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Supplement of

New evidence for atmospheric mercury transformations in the marine boundary layer from stable mercury isotopes

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Text S1. Details information of sampling and breakthrough experiments

TGM and total suspended particle (TSP) collection system was installed on the top deck of vessel, ~10 m upstream of the exhaust outlet of vessel's engine. All collection systems were turn off at 5 min before vessel stop for station work in cruises, and turn on at 5min after vessel sailing to minimize the influences of funnel emissions.

The TGM collection system was composed by a PFA filter holder (fixed with 90 mm quartz fiber membrane, Savillex, USA), chloride active carbon (CIC) trap, mass flow rate meter (MF5700, Siargo Ltd., China), and vacuum pump (2562C-50, Welch[®], USA). All components were connected with PFA tube (1/4" OD). The flow rate was maintained at ~ 10 L min⁻¹ during sampling.

TSP samples were collected using atmospheric particulate sampler (Model 2031, Laoying Instrument, China) for 12 h with quartz fiber filter (Grade QM-A, 8 × 10 inch, Whatman[®]). The flow rate was maintained at ~ 1 m³ min⁻¹ during sampling.

After each sampling, the CIC trap was sealed and stored in a polyethylene bag, and the filter was folded in half, sandwiched between aluminum foil, and sealed in polyethylene bags. All of the samples were then frozen until the pre-concentration step.

Breakthrough experiments were conducted in lab of Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, in Beijing, China to evaluate the performance of TGM collection system. Two CIC trap tubes were connected in series and then installed in TGM sampling system. The flow rate was maintained in 10 L min⁻¹ and the sampling last for 24h. The collected samples were treated using the same methods as field samples. The concentration of THg in blank CIC trap was ~0.4 ng g⁻¹. ~0.5 g CIC was loaded in each trap. The breakthrough was measured as 5.68±1.94% (1σ, n = 4). The results were showed in Table S2.

Text S2. Details on pre-concentration

Double-stage tube furnace with acid-trapping systems were installed in lab of Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, in Beijing, China, following publications.(Sun et al., 2013) CIC extracted from trap tube or one of paralleling sampled quartz fiber filter was individually installed in the upstream tube furnace, which was programmed to heat the samples from room temperature to 1000°C within 3.5h and maintained for 0.5h. The downstream tube furnace was programmed to maintain the temperature at 1000°C during sample processing. 5 mL 40% (v/v, HNO₃/HCl = 2/1) acid-trapping solution was installed in bubbler connected at the vent of the furnace to capture the released Hg. The Hg concentrations in the trapping solutions were then measured by cold vapor atomic fluorescence spectrometry (MERX, Brooks Rand Instruments, USA) following USEPA Method 1631.

In this study, the trapping solution with Hg concentration < 2.0 ng mL⁻¹ were grouped based on daytime and nighttime sampling. In each group, trapping solution were added into 1 bubbler and 1 mL 30% (m/m) SnCl₂ solution were added to reduce the contained Hg(II) into Hg⁰. The mixed solution were subsequently bubbled for 20 min. Same acid trapping solution used in pre-concentration stage was installed at the outlet of bubbler to collect the exhausted Hg⁰. NIST SRM 3133 was used to calculate the recoveries of this treatment.

Text S3. Back-trajectory analysis

72 h Back-trajectory analysis with time resolution of 3 h was performed using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4) Model (Rolph et al., 2017; Stein et al., 2015). The 3-hourly archived meteorological data was obtained from National Centers for Environmental Prediction's Global Data Assimilation System (GDAS-0.5 degree). During data processing, the arriving heights of air masses were settled to 100 m above sea level. The top of model was settled to 10000 m above sea level. 3 h intervals back-trajectories were calculated with starting locations extracted from the track line of the vessel. Arbitrary grid ($0.5^{\circ} \times 0.5^{\circ}$) over the domain of calculated trajectories was created and the number of trajectories that intersect each grid cell were counted and divided by the total number of trajectories, as the trajectory frequencies. The grid data was then processed using ArcGIS 10.1 and the trajectory frequencies (%) was illustrated following the Kriging geostatistical method. For each cruise, calculated trajectories associated with higher $\Delta^{199}\text{Hg}$ values (higher than averaged value) or lower $\Delta^{199}\text{Hg}$ values (lower than averaged value) were illustrated into trajectory frequencies plots (Fig. S1).

