# Supporting Information (SI) to

## Mercury isotope fractionation in the subsurface of a Hg(II)-chloride-contaminated industrial legacy site

*Flora M. Brocza[1,2], Harald Biester[3], Jan-Helge Richard[3,4], Stephan M. Kraemer[1], Jan G. Wiederhold[1*]*

[1] Environmental Geosciences, Centre for Microbiology and Environmental Systems Science, University of Vienna, Althanstrasse 14, UZA II, 1090 Vienna, Austria

[2] School of Chemical and Process Engineering, University of Leeds, 211 Clarendon Rd, Leeds LS2 9JT, United Kingdom

[3] Institut für Geoökologie, Technische Universität Braunschweig, Langer Kamp 19C, 38106 Braunschweig, Germany

[4] Institute for Hygiene and Environment, Marckmannstraße 129A, 20539 Hamburg, Germany

* corresponding author: jan.wiederhold@univie.ac.at

This supporting information contains 9 pages, 8 tables, and 4 figures.

Table of contents:

## Table S1: Hg concentrations and Hg isotopes of bulk soil samples from cores K2 and K3

| sample name | depth [m] | Hg [µg kg$^{-1}$] | $\delta^{202}$Hg [‰] | 2SD [‰] | $\Delta^{199}$Hg [‰] | 2SD [‰] | $\Delta^{200}$Hg [‰] | 2SD [‰] | $\Delta^{201}$Hg [‰] | 2SD [‰] | $\Delta^{204}$Hg [‰] | 2SD [‰] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **K2-1** | **0.2** | **34049** | | | | | | | | | | |
| **K2-2** | **0.4** | **14432** | | | | | | | | | | |
| **K2-3** | **0.6** | **3643** | | | | | | | | | | |
| **K2-4** | **0.8** | **201538** | **-0.22** | 0.06 | **-0.01** | 0.08 | **0.09** | 0.15 | **-0.02** | 0.04 | **-0.01** | 0.04 |
| **K2-5** | **1.9** | **42647** | **-0.14** | 0.06 | **-0.17** | 0.08 | **-0.12** | 0.15 | **-0.07** | 0.04 | **0.06** | 0.04 |
| **K2-6** | **2.1** | **528164** | **-0.36** | 0.06 | **-0.23** | 0.08 | **0.13** | 0.15 | **-0.10** | 0.04 | **0.06** | 0.04 |
| **K2-7** | **2.3** | **798542** | **-0.38** | 0.06 | **0.00** | 0.08 | **0.10** | 0.15 | **-0.05** | 0.04 | **0.00** | 0.04 |
| **K2-8** | **2.5** | **801531** | **-0.43** | 0.06 | **-0.02** | 0.08 | **0.00** | 0.15 | **-0.05** | 0.04 | **0.00** | 0.04 |
| **K2-9** | **2.7** | **191127** | **-0.29** | 0.06 | **-0.07** | 0.08 | **0.06** | 0.15 | **-0.05** | 0.04 | **-0.01** | 0.04 |
| **K2-10** | **2.9** | **20750** | **0.07** | 0.06 | **-0.10** | 0.08 | **0.21** | 0.15 | **-0.08** | 0.04 | **-0.03** | 0.04 |
| **K2-11** | **3.1** | **108335** | **-0.33** | 0.06 | **-0.02** | 0.08 | **-0.03** | 0.15 | **-0.07** | 0.04 | **0.02** | 0.04 |
| **K2-12** | **3.3** | **8114** | **-0.25** | 0.06 | **0.02** | 0.08 | **0.04** | 0.15 | **-0.05** | 0.04 | **0.01** | 0.04 |
| **K2-13** | **3.5** | **72945** | | | | | | | | | | |
| **K2-14** | **3.7** | **6743** | | | | | | | | | | |
| **K2-15** | **3.9** | **8952** | | | | | | | | | | |
| **K2-16** | **4.1** | **4463** | | | | | | | | | | |
| **K2-17** | **4.3** | **7420** | | | | | | | | | | |
| **K3-1** | **0.2** | **2255** | | | | | | | | | | |
| **K3-2** | **0.4** | **99633** | **-0.06** | 0.06 | **0.01** | 0.08 | **0.02** | 0.15 | **-0.01** | 0.04 | **-0.01** | 0.04 |
| **K3-3** | **0.6** | **99583** | **0.08** | 0.06 | **-0.10** | 0.08 | **-0.04** | 0.15 | **-0.04** | 0.04 | **0.01** | 0.04 |
| **K3-4** | **0.8** | **8903** | **-0.03** | 0.06 | **-0.02** | 0.08 | **-0.02** | 0.15 | **-0.01** | 0.04 | **0.02** | 0.04 |
| **K3-5** | **1.5** | **19644** | **-0.12** | 0.06 | **-0.02** | 0.08 | **0.02** | 0.15 | **-0.01** | 0.04 | **-0.01** | 0.04 |
| **K3-6** | **1.7** | **1544** | | | | | | | | | | |
| **K3-7** | **1.9** | **583** | | | | | | | | | | |
| **K3-8** | **2.1** | **75** | | | | | | | | | | |
| **K3-9** | **2.3** | **88** | | | | | | | | | | |
| **K3-10** | **2.5** | **2804** | | | | | | | | | | |
| **K3-11** | **2.7** | **2905** | | | | | | | | | | |
| **K3-12** | **2.9** | **76** | | | | | | | | | | |
| **K3-13** | **3.1** | **64** | | | | | | | | | | |
| **K3-14** | **3.3** | **170** | | | | | | | | | | |

Depth indicates midpoints of 20 cm core sections

Hg concentrations refer to dry mass of soil after determination of the water content on a separate aliquot.

Analytical precision of Hg concentration analysis was ±2.7 % (RSD, n=45) based on standard replicates.

2SD values for Hg isotopes refer to reproducibility of the ETH Fluka standard during measurement session.

