Supplementary Materials

Isotopic Characterization of Gaseous Mercury and Particulate Water-Soluble Organic Carbon Emitted from Open Grass Field Burning in Aso, Japan

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This supplementary material contains

6 pages
2 figures
6 tables
2 sub-sections

Table S1. Summary of noyaki sampling and types of samples collected.

	BAuT	Filter	Conventional trap
Noyaki sampling			
2019 March 24, Daikanpou	✓	✓	
2019 April 6, Namino	✓	✓	
2021 March 14, Komezuka		✓	
2021 March 23, Ubuyama	✓	✓	✓
2021 March 27, Kitayama	✓	✓	✓
Background air sampling			
2019 March 31, Namino	✓	✓	
2019 May 23, Namino	✓	✓	
2021 April 19, Komezuka	✓	✓	✓
2021 April 23, Ubuyama	✓	✓	✓
2021 May 10, Kitayama	✓	✓	✓
2021 May 25, Kitayama		✓	✓
2021 June 1, Namino		✓	✓

Table S2. TGM samples collected from noyaki studies.

Sample	Flow rate	Sampling duration	Air volume
	L min^{-1}	h	m^3
Noyaki samples			
2019 March 24, Daikanpou BAuT	75	0.9	4.2
2019 April 6, Namino BAuT	78	0.8	3.5
2021 March 23, Ubuyama BAuT	80	2.0	9.6
2021 March 27, Kitayama BAuT	85	2.0	10.2
Background air samples			
2019 March 31, Namino BAuT	54	2.1	6.7
2019 May 23, Namino BAuT	80	4.2	20.1
2021 April 19, Komezuka BAuT	90	3.0	16.4
2021 April 23, Ubuyama BAuT	90	3.5	18.9
2021 May 10, Kitayama BAuT	95	5.0	28.5

Table S3. Filter samples collected from noyaki studies.

Sample	Flow rate	Sampling duration	Air volume
	L min^{-1}	h	m^3
Noyaki sampling			
2019 March 24, Daikanpo 1st BAuT filter 1	73	0.63	2.76
2019 March 24, Daikanpo 1st BAuT filter 2	75	0.80	3.60
2019 March 24, Daikanpo 1st BAuT filter 3	75	0.93	4.18
2019 March 24, Daikanpo 2nd BAuT filter	75	0.67	3.00
2019 March 24, Daikanpo filter 1	35	0.63	1.33
2019 March 24, Daikanpo filter 2	35	0.80	1.68
2019 March 24, Daikanpo filter 3	35	0.93	1.95
2019 March 24, Daikanpo filter 4	37	0.67	1.48
2019 April 6, Namino BAuT filter	78	0.75	3.49
2019 April 6, Namino filter	38	0.75	1.69
2021 March 14, Komezuka BAuT filter	100	2.00	12.00
2021 March 23, Ubuyama BAuT filter	80	2.00	9.60
2021 March 27, Kitayama BAuT filter 1	85	1.05	5.36
2021 March 27, Kitayama BAuT filter 2	85	0.42	2.13
2021 March 27, Kitayama BAuT filter 3	85	0.53	2.72
Background air sampling			
2019 March 31, Namino BAuT filter	54	2.08	6.74
2019 May 23, Namino BAuT filter	80	4.18	20.08
2021 April 23, Ubuyama BAuT filter	90	3.50	18.90
2021 May 10, Kitayama BAuT filter	95	5.00	28.50
2021 May 25, Kitayama BAuT filter	90	5.17	27.90
2021 June 1, Namino BAuT filter	90	5.00	27.00

S.1. TGM recovery test through the overall procedure

Recovery tests through the overall procedure were conducted for total gaseous mercury (TGM) sampling using a BAuT. High trapping efficiency of TGM by BAuT and high recovery yields of plastic bag extraction have been demonstrated [24]. However, recovery yields and isotope measurements of yielded TGM through the overall procedure were not evaluated in the previous paper. Here, we conducted laboratory experiments to evaluate the overall procedure. In this test gaseous elemental mercury (GEM) prepared from the standard reference material 8610 (NIST, Gaithersburg, MD, USA), the stable mercury isotope ratios of which are provided by NIST, was introduced to the stream of 80 L min^{-1} air flow, in which TGM was removed through the front BAuT (Figure S1). The introduced GEM was then trapped at the backup BAuT, and the GEM captured was extracted and converted to Hg^{2+} through the procedure described in the previous paper referred earlier. Yielded solutions of 40% (v/v) reversed aqua regia containing Hg^{2+} was analyzed by a cold vapor generator (HGX-200, Teledyne CETAC Technologies, Omaha, NE, USA) coupled with a multi-collector inductively coupled plasma mass spectrometer (Neptune Plus, Thermo Fisher Scientific GmbH, Bremen, Germany) for yielded quantity and stable isotope ratios of mercury tested. Unfavorable isotope fractionation occurring at ICP section during the isotope ratio measurements was corrected by analyzing the simultaneously introduced SRM 997 thallium aerosol produced by an aerosol generator (Aridus II, Teledyne CETAC Technologies).

