An Environmentally Friendly Method for As, Cd, Cr, Cu, Ni, and Pb Determination in Terrestrial Moss Samples Using Ultrasonic Slurry Sampling Combined with Electrothermal Atomic Absorption Spectrometry

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ABSTRACT

Novel ultrasonic slurry sampling methods combined with the ETAAS determination of As, Cd, Cr, Cu, Ni, and Pb in terrestrial moss samples were developed without using corrosive acids. A pulverized moss sample between 1 to 50 mg (depending on element concentration) was placed into a 2.5 mL autosampler cup with 2 mL of HNO₃ (0.2 M), containing 0.01% of Triton X-100 reagent. The sample was then sonicated directly into the autosampler cup, using an ultrasonic probe at 85% power setting of 7 W for 25 seconds before injection.

Chemical modifiers were introduced directly into the graphite tube after sample introduction. An amount of 3 µg of Mg(NO₃)₂ and 5 µg of Pd was used as the chemical modifier for the As and Cu determination;

70 µg of NH₄H₂PO₄ and 4 µg of Mg(NO₃)₂ for Cd and Pb determination; and 20 µg of Mg(NO₃)₂ for Cr. Nickel (Ni) was determined without the addition of a chemical modifier. The methods were sensitive and precise, resulting in LODs of 51.3, 4.2, 94.4, 57.0, 124.7, 50.5 ng g⁻¹ for As, Cd, Cr, Cu, Ni and Pb, respectively, and RSDs of <10%. The accuracy was evaluated using certified reference materials GBW 07604 Poplar Leaves and Pseudoscleropodium purum (M2 and M3), and the results obtained were in good agreement with the certified values for all the elements studied.

The developed method was applied for element determination in real moss samples and to the best of our knowledge, no studies have previously reported trace element determination in moss samples using this methodology.

Commission for Europe, New York, USA) (15). Every five years, sampling surveys are performed across Europe, up to 4500 sites from 25 European countries in the last survey (15). The high number of samples and the number of elements usually determined in these studies requires reliable analytical techniques.

The trace elements included in ICP Vegetation reports are Al, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, V, and Zn (14). In the present study, we selected As, Cd, Cr, Cu, Ni, and Pb, most of which are included in the European Air Quality Directives. Several analytical techniques have been used for the determination of these elements in moss samples, such as electrothermal atomic absorption spectrometry (ETAAS), flame atomic absorption spectrometry (FAAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), instrumental neutron activation analysis (INAA), and atomic fluorescence spectrometry (AFS) (14). The use of these techniques varies among the studied elements. The most commonly used analytical techniques in moss analysis are ICP-MS and ICP-AES due to their high sensitivity and multi-elemental analysis capacity. However, this type of instrumentation is often too costly for some laboratories, while ETAAS is a technique available in most analytical laboratories and also offers high sensitivity for moss

INTRODUCTION

Several plants (Lichens, tree leaves, shrubs, Tillandsia, and mosses) were used in different studies for monitoring the atmospheric pollution (1–3). Among these, terrestrial mosses are the most commonly used biomonitors for trace metal atmospheric levels (4) and hundreds of scientific articles have been published (5–13).

These studies have shown that for some elements (e.g., Cd, Pb, etc.) there are significant correlations between bulk deposition and moss concentrations (10). For this reason, these organisms are studied by the International Cooperative Program on Effects of Air Pollution on Natural Vegetation and Crops, (ICP Vegetation) (13) who then report their findings of air pollutants to the Working Group on Effects of the Convention on Long-Range Transboundary Air Pollution (LRTAP, United Nation Economic

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analysis, especially for As, Cd, and Pb determination (7,14,16–18).

Microwave acid sample digestion was usually performed prior to trace metal determination in moss samples by ETAAS, ICP-OES, and ICP-MS (7–9,17). Nitric acid or mixtures of HNO₃ with H₂O₂ (7–9) were used for microwave acid digestion of moss samples for trace metal determination. The main drawbacks of sample acid digestion are the use of dangerous corrosive chemical products and the long time required for sample pre-treatment. An alternative methodology to conventional wet digestion procedures is the slurry sampling technique. This is a well-established methodology for the direct determination of trace metals in solid samples by atomic spectrometry (19), providing good analytical results and avoiding the use of dangerous and corrosive reagents. Although this methodology has been widely used for trace metal determination in several types of samples such as seafood (20,21), human hair (22), sediments and sludges (21,23,24), ambient aerosols (25), and plant materials (3,21,26,27), to the best of our knowledge, no studies have reported trace metal determination in moss samples using slurry sampling combined with ETAAS.

