

# Mercury concentrations, redox state, and isotope ratios in consecutive water extracts of Hg(II)-chloride contaminated soils

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## BACKGROUND & HYPOTHESES

Mercury (Hg) leaching from contaminated soils into groundwater or surface waters represents a serious environmental problem at industrial legacy sites. Sequential extraction protocols are commonly used to assess the mobility of Hg, thereby potentially underestimating the size of the water leachable, most mobile Hg soil pool by conducting only a single water extraction step [1].

Previous studies reported both heavier and lighter  $\delta^{202}\text{Hg}$  values in water leachates [1,2] compared to the respective bulk soil signature. Another recent study did not find a significant difference [3].

A variety of natural processes fractionate Hg stable isotopes e.g. sorption, precipitation, complexation and redox processes [4-6].

Mercury stable isotopes can consequently be used as a potential tool to trace biogeochemical processes in the environment.

This study aims to characterize the “water leachable Hg soil pool” in terms of Hg concentrations, redox state and isotopic signatures under differing biogeochemical conditions. We hypothesize that consecutive water extraction on Hg contaminated samples, under differing biogeochemical leaching conditions, result in different Hg concentrations and redox state in solution. Moreover, we expect distinct isotope signals in water leachates compared to the solid bulk value. With our results we aim to provide new insights on the possible use of Hg stable isotopes as process tracers in natural field systems.



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# METHODS

Consecutive water extractions were performed on three field samples (19 - 633 mg kg<sup>-1</sup> Hg) and one artificially contaminated aquifer material (ACAM1) under different extraction conditions and for time periods of up to 81 days (**Figure 1**).

The aquifer material was contaminated with a Hg<sup>II</sup> solution (NIST-3133) to ~20 mg kg<sup>-1</sup> Hg in the presence of chloride and buffered at pH ~9.

Hg redox state in solution was assessed by purging a solution aliquot with argon gas, Hg<sup>0</sup> was calculated by mass balance. Solid phase residues were digested with *aqua regia* after the respective extraction period.

Mercury concentrations were measured in all extracts by CV-AAS/AFS and isotopic signatures on selected samples using CV-MC-ICP-MS. Additional information on solid phase speciation was obtained by pyrolytic thermodesorption analysis (PTD). Multi-element (ICP-OES; major cations), pH, O<sub>2</sub>, and dissolved organic carbon (DOC) analysis was performed on all extracts.

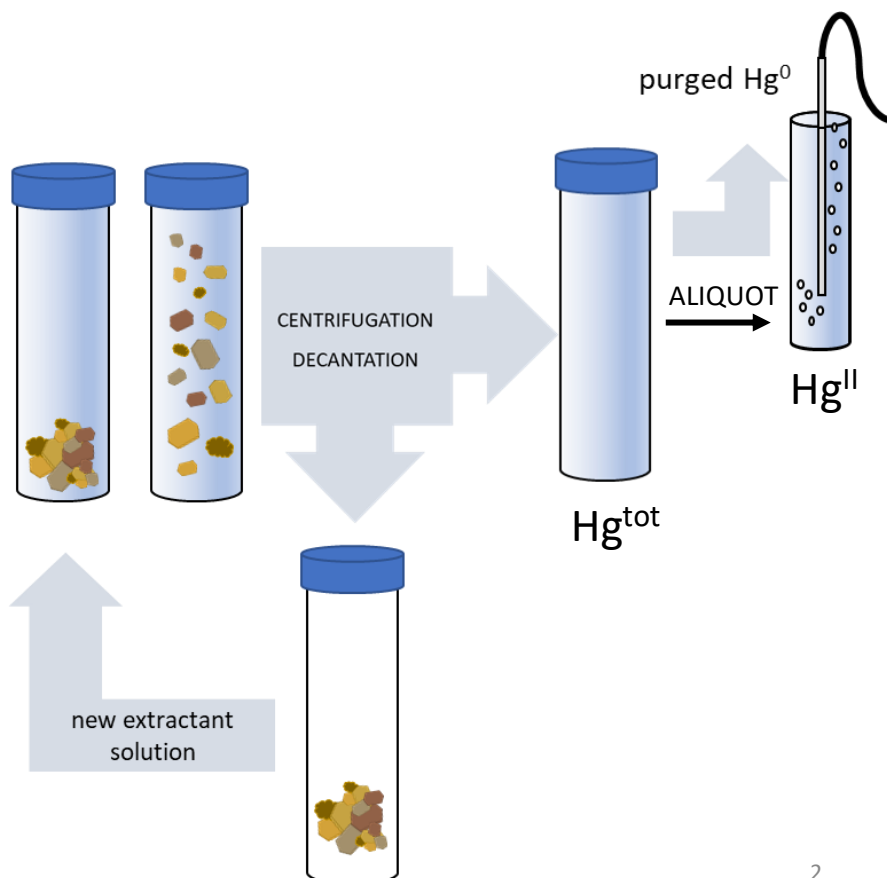
**Figure 1:**  
Illustration of the general experimental set-up for the consecutive water extractions. Batch experiments were conducted under different extraction conditions and for different time periods:

