An Isotopic Dilution Approach for Quantifying Mercury Lability in Soils

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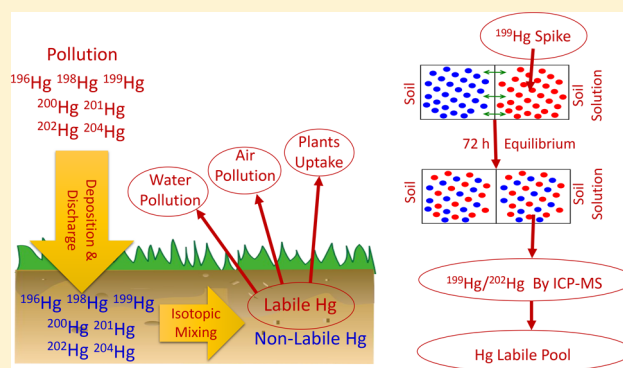
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[S] Supporting Information

ABSTRACT: The accurate estimation of soil mercury lability is crucial for risk assessment. In comparison to chemical fractionation and speciation, isotopic dilution (ID) offers precise definition of labile mercury fractions while maintaining the natural equilibrium. We developed and applied an ID protocol with ^{199}Hg to estimate the soil mercury (Hg) isotopically exchangeable (labile) pool or HgE using a range of industrially contaminated soils in Switzerland. The measured HgE values were consistent for the same soil against different spike levels (50, 100, and 200% of native ^{199}Hg), indicating that the spiked and soil isotopes achieved required dynamic equilibrium at the soil−water interface. Total soil Hg (THg; mg kg^{-1}) was the best predictor of HgE (mg kg^{-1}) and %HgE and accounted for 96 and 63% of the variance, respectively. Nonetheless, despite the wide range of THg values (0.37−310 mg kg^{-1}) in the studied soils, Hg lability spanned a narrow range (∼12−25% of THg), highlighting the large capacity of soils to sequester Hg in a very stable form. The "exchangeable pool" of Hg extracted by CH$_3$COONH$_4$ and MgCl$_2$ (<0.25 and <0.32% of THg, respectively) largely underestimated Hg lability in comparison to ID, suggesting the potential usefulness of the ID approach.

1. INTRODUCTION

Mercury (Hg) is a global pollutant that has created public concern because of its toxicity and substantial bioaccumulation.[1−3] The UNEP Minamata Convention on Mercury aims to reduce Hg use and to curb global anthropogenic emissions of Hg.[3,4] However, legacy Hg in soils and sediments will continue to pose significant risks through re-emission to the atmosphere and the surrounding environments. For example, the land−atmosphere flux may actually exceed the primary anthropogenic emissions of Hg^0 and thus prolongs its atmospheric residence.[5−7] Moreover, a considerable fraction of soil mercury can potentially accumulate in crops[8] or migrate to ground and surface waters.[9]

Soil Hg mobility and bioavailability are largely linked to its labile pool; therefore, accurate estimation of Hg lability is pivotal. To date, chemical extraction methods are the most popular way to liberate the labile fraction of soil Hg. Nonetheless, they suffer numerous limitations, e.g., interspecies conversion, re-adsorption, and redistribution of Hg between soil phases.[10,11] In addition, there is no universal protocol available such as the sequential extraction procedure developed by Tessier et al.[12] for classic hard metals,[10] and selecting the

type and sequence of extractants has always been an empirical decision based on the nature of soil or the targeted Hg species.[10,11] Moreover, when compared to the uptake of Hg by flora and fauna, good correlations were found between bioavailable Hg and Hg from all soil fractions, indicating that labile Hg is not exclusively bound to specific soil phases.[13,14] Isotopic dilution (ID) assesses the labile metal pool in soils by defining the fraction of metal that is isotopically exchangeable or its "E-value".[15] Currently, ID is the most promising method for estimating the potentially labile metal fraction regardless of its speciation or soil phase.[16] Isotopic dilution has been successfully applied to determine the E-values of several metals.[15−29]

