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Supplement of

Occurrence and spatial distribution of neutral perfluoroalkyl substances and cyclic volatile methylsiloxanes in the atmosphere of the Tibetan Plateau

Xiaoping Wang et al.

Correspondence to: Xiaoping Wang (wangxp@itpcas.ac.cn)

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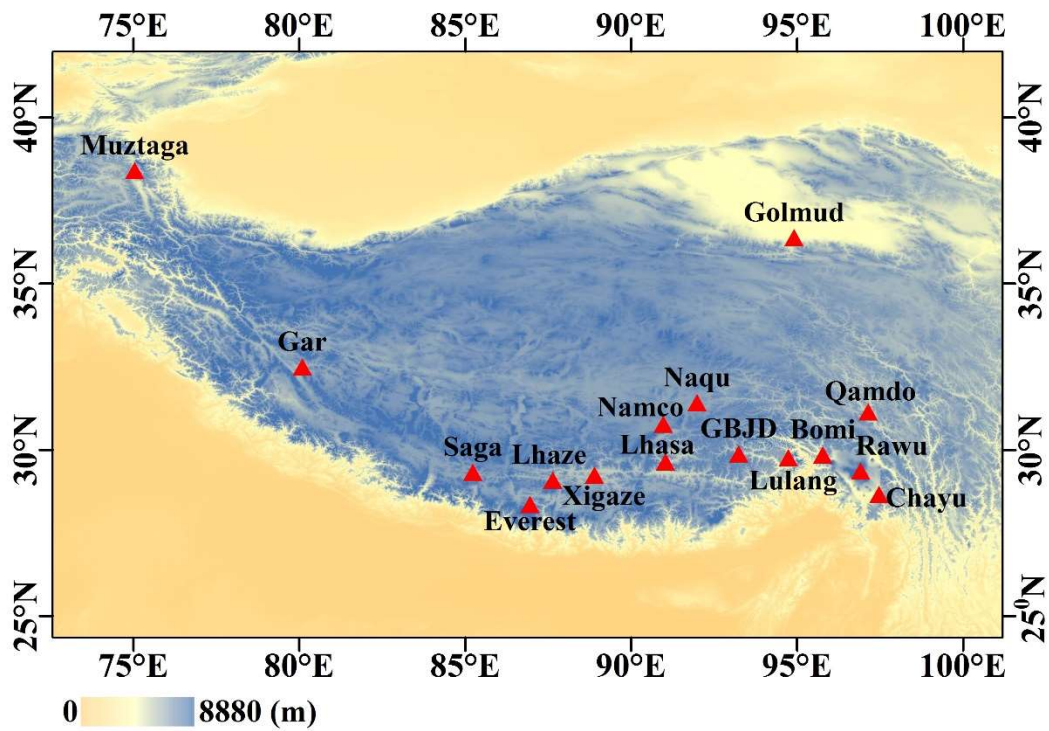


Figure S1. The passive air monitoring network comprising 16 sampling sites across the TP (Lhasa and Golmud are two booming cities, GBJD: Gongbujiangda)

Text SI 1 Details related to the depuration compounds (DCs)

DCs are some semi-volatile chemicals which are added to determine site-specific sampling rates. Before sampling, the PUF-disks were spiked with four depuration compounds (DCs, PCB-30, -54, -104, -188). This was achieved by adding 50ul of the DC mixture (each DC is 400pg/ul) to approximately 15ml of hexane and then evenly applying to both sides of the PUF disk using a pipette. DCs will experience volatilization losses if exposed to air. The amount of losses will depend on their volatility, exposure time, temperature and wind speed. Because the uptake of SOCs is air-side controlled, the rate of uptake of chemical will be the same as the rate of loss. Then, by measuring the losses of DCs in PUF disks, the site-specific air sampling rates can be obtained.

