

Application of the Sequential Extraction Scheme for Mercury in Contaminated Soil

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Abstract: The main aim of this study was to test and apply sequential extraction and quantification of different Hg phases in order to estimate the mobility and potential bioavailability of Hg in contaminated soils in the Idrija Hg-mine region, Slovenia. Separation of Hg phases was performed by means of a selective sequential extraction procedure complemented by volatilization of elemental mercury (Hg^0). Fractionation measurements indicated cinnabar as the predominant Hg fraction, followed by Hg^0 . Accumulation of cinnabar predominantly occurred in coarse grained flood plains sediments, where on average it constituted more than 80 % of total Hg. In contrast non-cinnabar fractions were found to be enriched in areas where fine grained material was deposited, reaching up to 62 % of total Hg. The strong positive correlation ($R^2=0.71-0.99$) among non-cinnabar fractions suggested that these fractions predominantly control the mobility and potential bioavailability of Hg. Sample pretreatment before fractionation influenced the partition of Hg between different fractions, and therefore fractionation in fresh, nontreated samples is suggested. Good agreement ($R^2=0.81-0.95$) was found between the non-cinnabar fractions and evaporation of Hg^0 . Both the temperature and sample moisture had significant effects on mercury volatilization.

Key words: mercury fractionation, soil, sequential extraction

INTRODUCTION

The biogeochemical and especially the ecotoxicological significance of Hg input is determined by its specific binding form and coupled reactivity rather than by its accumulation rate in the solid material. Consequently, these are the parameters that have to be determined in order to assess the potential for Hg transformation processes (such as methylation, reduction, demethylation), and to improve data for environmental risk assessment. One of the aims of the study presented here was differentiation of Hg compounds in soils into different behavioural classes by the sequential extraction scheme adopted from BLOOM ET AL.^[1] The sequential

extraction scheme 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).

Emissions of volatile mercury species from natural sources are believed to be a significant contributor to the atmospheric burden of mercury.^[2] In contrast to anthropogenic point sources of atmospheric Hg, natural sources are long lived ($>10^4$ years) and their emissions enter the global atmospheric Hg pool. In the past decade significant progress has been made in development of methods for the measurements of mercury emission, using both dynamic flux chambers and mi-

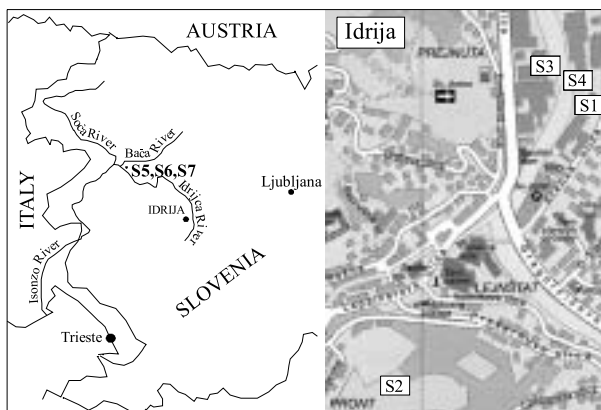


Figure 1. Sampling sites (S1-S7)

cro-meteorological methods. A good model should simulate all the processes in their proper importance, but as no *ideal* model of mercury soil-to-atmosphere emission exists, it is most important to know the relative importance of different parameters. For this purpose a simple mercury volatilization simulation experiment was applied. The study focuses on the estimation of the amount of volatile mercury in soil and on the influence of temperature and sample moisture content on mercury volatilization.

Samples were taken in the city of Idrija and its surroundings (Fig. 1). Two types of

samples were analysed: fresh and homogenized, to investigate the influence of sample pretreatment on fractionation results. The fresh part was stored under refrigeration until analysis. The other part was dried at 35 °C, homogenized and sieved through a mesh of 200 µm pore size. The procedure for simulation of mercury volatilization from soils was applied to fresh samples.