To the best of our knowledge, ID protocols have never been applied to try to measure the lability of soil Hg. Working with Hg isotopes is a challenging task because of (i) the low sensitivity of ICP-MS to Hg caused by its naturally occurring seven isotopes and its high first ionization energy[30] and (ii) the
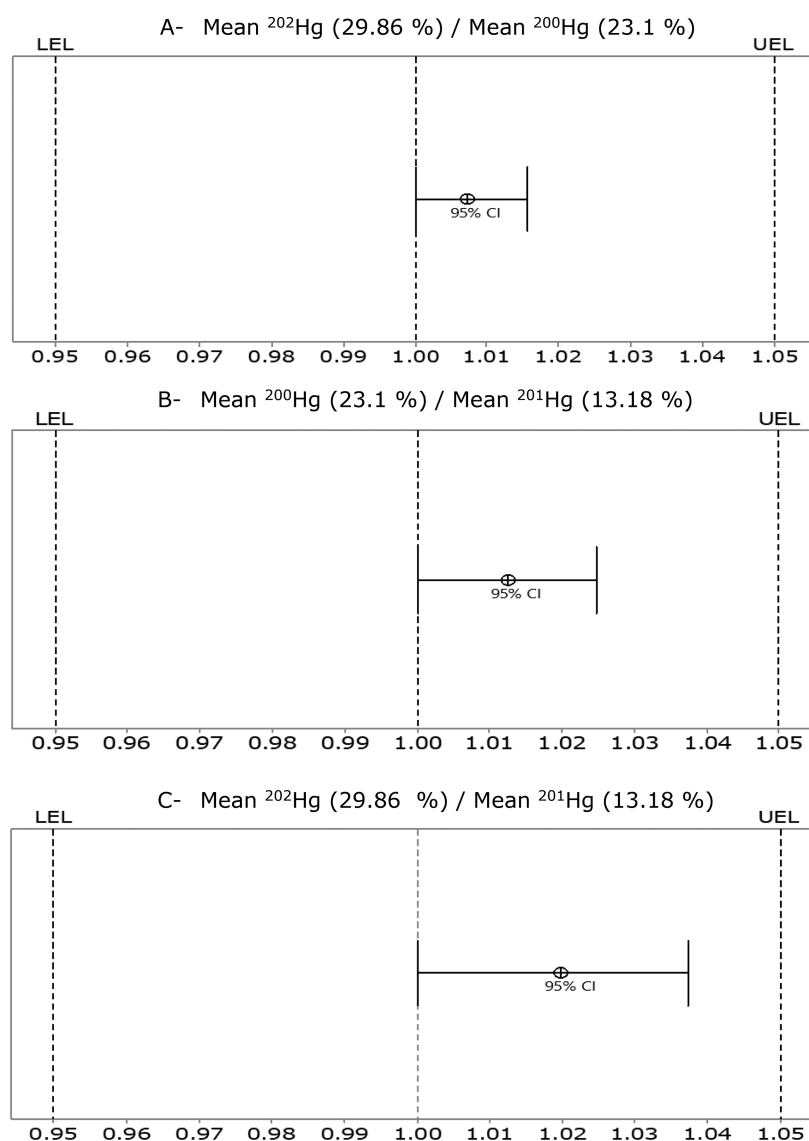
Figure 1. Comparison of equivalence tests (Minitab 17 package) showing the differences between the mean HgE values, at all sampling locations, measured by (A) ^{202}Hg vs ^{200}Hg, (B) ^{200}Hg vs ^{201}Hg, and (C) ^{202}Hg vs ^{201}Hg, as reference isotopes. Dashed lines represent the lower equivalence limit (LEL) and upper equivalence limit (UEL) set at a ±5% difference. Horizontal lines show the confidence interval (95%) for the difference in HgE measured by ^{202}Hg, ^{201}Hg, or ^{200}Hg. Three soil samples were taken from each location, and two spiked and two unspiked replicates were prepared for each sample.

potential reduction of soluble Hg^{2+} to Hg^0 and subsequent loss via evaporation or adsorption to glassware and the ICP-MS tubing system.[31] In view of the need to accurately estimate the availability of Hg in contaminated soils and to assess the associated environmental risks, this study aims to develop and apply a working ID protocol to quantify the pool size of labile soil Hg and to provide preliminary insights into the factors that likely control its mobility.

