	1	An Isotopic Dilution Approach for Quantifying Mercury Lability in
	2	Soils
	3 4	Waleed H. Shetaya ^{1, 2,*} , Stefan Osterwalder ¹ , Moritz Bigalke ³ , Adrien Mestrot ³ , Jen-How Huang ¹ , Christine Alewell ¹ .
	5 6	¹ Environmental Geosciences, University of Basel, Bernoullistrasse 30, 4056 Basel, Switzerland.
	7 8 9	² Air Pollution Department, Environmental Sciences Division, National Research Centre, 33 El-Bohouth St., Dokki, Giza 12622, Egypt.
	10 11	³ Institute of Geography, University of Bern, Hallerstrasse 12, 3012 Bern,
	12	Switzerland.
	13	* Corresponding Author: waleedhares.shetaya@unibas.ch,
	14	waleed.shetaya@outlook.com
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An Isotopic Dilution Approach for Quantifying Mercury Lability in

30 Supporting Information:

31 S.1. Materials and Methods:

32 S.1.1. Soil sampling and chemical characterisation

33 Soil samples were collected from nine different sites (located in some residential areas of Visp (46° 17' 32'' N, 7° 52' 58'' E) and Raron (46° 18' 36'' N, 7° 48'' E) towns, Canton 34 35 Valais, Switzerland, where a past industrial contamination with Hg is suspected. Three topsoil cores (collected at 0-10 cm depth) were taken from each plot within an area of 10 36 x 10 m or along a line-transect. One of these locations (VS2) was taken as a background 37 38 reference based on a previous investigation performed by Arcadis AG at this site (mixed samples n=16) which showed THg concentrations of < 0.1 mg kg⁻¹. Samples were 39 40 collected using a previously cleaned stainless steel auger and sealed in polyethylene bags for transport. Soils were air-died then sieved to < 2mm particle size for analysis. 41

42 Soil pH was measured using a glass electrode after 5 g of 2 mm sieved soils were equilibrated (end over end shaker) for 30 min in 12.5 mL of Milli-Q water. Soil organic 43 44 carbon content (%SOC) and organic nitrogen were determined by a Lyco CN 628 analyser. 45 About 0.25 g of ball milled soils were weighted into tin capsules and combusted at 1000°C. Carbon was measured by an infrared detector in oxygen rich environment while nitrogen 46 was measured by thermal conductivity in helium. Reactive Fe, Al and Mn oxides is soils 47 were extracted by the dithionite procedure developed by Kostka and Luther ¹. Finely 48 ground soils (agate ball mill) were suspended in 25 mL of a solution containing 0.22 M tri-49 sodium citrate, 0.11 M sodium hydrogen carbonate and 0.1 M sodium dithionite and 50 shaken for 16 hours in a water bath at 40°C. Centrifuged and filtered samples were 51 retained for analysis of Fe, AI, and Mn by ICP-OES and concentrations (mg kg⁻¹) of Fe₂O₃, 52 MnO₂, and Al(OH)₃ were calculated. Concentrations of metals in the dithionite and acid 53 54 extracts (diluted in 5% v/v HNO₃) were assayed by an Agilent ICP-OES 5100. Sample processing was undertaken using ICP Expert software (version 7.2). Total sulfur in soil 55 samples was extracted by the Swiss standard regulations on soil pollution protocol 56 (Verordnung über Belastungen des Bodens; VBBo)². In triplicates, 10 g of 2mm sieved 57

58 soils were extracted with 100 mL 2M analytical grade HNO₃ in a boiling water bath for 120 59 min. Total sulfur in the acid extracts was also assayed by ICP-OES. Total soil mercury (THg) was measured using a Perkin Elmer SMS100 atomic absorption spectrometer 60 61 according to the EPA standard method 7473. Soil samples were thermally decomposed at 62 750°C followed by amalgamation on a gold-trap and then analysis of Hg cold vapors. Certified reference lake sediment material (IAEA SL-1) was used for calibration. Replicate 63 64 samples and reference material were analyzed regularly (10% of the sampling sequence) and the precision was under 10% relative standard deviation (SD). 65

66 S.1.2. Determination of isotopically exchangeable Hg (Hg_E) in soil

Hamon, et al. ³ and Marzouk, et al. ⁴ 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. However, in practice, the amount of the added spike varied from c. 5% to 400% of the metal soil concentration and the 'appropriate' spike concentrations were usually selected based on the investigated metal, its concentration, soil properties and the robustness and accuracy of the isotopic ratio measurement ⁴⁻¹⁵.

