Supporting information：

Extraction of ultratrace dissolved gaseous mercury and reactive mercury in natural freshwater for stable isotope analysis

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Table S1 Recoveries and isotopic compositions of the injected and extracted Hg(0) for the DGM standard addition tests.

Sample ID	Temperature	Recovery	δ^{202}Hg	2sd	δ^{201}Hg	2sd	δ^{200}Hg	2sd	δ^{199}Hg	2sd	Δ^{201}Hg	2sd	Δ^{200}Hg	2sd	Δ^{199}Hg	2sd
	℃	%	(‰)		(‰)		(‰)		(‰)		(‰)		(‰)		(‰)	
Injected-Hg(0)-1	13.8	93.0	-1.79	0.15	-1.33	0.06	-0.96	0.05	-0.35	0.05	0.02	0.09	-0.06	0.06	0.10	0.05
Extracted-Hg(0)-1		108.1	-2.00	0.15	-1.44	0.06	-0.96	0.05	-0.35	0.05	0.06	0.09	0.04	0.06	0.17	0.05
Injected-Hg(0)-2	13.7	96.2	-2.06	0.12	-1.48	0.11	-1.03	0.10	-0.31	0.07	0.08	0.06	0.01	0.06	0.21	0.05
Extracted-Hg(0)-2		99.2	-1.97	0.12	-1.40	0.11	-0.96	0.10	-0.33	0.07	0.09	0.06	0.03	0.06	0.17	0.05
Injected-Hg(0)-3	15.7	86.3	-1.61	0.13	-1.22	0.06	-0.82	0.09	-0.34	0.05	0.00	0.06	-0.01	0.06	0.07	0.05
Extracted-Hg(0)-3		102.2	-1.61	0.13	-1.18	0.06	-0.82	0.09	-0.30	0.05	0.03	0.06	-0.01	0.06	0.10	0.05
Injected-Hg(0)-4	15.7	100.0	-1.77	0.10	-1.28	0.06	-0.85	0.06	-0.21	0.05	0.05	0.06	0.04	0.06	0.23	0.05
Extracted-Hg(0)-4		98.5	-1.63	0.10	-1.16	0.06	-0.77	0.06	-0.24	0.05	0.07	0.06	0.04	0.06	0.17	0.05
Injected-Hg(0)-5	16.3	101.4	-1.64	0.10	-1.16	0.06	-0.77	0.05	-0.22	0.05	0.07	0.09	0.05	0.06	0.19	0.05
Extracted-Hg(0)-5		100.6	-1.37	0.10	-1.00	0.06	-0.68	0.05	-0.22	0.05	0.03	0.09	0.01	0.06	0.13	0.05
Injected-Hg(0)-6	21.0	84.1	-1.79	0.22	-1.25	0.14	-0.87	0.12	-0.26	0.05	0.10	0.06	0.03	0.06	0.19	0.05
Extracted-Hg(0)-6		85.1	-1.71	0.22	-1.24	0.14	-0.82	0.12	-0.27	0.05	0.05	0.06	0.04	0.06	0.16	0.05
Injected-Hg(0)-7	15.1	86.6	-1.83	0.10	-1.26	0.06	-0.91	0.05	-0.32	0.05	0.12	0.06	0.01	0.06	0.14	0.05
Extracted-Hg(0)-7		115.9	-1.52	0.10	-1.07	0.06	-0.79	0.05	-0.25	0.05	0.07	0.06	-0.03	0.06	0.14	0.05
Injected-Hg(0)-8	13.7	93.6	-2.22	0.10	-1.58	0.10	-1.10	0.08	-0.40	0.08	0.09	0.06	0.02	0.06	0.16	0.06
Extracted-Hg(0)-8		87.1	-2.08	0.10	-1.50	0.10	-1.06	0.08	-0.43	0.08	0.07	0.06	-0.01	0.06	0.10	0.06
Injected-Hg(0)-9	14.1	95.2	-1.36	0.10	-0.89	0.10	-0.65	0.08	-0.17	0.08	0.13	0.06	0.03	0.06	0.17	0.06
Extracted-Hg(0)-9		98.4	-1.75	0.10	-1.27	0.06	-0.85	0.05	-0.24	0.05	0.05	0.06	0.03	0.06	0.20	0.05
Injected-Hg(0)-10	17.4	107.2	-1.88	0.10	-1.34	0.06	-0.90	0.05	-0.34	0.05	0.08	0.08	0.04	0.04	0.13	0.05
Extracted-Hg(0)-10		93.0	-1.86	0.10	-1.34	0.06	-0.90	0.05	-0.36	0.05	0.05	0.07	0.03	0.06	0.11	0.05
Injected-Hg(0)-11	15.7	83.2	-1.78	0.16	-1.25	0.22	-0.84	0.07	-0.28	0.05	0.09	0.10	0.05	0.06	0.17	0.05
Extracted-Hg(0)-11		97.5	-1.64	0.16	-1.16	0.22	-0.75	0.07	-0.24	0.05	0.07	0.10	0.08	0.06	0.17	0.05
Injected-Hg(0)--12	14.5	90.1	-1.85	0.10	-1.28	0.13	-0.85	0.05	-0.27	0.05	0.12	0.08	0.07	0.06	0.19	0.05
Extracted-Hg(0)-12		88.5	-1.78	0.10	-1.32	0.06	-0.91	0.05	-0.34	0.05	0.02	0.05	-0.04	0.06	0.11	0.05
Injected-Hg(0)-13	21.0	106.0	-1.50	0.10	-1.02	0.03	-0.74	0.07	-0.23	0.05	0.11	0.06	0.01	0.06	0.15	0.05
Extracted-Hg(0)-13		98.0	-1.55	0.10	-1.12	0.06	-0.67	0.10	-0.17	0.08	0.05	0.06	0.11	0.08	0.22	0.07
Injected-Hg(0)-14	21.6	100.5	-1.32	0.10	-0.96	0.07	-0.65	0.10	-0.17	0.08	0.03	0.06	0.02	0.08	0.16	0.07
Extracted-Hg(0)-14		101.0	-1.64	0.10	-1.11	0.05	-0.78	0.07	-0.23	0.08	0.12	0.06	0.04	0.06	0.19	0.08