**Table S2: Hg concentrations and relative Hg fractions of sequential extraction protocol (SEP)**

| sample name | depth [m] | bulk Hg [µg kg$^{-1}$] | F1: Hg [µg kg$^{-1}$] | f(F1) [‰] | F2: Hg [µg kg$^{-1}$] | f(F2) [‰] | F3: Hg [µg kg$^{-1}$] | f(F3) [‰] | F4: Hg [µg kg$^{-1}$] | f(F4) [‰] | SEP sum [µg kg$^{-1}$] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **K2-5** | **1.9** | **42647** | **730** | 1.97 | **3973** | 10.7 | **3158** | 8.52 | **29188** | 78.8 | **37049** |
| **K2-6** | **2.1** | **528164** | **3751** | 2.09 | **38941** | 21.7 | **50268** | 28.0 | **86572** | 48.2 | **179532** |
| **K2-7** | **2.3** | **798542** | **16460** | 1.73 | **158497** | 16.7 | **447864** | 47.1 | **327102** | 34.4 | **949924** |
| **K2-8-1** | **2.5** | **801531** | **17020** | 2.13 | **130453** | 16.3 | **313144** | 39.1 | **339586** | 42.4 | **800202** |
| **K2-8-2** | **2.5** | **801531** | **22260** | 3.21 | **132848** | 19.2 | **270905** | 39.1 | **266857** | 38.5 | **692869** |
| **K2-8-3** | **2.5** | **801531** | **18544** | 2.35 | **132971** | 16.8 | **320706** | 40.6 | **317665** | 40.2 | **789886** |
| **K2-8-4** | **2.5** | **801531** | **17223** | | **133182** | | **300596** | | | | |
| **K2-8-5** | **2.5** | **801531** | **20420** | | **174521** | | | | | | |
| **K2-8-6** | **2.5** | **801531** | **19200** | | | | | | | | |
| **K2-9** | **2.7** | **191127** | **456** | 0.22 | **26701** | 13.0 | **34164** | 16.6 | **144666** | 70.2 | **205988** |
| **K2-10** | **2.9** | **20750** | **1237** | 4.08 | **342** | 1.13 | **2039** | 6.73 | **26691** | 88.1 | **30309** |
| **K2-11** | **3.1** | **108335** | **202** | 3.35 | **156** | 2.59 | **275** | 4.58 | **5380** | 89.5 | **6013** |
| **K2-12** | **3.3** | **8114** | **168** | 3.06 | **70** | 1.28 | **325** | 5.93 | **4917** | 89.7 | **5480** |
| **K3-2** | **0.4** | **99633** | **1875** | 2.61 | **1325** | 1.85 | **6854** | 9.55 | **61689** | 86.0 | **71743** |
| **K3-3-1** | **0.6** | **99583** | **811** | 1.03 | **136** | 0.17 | **6703** | 8.51 | **71156** | 90.3 | **78807** |
| **K3-3-2** | **0.6** | **99583** | **567** | 0.88 | **43** | 0.07 | **5442** | 8.42 | **58559** | 90.6 | **64611** |
| **K3-3-3** | **0.6** | **99583** | **845** | 1.20 | **35** | 0.05 | **5932** | 8.39 | **63903** | 90.4 | **70715** |
| **K3-3-4** | **0.6** | **99583** | **718** | | **30** | | **5663** | | | | |
| **K3-3-5** | **0.6** | **99583** | **540** | | **38** | | | | | | |
| **K3-3-6** | **0.6** | **99583** | **356** | | | | | | | | |
| **K3-4** | **0.8** | **8903** | **312** | 2.73 | **356** | 3.11 | **2337** | 20.4 | **8427** | 73.7 | **11431** |
| **K3-5** | **1.5** | **19644** | **328** | 1.82 | **43** | 0.24 | **7964** | 44.1 | **9720** | 53.8 | **18055** |
| **NIST-2711-1** | | **6250** | **56** | 0.97 | **11** | 0.20 | **221** | 3.83 | **5484** | 95.0 | **5773** |
| **NIST-2711-2** | | **6250** | **41** | 0.72 | **13** | 0.23 | **165** | 2.89 | **5497** | 96.2 | **5717** |

f(Fx) refers to the fraction of total Hg in extract x relative to the sum of all extracts (x = F1, F2, F3, F4)

K2-8-y and K3-3-y (y = 1, 2, 3, 4, 5, 6) refer to replicate extracts of the same soil sample, with 4 to 6 being partial extracts

NIST-2711-1 and NIST-2711-2 refer to replicate extracts of the NIST standard reference material 2711 (Montana Soil)