**14 days (5 steps)**

- oxic (H<sub>2</sub>O)
- sub-oxic (H<sub>2</sub>O, low O<sub>2</sub>)
- CaCl<sub>2</sub> (2 mM)

**81 days (9 steps)**

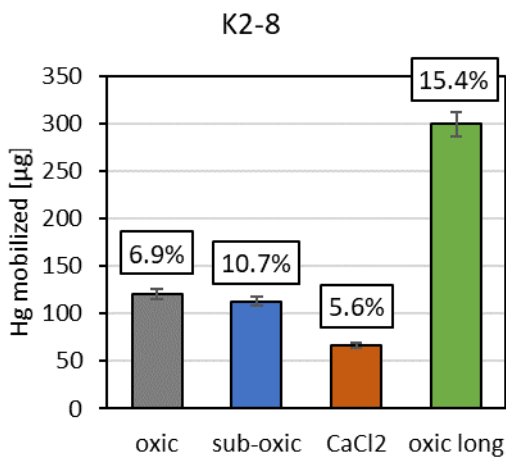
- oxic long (H<sub>2</sub>O)



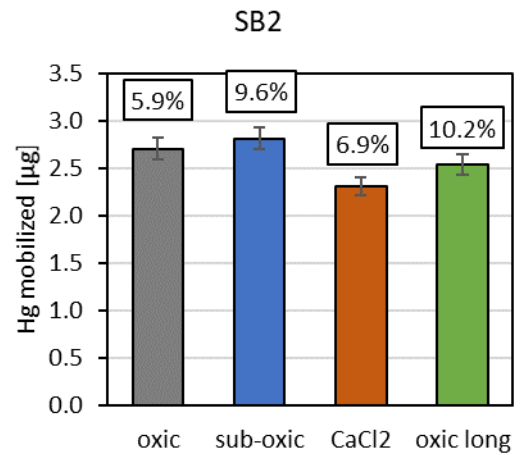
# RESULTS & DISCUSSION

## MERCURY MOBILIZATION

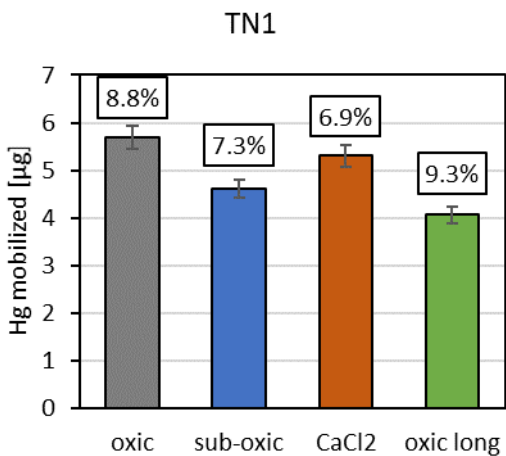
**Figure 2** illustrates results of leaching experiments and characteristics of the four different samples included in this study. Between 5.6% and 31% of the bulk  $Hg^{tot}$  were mobilized under varying leaching conditions. This resulted in high solution concentrations of around 369 to 9  $\mu g L^{-1}$  after 5 (14 days) and around 260 to 3  $\mu g L^{-1}$  after 9 extraction steps (81 days). No systematic difference, in terms of the proportion of mobilized Hg, was found between samples from the vadose vs. saturated zone. The absolute amount of Hg mobilized correlated with the solid  $Hg^{tot}$  and  $Hg^{tot}$  solution concentrations of up to 1200  $\mu g L^{-1}$  were found for the highest contaminated sample (K2-8).