Table S1 Details about the recovery standard and internal standard	
Analyte	Supplier (purity)
Recovery standard	
5:1 FTOH	Matrix Scientific, Columbia, SC, USA, 99%
7:1 FTOH	Interchim, Montlucon Cedex, France, 97%
9:1 FTOH	Interchim, Montlucon Cedex, France, 97%
11:1 FTOH	Interchim, Montlucon Cedex, France, 97%
[M+4]6:2 FTOH	Wellington Laboratories Inc, 98%
[M+5]8:2 FTOH	DuPont
[M+4]10:2 FTOH	Wellington Laboratories Inc, 98%
[M+3]NMeFOSA	Wellington Laboratories Inc, 98%
[M+5]NEtFOSA	Wellington Laboratories Inc, 98%
[M+7]NMeFOSE	Wellington Laboratories Inc, 98%
[M+9]NEtFOSE	Wellington Laboratories Inc, 98%
Internal standard	
13:1 FTOH	Interchim, Montlucon Cedex, France, 97%
13 C HCB	Cambridge Isotope Laboratories, Inc, 99%

Text S2 Detailed analysis regarding GC program and MS detection ions

Thermo DSQ GC–MS was used for analysis of neutral PFASs. The GC temperature program is as follows: 50 °C (held 1 min), ramped at 3 °C/min to 70 °C, ramped at 10 °C/min to 130 °C, then ramped at 20 °C/min to 225 °C (held 11.4 min), and finally cooled at 80 °C/min to 50 °C (total run time 32 min). A constant injection temperature of 200 °C was used, with a 2 mL splitless injection. Helium was employed as a carrier gas at a constant flow of 1 mL/min. The GC–MS transfer line temperature was set at 250 °C. Mass spectral analysis was performed in PCI-selected ion monitoring (PCI–SIM) mode, using methane as the reagent gas for quantification of target analytes (a seven point calibration curve (20, 50, 100, 200, 500, 1000 and 2000 pg injected) was used).

Quantification of cVMS was performed on a Trace GC Ultra (Thermo Electron Corp.) coupled to a MD800 MS detector (Fisons Instruments SpA) using electron ionization (EI). The GC temperature program incorporated an initial temperature of 40 °C with a hold time of 3 min, increased by 25 °C min⁻¹ to 190 °C, followed by a second temperature ramp of 40 °C min⁻¹ to 240 °C and held for 4 min. The MS was operated in selected ion monitoring (SIM) mode. The following ions were monitored in SIM mode: recording ions *m/z* 281/282 for D4, 355/267 for D5, 341/429 for D6, 284/285 for 13C4–D4, 360/270 for 13C5–D5, and 345/435 for 13C6–D6, respectively.

Table SI2 Amount (pg/sample) of PFASs in field blanks													
	8:2 FTO	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	12:2 FTOH	6:2 FTA	8:2 FTA	NMeFBSA	NMeFOSA	NEtFOSA	NMeFOSE	NetFOSE
F1	55	187	85	58	133	23	23	17	26	65	321	45	56
F2	28	155	47	35	93	15	34	17	33	44	288	43	27
F3	79	143	93	44	77	37	53	27	28	37	293	34	48
F4	44	102	69	38	120	45	28	16	32	29	189	45	59
F5	27	89	84	45	135	22	15	5	43	34	210	26	54
F6	36	177	93	34	103	18	34	9	22	52	203	47	53
Ave	45	142	79	43	111	27	31	15	31	43	251	40	49
MDL	104	261	131	69	179	63	69	37	52	83	419	64	84

Table SI3 Amount (ng/sample) of cVMS in field blanks				
	D3	D4	D5	D6
F1	35	70	520	87
F2	29.9	39.7	437	55.8
F3	38.4	45.6	763	47.9
F4	27.9	33.8	553	58.6
F5	30.7	65.4	327	57.2
F6	45.5	88.7	378	47.7
Ave	34.5	57.2	380	59.0
MDL	52.5	115	681	98.6