RESULTS AND DISCUSSION

Volatile mercury. Mercury fluxes were measured for 14 h in one-hour intervals follow-

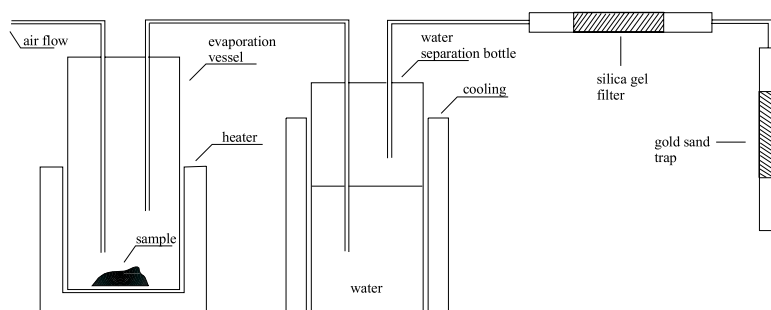


Figure 2. System for measuring soil Hg volatilisation: A sample is placed in a flow of Hg-free nitrogen in a teflon evaporation vessel connected to a water separation bottle and a gold sand trap. The gold sand trap is analysed by thermal desorption, double amalgamation and CVAFS.

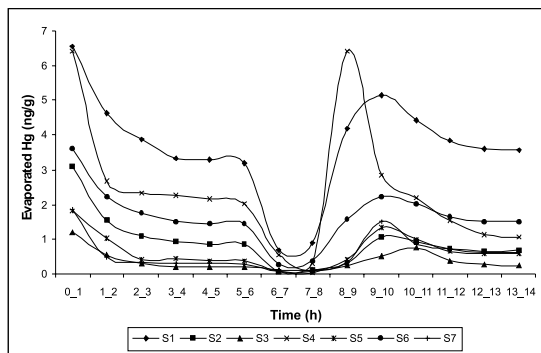


Figure 3. Results of Hg volatilization simulation experiment (one-hour intervals)

ing the procedure illustrated in Fig. 2. There is a similar trend in all samples (Fig. 3). The highest fluxes were determined in the first hour. Afterwards, during the second and third hour, fluxes gradually decreased. During the next three hours, when samples were already dry, fluxes within one-hour intervals became constant. This fact indicates the influence of moisture on mercury emission.

After six hours the samples were cooled down and fluxes measured for two hours at room temperature. Mercury fluxes at room temperature were 3 to 10-fold lower, showing no significant difference when the two one-hour intervals were compared. The sudden flux decrease in comparison with fluxes measured at 70 °C indicated the importance of temperature on mercury emission. To confirm the influence of both, moisture and temperature on mercury emission, samples were remoisted (sample weight to water volume was 1 to 1), heated at 70 °C once again and mercury fluxes measured for another six hours. The trend observed in the first six hours of the experiment was repeated (with a correlation coefficient $R^2=0.94$). Once again, the highest fluxes were measured in the first two hours (during the eighth and tenth hour respectively), then a gradual de-

crease followed until the fluxes become constant. A very strong correlation ($R^2=0.93$) between the sum of 14-hours fluxes and total Hg indicates the importance of total Hg concentrations on mercury volatilization.

Application of the sequential extraction scheme. The results obtained from homogenized samples differ from the fresh ones (Fig. 4). Evidently there must be some kind of alteration of Hg during homogenisation, drying and sieving of the samples, particularly in the case of fractions F1, F2 and F3. That is why we discuss here the results obtained from fresh samples, representing the actual situation in nature.

Hg was principally distributed between the cinnabar (F5) and elemental (F4) fraction. Although the percentage of first three fractions is rather small (the lowest quantities of Hg were extracted during the second extraction step at pH 2), absolute values of these mobile Hg fractions are quite high due to very high total Hg values in these samples (9 to 369 mg Hg kg⁻¹). In general, samples can be divided into two groups: samples of flood plains and others. Samples of flood plains (S4-S7) contain more cinnabar and less water soluble and elemental Hg when compared to others.