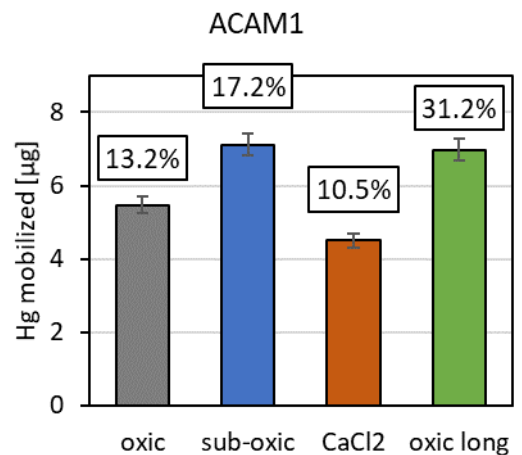
- vadose zone
- presence of  $Hg^0$  in the solid bulk (PTD)
- $Hg^{tot}$  633.5  $mg kg^{-1}$



- saturated zone
- all matrix bound- $Hg^{II}$  (PTD)
- $Hg^{tot}$  18.8  $mg kg^{-1}$



- saturated zone
- all matrix bound- $Hg^{II}$  (PTD)
- $Hg^{tot}$  32.4  $mg kg^{-1}$



- artificially contaminated aquifer material
- all matrix bound- $Hg^{II}$  (PTD)
- $Hg^{tot}$  20.1  $mg kg^{-1}$

**Figure 2:** Sample characteristics and leached proportions of Hg (sum of multiple extraction steps) for different biogeochemical conditions (Numbers indicate % of total soil Hg).

