Preparation and characterization of a soil reference material from a mercury contaminated site for comparability studies

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Abstract

The preparation and characterization of a soil reference material (SOIL-1) from a site polluted with mercury due to the past mercury mining in Idrija, Slovenia is reported. Homogeneity tests and intercomparison exercises for total (T-Hg) and methylmercury (MeHg) were performed. In addition, selective sequential extraction was applied for Hg fractionation, and multielemental analyses were performed by k_0 standardization neutron activation analysis (k_0-INAA) and inductively coupled mass spectrometry (ICP-MS) for other trace elements. Comparison of different analytical methods, as well as the distribution of data were critically evaluated using descriptive statistics and analysis of variance (ANOVA). Due to the nugget effect (cinnabar particles representing more than 90% of the mercury), homogeneity for T-Hg determination was difficult to achieve. The intercomparison exercise indicated that in order to obtain comparable results for total mercury (T-Hg) sample decomposition by HF must be performed. These data are then in good agreement with non-destructive methods such as k_0-INAA. Accepted reference values calculated taking into account the results obtained by six and three laboratories, respectively, were $67.1 \pm 11.3\,mg\,kg^{-1}$ for T-Hg and $4.0 \pm 1.3\,ng\,g^{-1}$ for MeHg (95% confidence intervals). However, the results obtained for Hg fractionation displayed significant differences in the organically bound fraction and elemental Hg. Results obtained by two laboratories using totally different analytical protocols for other elements showed excellent agreement for most elements. In summary, the results obtained for the SOIL-1 sample were of sufficient quality to suggest its use for quality control in laboratories dealing with mercury contaminated soils.

Keywords: Reference material; Mercury; Soils

1. Introduction

Soils and sediments are known to be accumulation pools for metals. Regarding mercury pollution, these environmental compartments are also critical from another point of view—they are important sites where Hg(II) is methylated to the most toxic Hg compound—methylmercury $MeHg^+$. Mercury in soil can also undergo other important transformation mechanisms such as reduction to elemental Hg and demethylation of $MeHg^+$. It is generally accepted that there is still a gap in our knowledge of the biogeochemistry of Hg in soils and sediments. In addition there is a lack of suitable "matrix" reference materials (RMs) for mercury analysis and speciation in contaminated soils. Only a few of them are certified, with

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concentrations ranging from 20 ng g^{-1} to about 6 μg g^{-1} with uncertainties from 8% to 31%. The stated concentrations refer to either "aqua regia extractable", "boiling HNO_3" or "cold HNO_3 extractable" mercury (IAEA, 1995). The present status of Hg in sediments is slightly better—there are a few RMs certified for both total (T-Hg) and methylmercury (MeHg), but they are mostly of marine origin (Horvat, 1999). Clearly, the existing RMs do not cover the needs for Hg studies and monitoring in contaminated areas where T-Hg concentrations are elevated (above several tens of μg g^{-1}).

Therefore, the aim of our work was to prepare a RM suitable for Hg studies in contaminated sites. Polluted soil (SOIL-1) from an area close to the Idrija mercury mine, Slovenia, was chosen. That soil is contaminated with Hg due to continuous deposition of particles enriched with Hg during flood events. Such a sample is representative of areas where mercury transport and deposition is governed by river hydrology, which is typical in a number of mercury contaminated environments. The work was conducted by the International Atomic Energy Agency (IAEA) and IJS in the framework of an IAEA Coordinated Research Project (CRP) "Health impacts of mercury cycling in contaminated environments studied by nuclear techniques". In this paper, the preparation and characterization of SOIL-1 by means of sample homogeneity measurements and interlaboratory studies are reported. All laboratories of the CRP participants were encouraged to participate in the data quality intercomparison exercises by analyzing total and MeHg in the samples by their usual techniques. The sample was also analyzed in two laboratories for other elements using INAA and ICP-MS methods. Further characterization included differentiation of Hg compounds in SOIL-1 into different behavioral classes by a sequential extraction scheme adopted from Bloom et al. (2003).

2. Methodology

2.1. Preparation of SOIL-1

2.1.1. Origin of SOIL-1

About 100 kg of soil sample was collected in polyethylene containers on 27th February 2001 from the grassland at Bača pri Modreju that is frequently flooded by the river Idrijca (Fig. 1). Surface soil was taken by a plastic shovel. The sample was then transported to the Department of Environmental Sciences at the Jožef Stefan Institute, Ljubljana for further preparation. The same sampling site has been regularly monitored since 1995 and the concentrations of total Hg were reported to be in the range between 40 and 50 mg kg^{-1} dry weight, while MeHg concentrations varied from 3 to 5 ng g^{-1}.

