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Observation and analysis of speciated atmospheric mercury in Shangri-La, Tibetan Plateau, China

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Table S1: The post hoc test (e.g., Tukey's HSD) for the TGM concentrations of different seasons. "I" refers to the mean TGM value of the first column. "J" refers to the mean TGM value of the second column. The differences of mean TGM value between spring and autumn and between spring and winter were 0.63 and 0.48 ng/m^3, respectively. The differences were statistically significant under the significance level of 5%. The TGM level was highest in spring (2.76 ng m^{-3}) and peaked in late April (Fig. 2), high TGM levels were frequently associated with northerly winds that carried domestic emissions from West China to the site. Fig. 8 also shows the back trajectories during April 26 to May 2 (first block in Fig.7). The air masses originated from Siberia moved over north Xinjiang, east Qinghai, Gansu and west Sichuan provinces. These are industrial areas in Northwest China that have major Hg emission sources (Fig. 1), mainly from the use of fossil fuels.

(I) code	(J) code	Mean Difference (I-J)	Std. Error Difference	P value	95% Confidence Interval of the Difference	
					Lower	Upper
Spring	Summer	0.33	0.14	0.083	-0.03	0.69
Spring	Autumn	0.63	0.15	<0.001	0.25	1.00
Spring	Winter	0.48	0.14	0.004	0.12	0.84
Summer	Autumn	0.29	0.15	0.183	-0.08	0.67
Summer	Winter	0.15	0.14	0.723	-0.22	-0.51
Autumn	Winter	0.15	0.15	0.745	-0.23	0.53

The level of significance is 0.05.

Table S2: The post hoc test (e.g., Tukey's HSD) for the GOM concentrations of different seasons. "I" refers to the mean TGM value of the first column. "J" refers to the mean TGM value of the second column. The differences of mean GOM value between winter and spring, between winter and summer and between winter and autumn were 12.10, 11.21 and 7.60 pg/m^3, respectively. The differences were statistically significant under the significance level of 5%. The GOM concentrations were highest in winter (14.62 pg m^{-3}). In winter, the air mass arriving in Shangri-La was primarily carried by the Westerlies with relatively higher wind speed (mean = 2.34 m s^{-1} in winter). These air masses passed through several strong source regions in South and Southeast Asia, potentially transporting mercury to the SAWRS. Then the high GOM could be caused by local photochemical transformation under low RH (54.7%).

(I) code	(J) code	Mean Difference (I-J)	Std. Error Difference	P value	95% Confidence Interval of the Difference	
					Lower	Upper
Spring	Summer	-0.90	1.84	0.961	-5.80	4.00
Spring	Autumn	-4.51	1.91	0.100	-9.60	0.59
Spring	Winter	-12.10	1.78	<0.001	-16.87	-7.35
Summer	Autumn	-3.61	1.79	0.198	-8.38	1.17
Summer	Winter	-11.21	1.66	<0.001	-15.62	-6.79
Autumn	Winter	-7.60	1.73	<0.001	-12.23	-2.97

The level of significance is 0.05.

Table S3: The post hoc test (e.g., Tukey's HSD) for the PBM concentrations of different seasons. "I" refers to the mean TGM value of the first column. "J" refers to the mean TGM value of the second column. The differences of mean PBM value between autumn and summer and between autumn and winter were 31.33 and 38.93 pg/m^3, respectively. The differences were statistically significant under the significance level of 5%. The PBM concentrations were high in autumn, with a peak concentration of 57.63 pg m^{-3}. Shangri-La is a remote area far away from large point sources, but there are several counties and some villages in Shangri-La area, due to high elevation (3850 m above sea level), the weather was cold in autumn. During this period, the domestic biofuel burning became more frequent than in summer, contributing to a high PBM level in Shangri-La. The PBM level was low in winter, this could be related to the high wind speed. In winter, the air mass arriving in Shangri-La was primarily carried by the Westerlies with the highest wind speed (mean = 2.34 m s^{-1}). This was benefit for the diffusion of PBM and result in a low PBM level.

(I) code	(J) code	Mean Difference (I-J)	Std. Error Difference	P value	95% Confidence Interval of the Difference	
					Lower	Upper
Spring	Summer	8.27	6.74	0.769	-12.61	29.16
Spring	Autumn	-23.06	8.39	0.071	-47.56	1.44
Spring	Winter	15.88	7.05	0.203	-5.46	37.21
Summer	Autumn	-31.33	6.12	0.001	-49.84	-12.82
Summer	Winter	7.60	4.10	0.356	-4.03	19.24
Autumn	Winter	38.93	6.46	<0.001	19.83	58.04

The level of significance is 0.05.