Figure S1. Trajectory Frequency in three cruises, based on trajectories associated with higher $\Delta^{199}\text{Hg}$ values (higher than averaged value) or lower $\Delta^{199}\text{Hg}$ values (lower than averaged value). a. 2016-summer with high $\Delta^{199}\text{Hg}$ values, b. 2016-summer with low $\Delta^{199}\text{Hg}$ values, c. 2016-winter with high $\Delta^{199}\text{Hg}$ values, d. 2016-winter with low $\Delta^{199}\text{Hg}$ values, e. 2018-summer with high $\Delta^{199}\text{Hg}$ values, f. 2018-summer with low $\Delta^{199}\text{Hg}$ values.

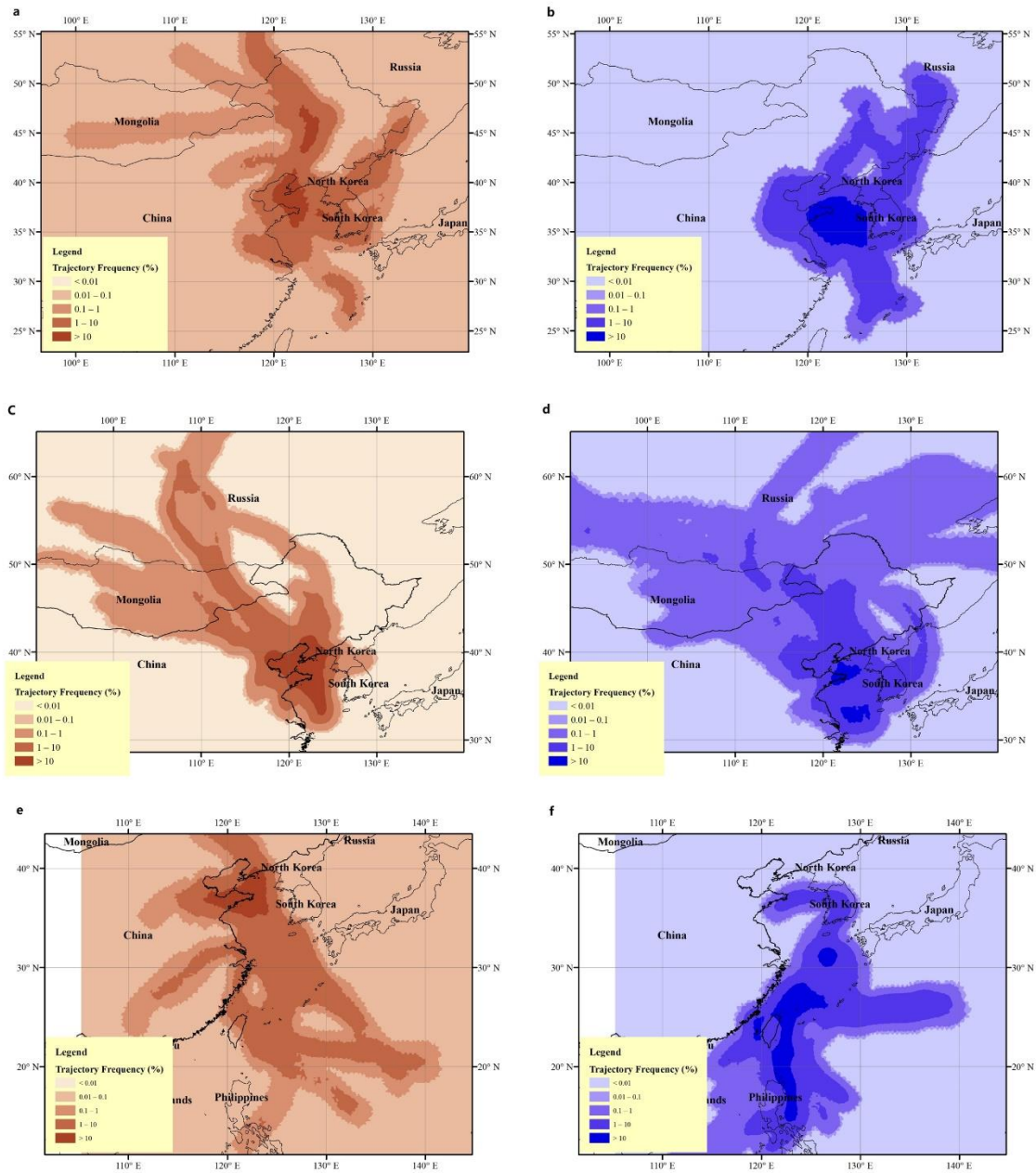


Table S1. Isotopic compositions and THg concentrations in TGM and PBM.

Sample	Speciation	Season	Year	TGM/PBM concentrations in ambient air ng (pg) m ⁻³ *	Sampling Duration**	$\delta^{202}\text{Hg}$ ‰	2 σ	$\Delta^{199}\text{Hg}$ ‰	2 σ	$\Delta^{200}\text{Hg}$ ‰	2 σ	$\Delta^{201}\text{Hg}$ ‰	2 σ
GS16w-1	TGM	winter	2017	1.04	1/10 20:00 - 1/11 20:00	-0.34	0.11	-0.15	0.07	-0.02	0.06	-0.18	0.08