TABLE I
Characteristics of Radiation Sources

Element	Wave-length (nm)	Spectral Bandwidth (nm)	Lamp Current (mA)
As	193.7	0.7	39 ^a
Cd	228.8	0.7	4 ^b
Cu	324.8	0.7	25 ^b
Cr	357.9	0.7	30 ^b
Ni	232.0	0.7	25 ^b
Pb	283.3	0.7	10 ^b

^a EDL= Electrodeless discharge lamp;

^b HCL= Hollow cathode lamp.

The objective of this study was to develop sensitive, reliable, relatively rapid, and environmentally friendly methods for As, Cd, Cr, Cu, Ni, and Pb determination in real terrestrial moss samples using ultrasonic slurry sampling combined with ETAAS.

EXPERIMENTAL

Instrumentation

For this study, a PerkinElmer AAnalyst™ 600 atomic absorption spectrometer with Zeeman background correction was used, equipped with an AS 800 autosampler, provided with a USS 800 titanium ultrasonic probe (PerkinElmer, Inc., Shelton, CT, USA). The radiation sources were hollow cathode lamps for Cd, Cu, Cr, Ni, and Pb and an electrodeless discharge lamp operated from an external power supply for As. The instrumental operating conditions are listed in Tables I and II. Pyrolytically coated graphite tubes with L'vov platforms were used for the elements studied. Integrated absorbance with an integration time of 3 seconds was used for As, Cd, and Pb, and 5 seconds for Cu, Cr, and Ni. The injected sample volume was 20 µL.

An ultracentrifuge mill ZM 200 (Retsch, Haan, Germany), equipped with titanium components, was used to reduce the particle size of the moss samples (less than 50 µm). A microbalance Excellence Plus,

XP 26 (± 0.001 mg) from Mettler Toledo® (Greifensee, Switzerland) was used to weigh the samples.

Standard Solutions and Reagents

Stock standard solutions for As, Cd, Cu, Cr, Ni, and Pb of 1000 µg L⁻¹ each were obtained from Panreac (Spain). Each test solution was prepared with ultrapure water (obtained from a Milli-Q® water-purification system, Millipore Corporation, USA) immediately before use.

Triton® X-100, polyethylene glycol mono(p-1,1,3,3-tetramethyl-phenyl) ether, was obtained from Merck (Darmstadt, Germany).

Palladium nitrate 10 g L⁻¹ in HNO₃ (15%) (Merck, Darmstadt, Germany), magnesium nitrate (Merck), and NH₄H₂PO₄ (99.999%) (Aldrich Chemical, Milwaukee, WI, USA) were used as the chemical modifiers.

Certified reference material GBW 07604 Poplar Leaves (Institute of Geophysical and Geochemical Exploration, Langfang, P.R. China) was used in the accuracy study. Also used were two moss samples (*Pleurozium scherberi*) M2 and M3 (collected in Harjavalta near a metal smelter at 61°22'N 22°12'E) and obtained for inter-laboratory comparison studies with the University of Santiago de Compostela, Spain (28).

TABLE II
AAnalyst 600 AAS Graphite Furnace Programs for As, Cd, Cu, Cr, Ni, and Pb Determination in Terrestrial Moss Samples

Step	Temperature (°C)	Ramp Time (s)	Hold Time (s)	Argon flow (mL min ⁻¹)
Dry 1	110	1	30	250
Dry 2	130	15	30	250
Pyrolysis	Var.	10	20, 30 ^a	250
Atomization	Var.	0	3 ^b , 5 ^c	0 (read)

^a For Pb; ^b As, Cd, and Pb; ^c for Cu, Cr, and Ni.

Sample Preparation

Terrestrial moss samples were collected around a ferrous smelter (Meg), a non-ferrous smelter (Alc), and in a background area (OSE). Collection of the moss samples was performed according to the methods developed for this moss species (29–32). The samples were picked by hand using gloves (talcum-free) and placed into polyethylene bags. In the laboratory, the samples were stored at 4 °C until sample processing (within 24–48 hours). After this, the apices of the shoots (3–4 cm) were cut from the moss *Pseudoscleropodium purum*. The samples were then dried to constant weight in a Dry-Big forced-air oven (Selecta) at 40°C. The dried samples were then pulverized in a Retsch ZM200 metal-free mill (particle size of less than 100 µm, Retsch Haan, Germany) and stored in a polyethylene vial (acid-washed with 10% v/v nitric acid for 24 hours) until ETAAS analysis.