2.1.2. Preparation of bulk material and bottling

The soil was air dried at 40 °C in a drying oven for 3 days. Samples were then ground and homogenized in a rotating ceramic ball mill for 60 min, sieved first through a 1.4 mm screen and then through a 250 μm screen. Since the preliminary data on bulk homogeneity indicated noticeable non-homogeneities, it was decided to re-homogenize the samples. The results were still not satisfactorily homogeneous, therefore sieving through a 125 μm screen had to be conducted. The whole content of the sample was then homogenized in a plastic rotating container for 3 days. Based on demonstrated homogeneity of the bulk material for a 500 mg sample the material was sub-sampled into 300 polyethylene bottles (100 mL), each containing about 70 g of sample. A flow chart for soil preparation is shown in Fig. 2.

2.1.3. Homogeneity studies

2.1.3.1. Bulk homogeneity test. In order to ensure the suitability of the material for an intercomparison, preliminary tests were performed for T-Hg at different particle sizes and sample intakes. To test the homogeneity of the material prior to final bottling, between-bottle homogeneity was verified based on aliquots from 10 bottles taken randomly. Due to high Hg concentrations the initial bulk homogeneity test was done on a 200 mg sample intake for <250 μm particle size. Total Hg was analyzed by cold vapor atomic absorption spectrophotometry (CV AAS) after digestion of the samples with nitric and sulfuric acid at 70 °C for 12 h in a closed Teflon digestion vessel on a LCD Milton Roy instrument (Horvat et al., 1991). The digested samples of <250 particle size and 200 mg sample intake were also measured by a SANSO SEISHAKUSHO CV AAS Hg analyzer, Instrument Model 910, Japan, without amalgamation to check for possible interferences during the measurement step. A repeated bulk homogeneity test was done on the <125 μm fraction with the same sample intake. Due to relatively poor homogeneity the sample intake was increased to 500 mg, which resulted in more acceptable CVs.

2.1.3.2. Final homogeneity test. A final homogeneity test was conducted after completion of the bottling of the sample material. A more rigorous digestion was employed, as the bulk homogeneity test did not come up with fully satisfactory results. Samples were analyzed by CV AAS after complete dissolution by a mixture of hydrofluoric, nitric and hydrochloric acids at 135 °C for 12 h. The between-bottle homogeneity was tested by the determination of T-Hg based on sample weights of 100 mg taken from six bottles. The within-bottle homogeneity was assessed by three replicate determinations on the content of each bottle.

2.2. Intercomparison exercise

An intercomparison exercise was conducted between the participating laboratories on SOIL-1. This study was intended to give the laboratories responsible for mercury analyses an opportunity to check the accuracy of their analytical results and analytical performance.