Table S4: The independent samples test for the TGM concentrations associated with different clusters. The mean TGM concentrations were not statistically different between cluster 1 and 4, between cluster 2 and 4 and between cluster 3 and 4 at the 5% significance level. The mean TGM concentrations associated with clusters 1 and 2 and clusters 2 and 3 that are not significantly different. Cluster 4, although relatively infrequent (4%), was associated with the highest TGM concentrations (mean = 3.9 ng m^{-3}) due to the passing of air masses over known source regions in Sichuan province. The area has a high background TGM level caused by industrial and domestic coal combustion, smelting industries, cement production, and biomass burning. Air masses of cluster 3, the most frequent transport sector, also had high TGM concentrations (mean = 2.6 ng m^{-3}). Cluster 3 had the shortest trajectories that move across Southeast Asian regions where extensive biomass burning occurred during early spring. The height of trajectories was very low can transport mercury emitted from surface to SAWRS (Fig.11&12).

	t-test for Equality of means						
	t	df	P value (2-tialed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference	
						Lower	Upper
Cluster 1&2	-1.23	94	.222	-0.13	0.11	-0.34	0.08
Cluster 1&3	-1.92	174	.056	-0.22	0.11	-0.44	0.01
Cluster 1&4	-3.62	61	.001	-0.81	0.22	-1.26	-0.36
Cluster 2&3	-0.71	162	.479	-0.09	0.12	-0.33	0.15
Cluster 2&4	-3.17	49	.003	-0.68	0.21	-1.11	-0.25
Cluster 3&4	-2.25	129	.026	-0.59	0.26	-1.11	-0.07

The level of significance is 0.05.

Description of the denuder-based sampling and analysis unit

The measurement of GOM and PBM was achieved by a manual method. The procedure of sampling and analysis of the manual method is analogous to the Tekran speciation system using similar denuders (Fig. S1) to the Tekran system with KCl coating. The only difference was the manual operation.

For GOM analysis, the manual denuder-based sampling system is analogous to the one used in the Tekran speciation unit. As shown in Fig. S2, the denuder, the inlet and impactor was the similar to Tekran speciation unit, and the temperature conditioner can keep a 40-50 ^{0}C for denuder during the sampling period via the heating tape. And the flow meter and vacuum pump was connected to the outlet of denuder, therefore we could get the total volume of sample gas in the two-hours sampling period. Fig. S3 shows the installation of denuder-based sampling unit at the site. Fine particulate (<2.5 μm) mercury samples were collected onto the filters. The GOM and PBM were collected simultaneously during sampling cycle via the denuder-based sampling unit. TGM is continuously measured Tekran 2537 except when collected GOM/PGM are being measured. This procedure is similar to the sampling and measurement cycle as the Tekran speciation unit.

The 47-mm quartz filter used for PBM sampling was the Whatman Grade QM-H Quartz Filter (http://www.gelifesciences.com/webapp/wcs/stores/servlet/catalog/zh/GELifeSciences/products/AlternativeProductStructure_21531/28418567). It is constructed with fine quartz fibers with low heavy metal content. This filter can withstand a heating temperature up to 900 ℃. The other difference of the filter is that the filter of manual method is of 47-mm diameter compared to the 21-mm filter used in the Tekran system. Fine particulate (<2.5 μm) mercury samples were collected onto the filters. The glass inlet and impactor are indentical to the apparatus of Tekran speciation system. Our apparatus followed the setup of J. Munthe et al. (2001), Mary M. Lynam et al. (2002), Landis et al. (2002). Such a sampling procedure is similar to Tekran speciation system.

For mercury detection, microwave digestion was NOT carried out. Instead, thermal desorption followed by Tekran detection was utilized (Fig.S4). The layout in the monitoring station is also shown in Fig. S5. A denuder from URG Corporation was used for the GOM sampling (Fig. S6). A separate PBM quartz trap of similar connector was used for PBM sampling. The denuders and traps are heated in the furnace that fits the size of denuder. The end caps were the URG plastic caps (Fig. S5) and not heated during the analysis. Air-cooler was used for decreasing the temperature of caps. The detection of PBM signals was achieved using the Lindberg Blue clamshell furnace at 900 ^{0}C. During the heating, the Teflon holder was NOT heated. We recognize that Tekran uses quartz chip to prevent mercury deposition in the Regenerable Particulate Filter (RPF) Assembly in the 1135 unit. The Teflon line from the trap to the inlet of Tekran 2537A is short (~1 m, Fig. S4) and therefore mercury deposition in the Teflon line is negligible.

Fig. S1: Quartz denuder.