# RESULTS & DISCUSSION

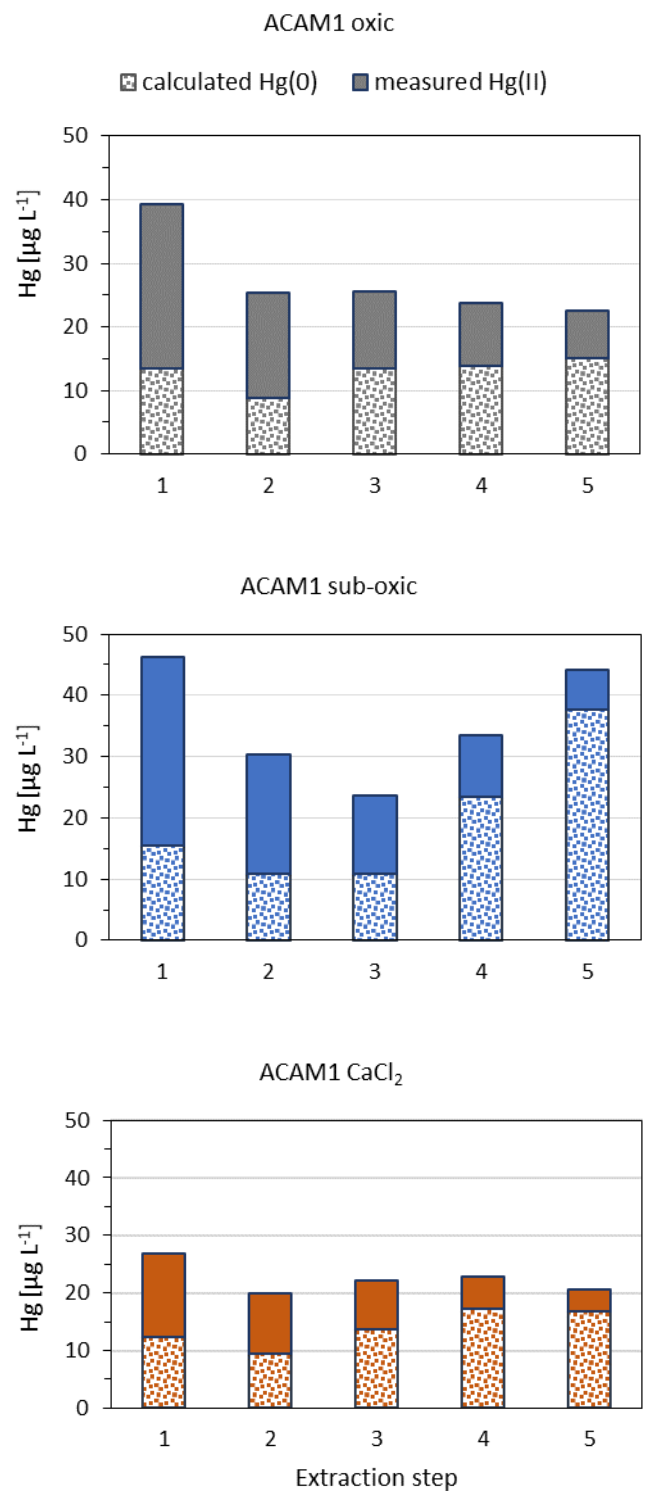
## MERCURY REDOX STATE

Different biogeochemical extraction conditions led to a difference in solution concentrations ( $Hg^{tot}$ ) as shown in **Figure 3** for the artificially contaminated sample.

The proportion of  $Hg^0$  of  $Hg^{tot}$  in solution was strikingly high over the course of the extraction, given that according to pyrolytic thermodesorption analysis only sample K2-8 contained  $Hg^0$  in the solid sample. For all other samples PTD indicated that Hg was predominantly matrix-bound  $Hg^{II}$ .

Up to 85% of the Hg in solution was present in the reduced form. In general, a higher proportion of  $Hg^0$  was found under sub-oxic extraction conditions for all samples. No correlation of dissolved Hg or  $Hg^0$  concentrations in extracts with any of the major elements measured by ICP-OES or DOC was found for oxic and sub-oxic extracts.

**Lower  $Hg^{tot}$  solution concentrations correlated with lower Fe and Al concentrations in  $CaCl_2$  compared to oxic and sub-oxic extracts.**



**Figure 3:** Hg solution concentrations over the course of 5 extraction steps (increasing duration) for the artificially contaminated aquifer material (ACAM1).

# RESULTS & DISCUSSION

## MERCURY STABLE ISOTOPES

Mercury stable isotopes were measured on selected extracts and showed a large variability among samples and treatments. A correlation between the fraction of  $\text{Hg}^0$  in solution and  $\delta^{202}\text{Hg}^{\text{tot}}$  was found for all samples. The correlation was found to be significant for ACAM1 in the oxic  $R^2=0.7945$  ( $p=0.0423$ ) and sub-oxic leachates  $R^2=0.9429$  ( $p=0.0059$ ). For this sample, all extracts were enriched in light Hg isotopes relative to the bulk soil Hg (here: NIST-3133 with  $\delta^{202}\text{Hg} = 0\text{‰}$ ). We also observed a significant correlation for sample TN1 in oxic  $R^2=0.9482$  ( $p=0.0051$ ), sub-oxic  $R^2=0.9662$  ( $p=0.0027$ ) and  $\text{CaCl}_2$  extracts  $R^2=0.7908$  ( $p=0.0435$ ). An enrichment of heavy or light isotopes in solution was found for TN1 relative to the bulk soil Hg (**Figure 4**).