GS16w-2	TGM	winter	2017	1.78	1/11 20:00 - 1/12 20:00	-0.40	0.11	-0.10	0.07	-0.02	0.06	-0.10	0.08
GS16w-3	TGM	winter	2017	1.16	1/12 20:00 - 1/13 20:00	0.59	0.11	-0.13	0.07	-0.01	0.06	-0.15	0.08
GS16w-4	TGM	winter	2017	2.01	1/4 20:00 - 1/6 20:00	0.48	0.11	-0.18	0.07	-0.06	0.06	-0.17	0.08
GS16w-5	TGM	winter	2017	1.72	1/6 20:00 - 1/7 20:00	0.33	0.11	-0.15	0.07	-0.06	0.06	-0.11	0.08
GS16w-6	TGM	winter	2017	2.14	1/7 20:00 - 1/8 20:00	0.42	0.11	-0.10	0.07	-0.04	0.06	-0.06	0.08
GS16w-7	TGM	winter	2017	1.65	1/8 20:00 - 1/9 20:00	-0.03	0.11	-0.17	0.07	-0.05	0.06	-0.18	0.08
GS16w-8	TGM	winter	2017	1.28	1/13 20:00 - 1/14 20:00	0.33	0.11	-0.12	0.07	-0.03	0.06	-0.13	0.08
GS16w-9	TGM	winter	2017	1.35	1/14 20:00 - 1/15 20:00	0.38	0.11	-0.18	0.07	-0.03	0.06	-0.15	0.08
GS16w-10	TGM	winter	2016	2.13	12/29 20:00 - 12/30 20:00	0.17	0.11	-0.12	0.07	-0.04	0.06	-0.07	0.08
GS16w-11	TGM	winter	2016	2.26	12/31 20:00 - 1/1 20:00	0.19	0.11	-0.14	0.07	-0.04	0.06	-0.11	0.08
GS16w-12	TGM	winter	2017	1.57	1/1 20:00 - 1/2 20:00	0.43	0.14	-0.17	0.07	-0.02	0.06	-0.14	0.08