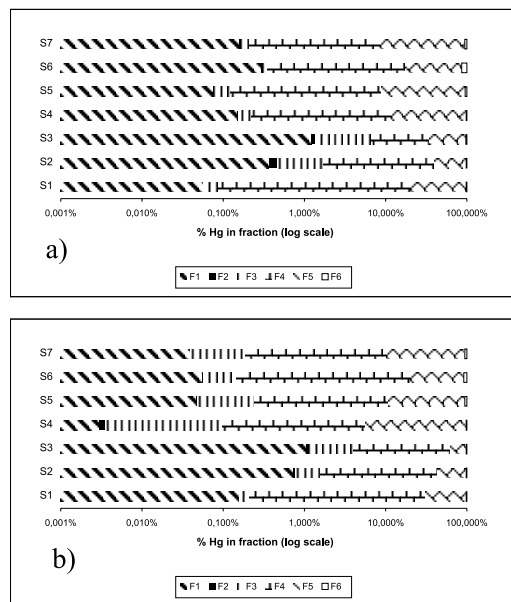


Figure 4. Sequential extraction results. a) homogenized samples, b) fresh samples

The third, organo-chelated Hg fraction, is presumably the most important one, as it is most strongly correlated with methylation potential.^[1] The expectation was that fraction F3 would be more abundant in samples with a higher amount of organic matter, as Hg that appears in this fraction is associated mostly with humic organic matter. On the contrary, the results showed a decline in the amount of organo-chelated Hg with increasing percentage of organic matter. Thus, the only significant fraction F3 was measured in samples S2-S4 (between 0.3 and 0.46 mg kg⁻¹), containing less than 4 % of organic matter. The measurements of the Hg after fourth extraction step may be interpreted as an estimate of total Hg⁰. This assumption was also confirmed by the very high correlation ($R^2=0.81$) between the rela-

tive amount of fraction F4 and relative amount of Hg evaporated during the volatilization experiments described above.

Grain size effect, relations between fractions and the amount of evaporated mercury. Cinnabar is especially concentrated in coarse-grained alluvial samples, where it constitutes on average more than 73 % of total Hg. In contrast, noncinnabar fractions were found to be enriched in areas where fine grained material was deposited, reaching up to 62 % of total Hg. An increased amount of any one fraction F1, F2, F3 or F4 lead to an increase of the remaining three fractions ($R^2=0.71-0.99$). On the other hand, an increased amount of fraction F5 resulted in decreased amounts of fractions F1 to F4 ($R^2=0.71-0.98$). This suggested that most chemical processes involved in mercury cycling in the soil occur within the noncinnabar mercury forms (F1-F4), as cinnabar (F5) is a very resistant insoluble form of mercury that does not enter in the mercury cycle. The relative amount of volatile (mainly Hg⁰) mercury obtained during the emission simulation experiment increased when the relative amount of the F1, F2, F3 and F4 fractions increased, and decreased when the percentage of F5 fraction increased. The suggestion is that Hg bound in the fractions F1 to F4 is mobile and potentially bioavailable, while Hg bound in fraction F5 is not, and therefore less harmful to the environment.

CONCLUSIONS

The simulation of the mercury vaporization from soil revealed that soil temperature and to a less extent added moisture are the main factors affecting the evaporation of mercury. Since a constant evaporation rate is obtained after 6 hours, we recommend that the procedure to assess the potential for mercury volatilization from soils should be completed after this period of time. We suggest that further investigations need to be performed to optimize the selected temperature. This is supported by the fact that bacteria may also be responsible for Hg reduction and volatilization, and the selected temperature should not kill the bacterial activity, as may be the case at 70 °C.

Sequential extraction of soils revealed that cinabarite and elementary mercury prevail.

Biogeochemical conversion between noncinnabar mercury forms provides the basis for mercury's complex distribution pattern in the soil, for its biological enrichment, and its atmospheric enrichment as well. Our results suggest that data on the amount of the mobile fraction of mercury are more relevant than data on total mercury content. The total mercury concentrations are high due to high contents of cinabarite, which is not soluble and does not enter the processes of mercury transformation. One of the important conclusions of this work is also related to the effect of the sample preparation procedure and unspecific leaching on the results obtained by the sequential extraction. This suggests that further development and standardization of the method is of paramount importance to obtain results comparable with other studies.

REFERENCES

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