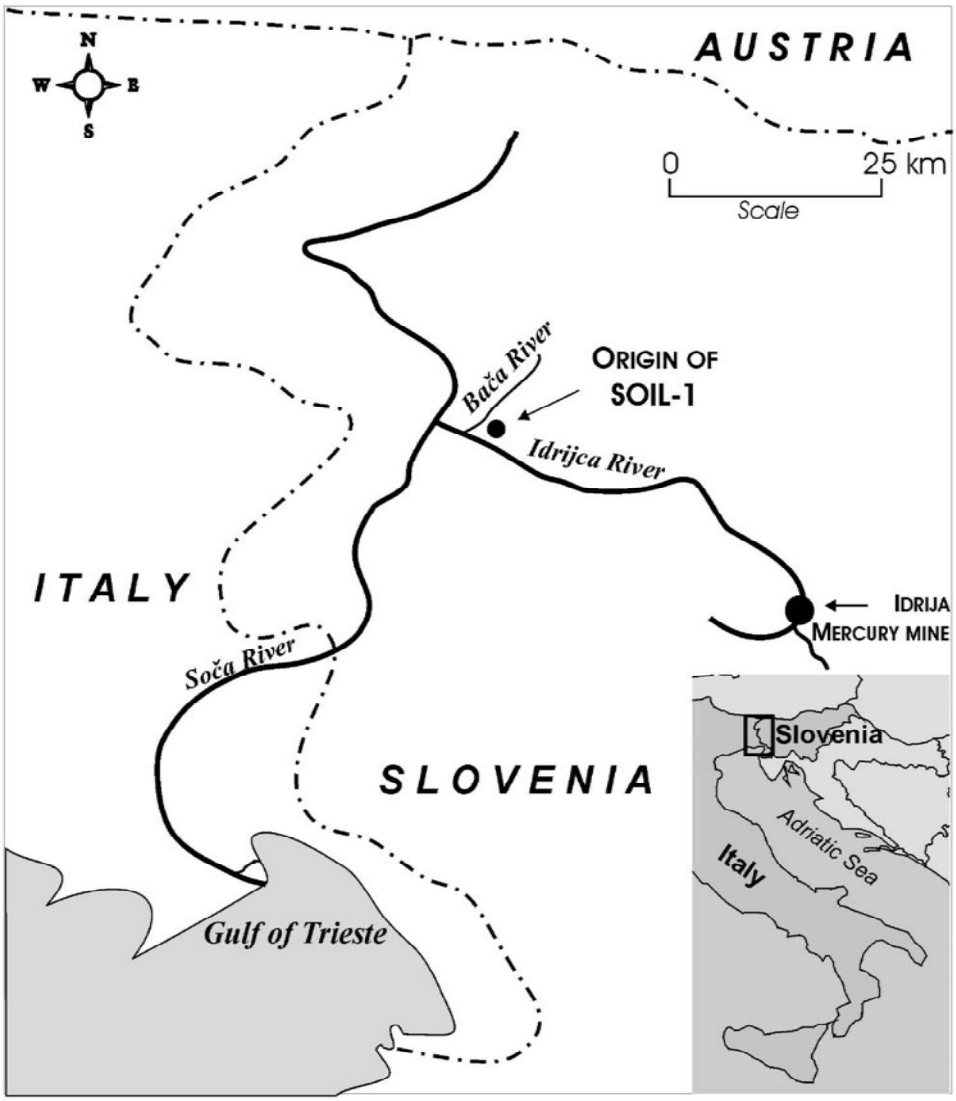

Fig. 1. Origin of SOIL-1 material.

The bottles of sample material were dispatched to all CRP participants and other laboratories interested in participating. Participating laboratories were requested to determine T-Hg and MeHg by their routine procedures. The IAEA and IJS were also interested in receiving results for any other element(s) that participating laboratories determined routinely. Participating laboratories were requested to make at least three, but preferably six, independent replicate determinations and to report all results, including the average weight of the sample taken for analysis, the concentration of each independent replicate determination, the arithmetic mean and the standard deviation of the replicate determinations and the detection limit of the method. Additionally, information requested included a summary of quality control procedures routinely employed within their laboratory, the results for Certified RMs analyzed concurrently and the instrumental method used for the quantitative determination.

In total, six laboratories from six countries participated in this intercomparison exercise. Total Hg results were provided by six laboratories, methylmercury by three and multielemental results by two. The analytical methods used by different laboratories accompanied by a short description are summarized in Table 1.

2.3. Sequential extraction procedure

A six-step sequential extraction scheme (SES) was applied to SOIL-1 in two laboratories (Frontier Geosciences Inc., Seattle and IJS, Ljubljana). Analyses were performed on 9 and 4 replicate samples, respectively. The SES consisted of six steps: including (a) water soluble (F1), (b) "human stomach acid" soluble (F2), (c) organo-chelated (F3), (d) elemental Hg (F4), (e) mercuric sulfide (F5) and residual fraction (F6). The sequential extraction procedure steps and the reagents used are described in Table 2.