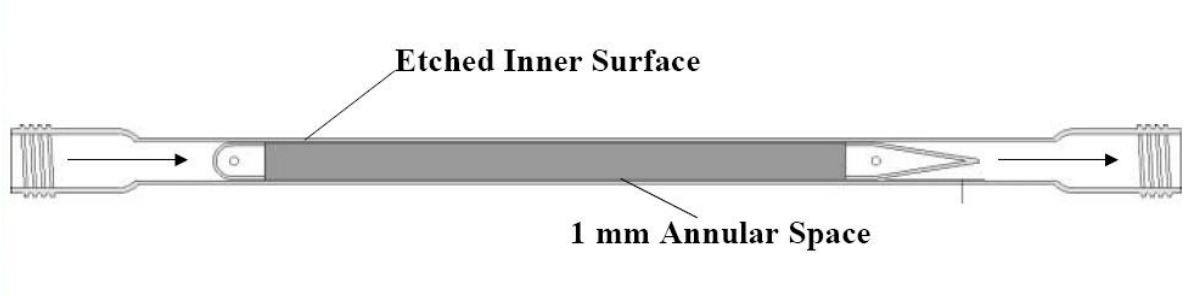

Fig. S2: The denuder-based sampling unit: the entire sampling train (left) and the detailed view of the denuder system (right).

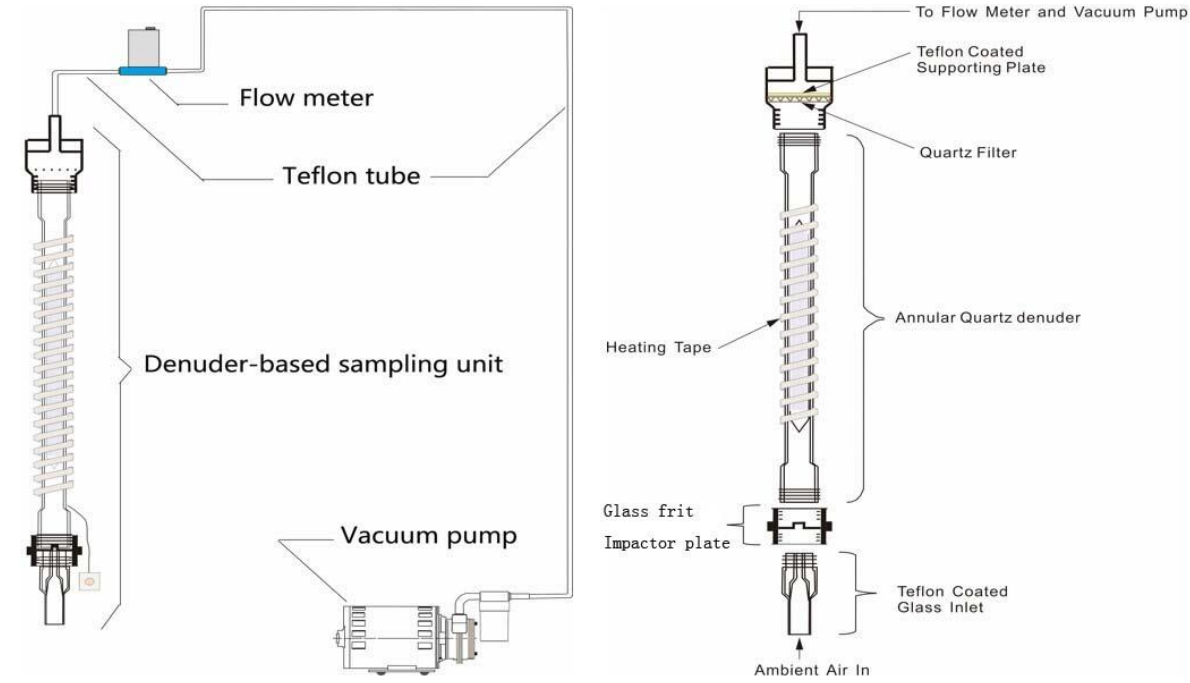

Fig.S3: The picture of denuder-based sampling unit.

