

1 **Supplementary Information**

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3 **Species-specific isotope dilution analysis of monomethylmercury in sediment using**
4 **GC/ICP-ToF-MS and comparison with ICP-Q-MS and ICP-SF-MS**

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25 **S1 Preparation of samples for determination of MMHg in sediment.**

26 A sample mass of 250 mg was weighed into a 15 mL centrifuge tube. Then, 1 mL of aqueous
27 CuSO_4 solution (1 mol/L) and the ^{201}Hg -enriched MMHg spike solution were added. The
28 required volume of spike solution was estimated for every sample to target an $^{201}\text{Hg}/^{202}\text{Hg}$ ratio
29 of approximately 1 and the actual amount of spike solution added was determined
30 gravimetrically. To assess the required volume of spike solution, the MMHg concentration of
31 the samples had been screened with an external calibration technique beforehand. The
32 sample-spike mixture was vortexed thoroughly to ensure complete mixing. A volume of 4 mL
33 HNO_3 (3 mol/L) and 5 mL of DCM were added for simultaneous extraction of MMHg from the
34 sediment and liquid-liquid extraction into DCM for separation from inorganic Hg. The tube was
35 vortexed in the dark for 30 min and subsequently centrifuged for 30 min at 3000 min^{-1} . The
36 DCM phase was separated over a phase separation filter and mixed with 4.5 mL of aqueous
37 $\text{Na}_2\text{S}_2\text{O}_3$ solution (0.1 mmol/L) to back extract MMHg into the aqueous phase for derivatization.
38 The tube was shaken for 30 min at 300 min^{-1} on a horizontal shaker and subsequently
39 centrifuged for 10 min at 3000 min^{-1} . A volume of 4 mL of the top aqueous phase was
40 transferred into a new 50 mL centrifuge tube. For derivatization, 19 mL of a buffer mixture
41 containing glacial acetic acid, methanol, and ultrapure water in a ratio of 1:1:1.5 adjusted to
42 pH 4.5 with NaOH solution (0.32 kg/kg) was added to the MMHg extract. Then, 1 mL of a
43 solution of the derivatization agent NaBPr_4 in THF (20 g/L) and 1 mL of n-hexane for extraction
44 of the derivatized MMHg were added. The derivatization took place during 1 h of shaking at
45 240 min^{-1} on a horizontal shaker. Afterwards, the tube was centrifuged for 10 min at 3500 min^{-1} ,
46 and the hexane phase was transferred into a 2 mL microcentrifuge tube. The derivatization
47 procedure was repeated by adding another 1 mL of NaBPr_4 solution in THF (20 g/L) and 1 mL
48 of n-hexane to the 50 mL centrifuge tube. After shaking and centrifuging, the hexane phase
49 was unified with the first one in the microcentrifuge tube. The tube was vortexed, and
50 anhydrous Na_2SO_4 was added to bind traces of residual water. Finally, 1 mL of the sample
51 solution was transferred into a 2 mL amber glass GC vial for analysis. Very low concentrated
52 sediment samples (IAEA-456 and samples 1 and 8) were prepared with a sample amount of
53 1 g and the twofold volume of reagents in the extraction procedure. All other steps were the
54 same as for higher concentrated samples. Procedural blanks were prepared by following the
55 whole sample preparation procedure without sediment and with (for determination of LOQ) and
56 without ^{201}Hg -enriched MMHg spike.

57 **Table S1** Details of the sampling site

Sample	Material	Chainage km	Coordinates
1	Sediment	57.4	52°50'45.1"N 13°32'32.1"E
2	Sediment	62	52°50'21.7"N 13°36'10.5"E
3	Sediment	73.86	52°50'35.2"N 13°46'10.0"E
4	Sediment	75.9	52°50'19.3"N 13°47'31.6"E
5	Sediment	77.94	52°50'10.5"N 13°49'15.0"E
W	Soil	79.5	52°50'42.5"N 13°50'23.2"E
6	Sediment	80.99	52°50'57.8"N 13°51'21.0"E
7	Sediment	88.91	52°50'55.1"N 13°57'09.7"E
8	Sediment	96	52°51'51.2"N 14°02'56.8"E
9	Sediment	104	52°52'30.4"N 14°08'55.3"E

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59 **Table S2** Details of the ²⁰¹Hg-enriched spike and reference materials

Material	MMHg mass fraction (mg/kg)	Total Hg mass fraction (mg/kg)	Isotopic composition
MMHg spike for SSID (MMHg in 3:1 acetic acid/methanol)	5.1 ± 0.3 (as MMHg)	/	¹⁹⁶ Hg: < 0.1 % ¹⁹⁸ Hg: (0.10 ± 0.03) % ¹⁹⁹ Hg: (0.41 ± 0.06) % ²⁰⁰ Hg: (2.29 ± 0.05) % ²⁰¹ Hg: (94.7 ± 0.1) % ²⁰² Hg: (2.32 ± 0.06) % ²⁰⁴ Hg: (0.11 ± 0.02) %
Hg spike for ID (solid HgO)	/	0.92×10 ⁶	¹⁹⁶ Hg: < 0.05 % ¹⁹⁸ Hg: (0.08 ± 0.010) % ¹⁹⁹ Hg: (0.10 ± 0.010) % ²⁰⁰ Hg: (0.45 ± 0.010) % ²⁰¹ Hg: (98.11 ± 0.030) % ²⁰² Hg: (1.18 ± 0.02) % ²⁰⁴ Hg: (0.08 ± 0.010) %
IAEA-456 (marine sediment)	0.0125×10 ⁻³ ± 0.019×10 ⁻³ (as Hg)	0.077 ± 0.005	/
ERM-CC020 (river sediment)	/	27.4 ± 0.6	/
ERM-CC580 (estuarine sediment)	0.0755 ± 0.0037 (as MMHg)	132 ± 3	/

