

# **An Isotopic Dilution Approach for Quantifying Mercury Lability in Soils**

Waleed H. Shetaya<sup>1, 2,\*</sup>, Stefan Osterwalder<sup>1</sup>, Moritz Bigalke<sup>3</sup>, Adrien Mestrot<sup>3</sup>, Jen-How Huang<sup>1</sup>, Christine Alewell<sup>1</sup>.

<sup>1</sup> Environmental Geosciences, University of Basel, Bernoullistrasse 30, 4056 Basel, Switzerland.

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

<sup>3</sup> Institute of Geography, University of Bern, Hallerstrasse 12, 3012 Bern, Switzerland.

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

waleed.shetaya@outlook.com

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  $^{199}\text{Hg}$  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  $^{199}\text{Hg}$ ) indicating that the spiked and soil isotopes  
50 achieved required dynamic equilibrium at the soil-water interface. Total soil Hg (THg; mg  
51  $\text{kg}^{-1}$ ) was the best predictor of HgE (mg  $\text{kg}^{-1}$ ) 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  $\text{kg}^{-1}$ ) 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  $\text{MgCl}_2$  ( $<0.25\%$  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 <sup>1-3</sup>. The UNEP Minamata Convention on Mercury aims to  
71 reduce Hg use and to curb global anthropogenic emissions of Hg <sup>3, 4</sup>. 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 Hg<sup>0</sup> and thus prolongs its  
75 atmospheric residence <sup>5-7</sup>. Moreover, a considerable fraction of soil mercury can  
76 potentially accumulate in crops <sup>8</sup> or migrate to ground and surface waters <sup>9</sup>.

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 <sup>10, 11</sup>. In addition, there is no universal protocol available such as the sequential  
82 extraction procedure developed by Tessier, et al. <sup>12</sup> for classic hard metals <sup>10</sup> 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 <sup>10, 11</sup>. 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 <sup>13, 14</sup>.  
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' <sup>15</sup>. Currently, ID is the most promising  
89 method to estimate the potentially labile metal fraction regardless of its speciation or soil  
90 phase <sup>16</sup>. Isotopic dilution has been successfully applied to determine the E-value of several  
91 metals <sup>15-29</sup>.

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 <sup>30</sup>, and (ii) the potential reduction of soluble Hg<sup>+2</sup> to Hg<sup>0</sup> and subsequent loss via  
96 evaporation or adsorption to glassware and ICP-MS tubing system <sup>31</sup>. 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 (HgCl<sub>2</sub>, Trace Sciences Inc., Texas, USA, certified isotopic  
109 abundances of 30% for <sup>196</sup>Hg and 36.8% for <sup>199</sup>Hg) was dissolved in 2 % HNO<sub>3</sub> and 1%  
110 HCl to prevent Hg volatilization and improve its washout during analysis <sup>30, 31</sup>.

### 111 **2.3. Determination of isotopically exchangeable (labile) Hg (Hg<sub>E</sub>) in soil**

112 Our ID protocol was adapted from several protocols developed for other heavy metals <sup>17</sup>,  
113 <sup>18, 20, 25</sup>. For all soils, two sets of soil suspensions (2 g dry soils in 30 mL 0.01 M Ca (NO<sub>3</sub>)<sub>2</sub>),  
114 each with 4 replicates, were prepared and shaken for 72 h. Two of the four replicates were  
115 then spiked with enriched <sup>196</sup>Hg or <sup>199</sup>Hg before all tubes were re-shaken for another 72 h.  
116 Spiking solutions were prepared to deliver 50%, 100% and 200% of native <sup>196</sup>Hg or <sup>199</sup>Hg  
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 <sup>196</sup>Hg/<sup>200</sup>Hg, <sup>196</sup>Hg/<sup>201</sup>Hg, <sup>196</sup>Hg/<sup>202</sup>Hg, <sup>199</sup>Hg/<sup>200</sup>Hg, <sup>199</sup>Hg/<sup>201</sup>Hg and <sup>199</sup>Hg/<sup>202</sup>Hg, 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 <sup>20, 24, 32</sup> (details in SI; S.1.3.). The isotopically exchangeable Hg  
124 pool or HgE (mg kg<sup>-1</sup>) of each soil was calculated from Equation 1 (adapted from Garforth,  
125 et al. <sup>20</sup>).