73 In this work, spike levels were chosen based on a preliminary experiment involving 3 soils 74 with high, medium and low THg contents which showed that at least 50% increase in the soil ¹⁹⁹Hg and ¹⁹⁶Hg content was required for robust isotopic ratio (IR) measurements. This 75 76 was mainly due to our carryover elimination strategy (SI, S.1.3), which included diluting 77 all solutions to < 2 μ g L⁻¹ Hg. Therefore, a careful balance was required between maintaining analytical precision while keeping spike concentrations to the minimum to 78 avoid possible perturbation of the natural equilibrium ^{3, 7}. The original plan was not to 79 exceed 100% of soil ¹⁹⁶Hg or ¹⁹⁹Hg; however, this was impractical for ¹⁹⁶Hg in all soils due 80 81 to its very low natural abundance. The authenticity of the estimated values of HgE was determined by checking their consistency against different spike levels ^{3, 4, 16}. The possible 82 83 precipitation of Hg isotopes at high spike concentrations was modelled with Visual MINTEQ 3.1 for the highest spike level in our range (4.1 μ g mL^{-1 199}Hg). Results showed that, under 84

our experimental conditions, both Hg(OH)₂ and HgCl₂ displayed negative saturation
indexes (-7.4 and -1.2, respectively) indicating negligible precipitation.

87 S.1.3. Measuring equilibrium Hg isotopic abundances

Isotopic abundances of ¹⁹⁶Hg, ¹⁹⁹Hg, ²⁰⁰Hg, ²⁰¹Hg and ²⁰²Hg in both spiked and un-spiked samples were assayed by an Agilent 7700x ICP-MS in helium collision mode. A three steps washing sequence between samples was used to eliminate memory effect and cross contamination; this included (i) a solution of 1 g L⁻¹ EDTA, 0.08 g L⁻¹ Triton X-100 and 6 g L⁻¹ NH₄OH, (ii) technical grade 5% HNO₃/HCl and (iii) the matrix solution (ultra-pure 1% HNO₃/ 0.5% HCl). In addition, all samples and standards were diluted to a 0.05 - 2 μ g L⁻¹ range of total Hg.

For internal mass bias correction, TI solution (10 μ g L⁻¹), in a matrix of ultra-pure 1% HNO₃ and 0.5% HCl, was introduced in the internal standard line via a T-piece and the variation in the ²⁰³Tl/²⁰⁵Tl ratios was used to correct shifts in Hg isotopic ratios ^{6, 17, 18}. Moreover, external mass discrimination correction was applied by repeatedly analyzing a 2 μ g L⁻¹ Hg ICP-MS standard every three samples ¹⁹. Changes in the measured count rate (CPS) ratios of the bracketing Hg standard were applied by linear extrapolation to the intervening samples ^{5, 11}.

102 The abundance of ¹⁹⁵Pt was measured to monitor and correct for possible isobaric 103 interference between ¹⁹⁶Pt and ¹⁹⁶Hg although in practice Pt concentrations were below 104 detection limits in all samples.

To ensure high level of measurement precision, repeated runs of very short quadrupole dwell times were applied. Five runs, each composed of 1000 sweeps, were applied to each sample and the dwell times were 5.01 ms for ¹⁹⁵Pt, ¹⁹⁶Hg, ¹⁹⁹Hg, ²⁰⁰Hg, ²⁰¹Hg, ²⁰²Hg, ²⁰³Tl and ²⁰⁵Tl. RSDs between the measured counts per second (CPS) of the five runs, for each isotope, were always kept below 1%; data were rejected and repeated if RSD exceeded 1% for any single isotope in the sequence. To allow for the fast jumping quadrupole to

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settle locally before sweeping through the main isotopes ⁴, ¹⁹⁴Pt (0.3 ms) was also added
to the sequence to work as a resting mass.

