

An Isotopic Dilution Approach for Quantifying Mercury Lability in Soils

Waleed H. Shetaya^{1, 2,*}, Stefan Osterwalder¹, Moritz Bigalke³, Adrien Mestrot³, Jen-How Huang¹, Christine Alewell¹.

¹ Environmental Geosciences, University of Basel, Bernoullistrasse 30, 4056 Basel, Switzerland.

² Air Pollution Department, Environmental Sciences Division, National Research Centre, 33 El-Bohouth St., Dokki, Giza 12622, Egypt.

³ Institute of Geography, University of Bern, Hallerstrasse 12, 3012 Bern, Switzerland.

* Corresponding Author: waleedhares.shetaya@unibas.ch,

waleed.shetaya@outlook.com

13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41

42 **Abstract**

43 The accurate estimation of soil mercury lability is crucial for risk assessment. In
44 comparison to chemical fractionation and speciation, isotopic dilution (ID) offers precise
45 definition of labile mercury fractions while maintaining natural equilibrium. We developed
46 and applied an ID protocol with ^{199}Hg to estimate the soil mercury (Hg) isotopically
47 exchangeable (labile) pool or HgE using a range of industrially contaminated soils in
48 Switzerland. The measured HgE values were consistent for the same soil against different
49 spike levels (50, 100 and 200% of native ^{199}Hg) indicating that the spiked and soil isotopes
50 achieved required dynamic equilibrium at the soil-water interface. Total soil Hg (THg; mg
51 kg^{-1}) was the best predictor of HgE (mg kg^{-1}) and %HgE and accounted for 96 and 63 %
52 of the variance, respectively. Nonetheless, despite the wide range of THg (0.37 - 310 mg
53 kg^{-1}) in the studied soils, Hg lability spanned across a narrow range ($\sim 12 - 25$ % of THg),
54 highlighting the large capacity of soils to sequester Hg in a very stable form. The
55 'exchangeable pool' of Hg extracted by $\text{CH}_3\text{COONH}_4$ and MgCl_2 ($<0.25\%$ and $<0.32\%$ of
56 THg, respectively) largely underestimated Hg lability in comparison to ID suggesting the
57 potential usefulness of the ID approach.

58

59 **Keywords:**

60 Soil pollution, Air pollution, Heavy metals, Stable isotopes, ICP-MS

61

62

63

64

65

66

67

68 **1. Introduction**

69 Mercury (Hg) is a global pollutant that has drawn public concern due to its toxicity and
70 substantial bioaccumulation ¹⁻³. The UNEP Minamata Convention on Mercury aims to
71 reduce Hg use and to curb global anthropogenic emissions of Hg ^{3, 4}. However, legacy Hg
72 in soils and sediments will continue to pose significant risks through re-emission to the
73 atmosphere and the surrounding environments. For example, the land-atmosphere flux
74 may actually exceed the primary anthropogenic emissions of Hg⁰ and thus prolongs its
75 atmospheric residence ⁵⁻⁷. Moreover, a considerable fraction of soil mercury can
76 potentially accumulate in crops ⁸ or migrate to ground and surface waters ⁹.

77 Soil Hg mobility and bioavailability are largely linked to its labile pool; therefore, accurate
78 estimation of Hg lability is pivotal. To date, chemical extraction methods are the most
79 popular way to liberate the labile fraction of soil Hg. Nonetheless, they suffer numerous
80 limitations e.g. inter-species conversion, re-adsorption and redistribution of Hg between
81 soil phases ^{10, 11}. In addition, there is no universal protocol available such as the sequential
82 extraction procedure developed by Tessier, et al. ¹² for classic hard metals ¹⁰ and selecting
83 the type and sequence of extractants has always been an empirical decision based on the
84 nature of soil or the targeted Hg species ^{10, 11}. Moreover, when compared to Hg uptake by
85 flora and fauna, good correlations were found between bioavailable Hg and Hg from all soil
86 fractions indicating that labile Hg is not exclusively bound to specific soil phases ^{13, 14}.
87 Isotopic dilution (ID) assesses the labile metal pool in soils by defining the fraction of metal
88 that is isotopically-exchangeable or its 'E-Value' ¹⁵. Currently, ID is the most promising
89 method to estimate the potentially labile metal fraction regardless of its speciation or soil
90 phase ¹⁶. Isotopic dilution has been successfully applied to determine the E-value of several
91 metals ¹⁵⁻²⁹.

92 To our knowledge, ID protocols have never been applied to try and measure the lability of
93 soil Hg. Working with Hg isotopes is a challenging task due to (i) ICP-MS low sensitivity
94 towards Hg caused by its naturally occurring seven isotopes and its high first ionization

95 energy ³⁰, and (ii) the potential reduction of soluble Hg⁺² to Hg⁰ and subsequent loss via
96 evaporation or adsorption to glassware and ICP-MS tubing system ³¹. In view of the need
97 to accurately estimate the availability of Hg in contaminated soils and to assess the
98 associated environmental risks, this study aims to develop and apply a working ID protocol
99 to quantify the pool size of labile soil Hg, and to provide preliminary insights into the
100 factors that likely control its mobility.

101 **2. Materials and Methods**

102 **2.1. Soil sampling and characterisation**

103 Three topsoil cores (0-10 cm) were taken in 9 residential areas in South-Switzerland where
104 past industrial contamination with Hg is suspected (more in SI; S.1.1). Soils were air dried
105 and sieved to <2 mm and soil properties including pH, organic carbon (Org-C), and total
106 soil Hg (THg) were determined as described in SI (S.1.1).

107 **2.2. Preparation of Hg stable isotope standards**

108 Enriched mercury standard (HgCl₂, Trace Sciences Inc., Texas, USA, certified isotopic
109 abundances of 30% for ¹⁹⁶Hg and 36.8% for ¹⁹⁹Hg) was dissolved in 2 % HNO₃ and 1%
110 HCl to prevent Hg volatilization and improve its washout during analysis ^{30, 31}.