**Table S3: Hg isotope data of sequential extraction protocol (SEP)**

| sample name | SEP fraction | fraction Hg [%] | n | $\delta^{202}$Hg [‰] | 2SD [‰] | $\Delta^{199}$Hg [‰] | 2SD [‰] | $\Delta^{200}$Hg [‰] | 2SD [‰] | $\Delta^{201}$Hg [‰] | 2SD [‰] | $\Delta^{204}$Hg [‰] | 2SD [‰] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **K2-5** | **F1** | **1.97** | **3** | **-0.34** | 0.06 | **-0.04** | 0.01 | **0.03** | 0.07 | **-0.06** | 0.04 | **0.00** | 0.06 |
| | **F2** | **10.7** | **1** | **0.15** | 0.11 | **-0.10** | 0.05 | **-0.03** | 0.13 | **-0.09** | 0.05 | **0.05** | 0.08 |
| | **F3** | **8.52** | **1** | **0.21** | 0.11 | **-0.06** | 0.05 | **-0.11** | 0.13 | **-0.10** | 0.05 | **0.02** | 0.08 |
| | **F4** | **78.8** | **2** | **-0.22** | 0.08 | **-0.07** | 0.06 | **-0.05** | 0.11 | **-0.06** | 0.06 | **-0.02** | 0.14 |
| | *calc. bulk* | **100** | | *-0.15* | | *-0.07* | | *-0.05* | | *-0.07* | | *-0.01* | |
| | **meas. bulk** | | | **-0.14** | 0.06 | **-0.17** | 0.08 | **-0.12** | 0.15 | **-0.07** | 0.04 | **0.06** | 0.04 |
| **K2-6** | **F1** | **2.09** | **1** | **-0.47** | 0.09 | **-0.03** | 0.04 | **-0.01** | 0.15 | **-0.03** | 0.06 | **0.01** | 0.06 |
| | **F2** | **21.7** | **1** | **-0.15** | 0.09 | **-0.09** | 0.04 | **-0.03** | 0.15 | **-0.07** | 0.06 | **0.02** | 0.06 |
| | **F3** | **28.0** | **1** | **-0.19** | 0.09 | **-0.04** | 0.04 | **0.03** | 0.15 | **-0.01** | 0.06 | **-0.02** | 0.06 |
| | **F4** | **48.2** | **1** | **-0.43** | 0.09 | **-0.02** | 0.04 | **-0.01** | 0.15 | **-0.04** | 0.06 | **-0.07** | 0.06 |
| | *calc. bulk* | **100** | | *-0.30* | | *-0.04* | | *0.00* | | *-0.04* | | *-0.04* | |
| | **meas. bulk** | | | **-0.36** | 0.06 | **-0.23** | 0.08 | **0.13** | 0.15 | **-0.10** | 0.04 | **0.06** | 0.04 |
| **K2-7** | **F1** | **1.73** | **2** | **-0.30** | 0.03 | **0.00** | 0.04 | **0.00** | 0.06 | **-0.04** | 0.01 | **0.02** | 0.13 |
| | **F2** | **16.7** | **1** | **0.04** | 0.11 | **-0.15** | 0.05 | **-0.07** | 0.13 | **-0.09** | 0.05 | **0.02** | 0.08 |
| | **F3** | **47.1** | **1** | **-0.37** | 0.11 | **-0.04** | 0.05 | **-0.05** | 0.13 | **-0.04** | 0.05 | **-0.03** | 0.08 |
| | **F4** | **34.4** | **1** | **-0.57** | 0.11 | **-0.01** | 0.05 | **-0.05** | 0.13 | **-0.05** | 0.05 | **-0.01** | 0.08 |
| | *calc. bulk* | **100** | | *-0.37* | | *-0.05* | | *-0.05* | | *-0.05* | | *-0.01* | |
| | **meas. bulk** | | | **-0.38** | 0.06 | **0.00** | 0.08 | **0.10** | 0.15 | **-0.05** | 0.04 | **0.00** | 0.04 |
| **K2-8-1** | **F1** | **2.13** | **1** | **0.08** | 0.24 | **-0.06** | 0.04 | **0.01** | 0.15 | **-0.07** | 0.08 | **0.03** | 0.10 |
| | **F2** | **16.3** | **1** | **-0.28** | 0.24 | **-0.05** | 0.04 | **0.13** | 0.15 | **-0.02** | 0.08 | **0.04** | 0.10 |
| | **F3** | **39.1** | **1** | **-0.45** | 0.24 | **-0.05** | 0.04 | **0.03** | 0.15 | **-0.16** | 0.08 | **0.00** | 0.10 |
| | **F4** | **42.4** | **1** | **-0.55** | 0.24 | **-0.02** | 0.04 | **0.02** | 0.15 | **-0.11** | 0.08 | **-0.05** | 0.10 |
| | *calc. bulk* | **100** | | *-0.45* | | *-0.04* | | *0.04* | | *-0.11* | | *-0.01* | |
| | **meas. bulk** | | **3** | **-0.43** | 0.02 | **-0.02** | 0.07 | **0.00** | 0.06 | **-0.05** | 0.02 | **0.00** | 0.02 |
| **K2-8-2** | **F1** | **3.21** | **2** | **0.12** | 0.05 | **-0.06** | 0.02 | **-0.11** | 0.23 | **-0.09** | 0.00 | **0.00** | 0.05 |
| | **F2** | **19.17** | **1** | **-0.25** | 0.09 | **-0.08** | 0.04 | **-0.15** | 0.15 | **-0.03** | 0.06 | **0.03** | 0.06 |
| | **F3** | **39.10** | **1** | **-0.36** | 0.09 | **-0.04** | 0.04 | **0.02** | 0.15 | **-0.01** | 0.06 | **-0.01** | 0.06 |
| | **F4** | **38.51** | **1** | **-0.42** | 0.09 | **-0.02** | 0.04 | **0.03** | 0.15 | **-0.02** | 0.06 | **0.03** | 0.06 |
| | *calc. bulk* | **100** | | *-0.35* | | *-0.04* | | *-0.01* | | *-0.02* | | *0.02* | |
| | **meas. bulk** | | **3** | **-0.43** | 0.02 | **-0.02** | 0.07 | **0.00** | 0.06 | **-0.05** | 0.02 | **0.00** | 0.02 |
| **K2-9** | **F1** | **0.22** | **1** | **-0.11** | 0.09 | **-0.04** | 0.04 | **0.02** | 0.15 | **-0.03** | 0.06 | **0.02** | 0.06 |
| | **F2** | **12.96** | **1** | **0.06** | 0.09 | **-0.12** | 0.04 | **0.01** | 0.15 | **-0.07** | 0.06 | **0.00** | 0.06 |
| | **F3** | **16.59** | **1** | **-0.08** | 0.09 | **-0.09** | 0.04 | **-0.05** | 0.15 | **-0.06** | 0.06 | **-0.04** | 0.06 |
| | **F4** | **70.23** | **1** | **-0.33** | 0.09 | **0.00** | 0.04 | **0.08** | 0.15 | **0.06** | 0.06 | **-0.12** | 0.06 |
| | *calc. bulk* | **100** | | *-0.24* | | *-0.03* | | *0.05* | | *0.02* | | *-0.09* | |
| | **meas. bulk** | | **1** | **-0.29** | 0.06 | **-0.07** | 0.08 | **0.06** | 0.15 | **-0.05** | 0.04 | **-0.01** | 0.04 |
| **K2-10** | **F1** | **4.08** | **2** | **0.03** | 0.05 | **-0.03** | 0.03 | **0.02** | 0.14 | **-0.04** | 0.09 | **0.00** | 0.03 |
| | **F2** | **1.13** | **1** | **-0.03** | 0.09 | **-0.06** | 0.04 | **-0.02** | 0.15 | **-0.04** | 0.06 | **0.03** | 0.06 |
| | **F3** | **6.73** | **2** | **0.28** | 0.01 | **-0.06** | 0.03 | **0.03** | 0.08 | **-0.06** | 0.02 | **0.00** | 0.05 |
| | **F4** | **88.06** | **2** | **0.09** | 0.08 | **-0.04** | 0.01 | **0.06** | 0.00 | **-0.04** | 0.16 | **0.01** | 0.03 |
| | *calc. bulk* | **100** | | *0.10* | | *-0.04* | | *0.06* | | *-0.04* | | *0.01* | |
| | **meas. bulk** | | **1** | **0.07** | 0.06 | **-0.10** | 0.08 | **0.21** | 0.15 | **-0.08** | 0.04 | **-0.03** | 0.04 |
| **K3-2** | **F1** | **2.61** | **3** | **0.01** | 0.05 | **0.00** | 0.03 | **-0.02** | 0.13 | **0.02** | 0.08 | **0.00** | 0.07 |
| | **F2** | **1.85** | **1** | **-0.06** | 0.24 | **0.00** | 0.04 | **-0.13** | 0.15 | **-0.07** | 0.08 | **0.00** | 0.10 |
| | **F3** | **9.55** | **2** | **0.05** | 0.10 | **0.01** | 0.02 | **0.04** | 0.03 | **0.00** | 0.00 | **0.00** | 0.04 |
| | **F4** | **85.99** | **1** | **0.01** | 0.09 | **-0.03** | 0.04 | **0.14** | 0.15 | **-0.04** | 0.06 | **-0.01** | 0.06 |
| | *calc. bulk* | **100** | | *0.01* | | *-0.03* | | *0.12* | | *-0.03* | | *-0.01* | |
| | **meas. bulk** | | **1** | **-0.06** | 0.06 | **0.01** | 0.08 | **0.02** | 0.15 | **-0.01** | 0.04 | **-0.01** | 0.04 |
| **K3-3** | **F1** | **1.03** | **1** | **0.34** | 0.09 | **-0.02** | 0.04 | **-0.03** | 0.15 | **-0.05** | 0.06 | **0.02** | 0.06 |
| | **F2** | **0.17** | **1** | **0.26** | 0.09 | **-0.02** | 0.04 | **-0.21** | 0.15 | **0.03** | 0.06 | **-0.08** | 0.06 |
| | **F3** | **8.51** | **1** | **0.26** | 0.09 | **-0.03** | 0.04 | **0.03** | 0.15 | **-0.01** | 0.06 | **0.02** | 0.06 |
| | **F4** | **90.29** | **1** | **-0.01** | 0.09 | **-0.09** | 0.04 | **0.04** | 0.15 | **0.01** | 0.06 | **-0.03** | 0.06 |
| | *calc. bulk* | **100** | | *0.02* | | *-0.08* | | *0.04* | | *0.01* | | *-0.02* | |
| | **meas. bulk** | | **1** | **0.08** | 0.06 | **-0.10** | 0.08 | **-0.04** | 0.15 | **-0.04** | 0.04 | **0.01** | 0.04 |