Recovery yields determined showed 70% and 65% for 5 ng and 16 ng of mercury injection, respectively. For 41 ng injection, the recovery yields improved to 90%. Their stable mercury isotope ratios showed some biases, depending on the mass of isotope, and the biases were large (up to 0.9 ‰) when the amount of mercury injected was below 16 ng (Table S4). The biases were lowest with 41 ng GEM injection (up to 0.4 ‰). It is possible that the carrier gas, mercury-free air, used to transfer trapped GEM in the BAuT to a small conventional mercury trap may have oxidized some GEM during the transfer. The use of inertia gas, conveniently pure nitrogen, may improve this extraction.

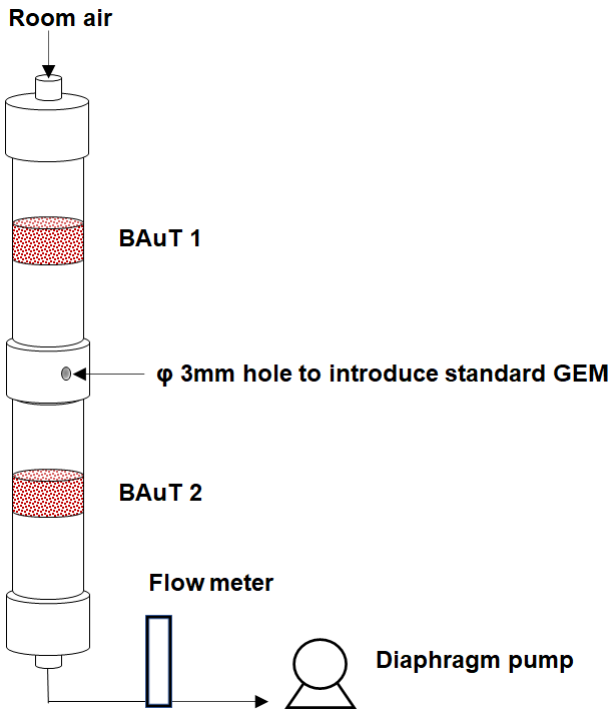

Figure S1. Experimental setup for BAuT recovery tests.

Table S4. Summary of recovery tests through overall procedure using SRM 8610.†

Injected quantity	Recovery yield	Accuracy in $\delta^{199}Hg$‡	Accuracy in $\delta^{200}Hg$‡	Accuracy in $\delta^{201}Hg$‡	Accuracy in $\delta^{202}Hg$‡	Accuracy in $\delta^{204}Hg$‡
ng	%	‰				
5.2	70.4 ± 3.1	0.08 ± 0.35	0.33 ± 0.18	0.47 ± 0.23	0.69 ± 0.55	0.89 ± 0.68
15.5	64.6 ± 7.1	0.05 ± 0.17	0.24 ± 0.20	0.33 ± 0.23	0.52 ± 0.24	0.90 ± 0.50
41.3	89.7 ± 8.0	-0.08 ± 0.12	-0.16 ± 0.09	-0.27 ± 0.15	-0.28 ± 0.17	-0.37 ± 0.22

†Values shown are average ± standard deviation (n = 3). ‡Accuracy = measured $\delta^{x}Hg$ – reference $\delta^{x}Hg$, ± 2×propagated uncertainty.

S2. Standard spike test of LV-WSOC

Recovery yields, precision, and accuracy of stable carbon isotope measurements for WSOC were evaluated by conducting standard spike tests with an aqueous solution of sucrose standard (IAEA-CH6, -10.8 ± 0.5 ‰). 4 – 40 μL of 10.0 μgC g^{-1} of sucrose solution in Milli-Q water (Milli-Q Integral 3, Merck KGaA, Darmstadt, Germany) was spiked to a 47 mm PTFE coated glass filter (Pallflex, Emfab, Pall Corp., Port Washington, NY, USA), and then left for approximately 30 min to dry. The standard spiked filters were then subjected to the quantitative and stable carbon isotope analysis, which is described

elsewhere[16, 30].