GS16w-13	TGM	winter	2017	2.83	1/2 20:00 - 1/3 20:00	0.06	0.11	-0.07	0.07	-0.01	0.06	-0.09	0.08
GS16w-14	TGM	winter	2017	2.39	1/3 20:00 - 1/4 20:00	-0.01	0.11	-0.05	0.07	0.00	0.06	-0.07	0.08
GS16s-1	TGM	summer	2016	1.95	07/11 04:00 - 07/11 20:00 07/12 04:00 - 07/12 20:00	-0.52	0.11	-0.04	0.09	-0.07	0.06	-0.07	0.08
GS16s-2	TGM	summer	2016	1.10	07/17 20:00 - 07/18 04:00 07/18 20:00 - 07/19 04:00 07/19 20:00 - 07/20 04:00	-1.42	0.11	-0.02	0.07	-0.05	0.06	-0.02	0.08
GS16s-3	TGM	summer	2016	1.32	07/09 04:00 - 07/09 20:00 07/10 04:00 - 07/10 20:00	-1.15	0.11	-0.08	0.07	-0.06	0.06	-0.09	0.08
GS16s-4	TGM	summer	2016	1.04	07/17 04:00 - 07/17 20:00 07/18 04:00 - 07/18 20:00	-2.30	0.11	0.06	0.07	0.06	0.06	0.03	0.08
GS16s-5	TGM	summer	2016	1.09	07/13 08:00 - 07/14 09:00	-1.91	0.11	0.05	0.07	-0.01	0.06	-0.01	0.08
GS16s-6	TGM	summer	2016	1.49	07/14 09:00 - 07/15 08:00	-1.65	0.11	0.10	0.07	-0.01	0.06	0.04	0.08
GS16s-7	TGM	summer	2016	0.92	07/15 08:00 - 07/16 08:00	-1.86	0.14	0.01	0.07	-0.05	0.06	-0.04	0.08

GS16s-8	TGM	summer	2016	1.49	07/19 04:00 - 07/19 20:00 07/20 04:00 - 07/20 16:00	-0.87	0.11	0.03	0.09	-0.01	0.06	-0.03	0.08
GS16s-9	TGM	summer	2016	1.36	07/07 20:00 - 07/08 20:00	-1.61	0.11	-0.01	0.09	-0.02	0.06	-0.02	0.08
GS18s-1	TGM	summer	2018	2.34	06/29 08:00 - 06/29 20:00	-0.47	0.11	-0.07	0.07	-0.05	0.06	-0.11	0.08
GS18s-2	TGM	summer	2018	2.79	06/28 08:00 - 06/28 20:00	-0.16	0.11	-0.09	0.07	-0.03	0.06	-0.10	0.08
GS18s-3	TGM	summer	2018	1.34	07/08 08:00 - 07/08 20:00	-0.16	0.11	-0.17	0.07	-0.07	0.06	-0.16	0.08
GS18s-4	TGM	summer	2018	1.63	06/30 08:00 - 06/30 20:00	-0.58	0.11	-0.02	0.07	0.00	0.06	-0.04	0.08
GS18s-5	TGM	summer	2018	1.10	07/01 08:00 - 07/01 20:00	0.38	0.11	-0.15	0.07	-0.01	0.06	-0.12	0.08
GS18s-6	TGM	summer	2018	0.99	07/07 08:00 - 07/07 20:00	0.90	0.11	-0.19	0.09	-0.04	0.06	-0.20	0.08
GS18s-7	TGM	summer	2018	1.35	07/14 08:00 - 07/14 20:00	0.21	0.11	-0.13	0.09	-0.08	0.12	-0.17	0.08
GS18s-8	TGM	summer	2018	1.32	07/05 08:00 - 07/05 20:00	-0.35	0.11	-0.16	0.07	-0.07	0.06	-0.17	0.08
GS18s-9	TGM	summer	2018	2.43	06/29 20:00 - 06/30 08:00	0.13	0.11	-0.08	0.07	-0.02	0.06	-0.09	0.08
GS18s-10	TGM	summer	2018	1.54	07/08 20:00 - 07/09 08:00	-0.23	0.11	-0.20	0.07	-0.06	0.06	-0.21	0.08
GS18s-11	TGM	summer	2018	2.06	07/13 20:00 - 07/14 08:00	-0.07	0.11	-0.18	0.07	-0.08	0.06	-0.14	0.08
GS18s-12	TGM	summer	2018	2.82	06/27 20:00 - 06/28 08:00	-0.59	0.13	-0.08	0.07	-0.02	0.06	-0.10	0.08