Procedure for Slurry Preparation

A mass of pulverized moss sample (between 1 and 50 mg) was placed into a 2.5 mL autosampler cup containing 2 mL of HNO₃ (0.2 M) and 0.01% of Triton X-100. The sample was then sonicated using an ultrasonic probe (at 85% power setting – 7 W) for 25 seconds before injection directly into the autosampler cup.

Element Determination by ETAAS

A volume of 20 µL of the slurry sample, prepared as described above, with 5 µL of the respective chemical modifiers used for the different elements, were introduced into the graphite furnace tube for analysis. Amounts of 3 µg Mg(NO₃)₂ and 5 µg Pd were the chemical modifiers for As and Cu determination; 70 µg NH₄H₂PO₄ and 4 µg Mg(NO₃)₂ for Cd and Pb determination; and 20 µg Mg(NO₃)₂ for Cr.

Nickel was determined without the addition of a chemical modifier. The instrumental conditions as well as the graphite furnace programs used for the determination of these elements are listed in Tables I and II.

RESULTS AND DISCUSSION

Optimization of Graphite Furnace Program

Experiments were performed to determine the optimum temperatures and times for the drying, mineralization, and atomization steps. The study was performed using an aqueous standard of the element studied and a moss slurry sample (prepared as described in the Procedure section above) and using Pd-Mg(NO₃)₂ as the chemical modifier for As and Cu, NH₄H₂PO₄-Mg(NO₃)₂ for Cd and Pb, and Mg(NO₃)₂ for Cr. Two drying steps (110 °C and 130 °C) were used (Table III).

Determination of the optimum mineralization temperatures were performed varying the mineralization temperature from 900 to 1400 °C for As, 500–1000 °C for Cd, 1000–1700 °C for Cr, 800–1500 °C for Cu, 800–1400 °C for Ni, and 600–1100 °C for Pb. Taking into account the results obtained, 1300 °C, 700 °C, 1200 °C, 1300 °C, 1200 °C, and 900 °C were selected as the optimum mineralization tempera-

tures for As, Cd, Cu, Cr, Ni, and Pb, respectively (Table III).

Optimization of the atomization temperatures was performed in the same way, working in the temperature ranges of 2000–2400 °C for As, 1200–1600 °C for Cd, 1600–2300 °C for Cu, 1500–2400 °C for Cr, 1800–2400 °C for Ni, and from 1300–1800 °C for Pb. The selected optimized temperatures were 2100 °C, 1300 °C, 1900 °C, 2200 °C, 2300 °C, and 1500 °C for As, Cd, Cu, Cr, Ni and Pb, respectively (Table III). These temperatures were selected taking into account the integrated absorbance as well as the peak profile. The influence of ramp times and hold times for each step was also studied, and the optimized graphite furnace programs are listed in Table II.

Amount of Chemical Modifier

Selection of the chemical modifiers used for ETAAS determination of the elements was based on previous studies (20,22,24,27,33–35) as well as per the manufacturer's (PerkinElmer, Inc.) recommendations (36,37). As listed above, Pd-Mg(NO₃)₂ was selected as the chemical modifier for As and Cu determination, NH₄H₂PO₄-Mg(NO₃)₂ for Cd and Pb, and Mg(NO₃)₂ for Cr determination. Ni was determined without the addition of a chemical modifier.

Experiments were performed to select the optimum amounts of these modifiers. A series of measurements were performed to determine the optimum quantities of both palladium and magnesium nitrate for As and Cu determination. Therefore, a series of measurements were performed adding different amounts of both modifiers. The amount of palladium varied from 0 to 6 µg and the amount of Mg(NO₃)₂ varied between 0 and 5 µg. Taking into account the integrated absorbance obtained and the peak profiles, amounts of 5 and 3 µg of palladium

TABLE III
Mineralization and Atomization Temperatures for As, Cd, Cr, Cu, Pb, and Ni Determination in Slurries of Moss Samples

Element	Mineralization Temperature (°C)	Atomization Temperature (°C)
As	1300	2100
Cd	700	1300
Cr	1300	2200
Cu	1200	1900
Pb	1200	2300

and magnesium nitrate, respectively, were selected for As and Cu determination.

Amounts of $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{Mg}(\text{NO}_3)_2$ were optimized for Cd and Pb determination. The amount of $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{Mg}(\text{NO}_3)_2$ required was studied in the range of 0–80 μg and 0–6 μg , respectively. Taking into account the integrated absorbance obtained, 70 and 4 μg of $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{Mg}(\text{NO}_3)_2$, respectively, were selected as the optimum amounts for the determination of both elements.