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

127 where  $M_{\text{sl}}$  and  $M_{\text{sp}}$  are the average atomic masses of Hg in soil and spike, respectively.  $C_{\text{sp}}$   
128 is the gravimetric concentration (mg L<sup>-1</sup>) of <sup>196</sup>Hg or <sup>199</sup>Hg in the spike solution,  $V_{\text{sp}}$  is the  
129 volume of the spike (L) and  $W_{\text{sl}}$  is the soil weight (kg).  ${}^{\text{sp}}\text{IA}_{\text{sp}}$ ,  ${}^{\text{rf}}\text{IA}_{\text{sp}}$  are the spike and  
130 reference isotopes abundances in the spike solution, respectively, and  ${}^{\text{sp}}\text{IA}_{\text{sl}}$ ,  ${}^{\text{rf}}\text{IA}_{\text{sl}}$  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<sup>-1</sup> 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 <sup>10, 33, 34</sup> (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<sup>-1</sup> (more in SI, S.2.1.).

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

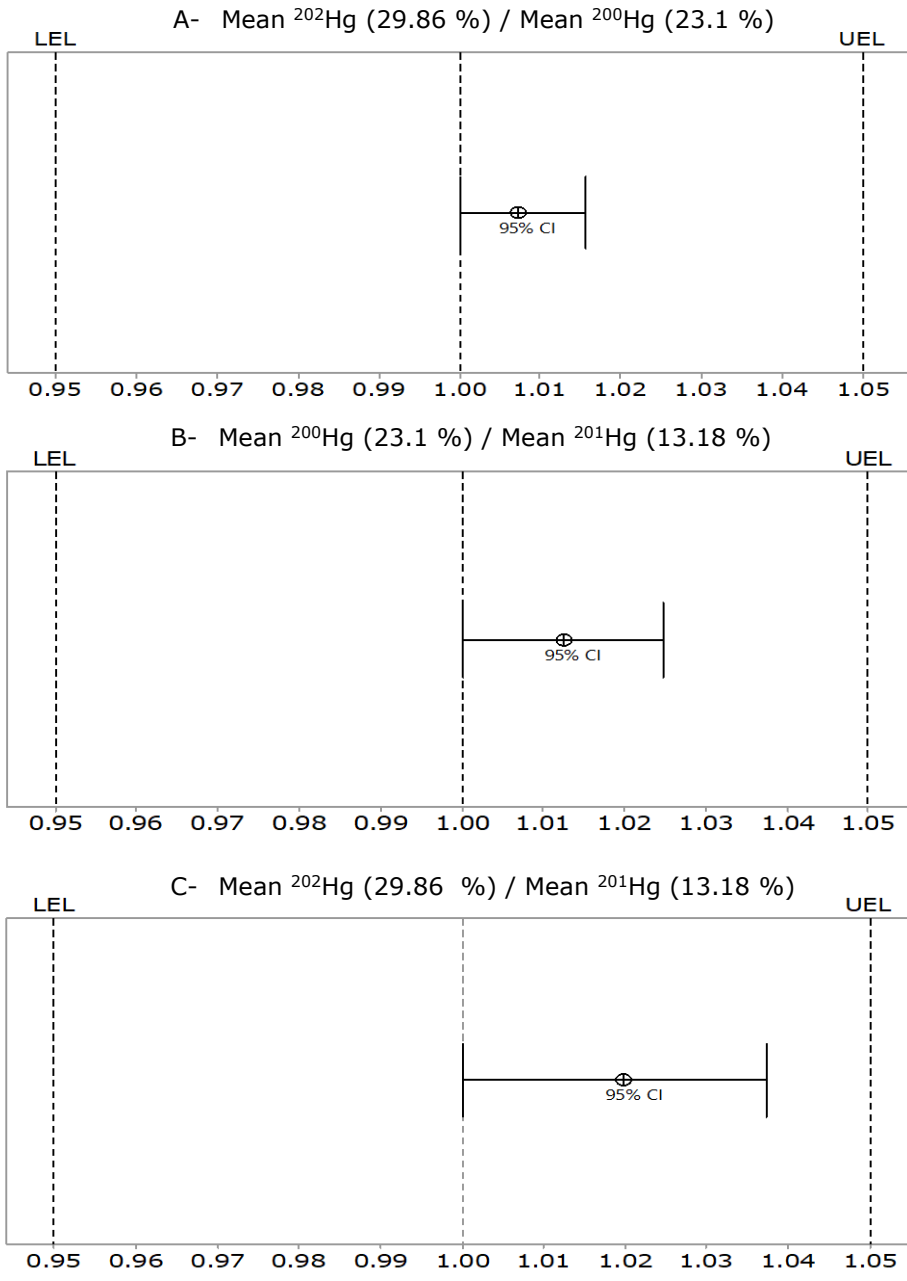
144 Mercury is a challenging element to analyse by ICP-MS because, in addition to its seven  
145 stable isotopes and high first ionization energy, soluble mercuric ions (Hg<sup>+2</sup>) can be readily