Table S4 Air concentrations of FTO, FTOHs, FBSA, FOSAs, FBSE and FOSEs (pg m⁻³).												
Sampling sites	8:2 FTO	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	12:2 FTOH	NMeFBSA	NMeFOSA	NEtFOSA	NMeFBSE	NMeFOSE	NEtFOSE
Bomi	1.93	67.5	6.15	61	6.75	3.11	3.655	5.11	4.26	1.77	0.57	0.185
Rawu	1.27	72	8.6	83.5	11.4	4.86	2.78	6.35	3.44	3.38	0.81	0.13
Lunang	1.56	59.5	5.75	88	7.85	2.72	2.445	4.27	2.34	1.09	0.42	0.08
Qamdo	2.28	53.5	4.66	40	4.77	1.68	1.61	3.84	1.77	0.83	0.24	0.11
Chayu	1.21	93.5	18.55	85.5	15.65	9.25	7.8	7.75	5.12	0.92	0.38	0.085
Nam Co	1.61	37.5	2.26	32.5	2.29	1.23	1.385	1.79	0.88	0.27	0.14	0.22
GBJD	0.99	51	5.8	66.5	7.45	3.16	1.79	1.36	1.62	0.48	0.42	0.18
Lhasa	1.04	43.5	16.85	71	29.1	22.2	3.495	2.94	0.94	1.43	0.89	0.13
Lhaze	1.33	35	4.39	54	5.2	2.17	0.655	1.99	0.39	0.32	0.46	0.13
Xigaze	0.83	44.5	3.275	51	3.81	1.88	1.445	1.11	0.26	0.21	0.38	0.075
Mt. Everest	0.44	39.5	4.2	34	7.165	2.9	0.49	0.89	0.36	0.11	0.32	0.16
Saga	0.34	47.5	3.44	51	4.29	2.11	0.615	1.92	1.39	0.19	0.17	0.19
Golmud	1.11	37.5	8.3	69.5	10.1	3.7	0.99	1.22	0.98	0.245	0.335	0.08
Naqu	0.88	22.5	2.67	38	3.16	2.17	0.62	1.38	0.235	0.61	0.19	0.11
Gar	0.18	17.5	2.435	42.5	2.585	0.61	0.66	1.90	0.445	0.365	0.19	0.17
Muztagata	1.12	38.5	4.475	30	4.13	1.59	1.61	3.82	0.365	0.34	0.31	0.095

Table S5 Relationships between Log K_{OA} of individual VMSs and Log (K_{SIP-A})

Relationships between temperature and octanol-air partition coefficient (Log K_{OA}) of individual VMSs			Relationships between Log K_{OA} of individual VMSs and Log (K_{SIP-A})*
Log (K_{OA}) = $m / (T) + b$ *			Log (K_{SIP-A}) = -0.05 Log K_{OA} +6.51
	m	b	
D3	1958	-2.7	
D4	2583	-3.2	
D5	3056	-3.4	
D6	3648	-3.7	

Text S2. Sampling rates (R_s) estimation using DCs

By measuring the losses of DCs in PUF disks during each sampling period, the relationship described in eq 1 could be used to calculate the site-specific air sampling rates (R_s , Moeckel et al., 2009).

$$R = \frac{-\ln\left(\frac{C_{DC}}{C_{DC-stable}}\right) \cdot K_{PAS-A} \cdot \rho_{PAS} \cdot V}{t} \quad (1)$$

$$K_{PAS-A} = 10^{0.6366 \log K_{OA} - 3.1774} \quad (2)$$

Where, C_{DC} and $C_{DC-stable}$ are the concentrations of DC and DC-stable at the end of the deployment period, respectively (ng sample⁻¹). K_{PAS-A} is the chemical's PAS-air partition coefficient with units of m³ g⁻¹ and it can be calculated according to the regression (eq 2) given by Shoeib and Harner (2002), ρ_{PAS} is the PAS bulk density (21300 g m⁻³), V is the volume of the PAS (0.000207 m³), and t is the deployment period in days. PCB-188 (average recovery is 81%) was used as DC-stable for correcting the losses of DCs. Only DCs that have recoveries within the desired range of between 20% and 80% should be used to estimate uptake rates. In our study (see Table SI-7), two proper DCs were PCB-30 (55%) and PCB-54 (73%).