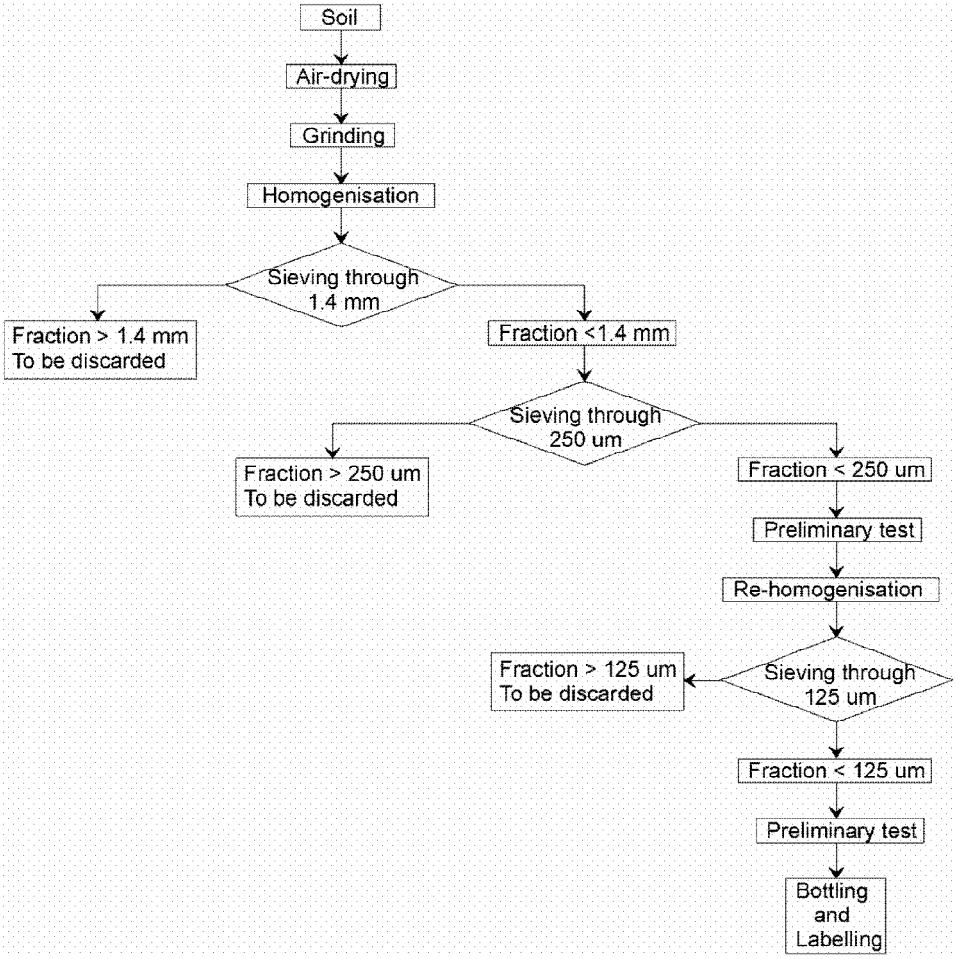

Fig. 2. Flow chart for the preparation of the SOIL-1.

Extractions were carried out using 0.4 g of sample. The sample weight to extractant volume ratio was 1–100. A total of 40 mL of extractant was added to the solid and subjected to end-over-end shaking at 250 rpm for 18 ± 4 h. The vials were then centrifuged at 3800 rpm for 10 min, and the supernatant liquid decanted for filtration through a membrane filter of 0.20 μm pore size. The extracted solution was then placed in a clean Teflon bottle and oxidized by adding 5 mL of 0.2 M BrCl. Total Hg in the oxidized extracted solution was determined using $SnCl_2$ reduction, gold trap amalgamation and CVAAS. In the subsequent extraction steps the above procedure was repeated. Owing to the very low expected Hg values in some fractions, the filters were rinsed with HNO_3, HCl and deionised water before filtration to avoid contamination. This SES is described in more detail elsewhere (Bloom et al., 2003).

The soil was prepared initially for comparability studies by the CRP participants. However, it was hoped that the material if satisfactory could serve a wider function to scientists working in the field of soil and environmental contamination.

3. Results and discussion

3.1. Homogeneity studies

3.1.1. Bulk homogeneity

The coefficients of variation (CV) obtained from replicate T-Hg analyses of different particle sizes and sample weights are presented in Table 3. The between bottles CVs revealed that the results obtained from the sample of the particle size <250 μm were not satisfactory. Re-homogenization and sieving through 125 μm pore size showed no better results when 200 mg of sample was analyzed. A larger sample intake (500 mg) showed a lower CV (about 7%), which was considered satisfactory based on the fact that soil samples from areas impacted by mining activities cannot be prepared completely homogeneous due to the nugget effect.