fraction Hg [%] refers to the fraction of total Hg in the extract relative to the sum of all extracts

K2-8-1 and K3-3-2 refer to replicate extracts of the same soil sample

"*calc. bulk* " refers to the calculated Hg isotope composition of the bulk sample based on the weighted sum of the four extracts

"meas. bulk" refers to the measured Hg isotope composition of the total soil digest (Table SI-1) from another sample aliquot

"n" indicates the number of replicate measurements of sample solution on MC-ICP-MS (average values are given)

2SD refers to sample replicates or to reproducibility of ETH Fluka during individual analytical session (for n = 1)

**Table S4: Hg concentrations and Hg isotope data of sequential water extractions of K2-8**

| extract name | dissolved Hg [µg $L^{-1}$] | soil Hg [µg $kg^{-1}$] | fraction bulk soil Hg [%] | n | $\delta^{202}$Hg [‰] | 2SD [‰] | $\Delta^{199}$Hg [‰] | 2SD [‰] | $\Delta^{200}$Hg [‰] | 2SD [‰] | $\Delta^{201}$Hg [‰] | 2SD [‰] | $\Delta^{204}$Hg [‰] | 2SD [‰] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **K2-8 F1A** | **429** | **10037** | **1.25** | **1** | **0.18** | 0.09 | **-0.11** | 0.04 | **0.11** | 0.15 | **-0.05** | 0.06 | **-0.01** | 0.06 |
| **K2-8 F1B** | **262** | **6510** | **0.81** | **1** | **0.13** | 0.09 | **-0.05** | 0.04 | **0.13** | 0.15 | **-0.01** | 0.06 | **-0.04** | 0.06 |
| **K2-8 F1C** | **216** | **6246** | **0.78** | **1** | **-0.05** | 0.09 | **-0.05** | 0.04 | **-0.03** | 0.15 | **-0.07** | 0.06 | **-0.02** | 0.06 |
| **K2-8 F1D*** | **165** | **3611** | **0.45** | **1** | **0.58** | 0.11 | **-0.06** | 0.05 | **0.08** | 0.13 | **-0.03** | 0.05 | **0.00** | 0.08 |
| **K2-8 F1E** | **148** | **3560** | **0.44** | **1** | **-0.21** | 0.11 | **-0.03** | 0.05 | **0.10** | 0.13 | **-0.05** | 0.05 | **0.00** | 0.08 |
| **K2-8 F1F** | **125** | **2858** | **0.36** | **1** | **-0.03** | 0.11 | **-0.02** | 0.05 | **-0.03** | 0.13 | **-0.07** | 0.05 | **0.01** | 0.08 |
| **K2-8 F1G** | **111** | **2693** | **0.34** | **2** | **-0.15** | 0.04 | **-0.02** | 0.02 | **0.04** | 0.17 | **-0.07** | 0.06 | **-0.02** | 0.01 |
| **K2-8 bulk** | | **801531** | **100** | **1** | **-0.43** | 0.06 | **-0.02** | 0.08 | **0.00** | 0.15 | **-0.05** | 0.04 | **0.00** | 0.04 |