2. MATERIALS AND METHODS

2.1. Soil Sampling and Characterization. Three topsoil cores (0−10 cm) were taken in nine residential areas in South Switzerland where past industrial contamination with Hg is suspected (more in section S.1.1). Soils were air-dried and sieved to <2 mm, and soil properties, including pH, organic carbon (Org-C), and total soil Hg (THg), were determined as described in section S.1.1.

2.2. Preparation of Hg Stable Isotope Standards. The enriched mercury standard ($HgCl_2$, Trace Sciences Inc., certified isotopic abundances of 30% for ^{196}Hg and 36.8% for ^{199}Hg) was dissolved in 2% HNO_3 and 1% HCl to prevent Hg volatilization and improve its washout during analysis.[30,31]

2.3. Determination of Isotopically Exchangeable (labile) Hg (HgE) in Soil. Our ID protocol was adapted from several protocols developed for other heavy metals.[17,18,20,25] For all soils, two sets of soil suspensions [2 g of dry soils in 30 mL of 0.01 M $Ca(NO_3)_2$], each with four replicates, were prepared and shaken for 72 h. Two of the four replicates were then spiked with enriched ^{196}Hg or ^{199}Hg before all tubes were again shaken for an additional 72 h. Spiking solutions were prepared to deliver 50, 100, and 200% of native ^{196}Hg or ^{199}Hg to the soil suspension in three major groups (section S.1.2). The volume of the acidic spike solution was minimized to avoid altering the natural soil pH. Suspensions were then centrifuged (3500 rpm for 25 min) and filtered with

0.45 μm syringe filters. The ^{196}Hg/^{200}Hg, ^{196}Hg/^{201}Hg, ^{196}Hg/^{202}Hg, ^{199}Hg/^{200}Hg, ^{199}Hg/^{201}Hg, and ^{199}Hg/^{202}Hg isotopic ratios, in the supernatants, were measured with an Agilent 7700x ICP-MS instrument, and the isotopic abundances of spike and reference isotopes in soil (unspiked soil suspensions) were then inferred from their natural abundances[20,24,32] (details in section S.1.3). The isotopically exchangeable Hg pool or HgE (milligrams per kilogram) of each soil was calculated from eq 1 (adapted from ref 20).

$$ \text{HgE} = \frac{M_{sl}C_{sp}V_{sp}(^{sp}IA_{sp} - ^{rf}IA_{sp}R)}{M_{sp}W_{sl}(^{rf}IA_{sl}R - ^{sp}IA_{sl})} \tag{1}$$

where M_{sl} and M_{sp} are the average atomic masses of Hg in soil and spike, respectively, C_{sp} is the gravimetric concentration (mg L^{-1}) of ^{196}Hg or ^{199}Hg in the spike solution, V_{sp} is the volume of the spike (L), W_{sl} is the soil weight (kg), $^{sp}IA_{sp}$ and $^{rf}IA_{sp}$ are the spike and reference isotopes abundances in the spike solution, respectively, $^{sp}IA_{sl}$ and $^{rf}IA_{sl}$ are their abundances in soils (unspiked solutions), and R is the equilibrium ratio of the spike to the reference isotope as measured by ICP-MS.

While HgE gives the absolute amount of isotopically exchangeable Hg (HgE; mg kg^{-1}), Hg lability (%HgE) is the percentage of HgE to total soil Hg (THg).

For comparison with chemical extraction, "exchangeable" soil Hg was extracted by ammonium acetate and magnesium chloride[10,33,34] (more details in section S.1.4).

3. RESULTS AND DISCUSSION

3.1. Soil Parameters. Key soil parameters are listed in Table S1. All soils were slightly acidic or alkaline (pH 6.2−8.2) with average Org-C content (2.6−4.5%). The total soil Hg (THg) ranged on average from 0.37 to 310 mg kg^{-1} (more in section S.2.1).

