) for Cd, Pb, Cu and Zn from solid soil to soil solution calculated as ratio of the concentration of the DGT-based labile fraction (c_{DGT}) and total dissolved concentration (c_{sol}) in soil solution. Error bars correspond to combined uncertainty (n = 3 measurement), while the red lines mark the limit value of 0.1 and 0.8 for low resupply capacity and sustained supply capacity, respectively.