The amount of $\text{Mg}(\text{NO}_3)_2$ varied from 0–40 μg for Cr determination and 20 μg of this modifier was selected.

Influence of Acid Media on Slurry Preparation

After preparation of the slurry and to mobilize several elements into the solution, several authors used an acid media. Thus, only a portion of the trace elements pre-

sent remained in the solid phase, which is nevertheless dispensed together with the enriched solution into the atomizer during sampling (38,39). Several acids have been reported in the literature for slurry preparation including HNO_3 (8,9,40), a combination of HNO_3 plus H_2O_2 (41,42), HNO_3 , H_2O_2 , plus HF (43), and HNO_3 plus HClO_4 (44). HNO_3 is widely used to prepare slurries of different types of samples such as seafood (20,21), hair (22), plants (3), or sediments (23). Taking into account the results reported in these reports, experiments were performed in our laboratory using HNO_3 (containing 0.01% of Triton X-100) as a liquid media to prepare the slurry. The influence of the HNO_3 concentrations was studied in the range of 0 to 1.0 M. The results obtained (Figure 1) show that the integrated absorbance increased with the HNO_3 concentration up to 0.2 M, and remained practically constant or slightly decreased at higher con-

centrations. Therefore, in order to obtain the best analytical response, for the present study 0.2 M HNO_3 (containing 0.01% of Triton X-100) was selected as the liquid medium to prepare the slurry of terrestrial moss samples.

Calibration and Analyte Addition Graphs

To obtain calibration graphs of standard aqueous solutions containing concentrations of 0–30 $\mu\text{g L}^{-1}$ for As, 0–6 $\mu\text{g L}^{-1}$ for Cd, 0–120 $\mu\text{g L}^{-1}$ for Cu and Pb, 0–90 $\mu\text{g L}^{-1}$ for Cr, and 0–60 $\mu\text{g L}^{-1}$ for Ni, appropriate amounts of Triton X-100 solution were added. The standard addition method was used in the same range of concentrations using a terrestrial moss sample. The slopes as well as the correlation coefficients (r) obtained for the calibration and addition graphs are shown in Table IV. Both the calibration and the addition graphs show good linearity, with correlation coefficients higher than 0.995 for all the

Fig. 1. Influence of HNO_3 concentration in the liquid media used to prepare the slurry in the integrated absorbance for the As, Cd, Cr, Cu, Ni and Pb determination by ETAAS.

elements studied. Moreover, both graphs exhibit similar slopes for all elements. This means that aqueous calibration is a real possibility, and this type of calibration was therefore used.

Sensitivity

Sensitivity was studied using three parameters: the limit of detection (LOD), the limit of quantification (LOQ), and the characteristic mass (m_0) (45). The LODs and LOQs obtained are listed in Table V. These limits were calculated based on 10 replicate determinations of the blank. The instrumental LODs obtained varied from 0.031 $\mu\text{g L}^{-1}$ for Cd to 0.94 $\mu\text{g L}^{-1}$ for Ni. These limits are lower than those obtained by Serpil (43) for the determination of these elements in lichen samples using ICP-OES (0.22, 2.3, 1.4, 2.3, and 7.4 $\mu\text{g L}^{-1}$ for Cd, Cr, Cu, Ni and Pb, respectively). The LOD and LOQ values for the moss sample, using 15 mg of sam-

ple and diluting it to a final volume of 2 mL to obtain the slurry, are also shown in Table V. These limits vary from 4.2 ng g^{-1} for Cd to 124.7 ng g^{-1} for Ni.

The characteristic mass (m_0) is defined as the mass of the analyte (in picograms) required to give a signal of 0.0044 for the integrated absorbance. The m_0 values obtained were 31.0 ± 6.2 , 1.3 ± 0.2 , 8.5 ± 1.6 , 15.8 ± 1.6 , 24.4 ± 0.4 , and 33.1 ± 3.6 pg for As, Cd, Cu, Cr, Ni and Pb, respectively. The characteristic mass values are in agreement with the manufacturer's recommendations (37).

Precision and Accuracy

The within-run precision (relative standard deviation, RSD) of the method was obtained for 10 replicate analyses of slurry of the internal reference material (*Pseudo-scleropodium purum*). The RSDs obtained were 4.5, 0.14, 3.7, 4.1, 2.2, and 3.7% for As, Cd, Cr, Cu, Ni

and Pb, respectively. These values are lower than 10%, indicating good precision.