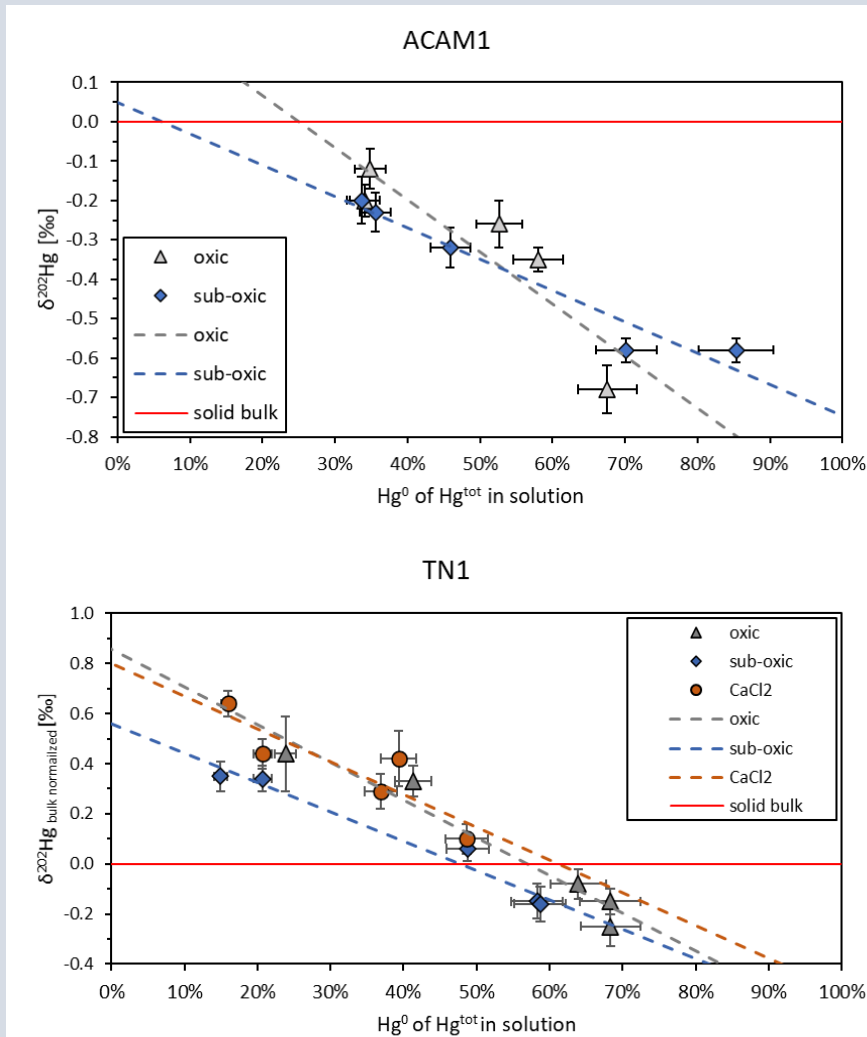


Figure 4: Correlation between the isotopic signature of  $\text{Hg}^{\text{tot}}$  and the proportion of  $\text{Hg}^0$  in solution for the artificial contamination and one sample from the saturated zone (TN1).

# RESULTS & DISCUSSION

## MERCURY STABLE ISOTOPES

Isotopic signatures for  $\delta^{202}\text{Hg}^0$  were calculated for selected samples by isotopic mass balance from measured  $\delta^{202}\text{Hg}^{\text{tot}}$  and  $\delta^{202}\text{Hg}^{\text{II}}$  values as illustrated in **equation 1**.

Calculated  $\delta^{202}\text{Hg}$  signatures of  $\text{Hg}^0$  in solution were isotopically light for all extracts as would be expected from an equilibrium between  $\text{Hg}^0$  and  $\text{Hg}^{\text{II}}$  solution species.

The enrichment factor ( $\epsilon^{202}\text{Hg}_{\text{Hg}^{\text{II}}-\text{Hg}^0}$ ) was calculated from  $\delta^{202}\text{Hg}$  signatures of  $\text{Hg}^0$  and  $\text{Hg}^{\text{II}}$  and was in good in agreement with theoretically predicted equilibrium fractionation between  $\text{Hg}^{\text{II}}$  solution species and  $\text{Hg}^0$  (**Figure 5**). We therefore hypothesize that  $\text{Hg}^0$  in solution was in equilibrium with  $\text{Hg}^{\text{II}}$  solution species during our leaching experiments.