3.1.2. Final homogeneity

The homogeneity test was done with three replicate determinations in six individual bottles. The between-bottles CV was 16.8% and within-bottles CVs varied

Table 1
Analytical methods used by participating laboratories accompanied with a short description

Code	Institution	Analyses	Detection	Digestion method
1A	IJS, Slovenia	T-Hg	CV AAS	HNO_3/H_2SO_4 digestion, $SnCl_2$ reduction, amalgamation
1B	IJS, Slovenia	T-Hg	CV AAS	$HF/HNO_3/HCl$ digestion, $SnCl_2$ reduction, amalgamation
1C	IJS, Slovenia	T-Hg multielemental	k_0-INAA	Thermal neutron flux irradiation in 250 kW TRIGA Mark II reactor, HPGe calibrated detector
1D	IJS, Slovenia	MeHg	CV AFS	$KBr/H_2SO_4/CuSO_4$ leaching, solvent extraction by CH_2Cl_2, derivatisation, ethylation, gas chromatography, pyrolysis
2	University of Dar es Salaam, Tanzania	T-Hg	CV AAS	HNO_3 digestion
3	Syddansk Universitet, Denmark	T-Hg	FAAS	Thermal decomposition at 550 ºC
4A	NIMD, Japan	T-Hg	CV AAS	HNO_3 digestion
4B	NIMD, Japan	MeHg	GC ECD	Acid leaching, solvent extraction of dithizonates
5A	University of Victoria, Canada	T-Hg	CV AFS	Aqua-regia (HCl/HNO_3) digestion with 0.01% $K_2Cr_2O_7$
5B	University of Victoria, Canada	multielemental	ICP MS	Aqua-regia (HCl/HNO_3) digestion with 0.01% $K_2Cr_2O_7$
6A	Frontier Geoscience, USA	T-Hg	CV AFS	$HF/HNO_3/HCl$ digestion, $SnCl_2$ reduction, amalgamation
6B	Frontier Geoscience, USA	MeHg	CV AFS	$KBr/H_2SO_4/CuSO_4$ leaching, solvent extraction by CH_2Cl_2, derivatisation, ethylation, gas chromatography, pyrolysis

Table 2
Sequential extraction scheme (SES): steps, reagents and fraction descriptions

Step	Reagents	Fraction description	Typical Hg species
F1	Milli-Q water	Water soluble	$HgCl_2$, $HgSO_4$
F2	pH 2 HCl/HOAc	"Human stomach acid" soluble	HgO
F3	1 N KOH	Organo-chelated	Hg in humic acids, Hg_2Cl_2
F4	12 N HNO3	Elemental	Hg^0, Hg_2Cl_2
F5	Aqua regia	Cinnabar	HgS, m-HgS, HgSe, HgAu
F6	$HF/HCl/HNO_3$	Residual	mineral lattice bound

Table 3
Bulk homogeneity test results

Sample intake (mg)	Particle size (μm)	n[a]	Average T-Hg (mg kg^{-1})	CV (%)[b]
200	<250	3	58.6	11.9
200	<250	3	56.3[c]	11.9
200	<125	1	47.1	11.0
500	<125	1	50.5	7.3

[a]Number of replicates in each of 10 bottles.
[b]Coefficient of variation.
[c]Without amalgamation.

between 10% and 18%. An F-test at a significance level of 0.05 did not detect any difference between the within- and between-bottle variances. Although the material homogeneity test showed poorer homogeneity than expected, for both the between- and within bottle homogeneity, the heterogeneity was measurable and, therefore, we concluded that the material was suitable for use as an intercomparison sample.

3.2. Intercomparison exercise results

3.2.1. Total mercury

The results obtained from participating laboratories were evaluated using statistical and graphical methods, including descriptive statistics and analysis of variance (ANOVA). For each of the data sets, the range of determinations, arithmetic means and standard deviations were compiled, based on the laboratory means. Some data were rejected on the basis of difficulties reported by the laboratories (e.g. too small a sample weight, high Hg vapor pressure, calibration range, no acceptable quality control, etc.).