111 **2.3. Determination of isotopically exchangeable (labile) Hg (Hg_E) in soil**

112 Our ID protocol was adapted from several protocols developed for other heavy metals ¹⁷,
113 ^{18, 20, 25}. For all soils, two sets of soil suspensions (2 g dry soils in 30 mL 0.01 M Ca (NO₃)₂),
114 each with 4 replicates, were prepared and shaken for 72 h. Two of the four replicates were
115 then spiked with enriched ¹⁹⁶Hg or ¹⁹⁹Hg before all tubes were re-shaken for another 72 h.
116 Spiking solutions were prepared to deliver 50%, 100% and 200% of native ¹⁹⁶Hg or ¹⁹⁹Hg
117 to the soil suspension in three major groups (SI, S.1.2). The volume of the acidic spike
118 solution was minimized to avoid altering natural soil pH. Suspensions were then
119 centrifuged (3500 rpm, 25 min) and filtered with 0.45 μm syringe filters. The isotopic
120 ratios ¹⁹⁶Hg/²⁰⁰Hg, ¹⁹⁶Hg/²⁰¹Hg, ¹⁹⁶Hg/²⁰²Hg, ¹⁹⁹Hg/²⁰⁰Hg, ¹⁹⁹Hg/²⁰¹Hg and ¹⁹⁹Hg/²⁰²Hg, in the

121 supernatants, were measured by an Agilent 7700x ICP-MS and the isotopic abundances of
122 spike and reference isotopes in soil (unspiked soil suspensions) were then inferred from
123 their natural abundances ^{20, 24, 32} (details in SI; S.1.3.). The isotopically exchangeable Hg
124 pool or HgE (mg kg⁻¹) of each soil was calculated from Equation 1 (adapted from Garforth,
125 et al. ²⁰).

$$126 \quad \text{HgE} = \frac{M_{\text{sl}} C_{\text{sp}} V_{\text{sp}} (\text{}^{\text{sp}}\text{IA}_{\text{sp}} - \text{}^{\text{rf}}\text{IA}_{\text{sp}} R)}{M_{\text{sp}} W_{\text{sl}} (\text{}^{\text{rf}}\text{IA}_{\text{sl}} R - \text{}^{\text{sp}}\text{IA}_{\text{sl}})} \quad (1)$$

127 where M_{sl} and M_{sp} are the average atomic masses of Hg in soil and spike, respectively. C_{sp}
128 is the gravimetric concentration (mg L⁻¹) of ¹⁹⁶Hg or ¹⁹⁹Hg in the spike solution, V_{sp} is the
129 volume of the spike (L) and W_{sl} is the soil weight (kg). $\text{}^{\text{sp}}\text{IA}_{\text{sp}}$, $\text{}^{\text{rf}}\text{IA}_{\text{sp}}$ are the spike and
130 reference isotopes abundances in the spike solution, respectively, and $\text{}^{\text{sp}}\text{IA}_{\text{sl}}$, $\text{}^{\text{rf}}\text{IA}_{\text{sl}}$ are their
131 abundances in soils (un-spiked solutions). R is the equilibrium ratio of the spike to the
132 reference isotope as measured by ICP-MS.

133 While HgE gives the absolute amount of isotopically exchangeable Hg (mg HgE kg⁻¹ soil),
134 Hg lability (%HgE) is the percentage of HgE to total soil Hg (THg).

135 For comparison with chemical extraction, 'exchangeable' soil Hg was extracted by
136 ammonium acetate and magnesium chloride ^{10, 33, 34} (more details in SI; S.1.4.).

137

138 **3. Results and Discussion**

139 **3.1. Soil parameters**

140 Key soil parameters are displayed in Table S1. All soils were slightly acidic or alkaline (pH
141 6.2 - 8.2) with average Org-C content (2.6 to 4.5 %). Total soil Hg (THg) ranged in average
142 from 0.37 to 310 mg kg⁻¹ (more in SI, S.2.1.).