Table S2 Recoveies and isotopic compositions of spiked SRM 3133, RM 8610 and BCR 482 for the RHg standard addition test.

Sample ID	Hg	Recovery	δ^{204}Hg	2sd	δ^{202}Hg	2sd	δ^{201}Hg	2sd	δ^{200}Hg	2sd	δ^{199}Hg	2sd	Δ^{204}Hg	2sd	Δ^{201}Hg	2sd	Δ^{200}Hg	2sd	Δ^{199}Hg	2sd
	ng	%			(‰)		(‰)		(‰)		(‰)				(‰)		(‰)		(‰)	
3133-1	10ng	91.4			-0.27	0.22	-0.31	0.06	-0.22	0.05	-0.07	0.06			-0.11	0.06	-0.09	0.08	-0.01	0.05
3133-2		106.5			-0.14	0.22	-0.10	0.08	-0.07	0.08	-0.02	0.07			0.01	0.06	0.01	0.08	0.02	0.08
3133-3		93.5			-0.01	0.22	-0.06	0.06	-0.05	0.05	0.01	0.05			-0.05	0.06	-0.04	0.08	0.01	0.05
3133-4		110.2			-0.19	0.22	-0.10	0.06	-0.07	0.05	0.01	0.05			0.04	0.06	0.02	0.08	0.06	0.05
3133-5		94.8			-0.08	0.22	-0.04	0.06	0.04	0.05	0.02	0.05			0.02	0.06	0.08	0.08	0.04	0.05
3133-6		81.3			0.12	0.22	-0.14	0.06	0.05	0.05	0.03	0.05			0.05	0.06	-0.01	0.08	0.00	0.05
3133-7		94.6			-0.22	0.22	-0.11	0.06	-0.08	0.05	-0.01	0.07			0.05	0.06	0.03	0.08	0.05	0.06
3133-8		90.7			-0.19	0.22	-0.08	0.06	-0.06	0.05	0.01	0.07			0.06	0.06	0.04	0.08	0.06	0.06
3133-9		103.8			-0.19	0.22	-0.06	0.06	-0.05	0.05	0.01	0.05			0.09	0.06	0.05	0.08	0.06	0.05
3133-10		92.7			0.04	0.22	0.06	0.06	0.04	0.05	0.05	0.05			0.03	0.06	0.02	0.08	0.04	0.05
3133-11		92.0			-0.25	0.22	-0.16	0.06	-0.12	0.07	-0.04	0.05			0.03	0.06	0.01	0.08	0.02	0.05
3133-12		100.0			-0.05	0.22	-0.01	0.06	0.06	0.05	0.00	0.05			0.03	0.06	0.08	0.08	0.01	0.05
3133-13		104.0			-0.05	0.22	0.09	0.06	-0.01	0.12	0.04	0.05			0.12	0.06	0.01	0.08	0.05	0.05
3133-14		117.0			-0.12	0.22	-0.11	0.07	-0.04	0.05	0.02	0.05			-0.01	0.06	0.02	0.08	0.05	0.06
3133-15		122.0			-0.17	0.22	-0.13	0.06	-0.08	0.05	-0.06	0.05			0.00	0.06	0.01	0.08	-0.02	0.05
8610-1	5ng	95.2	-0.62	0.16	-0.47	0.13	-0.35	0.09	-0.19	0.10	-0.16	0.08	0.08	0.14	0.00	0.06	0.04	0.06	-0.04	0.05