113 S.1.4. E-value comparison with extraction methods

114 Despite the popularity of extraction methods to estimate the available fraction of soil Hg, unfortunately there is no universal protocol available such as the sequential extraction 115 procedure developed by Tessier, et al. ²⁰ for classic hard metals ²¹. The type and sequence 116 117 of the selected extractants have always been an empirical decision depending on the nature of soil or the targeted Hg species ^{21, 22}. Moreover, when compared to Hg uptake by 118 119 flora or fauna, good correlations have been observed between bioavailable Hg and Hg from 120 all soil fractions indicating that labile Hg is not exclusively bound to specific soil phases ^{23,} 121 ²⁴. However, the first step of extraction using ammonium acetate or magnesium chloride to extract 'exchangeable Hg' was common in the available literature ^{21, 22, 25-27}. 122

For comparison with Hg E-value, 'Exchangeable' mercury in all soil samples was extracted by ammonium acetate or magnesium chloride as described by Han, et al. ²⁵ and Panyametheekul ²⁶. In duplicates, 2 g of <2mm sieved soils were suspended in 30 mL 1 M ammonium acetate or 0.5 M magnesium chloride and shaken for 1 h and 2 h, respectively, at room temperature. Centrifuged and filtered samples were diluted with 5 % HCl as necessary and Hg concentrations were measured by an Agilent ICP-OES 5100 fitted with Multimode Sample Introduction System (MSIS) for vapour generation.

130 S.2. Results and Discussion:

131 S.2.1. Soil Properties

Key soil parameters including total soil Hg (THg), pH, soil organic carbon (Org-C), total nitrogen, total S, reactive Fe, Mn and Al oxides are summarized by sampling site in Table S1. All soils were alkaline or slightly acidic with a mean pH range of 6.2 to 8.2. In general, soils showed average organic carbon content (2.6 to 4.5 %). Total soil Hg ranged in average from 0.37 to 310 mg kg⁻¹. All locations showed THg concentrations higher than the 0.37 mg kg⁻¹ measured in the VS2 background (reference) site. However, THg

- 138 concentrations were noticeably elevated (230 390 mg kg⁻¹) in location VS2 followed by
- 139 location TT2 indicating high levels of mercury contamination.

	THg		pН		Org-C		Ν		S		AI(OH)	3	MnO ₂		<i>Fe</i> ₂ <i>O</i> ₃	
Site	(mg kg	7 ⁻¹)			(%)		(%)		(%)		(g kg-1)	(g kg ⁻¹)	(g kg-1)
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
HW1	0.95	0.95	7.29	0.05	2.63	0.31	0.21	0.02	0.36	0.03	0.72	0.16	0.23	0.04	4.00	0.67
HK1	2.80	1.21	6.82	0.52	3.43	0.22	0.31	0.05	0.47	0.06	0.47	0.12	0.13	0.05	3.40	0.74
HK2	2.73	0.25	7.61	0.15	2.95	0.54	0.21	0.05	0.35	0.08	0.43	0.03	0.18	0.02	3.84	0.31
XX1	7.54	3.45	7.36	0.14	4.07	0.30	0.40	0.03	0.63	0.05	0.45	0.05	0.14	0.04	2.91	0.40
XX2	16.9	7.86	7.33	0.38	4.48	0.81	0.47	0.07	0.71	0.05	0.55	0.01	0.19	0.01	4.12	0.26
TT1	2.68	1.63	7.48	0.27	3.89	0.67	0.31	0.03	0.56	0.09	0.42	0.10	0.21	0.16	3.96	0.73
TT2	38.1	8.62	8.20	0.13	2.95	0.12	0.23	0.01	0.78	0.16	0.62	0.01	0.16	0.01	3.82	0.20
VS1	310	80	7.26	0.22	3.49	1.33	0.24	0.15	0.54	0.22	0.70	0.20	0.16	0.06	3.44	0.88
VS2	0.37	0.29	6.20	0.51	3.03	0.96	0.29	0.10	0.42	0.16	0.40	0.04	0.14	0.01	2.85	0.29

Table S1. Soil properties by sampling locations including total Hg (THg), pH, organic carbon (org-C), N, total S and reactive metal oxides in soils in Visp and Raron, Switzerland differently contaminated by Hg. SD= standard deviation.

Table S2. Mass bias correction factors in the ratios of spike isotopes (¹⁹⁶Hg and ¹⁹⁹Hg) to reference isotopes (²⁰⁰Hg, ²⁰¹Hg and ²⁰²Hg). The expected drift due to mass discrimination was corrected for by periodically running a 2 μ g L⁻¹ certified Hg standard and applying the changes in its isotopic ratios to the intervening samples. A, B and C are different soil sampled from the same location while 1 and 2 are replicates of the same soil. Isotopic ratios of the bracketing Hg standard used for mass bias correction are displayed in bold italic font in their exact position in the analysis sequence.