143 **3.2. Selection of spike and reference isotopes**

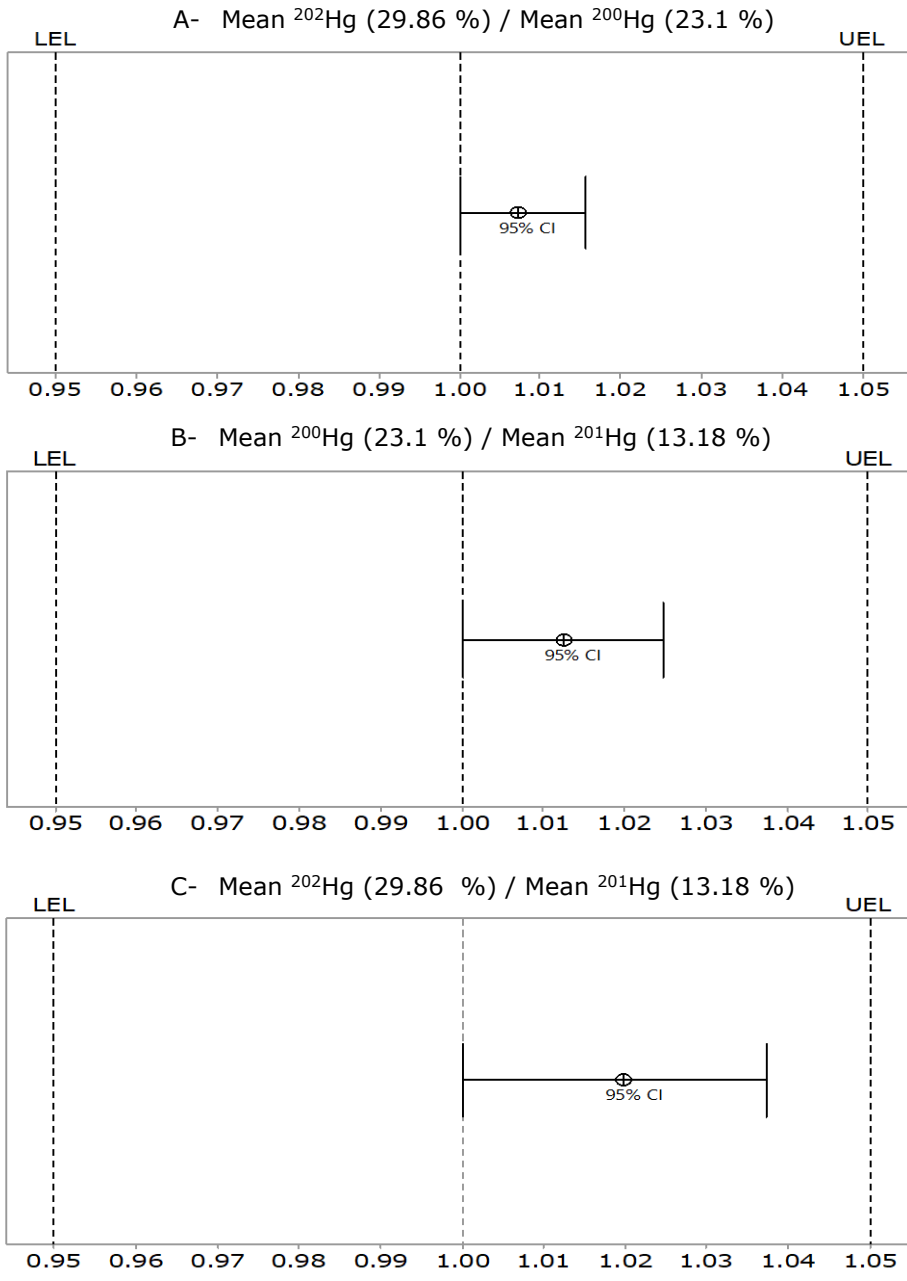
144 Mercury is a challenging element to analyse by ICP-MS because, in addition to its seven
145 stable isotopes and high first ionization energy, soluble mercuric ions (Hg⁺²) can be readily

146 reduced to elemental mercury (Hg^0) and lost from solution by sorption to containers' walls
147 and/or sample introduction system walls³⁰. To eliminate cross-contamination and memory
148 effect, all working solutions were prepared in a 0.5% ultra-pure HCl matrix to keep Hg in
149 its oxidised form and thus improve its washout from the system³¹; in addition, a triple-
150 step washing protocol (SI, S.1.3.) was adopted. Nevertheless, results still showed
151 substantial cross contamination in transition from ^{196}Hg spiked samples to the periodic Hg
152 standard. This was likely due to the very low natural abundance of ^{196}Hg in the periodic
153 standard. As a result, the natural isotopic ratio of the periodic Hg standard was significantly
154 distorted and fluctuated the external mass discrimination correction factors beyond
155 acceptable levels (0.59 - 0.93) (Table S2). In comparison, no significant cross-
156 contamination was observed for ^{199}Hg and the mass-bias correction factors were close to
157 the unity ($\pm < 0.02$; Table S2) rendering it more favourable as a spike isotope than ^{196}Hg .

158 Usually, unless significant isobaric interference is predicted, the 'main' isotope is selected
159 as a reference isotope for E-value calculations (Eq. 1); this is normally either the most
160 abundant isotope or the closest to the average mass e.g. ^{208}Pb , ^{65}Cu and ^{114}Cd ^{16, 17, 20}.
161 The values of HgE calculated using ^{201}Hg (average mass), ^{200}Hg and ^{202}Hg (most
162 abundant), were significantly different (paired t-test; $p < 0.05$, Table S3). Nevertheless,
163 equivalence analysis (Minitab 17) showed that the differences between HgE calculated by
164 any two reference Hg isotopes were within a range of $\pm 5\%$ of their means (95%
165 confidence interval, Figure 1.); moreover, systematic shifts of the confidence intervals
166 towards the more abundant isotopes were evident (Figure 1.). In other words, the
167 calculated HgE was directly proportional to the natural abundance of the selected reference
168 isotope which is most likely due to the higher sensitivity of ICP-MS for heavier and more
169 abundant isotopes³⁵. Accordingly, the HgE values calculated using ^{199}Hg as a spike isotope
170 and ^{202}Hg as a reference isotope were regarded the most precise of all.

171

172



173

174 **Figure 1.** Comparison of equivalence tests (Minitab 17 package) showing the differences
 175 between the mean HgE values, at all sampling locations, measured by: A- ²⁰²Hg vs ²⁰⁰Hg,
 176 B- ²⁰⁰Hg vs ²⁰¹Hg and C- ²⁰²Hg vs ²⁰¹Hg, as reference isotopes. Dashed lines represent
 177 Lower Equivalence Limit (LEL) and Upper Equivalence Limit (UEL) set at ± 5% difference.
 178 Horizontal lines show confidence interval (95%) for the difference in HgE measured by
 179 ²⁰²Hg, ²⁰¹Hg or ²⁰⁰Hg. Three soil samples were taken from each location and two spiked
 180 and two un-spiked replicates were prepared for each sample.