To study the accuracy of the method, three different slurries of the certified reference material GBW 07604 (for Cd, Cu, and Pb), M2 (As and Ni), M3 (Cr), and a blank were measured. The results listed in Table VI were compared with the certified concentrations using a Students *t*-test (95% significance) (46). No statistical differences between both concentrations were found; thus, it can be concluded that the method suggested is accurate.

The recovery was also calculated, and the mean recoveries obtained were $101 \pm 0.9\%$ for As (5, 10, 30 $\mu\text{g L}^{-1}$ added), $103 \pm 6\%$ for Cd (1, 2, 6 $\mu\text{g L}^{-1}$ added), $96 \pm 2\%$ for Cr (15, 30, 90 $\mu\text{g L}^{-1}$ added), $106 \pm 1\%$ for Cu (15, 30, 6 $\mu\text{g L}^{-1}$ added), $97 \pm 7\%$ for Ni (10, 20, 60 $\mu\text{g L}^{-1}$ added), and $106 \pm 2\%$ for Pb (30, 60, 120 $\mu\text{g L}^{-1}$ added). The recovery percentages

TABLE IV
Slopes and Correlation Coefficients for the Calibration and Addition Graphs

Element	Concentrations ($\mu\text{g L}^{-1}$)	Aqueous Calibration		Addition	
		Slope	r	Slope	r
As	0, 5, 10, 20, 30	0.0032	0.9991	0.0033	1.0000
Cd	0, 1, 2, 6	0.0629	0.9984	0.0615	0.9993
Cu	0, 15, 30, 60, 120	0.0052	0.9989	0.0053	0.9950
Cr	0, 15, 30, 90	0.0091	0.9978	0.0090	0.9995
Ni	0, 15, 30, 60, 120	0.0036	1.0000	0.0038	0.9990
Pb	0, 10, 20, 60	0.0025	0.9987	0.0023	0.9970

TABLE V
LOD and LOQ for As, Cd, Cr, Ni and Pb in Slurries of Terrestrial Moss Samples

Element	LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)	LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)
As	0.38	1.28	51.3	171.2
Cd	0.031	0.10	4.2	13.9
Cr	0.71	2.36	94.4	314.7
Cu	0.43	1.42	57.0	189.9
Ni	0.94	3.12	124.7	415.9
Pb	0.38	1.26	50.5	

TABLE VI
Accuracy of the Method

Element	CRM Material	Certified Content ($\mu\text{g g}^{-1}$)	Concentration Obtained (mean $\pm$ SD) ($\mu\text{g g}^{-1}$)
As	M2	0.98 ± 0.07	0.95 ± 0.02
Cd	CRM GBW 07604	0.32 ± 0.05	0.32 ± 0.01
Cu	CRM GBW 07604	9.3 ± 0.5	9.2 ± 0.2
Cr	M3	0.67 ± 0.19	0.66 ± 0.06
Ni	M2	16.3 ± 0.9	16.4 ± 0.4
Pb	CRM GBW 07604	1.5 ± 0.2	1.44 ± 0.1

were around 100% for all of the elements studied; therefore, the method shows good analytical recovery.

Application

The method was applied to the determination of As, Cd, Cu, Cr, Ni, and Pb in different terrestrial moss samples collected around a ferrous smelter (Meg), a non-ferrous smelter (Alc), and in a background area (OSE). Collection of the moss samples was performed according to the methods developed for this moss species (48–50).

The collected samples were then prepared as described in the Sample Preparation section. Two sub-samples from each moss sample were prepared as slurry, and the analysis of the slurry was performed in duplicate. The results in Table VII show that the As concentrations varied from 205.8 (OSE) to 734.1 $\mu\text{g kg}^{-1}$ and the arsenic concentrations in the terrestrial moss samples collected around both smelters were two or three times higher than the concentrations found in the background area. Cadmium concentrations at OSE varied from 70.2 to 1142.2 $\mu\text{g kg}^{-1}$ and the highest concentrations were found in the samples collected around a ferrous smelter (Meg) (398–1142 $\mu\text{g kg}^{-1}$). Chromium concentrations (OSE) varied from 0.82–71.4 mg kg^{-1} . Chromium concentrations in Meg

and Alc samples were from 4 to 87 times higher than the OSE sample (background area) and, in general, the highest concentrations were found in the Meg samples. Copper and nickel concentrations varied from 7.3 to 36.5 and from 2.1 to 36.5 mg kg^{-1} , respectively. Lead concentrations varied from 0.7 (OSE) to 165.5 (Meg) mg kg^{-1} . The highest lead concentrations were found in Meg samples.