Fig S4: The diagram of GOM and PBM analysis

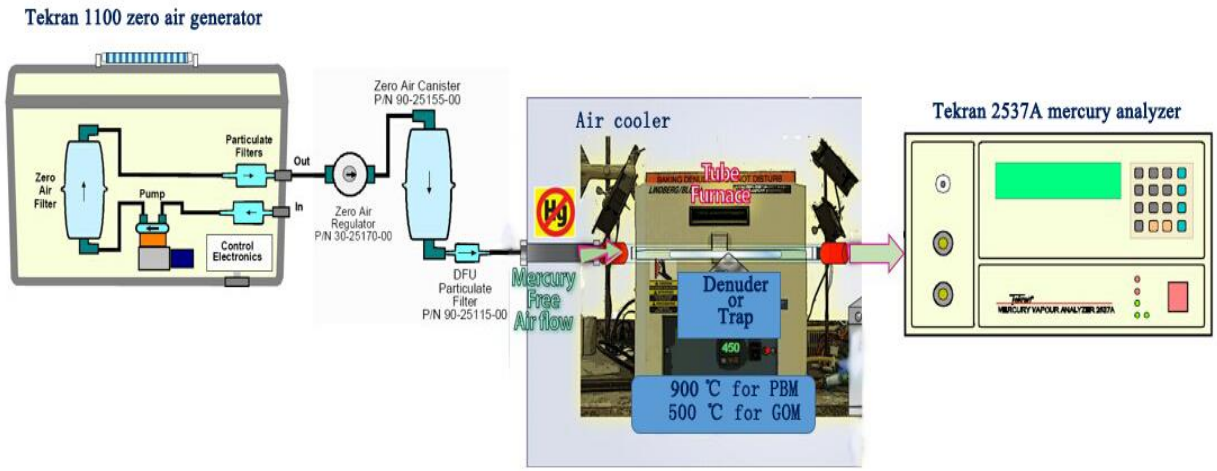

Fig S5: The diagram of analysis unit for measuring GOM and PBM.

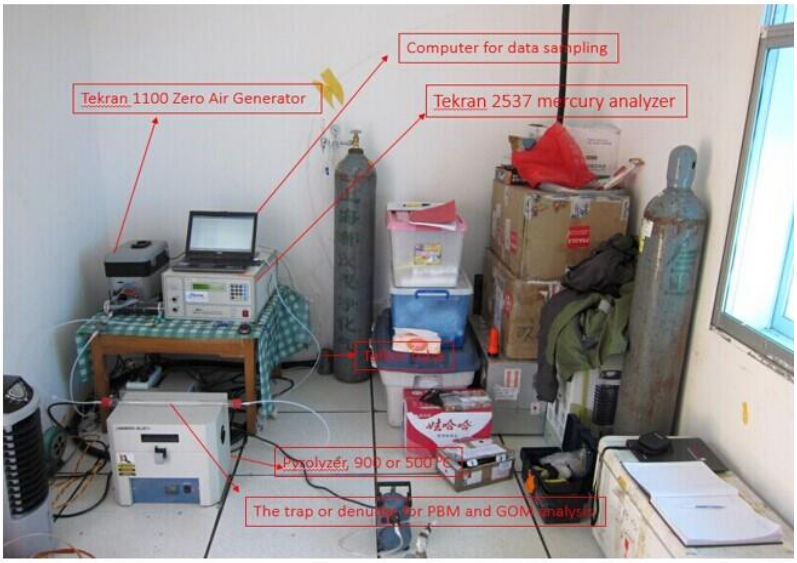

Fig. S6: The hollow quartz denuder from URG Corporation (middle).

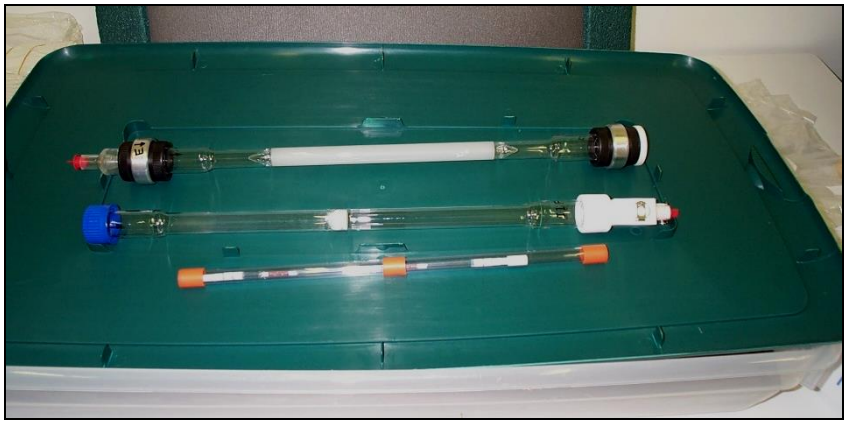

Fig S6: The synchronized locations of the back trajectory endpoints with the maps of MODIS fire hotspots. The high TGM concentrations (mean = 2.6 ng m^{-3}) associated with cluster 3 coincided with the fire hotspots. Therefore the most likely source region was Southeast Asia's biomass burning activities.