181

182

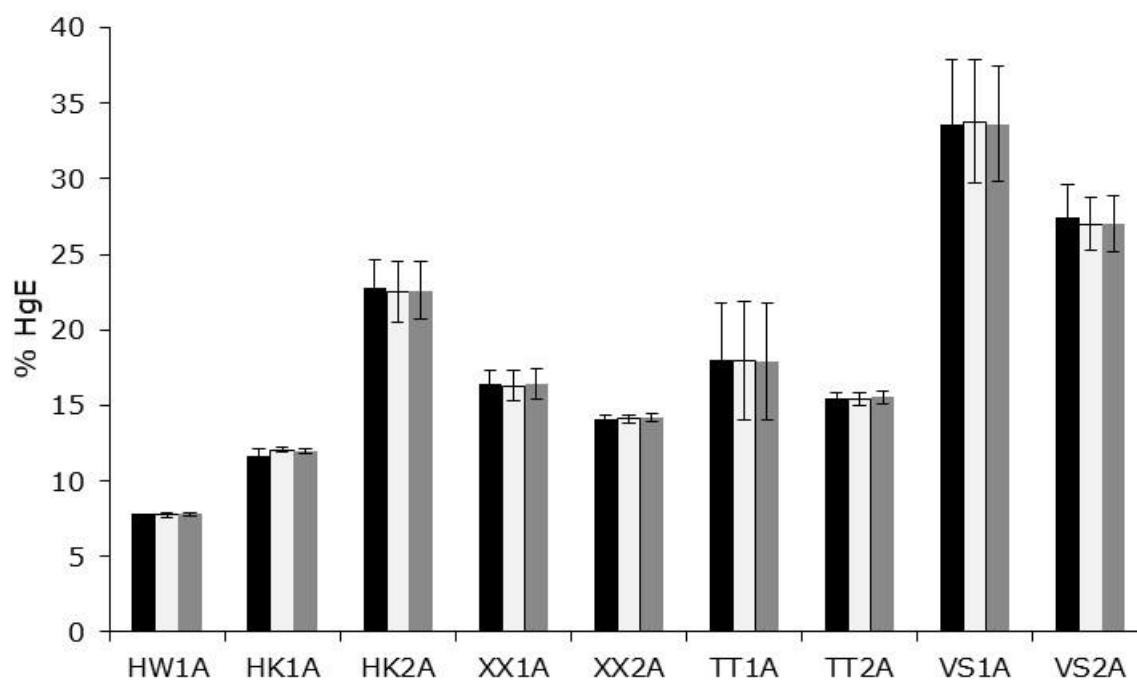
183

184 **3.3. Validation of Hg E-value**

185 In principle, E-value estimation is based on the assumption that the sorption reaction of
186 the spiked isotopes is reversible and that the isotopes in soil solution and solid phases are
187 in dynamic equilibrium ^{15, 16, 28, 29}. Hamon, et al. ³⁶ and Marzouk, et al. ²⁵ demonstrated
188 that the spiked isotopes may disturb the natural isotopic equilibrium leading to a
189 systematic variation in the measured E-values at higher spike levels. Moreover, in
190 elements with several oxidation states e.g. As, Se, interspecies conversion may produce
191 an error in the measured E-values rendering it no longer represents the 'isotopically
192 exchangeable' pools ^{37, 38}. Since Hg is known to interact significantly with organic matter
193 ^{3, 4, 39} and may undergo interspecies conversion e.g. evasion ^{40, 41} and methylation ^{1, 42, 43},
194 validation of the measured HgE was essential.

195 We examined the validity of the proposed protocol by comparing HgE in all soils at different
196 spike levels. Results showed that the apparent %HgE was consistent against different
197 ¹⁹⁹Hg spike concentrations (Figure 2 & Table S4). This indicates that the dominant process
198 is the reversible adsorption of Hg and that the potential chemical transformations of the
199 spiked Hg did not preclude the accurate determination of HgE. This is also true for the
200 expected disturbance in natural isotopic equilibrium at greater spike levels which seems
201 to have minimal effect on the measured HgE.

202



203

204 **Figure 2.** Hg lability (% HgE) in nine different soil from all sampling locations. Black, light
 205 grey and dark grey columns represent %HgE estimated at 50%, 100% and 200% ratios
 206 of spike to native ¹⁹⁹Hg, respectively. Error bars are standard error between 2 spiked (for
 207 each spike ratio) and 2 unspiked replicates. More data in Table S4.

