

## Evaluation of mercury bioavailability in soil samples using DGT and TD-AAS techniques: Case study of Baia Mare, NW Romania

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### Abstract

The aim of the present study is to evaluate the mercury (Hg) bioavailability in several soil samples collected from the Baia Mare area, NW Romania, using commercial Diffusive Gradients in Thin-films (DGT) devices and Thermal Desorption – Atomic Absorption Spectrometry method (TD-AAS) technique. Additionally, the method validation and measurement uncertainty estimation for the soil samples were studied. DGT devices specific for Hg (containing Spheron-Thiol resin in polyacrylamide as binding gel) were used for the experiments. Standard deviation of internal repeatability and reproducibility were determined to be 7 % and 10 %, respectively, while the relative expanded uncertainty was 21 %. It was found that only a small part (less than 0.5 %) of the total mercury content exist in bioavailable forms in the analysed soil.

**Key words:** diffusive gradients in thin-films (DGT), bioavailability, mercury, soil, Baia Mare

### Introduction

Mercury (Hg) is considered as one of the most toxic elements due to its impacts on the human health and environment, thus its environmental monitoring needs a special attention. Mercury can naturally occur in the Earth's crust, but also in anthropogenic sources due to mining activities, coal-burning power plants, waste incinerators and other industrial processes, which increase the level of mercury in the environment by a factor of 3–5 (Zierhut et al., 2010). Mercury has a high volatility in its elemental form, thus this element can be transported as a gas on very long distances through atmosphere and, because additionally has a very low degradability, it is worldwide dispersed (Senila et al., 2012). In 2006 the European Union (EU) excluded mercury use in measuring instruments such as thermometers, and also great efforts are made to replace the use of mercury in industrial processes (e.g. acetaldehyde production, chlorine-alkali electrolysis) by other substances (Leopold et al., 2010).

Hence, an accurate monitoring of mercury species in the environment is needed, and in addition to the determination of total metal concentration, the evaluation of its bioavailability provides very useful information for reliable risk assessment.

Different single or sequential extraction procedures are used in the current practice for mercury bioavailability assessment in soil and sediment samples (Zagury et al.,

2006), but it was shown that, for mercury, these procedures are not very selective and also poor reproducibility of the results was observed (Sahuquillo et al., 2003).

The technique of diffusive gradients in thin films (DGT), developed by Davison and Zhang (1994), provides an in situ tool of measuring labile metal species in aqueous solutions. This is very important, because the labile species are better correlated with metals bioavailability. In several studies DGT and TD-AAS were used for Hg bioavailability assessment in environmental samples. Dočekalová and Diviš (2005) investigated the DGT technique to measure mercury concentration in river water using two selective resins and contents of mercury trapped by DGT devices were measured by TD-AAS. Also, Diviš et al. (2005) used DGT and TD-AAS for mercury depth profiles measurement in river and marine sediments. Fernandez-Gomez et al. (2011) used TD-AAS technique for analysis of Spheron Thiol gels from DGT for the monitoring of mercury level in river water and it was showed that DGT present limitations for waters with a high biomass load, while in oligotrophic waters DGT offers accurate results. Cattani et al. (2008) analysed mercury species in soils by HPLC–ICP–MS and by DGT.

The present work describes the mercury determination in soil pore water collected from the Baia Mare area, NW Romania using commercial DGT devices specific for Hg ions (Spheron-Thiol resin gel) and TD-AAS technique. Method validation and measurement uncertainty estimation for these specific samples are also presented.

## Experimental

### Materials and instrumentation

All reagents used were of analytical grade. Ultrapure water was obtained by a Millipore Milli Q system. The DGT units for mercury determination were purchased from DGT Research Ltd. (Lanchester, UK). Each DGT unit consists of a plastic piston covered by a layer of polyacrylamide gel containing Spheron-Thiol resin (with – SH groups), an diffusive layer with a thickness of 0.76 mm and a 0.45 mm pore size filter membrane with a thickness of 0.13 mm, pressed by a plastic cap with a window 2 cm in diameter. A 1 000 mg L<sup>-1</sup> mercury standard solution (Merck, Germany) was used to calibrate the equipment used for the mercury determination. A soil certified reference material SRM 2709 San Joaquin Soil (New York, USA) was used for the quality control of total Hg determination.