The remaining laboratory data were used to calculate an overall arithmetic mean, standard deviation and 95% confidence interval. A summary of the results is presented in Fig. 3, which depicts S-plots showing all the laboratory mean values in order of increasing concentration, based on at least three independent determinations. It is evident from this plot that the data are relatively spread out with CV varying between 4% and 19%. In most cases CVs were about 10%, which is attributed to the relatively high heterogeneity of the material. For the determination of total Hg, most of the laboratories used a wet digestion procedure, followed by cold vapor techniques with detection by AAS or AFS. One laboratory used thermal decomposition (Lab code 3) and one non-destructive k_0-instrumental neutron activation analysis (k_0-INAA) (Lab code 1C). Out of eight reported datasets, three showed statistically significant different means for total Hg. (i.e., using ANOVA and the least significant difference multiple range test at $P = 0.05$) (Miller and Miller, 1993). Two of them showed higher values (Lab codes 1C and 6A) and one of them was significantly lower (Lab code 1A). Lower results were observed when wet digestion using H_2SO_4/HNO_3 acids followed by CV AAS was employed (Lab code 1A). The reason for the lower results obtained may be due to the incompleteness of the H_2SO_4/HNO_3 acid digestion where Hg could not be totally leached from the HgS (cinnabar). Lower results may also be a consequence of volatilization losses during an incorrect digestion procedure, as described in the literature (Trimm et al., 1998). Higher results were observed in the case of total sample digestion using HF (Lab codes 1B, 6A) and non-destructive k_0-INAA (Lab code 1C). Total decomposition with a mixture of acids including hydrofluoric acid is well known to produce higher results for heavy metals including mercury (Wyse et al., 2004). Also k_0-INAA showed good performance on environmental samples such as soil, sediments and sewage sludge in the past, especially when elevated mercury values ($>1\,mg\,kg^{-1}$) were involved (Jaćimović and Horvat, 2004), as is the case in our study. Methods employed by other laboratories were based on acid leaching without the presence of HF (Lab codes 1A, 2, 4A, 5A) and one thermal decomposition method (Lab code 3). Only Lab 1A showed a statistically significant difference for total Hg when these laboratories (Lab code 1A, 2, 3, 4A and 5A) were compared.

Although the data for Lab codes 1C, 1A and 6A were statistically different from the other results, we only excluded data for the lowest concentrations of total Hg (Lab. Code 1A). This decision was based on the fact that the same laboratory also reported data based on dissolution of the sample with the use of HF. All other data were then used for calculation of the mean value and 95% confidence intervals. Accepted laboratory means varied between 62.3 and 82.1 $mg\,kg^{-1}$. The recommended value is 67.1 $mg\,kg^{-1}$ with the 95% confidence interval from 55.8 to 78.4 $mg\,kg^{-1}$.

3.2.2. Methylmercury

Data obtained from three independent laboratories varied from 2.3 to 5.6 $ng\,g^{-1}$. These results are in accordance with previous observations at the location where the material for SOIL-1 was taken (Horvat et al., 2002). A summary of the results is presented in Fig. 4, which depicts S-plots showing the laboratory mean values in increasing concentrations. All laboratories' CVs are less than 7%. Methods used by laboratories 1D and 6B were practically the same. The protocol is based on acid

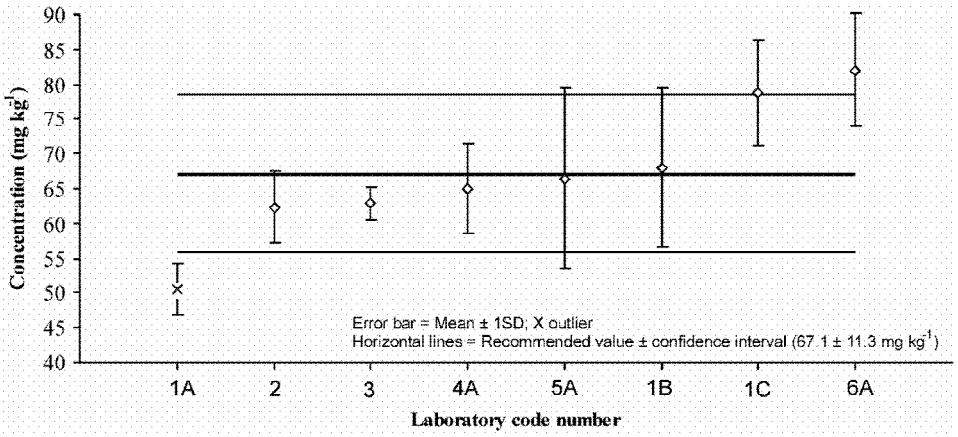

Fig. 3. Figure of laboratory T-Hg mean values, standard deviations and 95% confidence interval.