208

209

210

211

212

213

214

215

216

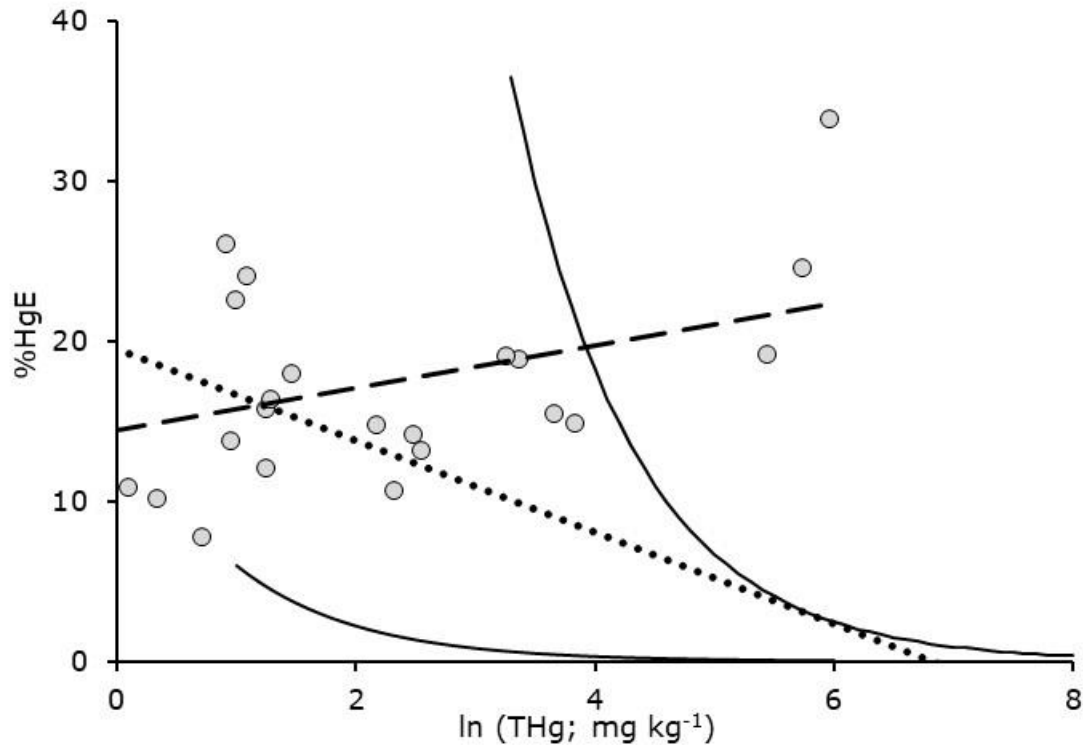
217

218 **3.4. Mercury lability and soil properties**

219 Across the whole range of data, both HgE (mg kg⁻¹) and %HgE showed good correlations
220 (r= 0.96, 0.63, respectively) with THg while they showed no significant correlation with
221 any other soil parameter (Table S5). Stepwise regression, performed by Minitab 17,
222 confirmed that THg is solely the best predictor of both HgE and %HgE accounting for 96
223 and 63 % of the variance, respectively (Table S6). Figures S1 and S2 show that although
224 a very good 'power' relationship (R²=0.97) between HgE and THg is evident, there is only
225 a very broad 'logarithmic' relationship (R²=0.18) between THg and %HgE. For HgE (mg
226 kg⁻¹), the strong correlation with THg is expected since THg spanned across four orders of
227 magnitude while falls within a relatively narrow range of pH (6.2 - 8.2) and Org-C (2.63 -
228 4.48 %) (Table S1). The broad correlation of THg with %HgE may reflect that
229 anthropogenic Hg remains more mobile than geogenic Hg or indicates a greater Hg
230 reactivity due to weaker adsorption at higher THg. However, this relationship could
231 possibly be an artefact especially that THg is used to calculate %HgE. To investigate this,
232 we used the 'lognorm.inv' function in Microsoft Excel to produce random distributions of
233 THg and %HgE at 10000 values. In addition, %HgE was estimated against ln(THg)
234 assuming that HgE (mg kg⁻¹) values are constant around their means ± standard deviation
235 ⁴⁴. Figure 3 clearly shows that, opposite to the experimental data, the calculated random
236 relationships between THg and %HgE displayed negative trends.

237

238



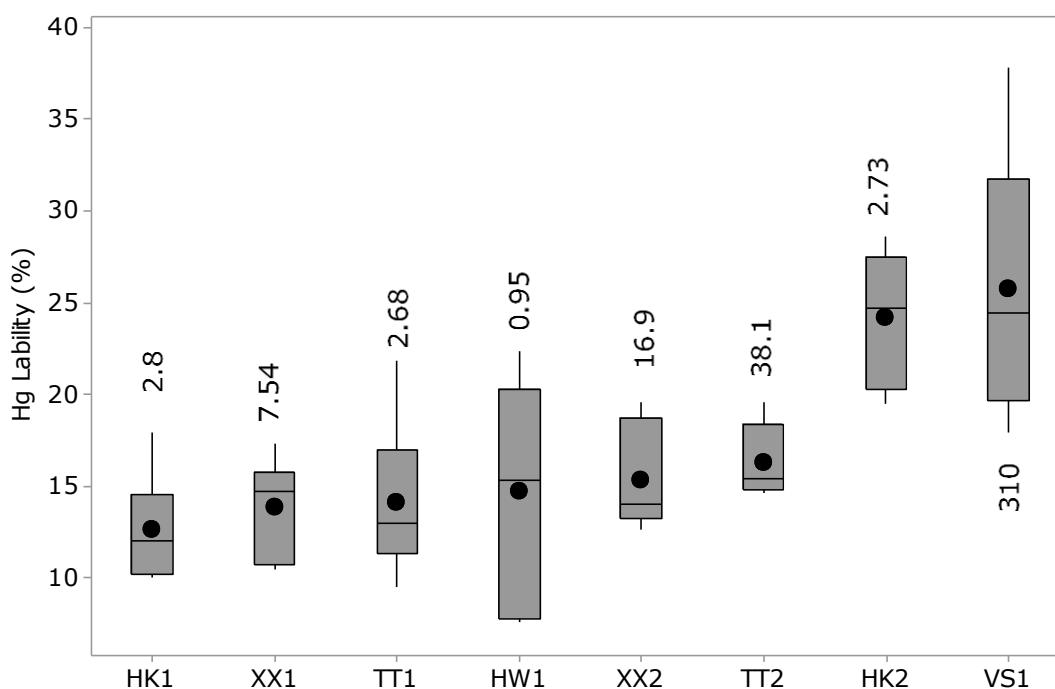
239

240 **Figure 3.** Relationship between $\ln(\text{THg}; \text{mg kg}^{-1})$ and experimentally measured %HgE
 241 values is displayed as grey circles and the dashed line is the a linear regression of the
 242 data. The dotted line represents linear regression of 10000 random pairs of %HgE and
 243 $\ln(\text{THg})$ allocated using the 'lognorm.inv(rand)' function of Microsoft Excel. The two solid
 244 curves assumes that HgE values are fixed at the means of $\ln(\text{HgE}) \pm \text{SD}$, thus resulting in
 245 a variation of %HgE with $\ln(\text{THg})$.