The measurements of mercury from resin gels and solid samples were carried out using an Automated Direct Hg Analyzer Hydra-C (Teledyne Instruments, Leeman Labs, USA) based on thermal desorption – atomic absorption spectrometry (TD-AAS). General soil properties, comprising pH, cation exchange capacity (CEC) and organic matter (OM), and water pH were determined by using standardized analytical methods.

### Sampling and analytical methods

Soils samples were sampled from private gardens from a village of Recea, located in the vicinity of Baia Mare, NW Romania, in an area with a long-history of ore mining and processing. For DGT determinations, amounts of 30 g of soil samples were mixed with ultrapure water until 100 % water holding capacities (WHC), in plastic containers, and kept for 24 h at 25 ± 2 °C, for equilibration. The DGT devices were introduced into the soil slurries and kept for a known time at 25 °C. After retrieval, the DGTs were carefully washed with ultrapure water and the resin gels were introduced directly in Hg-analyser and the mass (M) of Hg accumulated in the resin was measured. The average time concentration of mercury (Hg<sub>DGT</sub>) was calculated according to (Eq. 1) (DGT Research Ltd.):

$$\text{Hg}_{\text{DGT}} = M \Delta g / D t A \quad (1)$$

where  $\Delta g$  is the thickness of the diffusive gel and membrane filter,  $D$  is the diffusion coefficient of the Hg in the resin gel at 25 °C ( $8.50 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ ),  $t$  is the deployment time in seconds, and  $A$  is the area of the sampling window of the DGT device ( $3.14 \text{ cm}^2$ ).

To measure the Hg concentration in soil solution (Hg<sub>soil</sub>), a portion of the soil paste prepared for the DGT