"dissolved Hg" refers to concentration in extract solution

"soil Hg" refers to amount of extracted Hg relative to soil mass

"fraction bulk soil Hg" refers to relative fraction of extracted Hg relative to bulk digest

"n" indicates the number of replicate measurements of sample solution on MC-ICP-MS (average values are given)

2SD refers to sample replicates or to reproducibility of ETH Fluka during individual analytical session (for n = 1)

* indicates sample that was potentially affected by artifact (Hg loss) due to longer storage time before extraction was continued (see text)

**Table S5: Hg concentrations and Hg isotope data of groundwater samples**

| groundwater well | dissolved Hg [µg $L^{-1}$] | $\delta^{202}$Hg [‰] | 2SD [‰] | $\Delta^{199}$Hg [‰] | 2SD [‰] | $\Delta^{200}$Hg [‰] | 2SD [‰] | $\Delta^{201}$Hg [‰] | 2SD [‰] | $\Delta^{204}$Hg [‰] | 2SD [‰] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **BK-B3** | **75.6** | **0.75** | 0.06 | **-0.09** | 0.05 | **0.00** | 0.05 | **-0.07** | 0.04 | **-0.06** | 0.06 |
| **BK-B10** | **188.9** | **-0.08** | 0.06 | **-0.07** | 0.05 | **-0.08** | 0.05 | **-0.07** | 0.04 | **0.00** | 0.06 |
| **BK-B8** | **192.4** | **-0.13** | 0.06 | **-0.03** | 0.05 | **0.01** | 0.05 | **-0.05** | 0.04 | **0.01** | 0.06 |

"dissolved Hg" refers to Hg concentration in filtered groundwater sample (0.45 µm)

2SD refers to reproducibility of ETH Fluka during individual analytical session

**Table S6: Hg isotope data of ´ETH Fluka´ standard from this study and selected literature sources[1-10]**

| data source | MC-ICP-MS laboratory | n | $\delta^{202}$Hg [‰] | 2SD [‰] | $\Delta^{199}$Hg [‰] | 2SD [‰] | $\Delta^{200}$Hg [‰] | 2SD [‰] | $\Delta^{201}$Hg [‰] | 2SD [‰] | $\Delta^{204}$Hg [‰] | 2SD [‰] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **this study (Brocza et al.)** | University of Vienna | **52** | **-1.43** | 0.13 | **0.08** | 0.05 | **0.02** | 0.16 | **0.03** | 0.08 | **0.00** | 0.07 |
| **Grigg et al. (2018)** | University of Vienna | **55** | **-1.44** | 0.13 | **0.08** | 0.04 | **0.03** | 0.14 | **0.03** | 0.08 | **-0.01** | 0.07 |
| **Smith et al. (2015)** | ETH Zurich | **12** | **-1.45** | 0.07 | **0.09** | 0.04 | **0.03** | 0.02 | **0.03** | 0.03 | **-0.02** | 0.05 |
| **Jiskra et al. (2017)** | ETH Zurich | **26** | **-1.43** | 0.12 | **0.07** | 0.05 | **0.01** | 0.05 | **0.03** | 0.07 | **0.01** | 0.11 |
| **Enrico et al. (2016)** | GET Toulouse | **57** | **-1.43** | 0.14 | **0.08** | 0.06 | n.r. | n.r. | n.r. | n.r. | n.r. | n.r. |
| **Obrist et al. (2017)** | GET Toulouse | **38** | **-1.43** | 0.19 | **0.08** | 0.07 | **0.02** | 0.07 | n.r. | n.r. | n.r. | n.r. |
| **Du et al. (2018)** | GET Toulouse | **9** | **-1.47** | 0.23 | **0.09** | 0.05 | **0.03** | 0.04 | **0.02** | 0.10 | n.r. | n.r. |
| **Hansson et al. (2018)** | GET Toulouse | **9** | **-1.47** | 0.27 | **0.08** | 0.09 | n.r. | n.r. | **0.01** | 0.06 | n.r. | n.r. |
| **Xu et al. (2019)** | GET Toulouse | **10** | **-1.44** | 0.10 | **0.08** | 0.06 | **0.03** | 0.04 | **0.00** | 0.04 | **-0.02** | 0.18 |
| **Goix et al. (2019)** | GET Toulouse | **10** | **-1.45** | 0.08 | **0.08** | 0.05 | **0.00** | 0.04 | **0.02** | 0.06 | n.r. | n.r. |
| **Jiskra et al. (2019)** | GET Toulouse | **10** | **-1.45** | 0.19 | **0.08** | 0.09 | **0.02** | 0.09 | **0.03** | 0.09 | **-0.03** | 0.20 |

n.r. = not reported

**Table S7:** Definition of the estimated source signature for industrial Hg based on the literature survey published by Grigg et al.[1] (Fig. 3 and Supplementary material)

| | $\delta^{202}$Hg [‰] average | | | | $\Delta^{199}$Hg [‰] average | | | |
|---|---|---|---|---|---|---|---|---|
| | Ore* | Hg(0)^ | Sed.+ | **Mean** | Ore* | Hg(0)^ | Sed.+ | **Mean** |
| **Average** | -0.46 | -0.51 | -0.61 | **-0.52** | 0.01 | 0.00 | -0.01 | **0.00** |
| **1 SD** | 0.56 | 0.30 | 0.37 | **0.41** | 0.11 | 0.03 | 0.12 | **0.09** |
| **n** | 22 | 8 | 27 | **57** | 16 | 5 | 27 | **48** |