8610-2		102.2	-0.58	0.16	-0.44	0.13	-0.36	0.09	-0.20	0.10	-0.13	0.08	0.08	0.14	-0.03	0.06	0.03	0.06	-0.02	0.05
8610-3		99.2	-0.62	0.16	-0.44	0.13	-0.36	0.09	-0.22	0.10	-0.13	0.08	0.03	0.14	-0.04	0.06	0.00	0.06	-0.02	0.05
8610-4	10ng	90.1	-0.74	0.16	-0.50	0.13	-0.46	0.09	-0.27	0.10	-0.16	0.08	0.01	0.14	-0.08	0.06	-0.01	0.06	-0.04	0.05
8610-5		90.2	-0.72	0.16	-0.59	0.13	-0.42	0.09	-0.33	0.10	-0.21	0.08	0.17	0.14	0.03	0.06	-0.03	0.06	-0.06	0.05
8610-6		90.0	-0.54	0.16	-0.38	0.13	-0.33	0.09	-0.18	0.10	-0.10	0.08	0.03	0.14	-0.04	0.06	0.01	0.06	0.00	0.05
8610-7	20ng	110.3	-0.54	0.16	-0.38	0.13	-0.31	0.09	-0.18	0.10	-0.08	0.08	0.02	0.14	-0.03	0.06	0.01	0.06	0.01	0.05
8610-8		96.2	-0.72	0.16	-0.43	0.13	-0.38	0.09	-0.24	0.10	-0.11	0.08	-0.07	0.14	-0.05	0.06	-0.02	0.06	0.00	0.05
8610-9		102.3	-0.71	0.16	-0.46	0.13	-0.35	0.09	-0.26	0.10	-0.14	0.08	-0.02	0.14	0.00	0.06	-0.03	0.06	-0.03	0.05
BCR-1	5ng	99.6	-2.67	0.24	-1.70	0.14	-1.96	0.14	-0.81	0.08	-1.08	0.09	-0.14	0.14	-0.68	0.05	0.05	0.06	-0.65	0.07
BCR-2		112.6	-2.68	0.24	-1.71	0.14	-1.95	0.14	-0.82	0.08	-1.12	0.09	-0.12	0.11	-0.66	0.05	0.05	0.06	-0.69	0.07
BCR-3		99.6	-2.64	0.24	-1.69	0.14	-1.93	0.14	-0.82	0.08	-1.06	0.09	-0.11	0.11	-0.65	0.09	0.03	0.06	-0.63	0.07
BCR-4	10ng	90.7	-2.35	0.24	-1.52	0.14	-1.75	0.14	-0.69	0.08	-0.95	0.09	-0.08	0.11	-0.61	0.08	0.07	0.06	-0.57	0.07
BCR-5		89.7	-2.73	0.24	-1.76	0.14	-1.95	0.14	-0.82	0.08	-1.04	0.09	-0.10	0.11	-0.63	0.08	0.06	0.06	-0.60	0.07
BCR-6		100.6	-2.57	0.24	-1.61	0.14	-1.86	0.14	-0.77	0.08	--1.07	0.09	-0.16	0.11	-0.64	0.08	0.04	0.06	-0.66	0.07
BCR-7	20ng	98.6	-2.49	0.24	-1.61	0.14	-1.86	0.14	-0.78	0.08	--1.04	0.09	-0.09	0.11	-0.64	0.05	0.03	0.06	-0.63	0.07
BCR-8		95.7	-2.68	0.24	-1.68	0.14	-1.90	0.14	-0.78	0.08	-1.05	0.09	-0.18	0.11	-0.64	0.05	0.06	0.06	-0.63	0.07
BCR-9		98.3	-2.63	0.24	-1.63	0.14	-1.82	0.14	-0.78	0.08	-1.03	0.09	-0.20	0.11	-0.60	0.05	0.04	0.06	-0.62	0.07