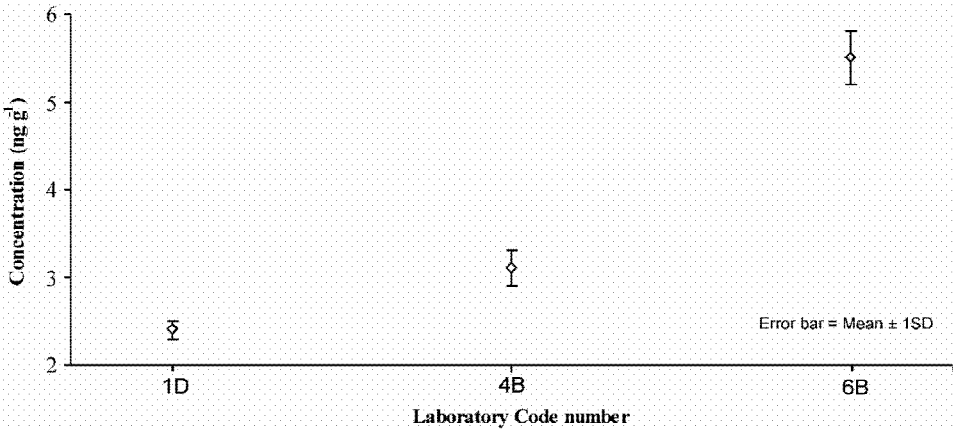

Fig. 4. Figure of laboratory MeHg mean values and standard deviations.

Table 4
Comparison of laboratory code no. 1 and no. 6 SES results

Fraction	Laboratory			
	Lab code no.1 ($n = 4$)[a]		Lab code no.6 ($n = 9$)	
	Average T-Hg (mg kg^{-1})	CV (%)	Average T-Hg (mg kg^{-1})	CV (%)
F1	0.032	36	0.018	5.7
F2	0.002	40	0.0013	21
F3	0.106	26	1.02	4
F4	5.87	3	3.43	7.3
F5	64.8	4	67.8	9.3
F6	0.032	35	—	—

[a] n, Number of replicates.

leaching, solvent extraction, derivatization by ethylation and detection by gas chromatography, pyrolysis and CV AFS detection (Logar et al., 2002). However, the results differ significantly. This difference could be attributed to the artifact MeHg production during the extraction step (Hintelmann et al., 1997), although the use of $KBr/H_2SO_4/CuSO_4$ leaching should practically be artifact free (Bloom et al., 1997). These differences deserve further attention; as shown in a study by Liang et al. (2004), the recovery of MeHg in soil may be significantly affected by the amount of sample intake and extraction reagents used. Slight changes in analytical protocols may affect the results. The results presented in Fig. 4 are for information purposes only and might be useful to those that intend to use this material for method development and comparability studies.

3.3. Results for sequential extraction

The results of sequential extraction obtained from both laboratories revealed cinnabar (F5) and elemental Hg (F4) as the predominant fractions, followed by organo-chelated (F3), water soluble (F1) and "human acid" soluble (F2) mercury. The sum of all fractions was similar to the total content obtained after digestion of the homogenized sample with nitric, hydrofluoric and hydrochloric acid. Recoveries of 80–105% were reached in most cases. The difference between the sum of species and T-Hg can be due in part to small losses during the SES extraction (<5%) and unleachable Hg bound in the rock lattice. The latter was confirmed in one laboratory by the determination of the residual mercury content after digestion with nitric, hydrochloric and hydrofluoric acid. Trace amounts of mercury were measured (between 32 and 42 μg kg^{-1}). Comparison of parallel determination in each particular step showed a good agreement. The CV values varied from 3% to 9% in the case of elemental (F4) and cinnabar (F5) fractions. Bigger differences were observed among fractions less abundant in Hg (more than 30%), which can be related to analytical uncertainties.

Comparison of the results using the same SES protocol is shown in Table 4. A significant disagreement was observed for F3, where IJS reported 10 times lower values than Frontier Geosciences, while for fraction F4 the values reported by the IJS were higher by a factor of 2. The differences are difficult to interpret and it is suggested that further research is needed to confirm the suitability of the proposed fractionation scheme for soil samples.