* published data of ore samples from Hg mines around the world

^ published data of Hg(0) storebought chemical stocks, measurements from retorting experiments, and measurements of fluorescent light bulbs

\+ published data of Hg-contaminated sediments

**Table S8**: Calculation of the estimated maximum amount of DOC-(thiol)-bound mercury in water extracts (F1) of soil samples based on measured DOC concentrations, an estimated thiol content of DOC of 0.15 % (w/w), and the assumption that all mercury will form $Hg(SR\text{-}DOM)_2$ complexes, as suggested by Skyllberg (2011).[11]

| sample | Hg in F1 extract [µg $L^{-1}$] | DOC in F1 extract [µg $L^{-1}$] | SR groups in DOC [nmol $L^{-1}$] | $Hg(SR\text{-}DOM)_2$ [nmol $L^{-1}$] | $Hg_{max}$ bound to SR [µg $L^{-1}$] | $Hg_{max}$ bound to SR [‰] |
|---|---|---|---|---|---|---|
| **K2-5** | 15.1 | 1267 | 58.3 | 29.1 | 58.5 | **100** |
| **K2-6** | 153 | 1391 | 64.0 | 32.0 | 64.2 | **41.8** |
| **K2-7** | 406 | 2274 | 105 | 52.3 | 105 | **25.8** |
| **K2-8** | 882 | 1052 | 48.4 | 24.2 | 48.5 | **5.50** |
| **K2-9** | 122 | 1104 | 50.8 | 25.4 | 50.9 | **41.6** |
| **K2-10** | 20.8 | 1044 | 48.0 | 24.0 | 48.2 | **100** |
| **K2-11** | 5.40 | 956 | 44.0 | 22.0 | 44.1 | **100** |
| **K2-12** | 11.4 | 1247 | 57.4 | 28.7 | 57.5 | **100** |
| | | | | | | |
| **K3-2** | 40.4 | 2974 | 137 | 68.4 | 137 | **100** |
| **K3-3** | 21.4 | 2433 | 112 | 56.0 | 112 | **100** |
| **K3-4** | 11.0 | 2196 | 101 | 50.5 | 101 | **100** |
| **K3-5** | 10.5 | 2042 | 93.9 | 47.0 | 94.2 | **100** |

SR: thiol group, DOM: dissolved organic matter, DOC: dissolved organic carbon

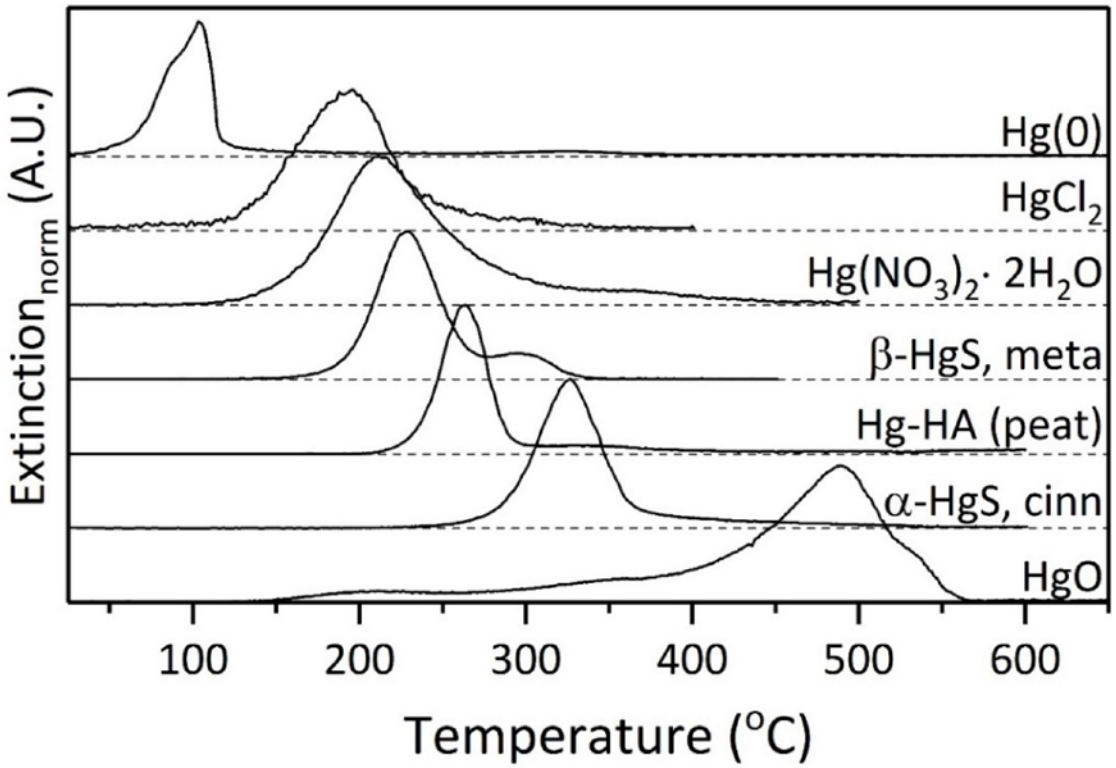


**Figure S1:** Typical Hg release curves of selected reference compounds during PTD (from top to bottom): Elemental Hg sorbed on quartz sand (Hg(0)), mercuric chloride ($HgCl_2$), mercury nitrate ($Hg(NO_3)_2 \cdot 2H_2O$), metacinnabar (β-HgS, meta), Hg in humic acid extracted from a peat (Hg-HA (peat)), cinnabar (α-HgS, cinn), and mercuric oxide (HgO). Figure reprinted with permission from Gilli et al.[12] Copyright 2018 Authors.