246

247 Overall, the observed range of %HgE (12.2 – 24.7; Figure 4) was very narrow as opposed
 248 to the very wide range of THg (0.37 - 310 mg kg^{-1} ; Table S1) and was considerably lower
 249 than other heavy metals' labilities e.g. Cd (up to 80%), Pb (up to 60%), and Zn (up to
 250 40%)^{17, 18, 20, 23, 24}. The exceptional affinity of Hg toward soil organic matter among heavy
 251 metals is well documented^{3, 45}. This highlights the extraordinarily large capacity of top
 252 soils and sediments with low/average organic content to scavenge high concentrations of
 253 Hg and mitigate its environmental mobility^{7, 46-48}.

254



255

256 **Figure 4.** Values of % Hg lability (% HgE of total Hg) in all sampling locations. The 'box
 257 and whisker' plot shows median (horizontal lines), mean (black circle symbols). The box
 258 demarcates the boundaries of the second and third quartile; the whiskers extend to the
 259 furthest data point within 1.5 box heights (of the box). Locations are arranged according
 260 to their mean %HgE values in an ascending order. Each sampling location is represented
 261 by three soil samples and 4 replicates (two spiked and two un-spiked). Numbers above or
 262 below boxes are average total Hg (THg) in each location (mg kg⁻¹).

263

264 3.5. Comparison with extraction methods

265 Ammonium acetate and magnesium chloride extractable Hg (exchangeable Hg) in our soils
 266 was only detectable in VS1 soils with pools of 0.01 to 0.25 % and 0.01 to 0.32 %, respectively,
 267 which is substantially lower than the labile Hg estimated by ID for the same
 268 location (19 – 33.7 %). This very low extractability was in line with previous findings
 269 (usually 0-5%)^{10, 34, 48} but was substantially lower than those of Pb, Zn and Cd (up to 30
 270 % at similar pH range)^{17, 23-25}. This reveals the clear distinction between Hg as a classic
 271 example of soft metal that has high affinity toward soft ligands e.g. S-bearing groups and
 272 organic matter as opposed to hard metals which tend to react with hard ligands such as
 273 O-bearing groups and Fe, Mn and Al hydrous oxides^{3, 47, 49, 50}. Therefore, in case of hard

274 acids (hard metals and protons), competition with Mg^{2+} and NH_4^+ on negatively charged
275 oxygen sites may displace large amounts of sorbed metals especially in acidic soils. On
276 the other hand, as a soft metal attached to soft ligands, Hg will face no such competition
277 and the amounts released to soil solution will be minimal over the whole natural soil pH
278 range ⁴⁷.

279 **3.6. Highlights, limitations and outlooks**

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

289 Nevertheless, our set of soils covered the pH (slightly acidic to slightly basic) and Org-C
290 (c. 2-5%) ranges mostly found in nature and the results demonstrated clearly that, under
291 common circumstance, THg was the most decisive factor for both HgE and %HgE and
292 highlighted the great capacity of surface soils and sediments to immobilize large quantities
293 of Hg. However, future work on Hg contaminated soils with wider range of parameters,
294 and studies that link HgE to bioavailable and reactive Hg (uptake by plants and animals,
295 migration and evasion) will be of great importance.

296

297

298

299

300 **Acknowledgments**

301 Waleed H. Shetaya acknowledges postdoctoral fellowship from the Swiss Government
302 Federal Department of Economic Affairs, Education and Research (EAER). Waleed H.
303 Shetaya likes also to thank Dr. Scott Young and Dr. Liz Bailey, the University of
304 Nottingham, UK, for the development of the original statistical random distribution models
305 used to generate Figure 3.

306 **Reference**

- 307 1. Mahaffey, K. R., Methylmercury: A new look at the risks. *Public Health Reports*
308 **1999**, *114*, (5), 397-+.
- 309 2. Eto, K.; Marumoto, M.; Takeya, M., The pathology of methylmercury poisoning
310 (Minamata disease). *Neuropathology* **2010**, *30*, (5), 471-479.
- 311 3. Beckers, F.; Rinklebe, J., Cycling of Mercury in the Environment: Sources, Fate,
312 and Human Health Implications-A Review. *Critical Reviews in Environmental Science and*
313 *Technology* **2017**, (just-accepted), 00-00.
- 314 4. Driscoll, C. T.; Mason, R. P.; Chan, H. M.; Jacob, D. J.; Pirrone, N., Mercury as a
315 Global Pollutant: Sources, Pathways, and Effects. *Environmental Science & Technology*
316 **2013**, *47*, (10), 4967-4983.
- 317 5. Grigal, D., Inputs and outputs of mercury from terrestrial watersheds: a review.
318 *Environmental Reviews* **2002**, *10*, (1), 1-39.
- 319 6. Reis, A. T.; Rodrigues, S. M.; Davidson, C. M.; Pereira, E.; Duarte, A. C.,
320 Extractability and mobility of mercury from agricultural soils surrounding industrial and
321 mining contaminated areas. *Chemosphere* **2010**, *81*, (11), 1369-1377.
- 322 7. Tipping, E.; Wadsworth, R. A.; Norris, D. A.; Hall, J. R.; Ilyin, I., Long-term mercury
323 dynamics in UK soils. *Environmental Pollution* **2011**, *159*, (12), 3474-3483.
- 324 8. Zhang, H.; Feng, X.; Larssen, T.; Qiu, G.; Vogt, R. D., In inland China, rice, rather
325 than fish, is the major pathway for methylmercury exposure. *Environmental Health*
326 *Perspectives* **2010**, *118*, (9), 1183.
- 327 9. Xue, T.; Wang, R. Q.; Zhang, M. M.; Dai, J. L., Adsorption and Desorption of
328 Mercury(II) in Three Forest Soils in Shandong Province, China. *Pedosphere* **2013**, *23*, (2),
329 265-272.
- 330 10. Issaro, N.; Abi-Ghanem, C.; Bermond, A., Fractionation studies of mercury in soils
331 and sediments: A review of the chemical reagents used for mercury extraction. *Analytica*
332 *Chimica Acta* **2009**, *631*, (1), 1-12.
- 333 11. Reis, A. T.; Lopes, C. B.; Davidson, C. M.; Duarte, A. C.; Pereira, E., Extraction of
334 available and labile fractions of mercury from contaminated soils: The role of operational
335 parameters. *Geoderma* **2015**, *259*, 213-223.