Location	Soil Spiked Sample		Isotopic ratios mass bias correction factors							
		Sample	¹⁹⁶ Hg/ ²⁰⁰ Hg	¹⁹⁶ Hg/ ²⁰¹ Hg	¹⁹⁶ Hg/ ²⁰² Hg	¹⁹⁹ Hg/ ²⁰⁰ Hg	¹⁹⁹ Hg/ ²⁰¹ Hg	¹⁹⁹ Hg/ ²⁰² Hg		
	Natura	l Ratio	0.006494	0.011381	0.005023	0.730303	1.279970	0.564970		
	Hg std.		0.006748	0.011737	0.00518	0.727679	1.265749	0.558636		
HW1	А	1	0.928	0.930	0.926	1.000	1.002	0.998		
		2	0.910	0.911	0.907	1.001	1.002	0.997		
	В	1	0.892	0.892	0.888	1.001	1.002	0.997		
		Hg std.	0.007287	0.01271	0.005611	0.725363	1.265201	0.558526		
		2	0.882	0.882	0.877	1.001	1.001	0.996		
	С	1	0.891	0.891	0.885	1.000	1.000	0.994		
		2	0.899	0.899	0.894	0.999	0.999	0.993		
		Hg std.	0.00697	0.012133	0.005354	0.726552	1.264826	0.55813		
HK1	А	1	0.886	0.886	0.880	0.999	0.999	0.993		
		2	0.864	0.864	0.859	0.999	0.998	0.993		
	В	1	0.843	0.842	0.838	0.999	0.998	0.994		
		Hg std.	0.007735	0.013497	0.00595	0.726829	1.26825	0.559124		
		2	0.825	0.825	0.821	0.999	0.999	0.994		
	С	1	0.829	0.830	0.825	0.999	1.000	0.995		
		2	0.833	0.834	0.829	1.000	1.001	0.995		
		Hg std.	0.00759	0.013194	0.005839	0.727214	1.264063	0.55947		
HK2	А	1	0.839	0.842	0.836	1.000	1.003	0.997		
		2	0.838	0.841	0.835	1.000	1.003	0.997		
	В	1	0.837	0.839	0.835	1.000	1.003	0.998		
		Hg std.	0.007637	0.013286	0.005867	0.727007	1.264733	0.558483		
		2	0.834	0.836	0.832	1.000	1.002	0.997		
	С	1	0.833	0.834	0.830	1.000	1.001	0.996		
		2	0.832	0.832	0.829	0.999	1.000	0.996		
		Hg std.	0.007662	0.013364	0.005892	0.727356	1.268739	0.55934		
XX1	А	1	0.818	0.818	0.815	0.999	0.999	0.995		
		2	0.806	0.807	0.803	1.000	1.000	0.995		
	В	1	0.794	0.795	0.790	1.000	1.000	0.995		
		Hg std.	0.008135	0.014177	0.006264	0.726427	1.266029	0.559366		
		2	0.764	0.765	0.761	0.999	1.000	0.994		
	С	1	0.746	0.747	0.743	0.998	0.999	0.994		
		2	0.728	0.729	0.726	0.997	0.998	0.993		
		Hg std.	0.007726	0.013443	0.005942	0.727105	1.265086	0.559147		
XX2	А	1	0.818	0.819	0.816	1.002	1.003	0.998		
		2	0.781	0.782	0.778	1.001	1.003	0.997		
	В	1	0.743	0.745	0.740	1.000	1.002	0.996		
		Hg std.	0.007802	0.013552	0.00599	0.728428	1.265264	0.559249		
		2	0.713	0.715	0.710	0.999	1.001	0.994		