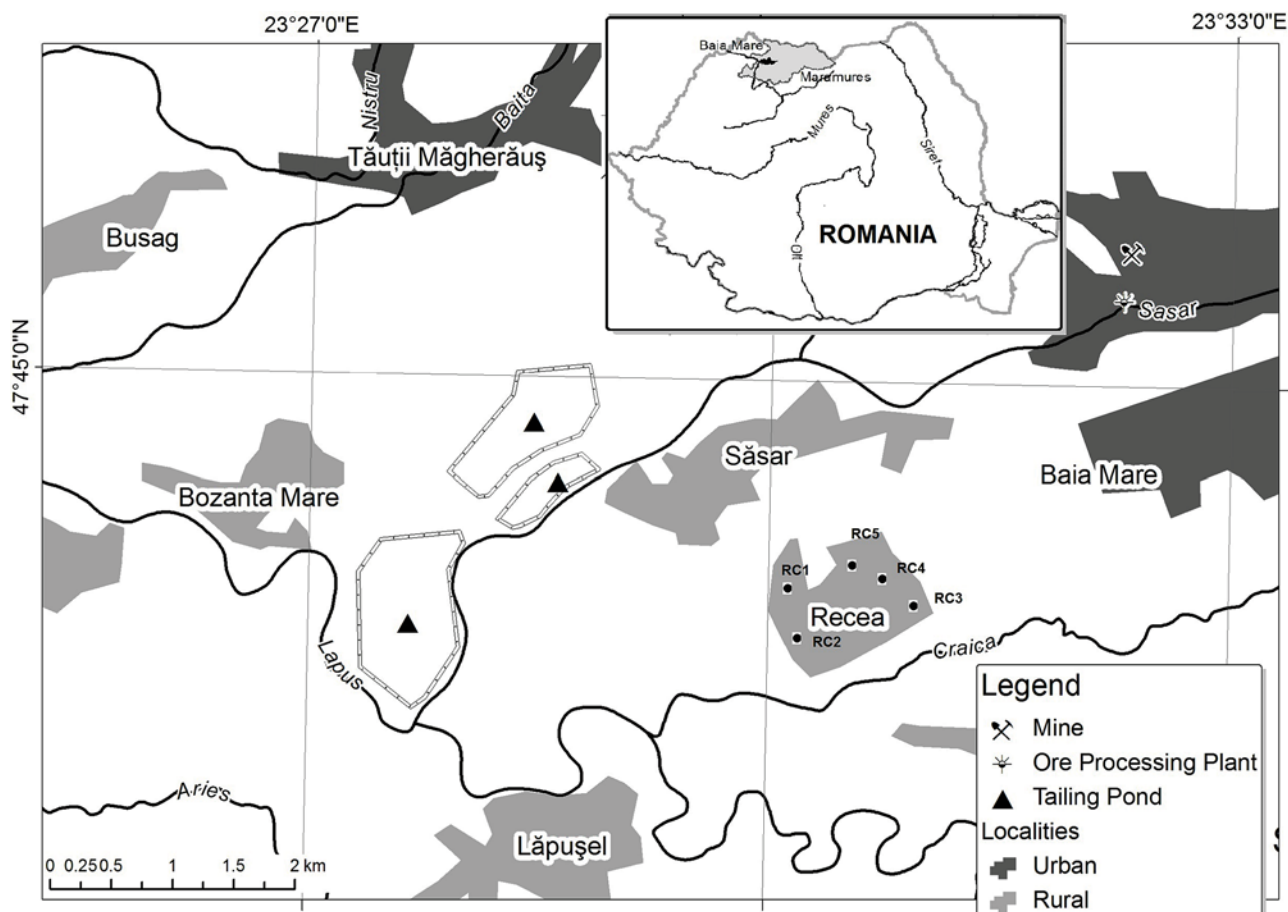


Fig. 1. Location sampling sites at Recea village in the vicinity of Baia Mare.

measurements was introduced in 25-mL polyethylene tubes and centrifuged at 5000 rpm for 20 minutes. The collected supernatant was filtered by means of a syringe connected to a 0.45- $\mu\text{m}$  pore size filter. The mercury concentrations in soil solutions were measured by CV-AFS.

## Results and discussion

Limit of Detection (LOD) and Limit of Quantitation (LOQ) were calculated using the 3s criteria. For TD-AAS method, the SBR was determined for the DGT device introduced for 24 h in a 100  $\mu\text{g L}^{-1}$  Hg in 0.01 mol  $\text{L}^{-1}$   $\text{NaNO}_3$  solution, while the relative standard deviation of the background (RSDB) was calculated from 10 successive measurements for the background signal at analytical wavelength of 253.65 nm. The detection limit of solid DGT sample analysis was determined to be 0.30 ng Hg. Relative standard deviation for ten replicates at lowest level of working range was 19.3 % and recovery in confirmation of lower working range concentration was 0.96, what is satisfactory performance.

Precision is usually evaluated by internal repeatability and reproducibility. Internal repeatability assay was conducted on 6 parallel samples (DGT devices immersed in a stirred solution of 100  $\mu\text{g L}^{-1}$  Hg in 0.01 mol  $\text{L}^{-1}$   $\text{NaNO}_3$  solution for 24 h at 25  $^\circ\text{C}$ ) using the same equipment by the same operator. The obtained value for the standard deviation of repeatability was 7 %, while the limit of repeatability was 20 %. The reproducibility study was conducted on 6 replicate solutions of 100  $\mu\text{g L}^{-1}$  Hg in 0.01 mol  $\text{L}^{-1}$   $\text{NaNO}_3$ , carried out by the same operator using the same equipment, but in different days. The obtained value for the standard deviation of reproducibility was 10 %.

Measurement uncertainty was estimated following the classical steps of specifying the measurand, identifying the uncertainty sources, quantifying uncertainty components and calculation of combined uncertainty. The main sources of uncertainty were identified as uncertainty associated with method calibration, trueness of the method (recovery) and overall repeatability of the procedure. Uncertainty sources were further divided to uncertainty components: uncertainty of volumetric operations, uncertainty of gravimetric operations, repeatability of operations and method recovery. The expanded uncertainty ( $U_E$ ) for a coverage factor ( $k = 2$ ) was 21 %. The main contribution to uncertainty came from the standard deviation of reproducibility for the DGT deployments.

### Hg available species in soil samples

Soil samples were collected from the village of Recea, located near to Baia Mare (NW Romania), an area known for a long history concerning mining activities. Surface soil samples (0–10 cm) were collected, transported to the laboratory, dried, crushed and sieved. The main soil properties (pH, OC, CEC, total Hg), determined according to the standardized methods, are presented in Tab. 1.