CONCLUSION

An environmentally friendly method for As, Cd, Cu, Cr, Ni, and Pb determination in slurries of terrestrial moss samples by ETAAS was developed. To the best of our knowledge, this is the first time that trace elements were determined in moss samples using this methodology. This method decreases the number of sample pretreatment steps (such as sample digestion) and avoids the use of corrosive reagents used in acid digestion methods. This reduces sample preparation time (requires less than five minutes) and reduces the possibility of sample contamination due to sample manipulation and reagents used. The USS 800 titanium ultrasonic slurry sampler used in this work is no longer commercially available. However, the slurry sample can be prepared using an external ultrasonic probe and then introduced into the

graphite tube using the autosampler.

The method was accurate and precise and presented high sensitivity for the elements studied, with detection limits lower (LODs from 0.031 $\mu\text{g L}^{-1}$ for Cd to 0.94 $\mu\text{g L}^{-1}$ for Ni) than those found in the literature (0.22, 2.3, 1.4, 2.3, 7.4 $\mu\text{g L}^{-1}$ for Cd, Cr, Cu, Ni and Pb, respectively) for the determination of these elements in these types of samples (43).

The method was applied to the determination of As, Cd, Cu, Cr, Ni, and Pb in different terrestrial moss samples collected around a ferrous smelter (Meg), non-ferrous smelter (Alc), and in a background area (OSE). Element concentrations varied from 205.8 to 734.1 $\mu\text{g kg}^{-1}$ for As; 70.2 to 1142.2 $\mu\text{g kg}^{-1}$ for Cd; 0.82 to 71.4 mg kg^{-1} for Cr; 7.3 to 36.5 mg kg^{-1} for Cu; 2.1 to 36.5 mg kg^{-1} for Ni, and 0.7 to 165.5 mg kg^{-1} for Pb. These concentrations were similar to those reported in the literature; moreover, the analytical method allows determining concentrations in a wide range of concentrations depending on the mass of the sample used for slurry preparation.

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TABLE VII
Concentration (mean $\pm$ Standard Deviation) of As, Cd, Cr, Cu, Ni, and Pb in Different Terrestrial Moss Samples

Sample	As (mg kg^{-1})	Cd (mg kg^{-1})	Cr (mg kg^{-1})	Cu (mg kg^{-1})	Ni (mg kg^{-1})	Pb (mg kg^{-1})
1Meg	480 $\pm$ 8.2	398.5 $\pm$ 34.7	2.27 $\pm$ 0.04	14.8 $\pm$ 0.84	3.7 $\pm$ 0.35	25.1 $\pm$ 0.6
2Meg	522 $\pm$ 42.5	606.6 $\pm$ 4.3	15.21 $\pm$ 2.1	20.4 $\pm$ 0.61	6.4 $\pm$ 0.12	48.5 $\pm$ 3.9
3Meg	434.2 $\pm$ 2.4	1126.5 $\pm$ 3.6	25.50 $\pm$ 3.56	33.2 $\pm$ 4.8	9.9 $\pm$ 0.24	111.9 $\pm$ 1.7
4Meg	734.1 $\pm$ 6.9	1142.2 $\pm$ 12.2	71.37 $\pm$ 4.35	36.8 $\pm$ 1.4	10.6 $\pm$ 2.1	165.5 $\pm$ 29.0
5Alc	571.5 $\pm$ 39.0	228.3 $\pm$ 0.2	9.05 $\pm$ 0.15	8.2 $\pm$ 0.30	21.4 $\pm$ 1.3	2.2 $\pm$ 0.013
6Alc	603.2 $\pm$ 63.1	186.5 $\pm$ 1.3	4.90 $\pm$ 0.90	12.1 $\pm$ 0.93	36.5 $\pm$ 2.9	6.0 $\pm$ 0.16
7Alc	598.0 $\pm$ 18.5	227.2 $\pm$ 1.3	3.28 $\pm$ 0.28	8.5 $\pm$ 0.1	14.8 $\pm$ 3.9	2.7 $\pm$ 0.5
8OSE	205.8 $\pm$ 30.4	70.2 $\pm$ 0.20	0.82 $\pm$ 8 $\times$ 10 ⁻⁴	7.3 $\pm$ 0.06	2.1 $\pm$ 0.18	0.7 $\pm$ 0.03

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