	С	1	0.722	0.722	0.718	0.999	1.000	0.994
		2	0.730	0.730	0.726	0.999	0.999	0.993
		Hg std.	0.00754	0.013134	0.005797	0.726265	1.265067	0.558402
TT1	А	1	0.833	0.835	0.831	1.001	1.002	0.998
		2	0.819	0.819	0.816	1.000	1.000	0.996
	В	1	0.804	0.804	0.801	0.999	0.998	0.994
		Hg std.	0.008032	0.014019	0.006174	0.727854	1.27036	0.559462
		2	0.795	0.794	0.791	0.998	0.998	0.994
	С	1	0.799	0.800	0.796	0.998	0.999	0.995
		2	0.804	0.806	0.802	0.999	1.001	0.996
		Hg std.	0.007456	0.013006	0.005741	0.725003	1.264739	0.558205
TT2	А	1	0.817	0.818	0.812	0.997	0.999	0.991
		2	0.816	0.817	0.811	0.997	0.999	0.991
	В	1	0.814	0.816	0.810	0.997	0.999	0.992
		Hg std.	0.009027	0.015686	0.006937	0.727826	1.264719	0.559305
		2	0.910	0.910	0.907	1.001	1.001	0.998
	С	1	0.889	0.890	0.887	1.001	1.002	0.999
		2	0.869	0.870	0.867	1.001	1.003	0.999
		Hg std.	0.008595	0.015009	0.006621	0.72658	1.268736	0.559692
VS1	А	1	0.751	0.750	0.746	0.999	0.998	0.993
		2	0.763	0.762	0.758	0.999	0.999	0.993
	В	1	0.775	0.775	0.770	0.999	0.999	0.993
		Hg std.	0.008069	0.01405	0.006207	0.726986	1.265819	0.559237
		2	0.729	0.730	0.725	0.997	0.998	0.991
	С	1	0.671	0.672	0.667	0.995	0.997	0.989
		2	0.614	0.615	0.610	0.994	0.995	0.987
		Hg std.	0.011371	0.01976	0.008739	0.731391	1.270962	0.562087

Table S3. E-values of Hg (mg kg⁻¹), for all collected samples, as calculated by equation 1 using ¹⁹⁹Hg as spike isotope and ²⁰⁰Hg, ²⁰¹Hg or ²⁰²Hg as reference isotopes. A, B and C represent different samples collected from the same location. Standard errors are displayed between brackets (two spiked and two un-spiked replicates).

Location	Sample	E-Value	E-Value	E-Value
HW1	Δ			
	B		0.06 (0.01)	0.10(0.00)
	C			
	^	0.00(0.01)	0.07 (0.00)	0.03(0.01)
UKI	A	0.41(0.02)	0.30 (0.03)	0.42(0.01)
	В	0.54 (0.06)	0.52 (0.09)	0.55 (0.08)
	С	0.14 (0.00)	0.13 (0.00)	0.14 (0.00)
HK2	А	0.62 (0.05)	0.57 (0.05)	0.61 (0.05)
	В	0.72 (0.03)	0.71 (0.25)	0.72 (0.14)
	С	0.64 (0.03)	0.61 (0.02)	0.65 (0.01)
XX1	А	0.56 (0.03)	0.54 (0.04)	0.59 (0.04)
	В	1.29 (0.02)	1.18 (0.04)	1.29 (0.01)
	С	1.08 (0.05)	1.01 (0.04)	1.09 (0.02)
XX2	А	1.69 (0.04)	1.59 (0.05)	1.69 (0.04)
	В	1.66 (0.23)	1.54 (0.15)	1.67 (0.05)
	С	4.91 (0.25)	4.70 (0.08)	4.95 (0.16)
TT1	А	0.78 (0.17)	0.75 (0.18)	0.78 (0.17)
	В	0.12 (0.01)	0.11 (0.02)	0.12 (0.01)
	С	0.35 (0.03)	0.32 (0.15)	0.36 (0.05)
TT2	А	5.99 (0.13)	5.80 (0.11)	5.99 (0.17)
	В	5.42 (0.17)	5.36 (0.48)	5.46 (0.25)
	С	6.83 (0.04)	6.69 (0.14)	6.85 (0.06)
VS1	А	131(16.8)	131 (16.7)	132 (15.9)
	В	74.9 (0.28)	73.7 (1.09)	75.9 (0.65)
	С	43.7 (2.69)	43.3 (3.01)	44.0 (1.89)

Table S4. Mercury lability (%HgE), for all samples, calculated by equation 1, against different ¹⁹⁹Hg spike to natural ratios. A, B and C are different samples from the same location. Standard errors are displayed between brackets for two spiked (for each spike level) and two un-spiked replicates.