Table S3 Concentrations and isotopic compositions of DGM and RHg for the duplicate samples. Samples were collected in HFL.

Sample ID	Hg concentration	$\delta^{199}Hg$	2sd	$\delta^{200}Hg$	2sd	$\delta^{201}Hg$	2sd	$\delta^{202}Hg$	2sd	$\delta^{204}Hg$	2sd	$\Delta^{199}Hg$	2sd	$\Delta^{200}Hg$	2sd	$\Delta^{201}Hg$	2sd	$\Delta^{204}Hg$	2sd
	pg L^{-1}	(‰)		(‰)		(‰)		(‰)		(‰)		(‰)		(‰)		(‰)		(‰)	
DGM-a-1	74.6	-0.13	0.05	-0.22	0.06	-0.32	0.11	-0.36	0.12	-0.54	0.29	-0.04	0.05	-0.05	0.06	-0.04	0.05	0.00	0.29
DGM-b-1	82.6	-0.21	0.05	-0.34	0.13	-0.49	0.29	-0.56	0.24	-0.95	0.44	-0.07	0.05	-0.06	0.06	-0.07	0.05	-0.11	0.29
DGM-a-2	109.2	-0.10	0.09	-0.21	0.12	-0.28	0.11	-0.46	0.12	-0.59	0.57	0.01	0.08	0.02	0.09	0.06	0.09	0.10	0.48
DGM-b-2	110.0	-0.10	0.08	-0.21	0.12	-0.35	0.11	-0.53	0.12	-0.73	0.48	0.04	0.08	0.06	0.09	0.05	0.09	0.07	0.49
DGM-a-3	125.7	-0.07	0.12	-0.23	0.09	-0.39	0.11	-0.56	0.12	-0.90	0.41	0.07	0.12	0.05	0.07	0.03	0.09	0.55	0.41
DGM-b-3	121.2	-0.07	0.12	-0.23	0.09	-0.31	0.11	-0.49	0.12	-1.02	0.41	0.06	0.12	0.01	0.07	0.06	0.09	-0.06	0.41
DGM-a-4	87.8	-0.10	0.08	-0.24	0.09	-0.44	0.12	-0.56	0.12	-0.77	0.29	0.05	0.08	0.05	0.07	-0.01	0.09	0.08	0.45
DGM-b-4	99.3	-0.07	0.08	-0.23	0.09	-0.41	0.12	-0.47	0.12	-0.90	0.29	0.04	0.08	0.01	0.07	-0.05	0.09	-0.20	0.45
DGM-a-5	89.0	-0.14	0.12	-0.22	0.09	-0.33	0.11	-0.39	0.12	-0.39	0.41	-0.04	0.12	-0.02	0.07	-0.03	0.09	0.43	0.41
DGM-b-5	91.5	-0.19	0.08	-0.19	0.09	-0.43	0.11	-0.47	0.12	-0.47	0.29	-0.07	0.09	0.04	0.07	-0.08	0.11	0.07	0.24