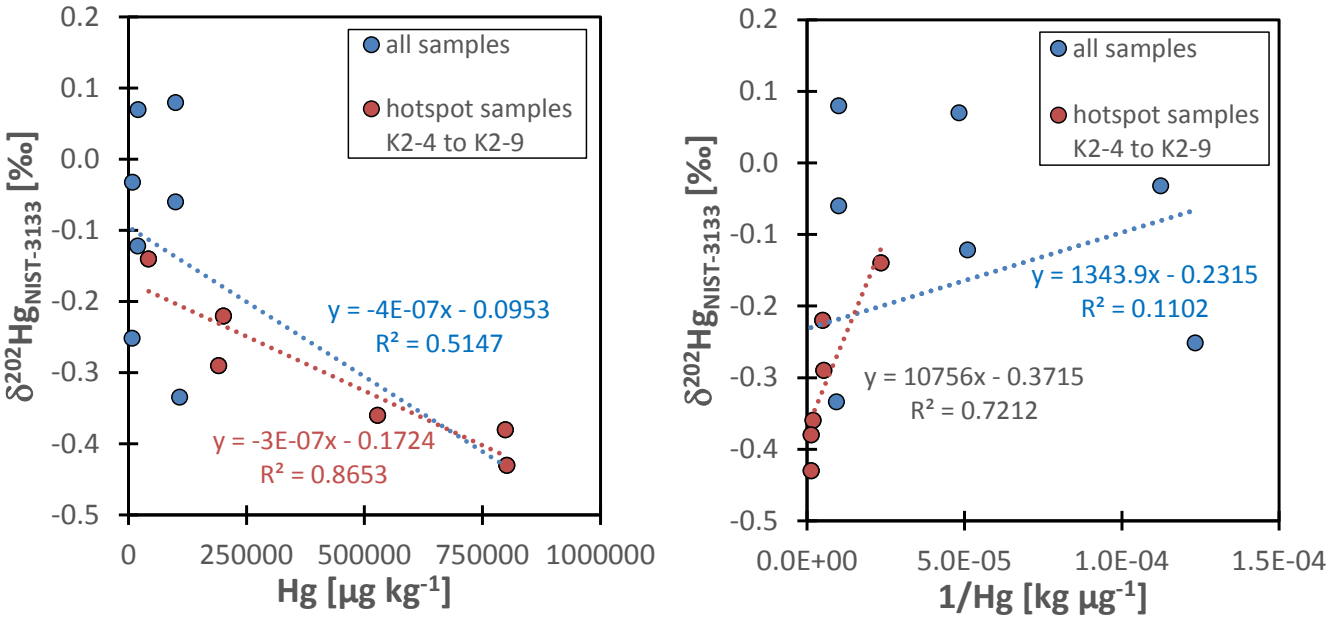


**Figure S2:** Plots of Hg isotope data (bulk samples) vs. Hg (left) and vs. 1/Hg (right)

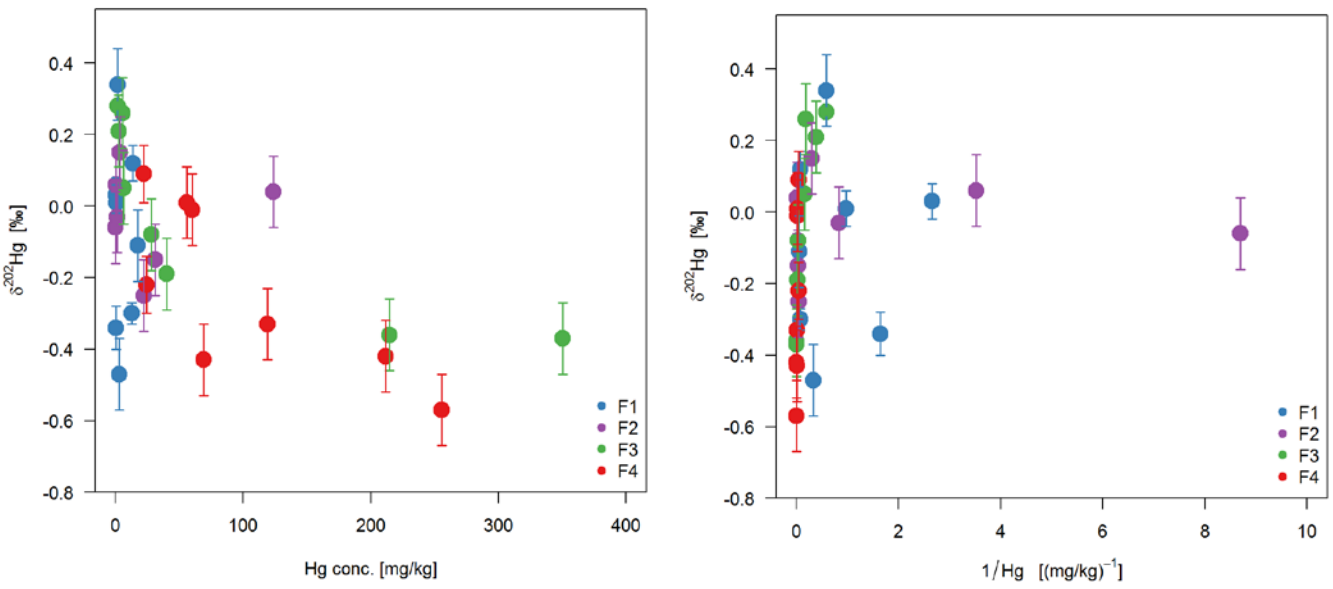


**Figure S3:** Plots of Hg isotope data (SEP samples) vs. Hg (left) and vs. 1/Hg (right)

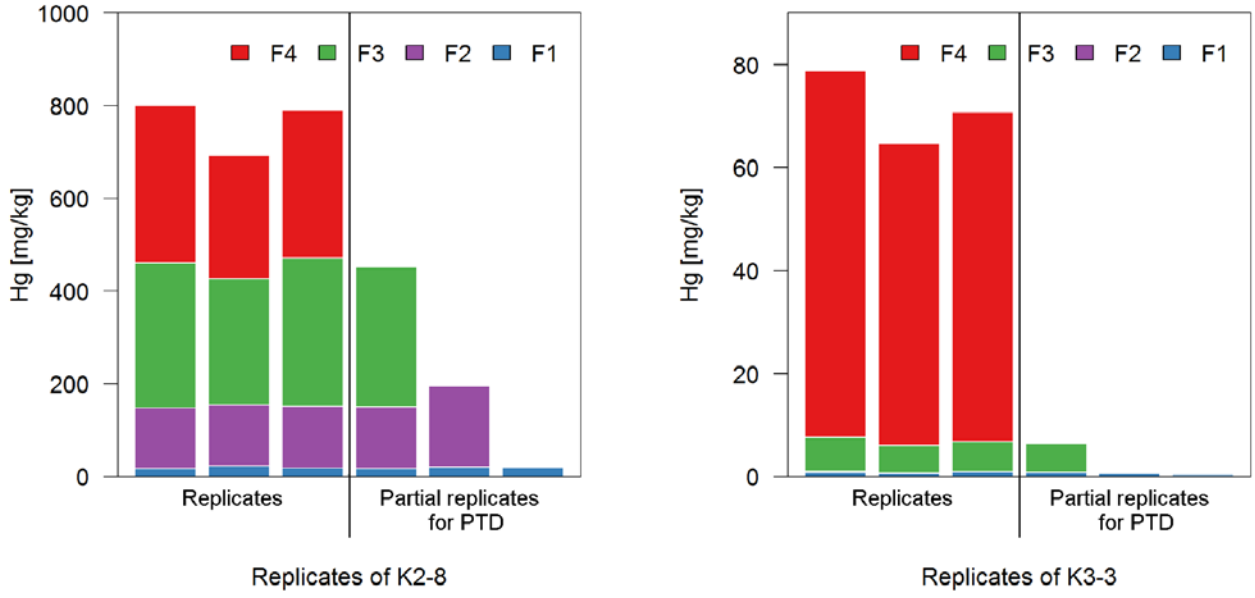


**Figure S4:** Results of replicate extractions of sample K2-8 and K3-3. Partial extractions are sequential extractions which were stopped after a particular extraction step.

**References used in SI:**


(1) Grigg, A. R. C.; Kretzschmar, R.; Gilli, R. S.; Wiederhold, J. G., Mercury isotope signatures of digests and sequential extracts from industrially contaminated soils and sediments. *Sci. Total Environ.* **2018**, 636, 1344-1354.

(2) Smith, R. S., Wiederhold, J. G., Jew, A. D., Brown Jr, G. E., Bourdon, B., Kretzschmar, R., Stable Hg isotope signatures in creek sediments impacted by a former Hg mine. *Environ. Sci. Technol.* **2015**, 49(2), 767-776.

(3) Jiskra, M., Wiederhold, J. G., Skyllberg, U., Kronberg, R. M., Kretzschmar, R., Source tracing of natural organic matter bound mercury in boreal forest runoff with mercury stable isotopes. *Environ. Sci. Process Impacts* **2017**, 19(10), 1235-1248.

(4) Enrico, M., Roux, G. L., Marusczak, N., Heimbürger, L. E., Claustres, A., Fu, X., Sun, R., Sonke, J. E., Atmospheric mercury transfer to peat bogs dominated by gaseous elemental mercury dry deposition. *Environ. Sci. Technol.* **2016**, 50(5), 2405-2412.

(5) Obrist, D., Agnan, Y., Jiskra, M., Olson, C. L., Colegrove, D. P., Hueber, J., Moore, C.W., Sonke, J. E., Helmig, D., Tundra uptake of atmospheric elemental mercury drives Arctic mercury pollution. *Nature* **2017**, 547(7662), 201-204.