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61 **Table S3** Operating conditions of the GC/ICP-MS interface for MMHg analysis

Parameter	Value
Column	TG5-SilMS (30 m x 0.25 mm i.d., 0.25 µm)
PTV Injector temperature program	250 °C to 400 °C with 10 °C/s
Injection volume (µL)	2
Carrier gas	Helium
Carrier gas flow rate (mL/min)	1
Oven temperature program	1 min hold 40 °C, 20 °C/min to 150 °C, 70 °C/min to 300 °C, 4.5 min hold 300 °C
Transfer line temperature (°C)	300
Make up gas flow rate (L/min)	0.600

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63 **Table S4** Operating conditions of the ICP-ToF-MS instrument for MMHg analysis

Parameter	Value
Cones	Platinum
RF power (W)	1200
Cool gas flow rate (L/min)	14
Auxiliary gas flow rate (L/min)	0.80
Nebulizer gas flow rate (L/min)	0.730
Integration time (s)	0.2
Isotopes	²⁰¹ Hg, ²⁰² Hg, ²⁰³ Tl, ²⁰⁵ Tl

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65 **Table S5** Operating conditions of the ICP-Q-MS instrument for MMHg analysis

Parameter	Value
Cones	Nickel
RF power (W)	1550
Cool gas flow rate (L/min)	14
Auxiliary gas flow rate (L/min)	0.80
Nebulizer gas flow rate (L/min)	0.730
Dwell time (s)	0.1
Isotopes	²⁰¹ Hg, ²⁰² Hg, ²⁰³ Tl, ²⁰⁵ Tl

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67 **Table S6** Operating conditions of the ICP-SF-MS instrument for MMHg analysis

Parameter	Value
Cones	Nickel
RF power (W)	1250
Cool gas flow rate (L/min)	16
Auxiliary gas flow rate (L/min)	0.85
Nebulizer gas flow rate (L/min)	0.530
Resolution	Low (300)
Mass window	20
Samples per peak	100
Sample time (s)	0.02
Isotopes	²⁰¹ Hg, ²⁰² Hg, ²⁰³ Tl, ²⁰⁵ Tl

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69 **Table S7** Operating conditions of the ICP-SF-MS instrument for total Hg analysis

Parameter	Value
Cones	Nickel
RF power (W)	1250
Cool gas flow rate (L/min)	16
Auxiliary gas flow rate (L/min)	1.00
Nebulizer gas flow rate (L/min)	1.160
Resolution	Low (300)
Mass window	5
Samples per peak	200
Dwell time (s)	0.002
Runs	10
Passes	500
Isotopes	²⁰⁰ Hg, ²⁰¹ Hg, ²⁰² Hg

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71 **Table S8** MMHg ($w(\text{Hg})_{\text{MMHg}}$) and Hg ($w(\text{Hg})_{\text{total}}$) mass fractions determined in sediment
72 reference materials and samples with expanded uncertainty U ($k = 2$) based on dry weight and
73 $n = 3$ replicates (exceptions annotated)

Sample	MMHg mass fraction ($\mu\text{g}/\text{kg}$)	Total Hg mass fraction (mg/kg)
ERM-CC020		27.5 ± 1.0
ERM-CC020 certified value		27.4 ± 0.6
ERM-CC580	$81.8 \pm 5.3^{\text{a}}$ $82.3 \pm 4.2^{\text{b}}$ $81.8 \pm 4.2^{\text{c}}$	$136.5 \pm 4.5^{\text{d}}$
ERM-CC580 certified value	75.5 ± 3.7	132 ± 3
IAEA-456	$0.132 \pm 0.013^{\text{e}}$	0.0823 ± 0.0070
IAEA-456 certified value	0.125 ± 0.019	0.077 ± 0.005
Sediment 1 (km 57.4)	0.180 ± 0.017	0.056 ± 0.013
Sediment 2 (km 62)	0.488 ± 0.043	0.259 ± 0.012
Sediment 3 (km 73.86)	26.3 ± 1.7	9.14 ± 0.27
Sediment 4 (km 75.9)	39.3 ± 5.5	41.4 ± 2.6
Sediment 5 (km 77.94)	20.5 ± 1.8	9.18 ± 0.69
Sediment 6 (km 80.99)	36.3 ± 2.7	126.1 ± 7.1
Sediment 7 (km 88.91)	33.0 ± 3.5	30.0 ± 4.2
Sediment 8 (km 96)	0.367 ± 0.033	0.549 ± 0.066
Sediment 9 (km 104)	6.37 ± 0.54	2.58 ± 0.12
Washing bed (W)	40.6 ± 3.7	117.2 ± 3.3

74 ^a as MMHg ($w(\text{MMHg})$), $n = 12$, determined with GC/ICP-ToF-MS

75 ^b as MMHg ($w(\text{MMHg})$), $n = 2$, determined with GC/ICP-Q-MS

76 ^c as MMHg ($w(\text{MMHg})$), $n = 2$, determined with GC/ICP-SF-MS

77 ^d as MMHg ($w(\text{MMHg})$)

78 ^e $n = 6$