3.2. Selection of Spike and Reference Isotopes. Mercury is a challenging element to analyze by ICP-MS because, in addition to its seven stable isotopes and high first ionization energy, soluble mercuric ions (Hg^{2+}) can be readily reduced to elemental mercury (Hg^0) and lost from solution by sorption to walls of containers and/or walls of the sample introduction system.[30] To eliminate cross-contamination and the memory effect, all working solutions were prepared in a 0.5% ultrapure HCl matrix to keep Hg in its oxidized form and thus improve its washout from the system;[31] in addition, a triple-step washing protocol (section S.1.3) was adopted. Nevertheless, results still showed substantial cross-contamination in the transition from ^{196}Hg-spiked samples to the periodic Hg standard. This was likely due to the very low natural abundance of ^{196}Hg in the periodic standard. As a result, the natural isotopic ratio of the periodic Hg standard was significantly distorted and led to fluctuation of the external mass discrimination correction factors beyond acceptable levels (0.59−0.93) (Table S2). In comparison, no significant cross-contamination was observed for ^{199}Hg, and the mass bias correction factors were close to unity [±<0.02 (Table S2)], rendering it more favorable as a spike isotope than ^{196}Hg.

Usually, unless significant isobaric interference is predicted, the "main" isotope is selected as a reference isotope for E-value calculations (eq 1); this is normally either the most abundant isotope or the closest to the average mass, e.g., ^{208}Pb, ^{65}Cu, and ^{114}Cd.[16,17,20] The values of HgE calculated using ^{201}Hg (average mass), ^{200}Hg, and ^{202}Hg (most abundant) were significantly

different [paired t test; $p < 0.05$ (Table S3)]. Nevertheless, equivalence analysis (Minitab 17) showed that the differences between HgE calculated by any two reference Hg isotopes were within a range of ±5% of their means [95% confidence interval (Figure 1)]; moreover, systematic shifts of the confidence intervals toward the more abundant isotopes were evident (Figure 1). In other words, the calculated HgE was directly proportional to the natural abundance of the selected reference isotope, which is most likely due to the higher sensitivity of ICP-MS for heavier and more abundant isotopes.[35] Accordingly, the HgE values calculated using ^{199}Hg as a spike isotope and ^{202}Hg as a reference isotope were regarded the most precise of all.

3.3. Validation of the Hg E-Value. In principle, E-value estimation is based on the assumption that the sorption reaction of the spiked isotopes is reversible and that the isotopes in soil solution and solid phases are in dynamic equilibrium.[15,16,28,29] Hamon et al.[36] and Marzouk et al.[25] demonstrated that the spiked isotopes may disturb the natural isotopic equilibrium leading to a systematic variation in the measured E-values at higher spike levels. Moreover, in elements with several oxidation states, e.g., As and Se, interspecies conversion may produce an error in the measured E-values, leading to it no longer representing the "isotopically exchangeable" pools.[37,38] Because Hg is known to interact significantly with organic matter[3,4,39] and may undergo interspecies conversion, e.g., evasion[40,41] and methylation,[1,42,43] validation of the measured HgE was essential.

We examined the validity of the proposed protocol by comparing HgE in all soils at different spike levels. Results showed that the apparent %HgE was consistent against different ^{199}Hg spike concentrations (Figure 2 and Table S4).
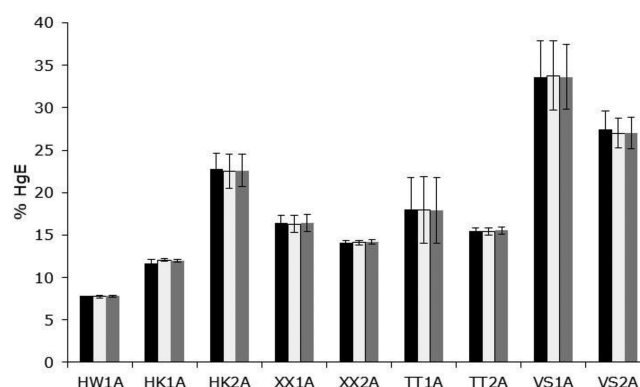

Figure 2. Hg lability (%HgE) in nine different soils from all sampling locations. Black, light gray, and dark gray columns represent %HgE estimated at 50, 100, and 200% ratios of spike to native ^{199}Hg, respectively. Error bars are standard errors between two spiked (for each spike ratio) and two unspiked replicates. More data in Table S4.