Location	Sample	Hg Lability (%HgE)				
Spike / Native ¹⁹⁹ Hg		50 %	100 %	200 %		
HW1	А	7.82 (0.01)	7.76 (0.14)	7.81 (0.12)		
	В	16.5 (3.65)	16.2 (3.45)	16.2 (3.48)		
	С	19.8 (2.34)	20.2 (2.23)	20.1 (2.2)		
HK1	А	11.7 (0.42)	12 (0.18)	12 (0.18)		
	В	15.5 (1.78)	15.7 (2.24)	15.7 (2.24)		
	С	10.1 (0.25)	10.2 (0.13)	10.1 (0.16)		
HK2	А	22.8 (1.82)	22.5 (2.01)	22.6 (1.92)		
	В	24.1 (4.32)	24.1 (4.54)	24.2 (4.5)		
	С	25.5 (1.29)	26 (1.17)	26 (1.11)		
XX1	А	16.5 (0.88)	16.3 (1.02)	16.4 (1)		
	В	14.6 (0.43)	14.7 (0.57)	14.7 (0.57)		
	С	10.6 (0.26)	10.7 (0.15)	10.7 (0.13)		
XX2	А	14.1 (0.28)	14.1 (0.3)	14.2 (0.29)		
	В	13 (0.26)	13.1 (0.42)	13.1 (0.41)		
	С	18.9 (0.59)	19 (0.61)	19.1 (0.6)		
TT1	А	18 (3.80)	18 (3.89)	17.9 (3.84)		
	В	10.7 (1.26)	10.8 (1.23)	10.7 (1.29)		
	С	13.5 (1.63)	13.7 (1.73)	13.7 (1.79)		
TT2	А	15.5 (0.33)	15.4 (0.43)	15.6 (0.43)		
	В	18.6 (0.93)	18.8 (0.85)	18.7 (0.83)		
	С	14.8 (0.99)	14.8 (0.09)	14.8 (0.13)		
VS1	А	33.6 (4.23)	33.8 (4.07)	33.6 (3.84)		
	В	24.2 (0.08)	24.5 (0.21)	24.5 (0.19)		
	С	19 (1.15)	19.1 (1.17)	19.1 (1.12)		
VS2	A	27.5 (2.16)	27.1 (1.78)	27 (1.85)		
	В	46 (8.31)	45.9 (8.07)	45.8 (8.15)		
	С	15.3 (0.64)	15.1 (0.61)	15.1 (0.64)		

Soil Parameter	Pearson Correlation (r) with HgE (mg kg ⁻¹)	Pearson Correlation (r) with %HgE
THg	0.98	0.63
рН	-0.07	0.14
Ν	-0.13	-0.26
Org-C	0.11	-0.03
S	0.11	-0.04
Al(OH)₃	0.47	0.08
MnO ₂	-0.06	-0.17
Fe ₂ O ₃	-0.03	0.00

Table S5. Pearson correlation coefficients of Hg labile pool (HgE; mg kg⁻¹) and Hg lability (%HgE) with soil parameters in all soils (n=27).

Table S6. Linear stepwise regression (Minitab 17) coefficients and P-values. Labile Hg (HgE; mg kg⁻¹) and Hg lability ($^{\circ}$ HgE) parameterised by all other soil parameters including THg, pH, N, Org-C, S and Al, Mn and Fe oxides.

	HgE (mg kg ⁻¹))	%HgE		
Regression	$R^2 = 0.96$		$R^2 = 0.63$		
	Coefficients	P-value	Coefficients	P-value	
Intercept	-4.98	0.90	-4.70	0.83	
THg	0.27	0.00	0.05	0.01	
рН	-1.92	0.73	2.70	0.39	
Ν	-46.2	0.47	1.85	0.96	
Org-C	7.57	0.32	-0.52	0.90	
S	0.00	0.85	0.00	0.45	
Al(OH)₃	2.89	0.88	-20.5	0.08	
MnO ₂	-1.44	0.98	-34.4	0.20	
Fe ₂ O ₃	1.58	0.77	5.85	0.07	



Figure S1. Total soil mercury (THg) (mg kg⁻¹) plotted against corresponding labile Hg (HgE; mg kg⁻¹) for all data points (n=27). The dashed line represents a 'power' relationship between x and y parameters.



Figure S2. Total soil mercury (THg) (mg kg⁻¹) plotted against Hg lability (%HgE) for all data points (n=27). The dashed line represents a 'logarithmic' relationship between x and y parameters.

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