- 336 12. Tessier, A.; Campbell, P. G.; Bisson, M., Sequential extraction procedure for the
337 speciation of particulate trace metals. *Analytical chemistry* **1979**, *51*, (7), 844-851.
- 338 13. Han, F. X.; Su, Y.; Shi, Z.; Xia, Y.; Tian, W.; Philips, V.; Monts, D. L.; Gu, M.;
339 Liang, Y., Mercury distribution and speciation in floodplain soils and uptake into native
340 earthworms (*Diplocardia* spp.). *Geoderma* **2012**, *170*, 261-268.
- 341 14. Jing, Y.; He, Z.; Yang, X.; Sun, C., Evaluation of Soil Tests for Plant-available
342 Mercury in a Soil–Crop Rotation System. *Communications in soil science and plant analysis*
343 **2008**, *39*, (19-20), 3032-3046.
- 344 15. Young, S. D.; Tye, A.; Carstensen, A.; Resende, L.; Crout, N., Methods for
345 determining labile cadmium and zinc in soil. *European Journal of Soil Science* **2000**, *51*,
346 (1), 129-136.
- 347 16. Gabler, H. E.; Bahr, A.; Heidkamp, A.; Utermann, J., Enriched stable isotopes for
348 determining the isotopically exchangeable element content in soils. *European Journal of*
349 *Soil Science* **2007**, *58*, (3), 746-757.
- 350 17. Atkinson, N. R.; Bailey, E. H.; Tye, A. M.; Breward, N.; Young, S. D., Fractionation
351 of lead in soil by isotopic dilution and sequential extraction. *Environmental Chemistry*
352 **2011**, *8*, (5), 493-500.
- 353 18. Chenery, S. R.; Izquierdo, M.; Marzouk, E.; Klinck, B.; Palumbo-Roe, B.; Tye, A.
354 M., Soil-plant interactions and the uptake of Pb at abandoned mining sites in the Rookhope
355 catchment of the N. Pennines, UK - A Pb isotope study. *Science of the Total Environment*
356 **2012**, *433*, 547-560.
- 357 19. Gäbler, H.-E.; Bahr, A.; Mieke, B., Determination of the interchangeable heavy-
358 metal fraction in soils by isotope dilution mass spectrometry. *Fresenius' journal of*
359 *analytical chemistry* **1999**, *365*, (5), 409-414.
- 360 20. Garforth, J. M.; Bailey, E. H.; Tye, A. M.; Young, S. D.; Lofts, S., Using isotopic
361 dilution to assess chemical extraction of labile Ni, Cu, Zn, Cd and Pb in soils. *Chemosphere*
362 **2016**, *155*, 534-541.
- 363 21. Izquierdo, M.; Tye, A.; Chenery, S., Sources, lability and solubility of Pb in alluvial
364 soils of the River Trent catchment, UK. *Science of the Total Environment* **2012**, *433*, 110-
365 122.
- 366 22. Mao, L.; Young, S.; Tye, A.; Bailey, E., Predicting trace metal solubility and
367 fractionation in Urban soils from isotopic exchangeability. *Environmental Pollution* **2017**.
- 368 23. Mao, L. C.; Bailey, E. H.; Chester, J.; Dean, J.; Ander, E. L.; Chenery, S. R.; Young,
369 S. D., Lability of Pb in soil: effects of soil properties and contaminant source.
370 *Environmental Chemistry* **2014**, *11*, (6), 690-701.
- 371 24. Marzouk, E. R.; Chenery, S. R.; Young, S. D., Predicting the solubility and lability
372 of Zn, Cd, and Pb in soils from a minespoil-contaminated catchment by stable isotopic
373 exchange. *Geochimica Et Cosmochimica Acta* **2013**, *123*, 1-16.
- 374 25. Marzouk, E. R.; Chenery, S. R.; Young, S. D., Measuring reactive metal in soil: a
375 comparison of multi-element isotopic dilution and chemical extraction. *European Journal*
376 *of Soil Science* **2013**, *64*, (4), 526-536.