RHg-a-1	246.1	-0.24	0.04	-0.53	0.10	-0.72	0.06	-1.11	0.10	-1.60	0.27	0.04	0.05	0.03	0.06	0.11	0.07	0.05	0.18
RHg-b-2	257.9	-0.27	0.04	-0.53	0.10	-0.77	0.06	-1.14	0.10	-1.74	0.27	0.02	0.05	0.04	0.06	0.09	0.07	-0.04	0.18
RHg-a-2	206.6	-0.20	0.08	-0.44	0.04	-0.73	0.06	-0.97	0.10	-1.62	0.20	0.05	0.10	0.05	0.08	0.00	0.05	-0.17	0.15
RHg-b-2	184.3	-0.24	0.08	-0.51	0.04	-0.73	0.06	-1.07	0.10	-1.69	0.20	0.03	0.10	0.03	0.08	0.08	0.05	-0.09	0.15
RHg-a-3	174.8	-0.20	0.08	-0.43	0.04	-0.55	0.06	-0.82	0.10	-1.23	0.20	0.01	0.10	-0.02	0.08	0.06	0.05	-0.02	0.15
RHg-b-3	201.5	-0.25	0.08	-0.45	0.04	-0.60	0.06	-0.91	0.10	-1.35	0.20	-0.02	0.10	0.01	0.08	0.08	0.05	0.00	0.15
RHg-a-4	209.6	-0.24	0.03	-0.58	0.03	-0.83	0.06	-1.19	0.13	-1.94	0.20	0.06	0.05	0.02	0.06	0.06	0.06	-0.16	0.15
RHg-b-4	228.0	-0.25	0.03	-0.55	0.03	-0.76	0.06	-1.16	0.13	-1.58	0.20	0.04	0.05	0.03	0.06	0.12	0.06	0.15	0.15
RHg-a-5	265.3	-0.17	0.06	-0.40	0.02	-0.56	0.06	-0.80	0.10	-1.23	0.20	0.03	0.05	0.01	0.06	0.04	0.06	-0.03	0.19
RHg-b-5	241.6	-0.20	0.06	-0.43	0.02	-0.64	0.06	-0.88	0.10	-1.32	0.20	0.03	0.05	0.02	0.06	0.02	0.06	0.00	0.19
RHg-a-6	211.3	-0.06	0.05	-0.34	0.02	-0.56	0.06	-0.69	0.10	-1.20	0.20	0.11	0.05	0.01	0.06	-0.04	0.06	-0.17	0.19
RHg-b-6	213.7	-0.02	0.05	-0.31	0.02	-0.51	0.06	-0.64	0.10	-1.14	0.27	0.14	0.05	0.01	0.06	-0.03	0.06	-0.18	0.15

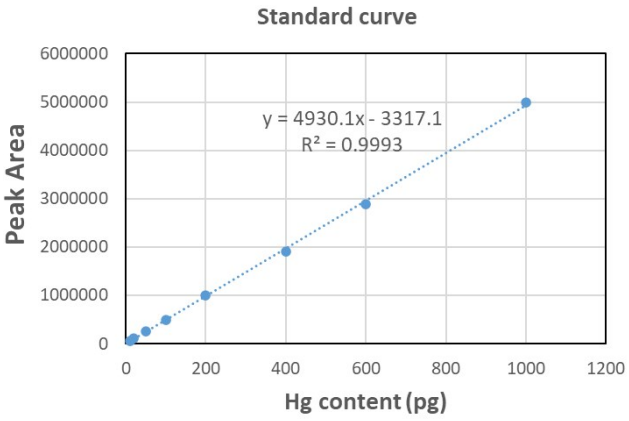
Table S4 Concentrations and isotopic compositions of dissolve mercury (DHg) in HFL.