146 reduced to elemental mercury ( $\text{Hg}^0$ ) and lost from solution by sorption to containers' walls  
147 and/or sample introduction system walls<sup>30</sup>. 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 system<sup>31</sup>; 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  $^{196}\text{Hg}$  spiked samples to the periodic Hg  
152 standard. This was likely due to the very low natural abundance of  $^{196}\text{Hg}$  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  $^{199}\text{Hg}$  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  $^{196}\text{Hg}$ .

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.  $^{208}\text{Pb}$ ,  $^{65}\text{Cu}$  and  $^{114}\text{Cd}$ <sup>16, 17, 20</sup>.  
161 The values of HgE calculated using  $^{201}\text{Hg}$  (average mass),  $^{200}\text{Hg}$  and  $^{202}\text{Hg}$  (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 isotopes<sup>35</sup>. Accordingly, the HgE values calculated using  $^{199}\text{Hg}$  as a spike isotope  
170 and  $^{202}\text{Hg}$  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-  $^{202}\text{Hg}$  vs  $^{200}\text{Hg}$ ,  
 176 B-  $^{200}\text{Hg}$  vs  $^{201}\text{Hg}$  and C-  $^{202}\text{Hg}$  vs  $^{201}\text{Hg}$ , as reference isotopes. Dashed lines represent  
 177 Lower Equivalence Limit (LEL) and Upper Equivalence Limit (UEL) set at  $\pm 5\%$  difference.  
 178 Horizontal lines show confidence interval (95%) for the difference in HgE measured by  
 179  $^{202}\text{Hg}$ ,  $^{201}\text{Hg}$  or  $^{200}\text{Hg}$ . 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