- 377 26. Nolan, A. L.; Ma, Y. B.; Lombi, E.; McLaughlin, M. J., Measurement of labile Cu in
378 soil using stable isotope dilution and isotope ratio analysis by ICP-MS. *Analytical and*
379 *Bioanalytical Chemistry* **2004**, *380*, (5-6), 789-797.
- 380 27. Sivry, Y.; Riotte, J.; Munoz, M.; Sappin-Didier, V.; Dupre, B., Study of labile Cd
381 pool in contaminated soil using stable isotope analysis, radioactive isotope dilution and
382 sequential extraction. *Geochimica Et Cosmochimica Acta* **2006**, *70*, (18), A594-A594.
- 383 28. Tongtavee, N.; Shiowatana, J.; McLaren, R. G.; Gray, C. W., Assessment of lead
384 availability in contaminated soil using isotope dilution techniques. *Science of the Total*
385 *Environment* **2005**, *348*, (1-3), 244-256.
- 386 29. Young, S.; Crout, N.; Hutchinson, J.; Tye, A.; Tandy, S.; Nakhone, L., Techniques
387 for measuring attenuation: isotopic dilution methods. *Natural attenuation of trace element*
388 *availability in soils* **2007**, 19-37.
- 389 30. McCurdy, E., Successful Low Level Mercury Analysis using the Agilent 7700 Series
390 ICP-MS. *Agilent ICP-MS J* **2011**, *45*, (1).
- 391 31. Nelms, S., Determination of Mercury in Urine. *AMERICAN BIOTECHNOLOGY*
392 *LABORATORY* **2004**, *22*, (2), 50-55.
- 393 32. Hieftje, G. M.; Barnes, J. H.; Grøn, O. A.; Leach, A. M.; McClenathan, D. M.; Ray,
394 S. J.; Solyom, D. A.; Wetzels, W. C.; Denton, M. B.; Koppelaar, D. W., Evolution and
395 revolution in instrumentation for plasma-source mass spectrometry. *Pure and applied*
396 *chemistry* **2001**, *73*, (10), 1579-1588.
- 397 33. Han, F. X.; Su, Y.; Monts, D. L.; Waggoner, C. A.; Plodinec, M. J., Binding,
398 distribution, and plant uptake of mercury in a soil from Oak Ridge, Tennessee, USA.
399 *Science of the Total Environment* **2006**, *368*, (2-3), 753-768.
- 400 34. Panyamethekul, S., An operationally defined method to determine the speciation
401 of mercury. *Environmental Geochemistry and Health* **2004**, *26*, (1), 51-57.
- 402 35. Nelms, S. M.; Beauchemin, D., *Inductively coupled plasma mass spectrometry*
403 *handbook*. Oxford, Boca Raton, FL: 2005.
- 404 36. Hamon, R. E.; Parker, D. R.; Lombi, E., Advances in isotopic dilution techniques in
405 trace element research: a review of methodologies, benefits, and limitations. *Advances in*
406 *agronomy* **2008**, *99*, 289-343.
- 407 37. Hamon, R. E.; Lombi, E.; Fortunati, P.; Nolan, A. L.; McLaughlin, M. J., Coupling
408 speciation and isotope dilution techniques to study arsenic mobilization in the
409 environment. *Environmental Science & Technology* **2004**, *38*, (6), 1794-1798.
- 410 38. Collins, R. N.; Tran, N. D.; Bakkaus, E.; Avoscan, L.; Gouget, B., Assessment of
411 isotope exchange methodology to determine the sorption coefficient and isotopically
412 exchangeable concentration of selenium in soils and sediments. *Environmental Science &*
413 *Technology* **2006**, *40*, (24), 7778-7783.
- 414 39. Fitzgerald, W.; Lamborg, C., Geochemistry of mercury in the environment.
415 *Environmental Geochemistry* **2005**, *9*, 107.
- 416 40. Fritsche, J.; Osterwader, S.; Nilsson, M. B.; Sagerfors, J.; Akerblom, S.; Bishop,
417 K.; Alewell, C., Evasion of Elemental Mercury from a Boreal Peat land Suppressed by Long-
418 Term Sulfate Addition. *Environmental Science & Technology Letters* **2014**, *1*, (10), 421-
419 425.

- 420 41. Schluter, K., Review: evaporation of mercury from soils. An integration and
421 synthesis of current knowledge. *Environmental Geology* **2000**, 39, (3-4), 249-271.
- 422 42. Morel, F. M. M.; Kraepiel, A. M. L.; Amyot, M., The chemical cycle and
423 bioaccumulation of mercury. *Annual Review of Ecology and Systematics* **1998**, 29, 543-
424 566.
- 425 43. Mousavi, A.; Chavez, R. D.; Ali, A. M. S.; Cabaniss, S. E., Mercury in Natural
426 Waters: A Mini-Review. *Environmental Forensics* **2011**, 12, (1), 14-18.
- 427 44. Shetaya, W. H.; Marzouk, E. R.; Mohamed, E. F.; Elkassas, M.; Bailey, E. H.; Young,
428 S. D., Lead in Egyptian soils: Origin, reactivity and bioavailability measured by stable
429 isotope dilution. *Science of The Total Environment* **2018**, 618, 460-468.
- 430 45. Tipping, E., Modelling the interactions of Hg(II) and methylmercury with humic
431 substances using WHAM/Model VI. *Applied Geochemistry* **2007**, 22, (8), 1624-1635.
- 432 46. Soares, L. C.; Egreja, F. B.; Linhares, L. A.; Windmoller, C. C.; Yoshida, M. I.,
433 Accumulation and oxidation of elemental mercury in tropical soils. *Chemosphere* **2015**,
434 134, 181-191.
- 435 47. Wallschlager, D.; Hintelmann, H.; Evans, R. D.; Wilken, R. D., VOLATILIZATION
436 OF DIMETHYLMERCURY AND ELEMENTAL MERCURY FROM RIVER ELBE FLOODPLAIN
437 SOILS. *Water Air and Soil Pollution* **1995**, 80, (1-4), 1325-1329.
- 438 48. Renneberg, A. J.; Dudas, M. J., Transformations of elemental mercury to inorganic
439 and organic forms in mercury and hydrocarbon co-contaminated soils. *Chemosphere*
440 **2001**, 45, (6-7), 1103-1109.
- 441 49. Schuster, E., THE BEHAVIOR OF MERCURY IN THE SOIL WITH SPECIAL EMPHASIS
442 ON COMPLEXATION AND ADSORPTION PROCESSES - A REVIEW OF THE LITERATURE.
443 *Water Air and Soil Pollution* **1991**, 56, 667-680.
- 444 50. Skyllberg, U.; Bloom, P. R.; Qian, J.; Lin, C.-M.; Blears, W. F., Complexation of
445 mercury (II) in soil organic matter: EXAFS evidence for linear two-coordination with
446 reduced sulfur groups. *Environmental science & technology* **2006**, 40, (13), 4174-4180.
- 447
- 448