Test results showed that recovery yields were in the range between 98% and 109% (Table S5). Measured $\delta^{13}C$, however, varied largely (from -11.03 ‰ to -14.31 ‰), which was significantly different from the reference $\delta^{13}C$. The large variation was due to the significant impact of the blank carbon, which was 10 μgC with $\delta^{13}C$ of -23.9 ‰ equivalent to 2.4% – 24% of the spiked carbon. Blank-corrected $\delta^{13}C$ (Table S5) showed agreement with the reference value within the propagated uncertainties. However, it is good to be aware of that the magnitude of the measurement uncertainties considerably changed as the spiked mass varied from 41 μgC to the carbon larger than 103 μgC. It is preferable to use the isotope data gained from the analysis higher than 113 μgC (= 103 + 10 μgC).

Table S5. Results of recovery test (n = 3 for each spiked carbon mass) using IAEA-CH-6 sucrose.

Spiked C mass	Recovery yield†	$\delta^{13}C$†
(μgC)	(%)	(‰)
41	109 ± 8	-11.9 ± 0.6
103	102 ± 10	-11.4 ± 0.2
411	98 ± 3	-10.9 ± 0.1

†Values were blank-corrected, and values shown are average ± 1 σ of standard error.

Table S6. Comparison between TGM concentrations determined using the conventional traps and BAuTs.

Sample	Conventional trap	BAuT	Hg Loss using BAuT†
	ng m^{-3}	ng m^{-3}	%
Noyaki 2021 March 23, Ubuyama	4.9	4.0	18
Noyaki 2021 March 27, Kitayama	5.0	4.3	14

Background air 2021 April 19, Komezuka	1.5	1.0	32
Background air 2021 April 23, Ubuyama	1.6	0.99	36
Background air 2021 May 10, Kitayama	2.4	1.3	44

†Values are reference to the concentrations determined by the conventional traps.

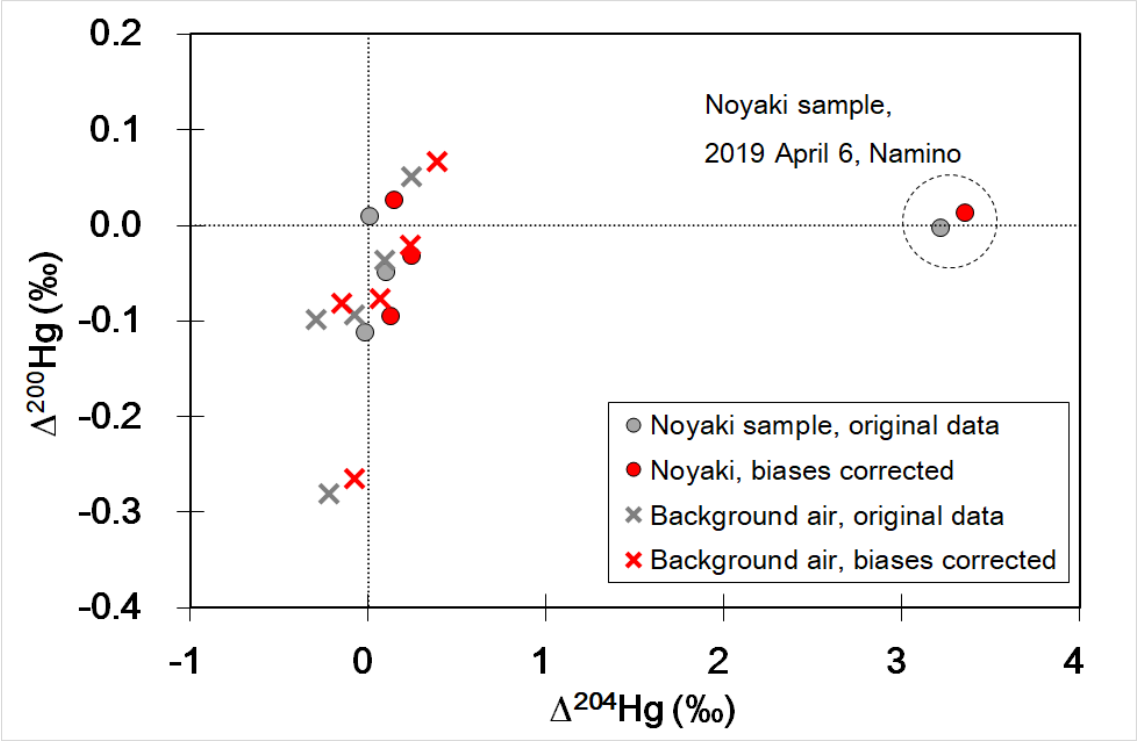

Figure S2. Scatter plot of Δ^{204}Hg versus Δ^{200}Hg for TGM from noyaki and background air samples before and after the corrections for the measurement biases were made.