Sample ID	Hg concentration	δ^{199}Hg	2sd	δ^{200}Hg	2sd	δ^{201}Hg	2sd	δ^{202}Hg	2sd	δ^{204}Hg	2sd	Δ^{199}Hg	2sd	Δ^{200}Hg	2sd	Δ^{201}Hg	2sd	Δ^{204}Hg	2sd
	ng L^{-1}	(‰)		(‰)		(‰)		(‰)		(‰)		(‰)		(‰)		(‰)		(‰)	
DHg-1	1.15	-0.13	0.05	-0.49	0.08	-0.71	0.05	-1.06	0.10	-1.67	0.29	0.14	0.05	0.04	0.06	0.09	0.05	-0.09	0.19
DHg-2	1.23	-0.15	0.05	-0.31	0.08	-0.67	0.05	-0.91	0.10	-1.46	0.14	0.08	0.05	0.14	0.06	0.01	0.05	-0.10	0.15
DHg-3	2.15	0.00	0.05	-0.38	0.08	-0.40	0.11	-0.79	0.10	-1.38	0.27	0.20	0.05	0.02	0.06	0.19	0.05	-0.19	0.11
DHg-4	1.58	-0.03	0.05	-0.45	0.08	-0.58	0.10	-0.90	0.10	-1.36	0.14	0.20	0.05	0.00	0.06	0.09	0.05	-0.02	0.11

Text S1 Instrumental conditions of CVAFS and CV-MC-ICP-MS

Hg concentrations in the acid-trapping solutions were measured by the Cold Vapor Atomic Fluorescence Spectrometry (CVAFS).[1] The detection limit of CVAFS for Hg has been determined to be 0.2 ng L^{-1}. Before the analysis of Hg, reagent materials and containers were carefully cleaned to eliminate possible contaminations.[1] Hg concentrations were calculated on basis of the standard curve determined by reducing a known amount of 3133 Hg standard (10-1000pg) with $SnCl_2$ solution (**Figure S1**). The samples were reduced with stannous chloride ($SnCl_2$) to convert Hg(Ⅱ) to gas Hg(0), which was then separated from the bubbler by purging with argon gas and collected onto a gold trap. Hg mass on gold trap was thermally desorbed and subsequently detected by CVAFS.[1]

Figure S1 Standard curve of the CVAFS, Tekran 2500



Prior to CV-MC-ICP-MS analysis, analytical grade acid (i.e., HNO_3, HCl), Mill-Q water and high-purity argon were prepared. Hg in trapping solutions were diluted to the concentration matching that of the NIST 3133 Hg standards bracketing solution (differences less than 10%).[2] To minimize risks of the cross-contamination between the samples and Hg standard, a 10% HNO_3 (V/V) blank solution was used to rinse the cold vapor generation system to eliminate memory efforts. The Hg standard (NIST SRM 3133) and thallium standard solutions (SRM 997) were diluted to concentrations of 1.0 ng Hg mL^{-1} and 20 ng Tl mL^{-1}, respectively, using 10% HCl (V/V) and 10% (V/V) HNO_3. Instrumental mass bias was corrected using certified Tl isotope standard introduced as aerosol and strict standard-sample-standard bracketing with 3133 Hg standard solution. Besides, acquisition parameters should be optimized to get the best internal precision on all Hg ratios (**Table S5**).[3-5]

Table S5 Instrumental operating conditions and parameters of CV-MC-ICP-MS

Plasma parameters	
Nebulizer gas	27.0 - 34.0 mL min^{-1}
Mix gas	0.07 - 0.13 mL min^{-1}
RF Power	1300 W
Apex system：Heater temperature	100℃
Apex system：Chiller temperature	2 ℃

cold vapor generation system: Solution uptake rate	0.75 ml min^{-1}
Sensitivity for ^{202}Hg	1.2-1.4 V (ng mL^{-1})

Reference:

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