GS18s-13	TGM	summer	2018	0.89	07/07 20:00 - 07/08 08:00	0.22	0.16	-0.24	0.07	-0.13	0.06	-0.22	0.08
GS18s-14	TGM	summer	2018	1.92	07/05 20:00 - 07/06 08:00	-0.03	0.11	-0.14	0.07	-0.05	0.09	-0.05	0.08
GS18s-15	TGM	summer	2018	0.86	07/12 20:00 - 07/13 08:00	-1.34	0.11	-0.09	0.07	-0.14	0.06	-0.13	0.08
GS18s-16	TGM	summer	2018	1.77	07/01 20:00 - 07/02 08:00	0.22	0.11	-0.13	0.07	-0.04	0.06	-0.17	0.09
GS18s-17	TGM	summer	2018	2.57	06/28 20:00 - 06/29 08:00	-0.04	0.11	-0.04	0.12	0.00	0.07	-0.06	0.08
GS18s-18	TGM	summer	2018	1.55	07/06 20:00 - 07/07 08:00	0.26	0.11	-0.14	0.07	-0.02	0.06	-0.15	0.08
PS18s-1	PBM	summer	2018	45.88	06/27 20:00 - 06 28 08:00	-0.93	0.13	0.28	0.07	0.03	0.06	0.03	0.08
PS18s-2	PBM	summer	2018	52.26	07/07 08:00 - 07/07 20:00	-1.11	0.11	0.06	0.07	0.02	0.06	-0.02	0.08
PS18s-3	PBM	summer	2018	3.60	06/28 08:00 - 06/28 20:00 06/29 08:00 - 06/29 20:00 06/30 08:00 - 06/30 20:00	-1.73	0.11	0.64	0.11	0.07	0.06	0.20	0.08
PS18s-4	PBM	summer	2018	1.96	06/28 20:00 - 06/29 08:00 06/29 20:00 - 06/30 08:00 06/30 20:00 - 07/01 08:00	-1.42	0.11	0.45	0.07	-0.04	0.06	0.28	0.08

PS18s-5	PBM	summer	2018	3.76	07/01 08:00 - 07/01 20:00 07/04 08:00 - 07/04 20:00 07/05 08:00 - 07/05 20:00	-0.23	0.11	0.29	0.12	0.00	0.06	0.08	0.09
PS18s-6	PBM	summer	2018	7.82	07/01 20:00 - 07/02 08:00 07/03 20:00 - 07/04 08:00 07/04 20:00 - 07/05 08:00	-0.07	0.14	0.49	0.09	0.01	0.09	0.07	0.12
PS18s-7	PBM	summer	2018	5.69	07/05 20:00 - 07/06 08:00 07/06 20:00 - 07/07 08:00 07/07 20:00 - 07/08 08:00	-0.57	0.20	0.70	0.07	0.02	0.07	0.12	0.08
PS18s-8	PBM	summer	2018	2.67	07/08 08:00 - 07/08 20:00 07/13 08:00 - 07/13 20:00 07/14 08:00 - 07/14 20:00	-0.97	0.11	0.22	0.07	0.00	0.07	0.01	0.08
PS18s-9	PBM	summer	2018	5.39	07/12 20:00 - 07/13 08:00 07/13 20:00 - 07/14 08:00 07/14 20:00 - 07/15 08:00	-0.18	0.20	0.49	0.09	0.01	0.06	0.07	0.08

*: The concentrations were calculated by measured THg concentrations in trapping solution and measured air volume during sampling. The TGM concentrations were reported in unit of ng m^{-3} , and PBM concentrations were reported in unit of pg m^{-3} .

** : Sampling duration with multiple periods were caused by merging samples.

*** : The mean for sample categories are reported in mean and 1σ other than 2σ in this table. And the isotopic compositions are reported in mean and 2σ .

Table S2. QA/QC data during sampling and measurements.

Second Referenced Standards isotopic measurements									
Standard	$\delta^{202}\text{Hg}$ ‰	2σ	$\Delta^{199}\text{Hg}$ ‰	2σ	$\Delta^{200}\text{Hg}$ ‰	2σ	$\Delta^{201}\text{Hg}$ ‰	2σ	n
BCR 482 (1ppb)	-1.68	0.11	-0.59	0.06	0.04	0.06	-0.60	0.03	4
NIST 3177 (1ppb)	-0.51	0.06	0.01	0.07	0.01	0.04	0.02	0.08	18
Thermal Decomposition Recoveries									
Standard	Measured Concentrations ng g⁻¹		σ	Referenced Concentrations ng g⁻¹		Recoveries %	σ	n	
BCR482	475.86		7.07	480		99.14	1.47	4	
Breakthrough Measurements									
THg in upstream CIC trap ng		σ	THg in downstream CIC trap ng		σ	Breakthrough %	σ	n	
13.27		1.56	0.74		0.22	5.68	1.94	4	
Method Blank									
CIC blank ng g⁻¹	σ	n		Acid-trapping solution blank pg			n		
0.41	0.06	3		< 10 pg			2		

Table S3. The averaged meteorological data during sampling, percentage of Hg(II) in PBM, and the speciated Br concentrations on PM.