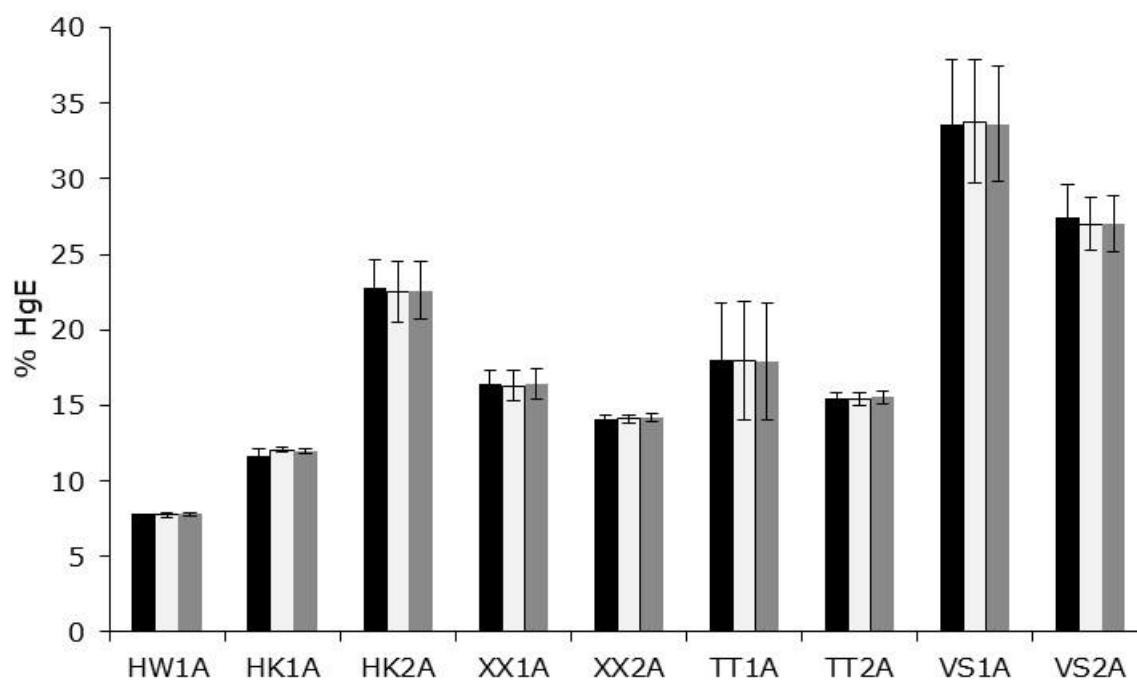
184 **3.3. Validation of Hg E-value**

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 <sup>15, 16, 28, 29</sup>. Hamon, et al. <sup>36</sup> and Marzouk, et al. <sup>25</sup> 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 <sup>37, 38</sup>. Since Hg is known to interact significantly with organic matter  
193 <sup>3, 4, 39</sup> and may undergo interspecies conversion e.g. evasion <sup>40, 41</sup> and methylation <sup>1, 42, 43</sup>,  
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 <sup>199</sup>Hg 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 <sup>199</sup>Hg, 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