This indicates that the dominant process is the reversible adsorption of Hg and that the potential chemical transformations of the spiked Hg did not preclude the accurate determination of HgE. This is also true for the expected disturbance in the natural isotopic equilibrium at greater spike levels, which seems to have a minimal effect on the measured HgE.

3.4. Mercury Lability and Soil Properties. Across the whole range of data, both HgE (milligrams per kilogram) and %HgE showed good correlations ($r = 0.96$ and 0.63, respectively) with THg, while they showed no significant correlation with

any other soil parameter (Table S5). Stepwise regression, performed by Minitab 17, confirmed that THg is solely the best predictor of both HgE and %HgE accounting for 96 and 63% of the variance, respectively (Table S6). Figures S1 and S2 show that although a very good "power" relationship ($R^2 = 0.97$) between HgE and THg is evident, there is only a very broad "logarithmic" relationship ($R^2 = 0.18$) between THg and %HgE. For HgE (mg kg^{-1}), the strong correlation with THg is expected because THg spanned 4 orders of magnitude while falling within relatively narrow ranges of pH (6.2−8.2) and Org-C (2.63−4.48%) (Table S1). The broad correlation of THg with %HgE may reflect the fact that anthropogenic Hg remains more mobile than geogenic Hg or indicates a greater Hg reactivity due to weaker adsorption at higher THg. However, this relationship could possibly be an artifact, especially because THg is used to calculate %HgE. To investigate this, we used the 'lognorm.inv' function in Microsoft Excel to produce random distributions of THg and %HgE at 10000 values. In addition, %HgE was estimated against ln(THg) assuming that HgE (mg kg^{-1}) values are constant around their means ± the standard deviation.[44] Figure 3 clearly shows that, opposite to the experimental data, the calculated random relationships between THg and %HgE displayed negative trends.
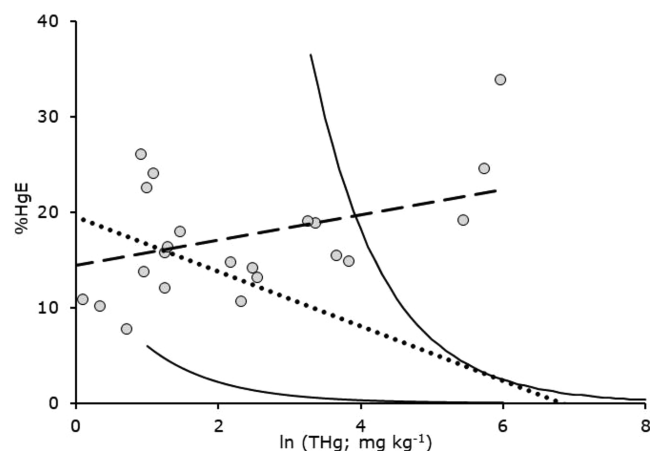

Figure 3. Relationship between ln(THg) and experimentally measured %HgE values displayed as gray circles. The dashed line is a linear regression of the data. The dotted line represents linear regression of 10000 random pairs of %HgE and ln(THg) allocated using the 'lognorm.inv(rand)' function in Microsoft Excel. The two solid curves assume that HgE values are fixed at the means of ln(HgE) ± the standard deviation, thus resulting in a variation of %HgE with ln(THg).