**The difference in isotopic signature of total extracts with varying fractions of  $\text{Hg}^0$  shows that  $\delta^{202}\text{Hg}^{\text{tot}}$  signatures were not solely governed by an equilibrium between  $\text{Hg}^{\text{II}}$  and  $\text{Hg}^0$  in solution.**

If so, the equilibrium between the two solution species would always result in an identical  $\delta^{202}\text{Hg}^{\text{tot}}$  signatures independent from the fraction of  $\text{Hg}^0$  in solution.

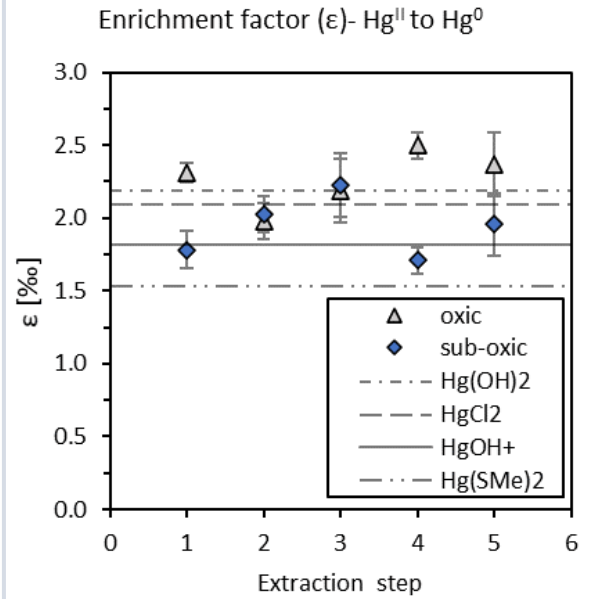


Figure 5: Calculated enrichment factors between  $\text{Hg}^{\text{II}}$  and  $\text{Hg}^0$  for sample ACAM1, oxic and sub-oxic treatment. Lines represent predicted enrichment factors for dominant  $\text{Hg}^{\text{II}}$  solution species relative to elemental  $\text{Hg}^0$  vapor [5].

### equation 1:

$$\delta^{202}\text{Hg}^0 = \frac{(\delta^{202}\text{Hg}^{\text{tot}} - (\delta^{202}\text{Hg}^{\text{II}} \times \text{fraction } \text{Hg}^{\text{II}}))}{\text{fraction } \text{Hg}^0}$$

The enrichment factor (e.g.  $\epsilon^{202}\text{Hg}$ ) was calculated from  $\delta^{202}\text{Hg}$  according to **equation 2** and indicates the direction and extent of isotopic fractionation between 2 reservoirs [7].

### equation 2:

$$\epsilon^{202}\text{Hg}_{\text{Hg}^{\text{II}} - \text{Hg}^0} = \delta^{202}\text{Hg}^{\text{II}} - \delta^{202}\text{Hg}^0$$

# CONCLUSIONS & OUTLOOK

We demonstrated that a surprisingly large amount of Hg can be mobilized by water from contaminated soil samples. Solution concentrations remained high over a leaching period of 81 days and 9 extraction steps (still between 3 and 260  $\mu\text{g L}^{-1}$  in 9<sup>th</sup> water extract) implying that the investigated samples could potentially release Hg over a long time period.

Although  $\text{Hg}^{\text{II}}$  was dominant in all solid samples a considerable proportion of  $\text{Hg}^0$  was found in solution with a high variability among treatments, indicating  $\text{Hg}^{\text{II}}$  reduction processes and active formation of  $\text{Hg}^0$  during the leaching experiments.

Our results show that isotopic ratios of mobilized Hg were distinct from bulk signatures and highlight the important influence of equilibrium isotope fractionation between Hg redox states for Hg isotope signatures in solution.

Potential kinetic isotope effects occurring during the mobilization step of Hg from the solid to the solution phase were presumably overprinted by secondary equilibration reactions.

Our results imply that Hg isotope variations may be used as a potential tracer for the complex biogeochemical processes and conditions involved in the mobilization of Hg from contaminated soil samples.

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