(6) Du, B., Feng, X., Li, P., Yin, R., Yu, B., Sonke, J. E., Guinot, B., Anderson, C. W. N., Maurice, L., Use of mercury isotopes to quantify mercury exposure sources in inland populations, China. *Environ. Sci. Technol.* **2018**, 52(9), 5407-5416.

(7) Hansson, S. V., Sonke, J., Galop, D., Bareille, G., Jean, S., Le Roux, G., Transfer of marine mercury to mountain lakes. *Sci. Rep.* **2017**, 7(1), 12719.

(8) Xu, H. M., Sun, R. Y., Cao, J. J., Huang, R. J., Guinot, B., Shen, Z. X., Jiskra, M. Lie, C.X., Du, B.Y.; He, C., Liu, S.X., Zhang, T., Sonke, J.E., Mercury stable isotope compositions of Chinese urban fine particulates in winter haze days: Implications for Hg sources and transformations. *Chem. Geol.* **2019**, 504, 267-275.

(9) Goix, S., Maurice, L., Laffont, L., Rinaldo, R., Lagane, C., Chmeleff, J., Menges, J., Heimbürger, L. E., Maury-Brachet, R., Sonke, J. E., Quantifying the impacts of artisanal gold mining on a tropical river system using mercury isotopes. *Chemosphere* **2019**, 219, 684-694.

(10) Jiskra, M., Marusczak, N., Leung, K. H., Hawkins, L., Prestbo, E. M., Sonke, J. E., Automated stable isotope sampling of gaseous elemental mercury (ISO-GEM)–Insights into GEM emissions from building surfaces. *Environ. Sci. Technol.* **2019**, 53, 4346−4354.

(11) Skyllberg, U., Chemical Speciation of Mercury in Soil and Sediment. John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2011; pp 219-258.

(12) Gilli, R., Karlen, C., Weber, M., Rüegg, J., Barmettler, K., Biester, H., Boivin, P., Kretzschmar, R., Speciation and mobility of mercury in soils contaminated by legacy emissions from a chemical factory in the Rhône valley in canton of Valais, Switzerland. *Soil Systems* **2018**, 2(3), 44.