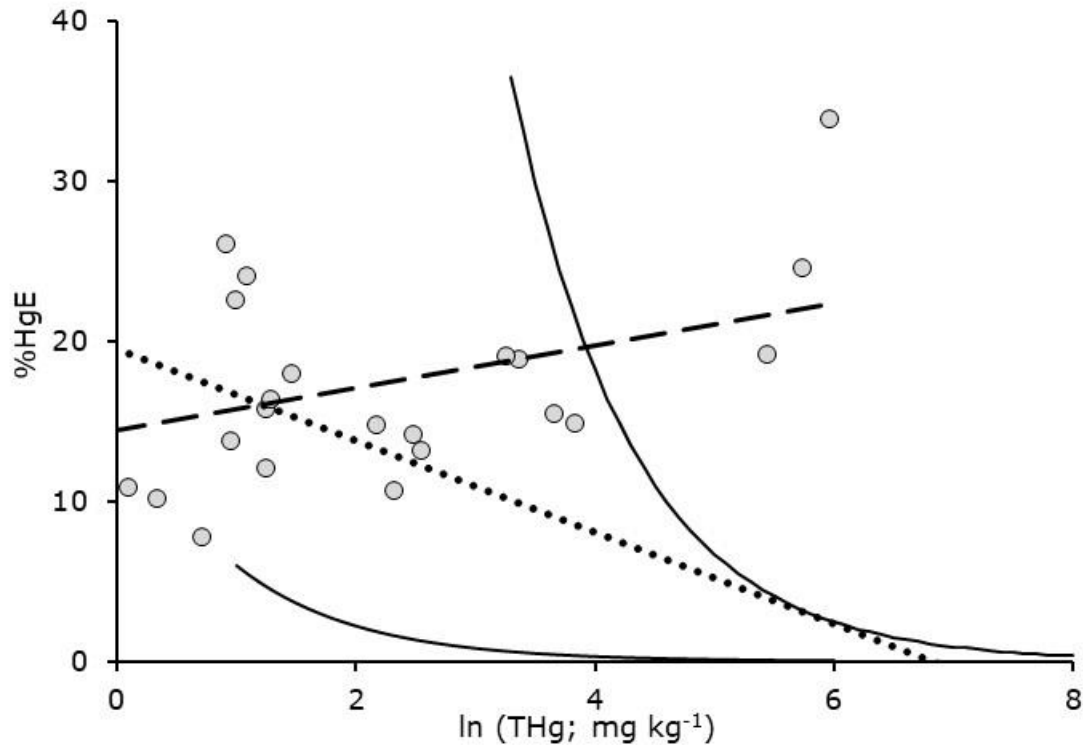
217

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

219 Across the whole range of data, both HgE (mg kg<sup>-1</sup>) 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 (R<sup>2</sup>=0.97) between HgE and THg is evident, there is only  
225 a very broad 'logarithmic' relationship (R<sup>2</sup>=0.18) between THg and %HgE. For HgE (mg  
226 kg<sup>-1</sup>), 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<sup>-1</sup>) values are constant around their means ± standard deviation  
235 <sup>44</sup>. Figure 3 clearly shows that, opposite to the experimental data, the calculated random  
236 relationships between THg and %HgE displayed negative trends.

237

238



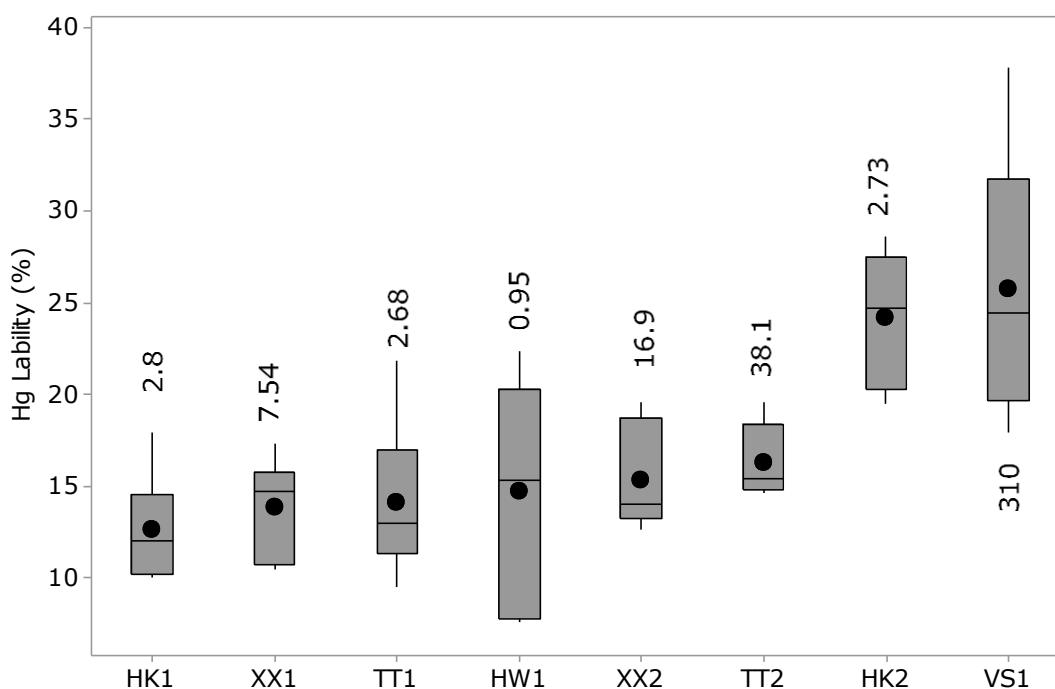
239

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  $\text{mg kg}^{-1}$ ; 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%)<sup>17, 18, 20, 23, 24</sup>. The exceptional affinity of Hg toward soil organic matter among heavy  
 251 metals is well documented<sup>3, 45</sup>. 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<sup>7, 46-48</sup>.

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<sup>-1</sup>).

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%)<sup>10, 34, 48</sup> but was substantially lower than those of Pb, Zn and Cd (up to 30  
 270 % at similar pH range)<sup>17, 23-25</sup>. 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<sup>3, 47, 49, 50</sup>. 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 <sup>47</sup>.

### 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 <sup>196</sup>Hg carryover issues we encountered  
288 enabling its usage as a spike isotope at much lower levels than <sup>199</sup>Hg.

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