3.4. Multielemental analysis results

In addition, multielemental analysis results obtained by two laboratories using k_0-INAA and ICP-MS are given in Table 5. The results are presented as the average values of three and six independent determinations, respectively, accompanied with relative standard deviations (RSD) and detection limits. Thirty-seven elements were determined

Table 5
Summary of the results of k_0-INAA and ICP-MS multielemental analyses

Analyte	k_0-INAA ($n = 3$)			ICP-MS ($n = 6$)		
	Mean (mg kg^{-1})	RSD (%)	LOD (mg kg^{-1})	Mean (mg kg^{-1})	RSD (%)	LOD[a] (mg kg^{-1})
Ag	<0.3		0.3			
As	9.3	1.18	0.4			
Au	<0.002		0.002			
Ba	197.0	1.52	10	200.6	3.2	0.28
Be				1.5	15.9	0.06
Bi				1.3	13.3	0.01
Br	6.1	0.98	0.3			
Ca	96739.0	1.38	500			
Ce						
Cd	2.0	0.00	1.50			
Ce	54.7	2.74	0.3			
Co	6.6	0.76	0.03			
Cr	36.4	1.37	0.5			
Cs	5.2	0.39	0.06	5.1	4.5	0.25
Dy				4.1	7.6	0.01
Er				2.4	4.8	0.01
Eu	0.8	3.57	0.1	0.8	4.4	0.03
Fe	19678.0	0.64	30			
Ga	<20		20			
Gd				4.8	6.9	0.56
Hf	5.5	0.72	0.05	3.0	5.4	0.01
Hg	78.75	7.62	0.2			
Ho				0.8	2.7	0.005
K	14431.0	2.75	500			
La	27.9	2.15	0.03	26.8	5.9	0.01
Li				32.5	8.0	1.47
Lu				0.3	4.4	0.01
Mo	1.4	23.53	0.5	1.2	6.7	0.14
Na	5479.0	0.55	15			
Nb				18.3	10.5	0.11
Nd	27.1	5.90	1	23.7	6.2	0.03
Pb				44.8	7.7	0.03
Pr				6.6	3.2	0.01
Rb	71.3	1.40	2	75.0	5.5	0.5
Sb	2.7	2.62	0.03			
Sc	7.6	0.53	0.005	7.6	7.9	0.05
Se	<0.4		0.4			
Sm	4.6	1.32	0.01	4.7	4.2	0.04
Sn	<20		20			
Sr	128.0	3.91	20	134.0	2.8	0.48
Ta	0.8	0.66	0.03	0.8	3.1	0.003
Tb	0.7	1.54	0.03	0.7	9.1	0.004
Te	1.0	19.80	0.9			
Th	10.0	1.00	0.05	10.2	10.2	0.02
Tl				0.5	7.0	0.05
Tm				0.3	4.5	0.01
U	3.2	2.21	0.05	3.4	5.6	0.01
V				49.1	5.7	0.06
W	2.2	2.74	1			
Y				25.9	4.6	0.01
Yb	2.4	1.67	0.05	2.3	6.9	0.03
Zn	88.5	5.42	2			
Zr	234.0	3.85	40	103.4	9.2	0.02

[a]LOD, limit of detection.

using k_0-INAA and 32 elements using ICP-MS. The RSD for all of the elements that are well measured by these two methods are quite low, less than 10%. This indicates that these elements are homogeneously distributed in SOIL-1 as opposed to Hg where significant heterogeneity was observed due to the specific nature of SOIL-1. The comparison of the results obtained by k_0-INAA and ICP-MS showed generally excellent agreement. However, there were some differences, since ICP-MS showed somewhat lower results for Hf and Zr.

4. Conclusions

Mercury polluted soil (SOIL-1) from the Idrija mercury mine region, Slovenia, was prepared and characterized for T-Hg and MeHg. Bulk homogeneity tests showed that it is very difficult to assure sufficient homogeneity for mercury determination in soils from Hg contaminated sites. This is probably due to the nugget effect, a term which describes particles of small size with a high amount of Hg (most probably cinnabar particles), as it was shown by a sequential extraction procedure that more than 90% of the mercury is contained in the cinnabar (F5) fraction. Moreover, the intercomparison exercise underscored the importance of complete decomposition of this kind of material with HF or the use of non-destructive methods such as k_0-INAA for obtaining accurate results for T-Hg. MeHg measurements obtained from different laboratories showed that the improvement of analytical procedures for MeHg in soil deserves further attention.

Two sets of data for multielemental analysis indicated that Hg in the SOIL-1 is distributed differently from other matrix elements. Considering the nature of the SOIL-1 sample (e.g. mercury mining), heterogeneity of Hg at the 17% level is acceptable and therefore the material is suggested for comparability studies. However, the generalization of such an assumption for other contaminated samples, prepared for similar purposes, should be made with caution, taking the origin of the sample into consideration.

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