SAMPLE	Temp °C	Press hPa	RH %	The percentage of Hg(II) in PBM* %	Br ⁻ on PM* ng m ⁻³	Organic Br on PM* ng m ⁻³	Soluable Br on PM* ng m ⁻³
GS16w-1	2.70	1022.26	54.71				
GS16w-2	0.22	1017.44	59.50				
GS16w-3	1.63	1016.95	55.93				
GS16w-4	7.03	1022.56	65.83				
GS16w-5	7.96	1017.83	78.96				
GS16w-6	5.13	1013.24	77.84				
GS16w-7	1.51	1016.50	60.09				
GS16w-8	-0.42	1024.54	54.53				
GS16w-9	-1.41	1029.99	52.02				
GS16w-10	4.63	1029.33	56.08				
GS16w-11	9.23	1023.00	73.14				
GS16w-12	11.97	1019.17	82.59				
GS16w-13	10.76	1021.48	74.48				
GS16w-14	9.74	1020.21	72.13				
GS16s-1	24.61	997.10	89.33				
GS16s-2	23.39	1004.61	90.64				
GS16s-3	23.98	1002.14	88.68				
GS16s-4	23.36	1004.16	86.83				
GS16s-5	24.64	1000.52	83.90				
GS16s-6	24.72	999.93	86.52				
GS16s-7	22.54	996.40	88.15				
GS16s-8	24.43	1002.82	91.12				
GS16s-9	23.60	1006.62	91.25				
GS18s-1	19.64	998.88	99.85		2.54	2.78	5.31
GS18s-2	20.05	994.87	99.78		2.72	1.38	4.10
GS18s-3	28.37	1002.71	92.05		1.93	1.58	3.51
GS18s-4	23.09	1002.81	100.30		4.91	2.22	7.13
GS18s-5	22.30	1001.21	92.47		2.09	1.28	3.36
GS18s-6	28.20	1000.18	67.13		4.83	1.95	6.78
GS18s-7	27.26	1005.17	90.39		1.49	1.11	2.61
GS18s-8	25.91	995.95	95.22		0.14	1.24	1.38
GS18s-9	22.38	1002.27	98.57		1.53	1.49	3.02
GS18s-10	28.02	1003.53	93.54		2.84	1.68	4.53
GS18s-11	26.90	1005.41	94.62		6.50	1.03	7.53
GS18s-12	20.26	994.68	98.33		6.51	3.27	9.78
GS18s-13	28.05	1001.89	99.88		0.00	1.91	1.91
GS18s-14	24.62	997.92	74.54		0.75	1.06	1.80
GS18s-15	27.02	1002.53	97.74		1.49	1.35	2.84
GS18s-16	22.17	1001.79	95.77		2.19	1.74	3.94
GS18s-17	17.69	996.67	100.30		0.64	0.36	1.01
GS18s-18	27.06	998.38	53.28		6.69	3.57	10.26

PS18s-1	20.26	994.68	98.33	70.90	6.51	3.27	9.78
PS18s-2	28.20	1000.18	67.13	71.87	4.83	1.95	6.78
PS18s-3	20.93	998.85	99.98	83.98	3.42	2.13	5.55
PS18s-4	20.63	1000.63	99.56	93.87	44.26	1.43	45.69
PS18s-5	24.57	997.80	83.95	86.31	0.91	1.47	2.38
PS18s-6	23.73	997.62	85.59	94.87	1.42	1.67	3.09
PS18s-7	26.70	999.68	66.35	57.02	1.87	2.00	3.87
PS18s-8	27.73	1003.74	92.17	82.97	11.70	1.64	13.34
PS18s-9	27.03	1004.69	94.15	66.00	3.50	1.31	4.81

*: results were calculated based on merged samples with multiple sampling durations.

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