Overall, the observed range of %HgE [12.2−24.7 (Figure 4)] was very narrow as opposed to the very wide range of THg [0.37−310 mg kg^{-1} (Table S1)] and was considerably lower than the labilities of other heavy metals, e.g., Cd (≤80%), Pb (≤60%), and Zn (≤40%).[17,18,20,23,24] The exceptional affinity of Hg for soil organic matter among heavy metals is well-documented.[3,45] This highlights the extraordinarily large capacity of top soils and sediments with low and/or average organic content to scavenge high concentrations of Hg and mitigate its environmental mobility.[7,46−48]

3.5. Comparison with Extraction Methods. Ammonium acetate and magnesium chloride extractable Hg (exchangeable Hg) in our soils could be detected only in VS1 soils with pools
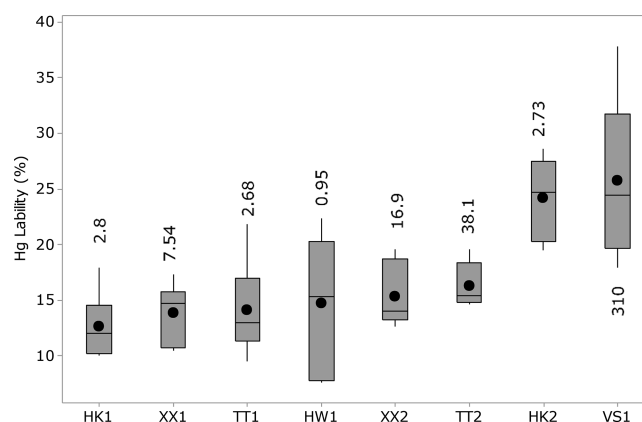

Figure 4. Values of %Hg lability (%HgE of total Hg) in all sampling locations. The "box and whisker" plot shows medians (horizontal lines) and means (black circles). The box demarcates the boundaries of the second and third quartiles; the whiskers extend to the furthest data point within 1.5 box heights (of the box). Locations are arranged according to their mean %HgE values in ascending order. Each sampling location is represented by three soil samples and four replicates (two spiked and two unspiked). Numbers above or below boxes are the average total Hg (THg) in each location (mg kg^{-1}).

of 0.01−0.25 and 0.01−0.32%, respectively, which is substantially lower than the labile Hg estimated by ID for the same location (19−33.7%). This very low extractability was in line with previous findings (usually 0−5%)[10,34,48] but was substantially lower than those of Pb, Zn, and Cd (≤30% over a similar pH range).[17,23−25] This reveals the clear distinction between Hg as a classic example of a soft metal that has high affinity for soft ligands, e.g., S-bearing groups and organic matter, as opposed to hard metals that tend to react with hard ligands, such as O-bearing groups and Fe, Mn, and Al hydrous oxides.[3,47,49,50] Therefore, in the case of hard acids (hard metals and protons), competition with Mg^{2+} and NH_4^+ on negatively charged oxygen sites may displace large amounts of sorbed metals, especially in acidic soils. On the other hand, as a soft metal attached to soft ligands, Hg will face no such competition, and the amounts released to the soil solution will be minimal over the whole natural soil pH range.[47]

3.6. Highlights, Limitations, and Outlooks. The soils used in this study were sampled at sites relatively close to each other that had been contaminated by one industrial Hg point source. They were thus relatively homogeneous in their Hg speciation, and this may have contributed to the apparent consistency of HgE at different spike levels. Highly acidic/alkaline soils or those soils enriched with Org-C that are simultaneously highly mineralized with Hg are scarce, and the investigation of HgE in pristine soils will require an analytical system that offers greater detection limits, e.g., by using a cold vapor introduction system and/or higher-resolution ICP-MS. This may also help in overcoming the ^{196}Hg carryover issues we encountered, enabling its usage as a spike isotope at levels much lower than that of ^{199}Hg.

Nevertheless, our set of soils covered the pH (slightly acidic to slightly basic) and Org-C (∼2−5%) ranges mostly found in nature, and the results demonstrated clearly that, under common circumstances, THg was the most decisive factor for both HgE and %HgE and highlighted the great capacity of surface soils and sediments to immobilize large quantities of Hg. However, future work on Hg-contaminated soils with a wider range of parameters and studies that link HgE to

bioavailable and reactive Hg (uptake by plants and animals, migration, and evasion) will be of great importance.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.7b00510.

Additional materials, methods, results, and discussion (PDF)

■ AUTHOR INFORMATION

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Notes

The authors declare no competing financial interest.

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