The pH of soil samples examined was in the neutral range. The organic carbon content ranged between 1.8–2.6 %, while the CEC values were in the range of

15.8–20.3  $\text{cmol kg}^{-1}$ . Values of the total mercury concentration were generally homogeneously distributed, ranging between 488–851  $\mu\text{g kg}^{-1}$  dw (dry weight).

The DGT Hg concentrations in soil correspond to the concentration at the interface of the DGT device and the soil. Mercury is continuously taken up from the solution of soil and is trapped by the resin gel of DGT devices, which induce a decrease of Hg in the pore water and a resupply from the solid phase (Cattani et al., 2009). DGT Hg concentrations were measured by deploying the DGT devices in soil samples, mixed with ultrapure water until 100 % water holding capacities (WHC) for 24 h. Slurries were collected from the same soil, soil solutions were prepared by centrifugation and analysed for total Hg concentration.

Hg content in soil solutions ( $\text{Hg}_{\text{soln}}$ ) ranged between 2.5–4.6  $\mu\text{g L}^{-1}$ , which generally represent less than 0.5 % of the total Hg content in soil.  $\text{Hg}_{\text{DGT}}$  concentrations were in the range of 2.2–3.8  $\mu\text{g L}^{-1}$ . In order to measure resupply from solid phase, the ratio R between  $\text{Hg}_{\text{DGT}}$  and  $\text{Hg}_{\text{soln}}$  was calculated. When R is higher than 0.95, the metal is present as mobile and kinetically labile species in the solid phase. That capacity of the solid phase to resupply the pore water is high. An R value approaching 0 suggests very limited or no metal resupply from the solid phase (DGT Research Ltd, Lancaster, UK). The R ratios in our case ranged between 0.76–0.92, indicating that Hg in solution is quickly replaced from the solid phase, where it is found in an available form. Cattani et al. (2008) also reported high availability of Hg found in soil solution. Even if the Hg

Tab. 1  
Soil properties in the selected area

Sample	pH	CEC ( $\text{cmol kg}^{-1}$ )	OM (%)	THg ( $\mu\text{g kg}^{-1}$ dw)
RC1	7.6	18.4	2.3	630
RC2	7.2	16.7	2.1	544
RC3	7.4	20.3	2.6	845
RC4	7.8	15.8	1.8	488
RC5	7.4	18.6	2.2	851

CEC – cation exchange capacity; OM – organic matter; THg – Total Hg

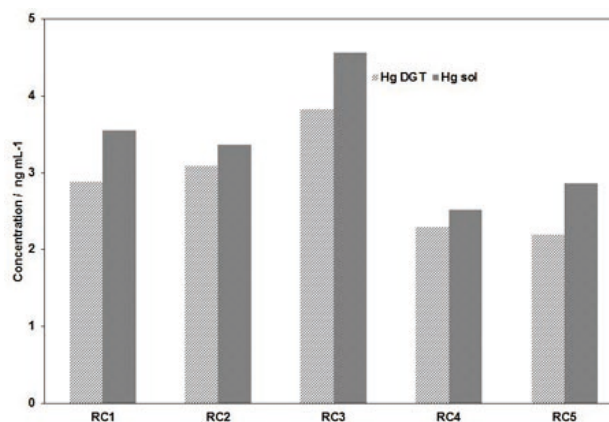


Fig. 2. Mercury in soil solution ( $\text{Hg}_{\text{soln}}$ ) and mercury measured by DGT ( $\text{Hg}_{\text{DGT}}$ ) in soils.

concentration in soil solution is low, the high bioavailability in soil solution can explain the hyperaccumulation of Hg in several plant species due to the re-supply of Hg from soil solid phase).

### Conclusions

Standard deviation of internal repeatability and reproducibility were determined to be 7 % and 10 %, respectively, while the relative expanded uncertainty was 21 %. Hg bioavailability was assessed in several soil samples from a mining area from NW Romania. Only a small part of the total mercury (less than 0.5 %) was found to be in bioavailable forms in the soil.

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