References:

Moeckel, C., Harner, T., Nizzetto, L., Strandberg, B., Lindroth, A., Jones, K.C., 2009.

Use of depuration compounds in passive air samplers: Results from active sampling-supported field deployment, potential uses, and recommendations. Environ. Sci. Technol. 43, 3227-3232.

Shoeib, M., Harner, T., 2002. Characterization and comparison of three passive air samplers for persistent organic pollutants. Environ. Sci. Technol. 36, 4142-4151.

Table S6. Summary of the recoveries of DCs (%) and calculated R_s values for different sampling site						
Sampling site	PCB-30	PCB-54	PCB-104	PCB-188	R_s (m^3/day)	k_A (m/day)
Bomi	61	42	10	98	4.8	125
Rawu	41	75	22	114	4.6	120
Lunang	55	78	20	99	4.4	114
Qamdo	50	85	21	107	3.9	101
Chayu	56	76	14	99	4.3	112
Nam Co	31	46	20	91	6.2	161
GBJD	70	78	19	85	3.8	99
Lhasa	40	68	8	80	4.5	117
Lhaze	60	60	24	119	4.3	112
Xigaze	60	70	16	88	4.2	109
Mt. Everest	28	32	7	93	6.1	159
Saga	32	46	27	107	5.7	148
Golmud	31	39	10	78	6.0	156
Gaerze	15	28	7	93	6.8	177
Gar	18	35	8	80	6.5	169
Muztagata	27	30	16	81	6.4	166

	D3	D4	D5	D6
Bomi	6.30	6.21	6.14	6.05
Rawu	6.28	6.19	6.12	6.02
Lulang	6.29	6.21	6.13	6.04
Qamdo	6.30	6.21	6.13	6.04
Chayu	6.30	6.22	6.14	6.06
NamCo	6.28	6.19	6.12	6.02
GBJD	6.29	6.21	6.13	6.04
Lhasa	6.30	6.21	6.14	6.05
Lhaze	6.30	6.21	6.13	6.04
Xigaze	6.29	6.21	6.13	6.04
Mt. Everest	6.29	6.20	6.13	6.04
Saga	6.29	6.21	6.13	6.04
Golmud	6.29	6.21	6.13	6.04
Naqu	6.28	6.21	6.12	6.02
Gar	6.29	6.21	6.12	6.03
Muztagata	6.28	6.19	6.11	6.01

	V_{air} (m³)				Average
	D3	D4	D5	D6	
Bomi	83	101	119	147	112
Rawu	82	101	120	149	113
Lulang	76	93	110	136	104
Qamdo	67	82	97	119	91
Chayu	73	89	105	129	99
NamCo	110	135	161	200	152
GBJD	66	80	96	118	90
Lhasa	77	95	112	138	105
Lhaze	74	91	108	133	101
Xigaze	72	89	105	129	99
Mt. Everest	106	130	155	191	145
Saga	98	120	142	175	134
Golmud	104	127	151	186	142
Naqu	120	148	176	218	166
Gar	114	140	167	206	157
Muztagata	115	141	169	211	159

Table S9 Air concentrations of D3, D4, D5 and D6 (ng m⁻³)				
Sampling sites	D3	D4	D5	D6
Bomi	44.4	37.8	74.0	1.2
Rawu	33.0	54.2	103.6	2.9
Lunang	17.8	43.5	48.1	1.0
Qamdo	43.1	53.5	145.6	1.3
Chayu	60.9	96.6	79.8	2.3
Nam Co	11.2	20.2	4.0	0.9
GBJD	71.1	59.5	130.0	1.7
Lhasa	44.8	54.6	464.6	1.3
Lhaze	12.7	42.7	80.8	2.8
Xigaze	42.3	34.3	36.9	0.4
Mt. Everest	39.5	27.8	6.6	0.2
Saga	8.2	15.8	11.7	1.3
Golmud	26.8	48.6	208.1	2.8
Naqu	4.8	11.2	5.1	1.6
Gar	3.4	13.5	9.5	2.9
Muztagata	2.3	6.1	9.1	0.9
average	29.1	38.8	88.6	1.6

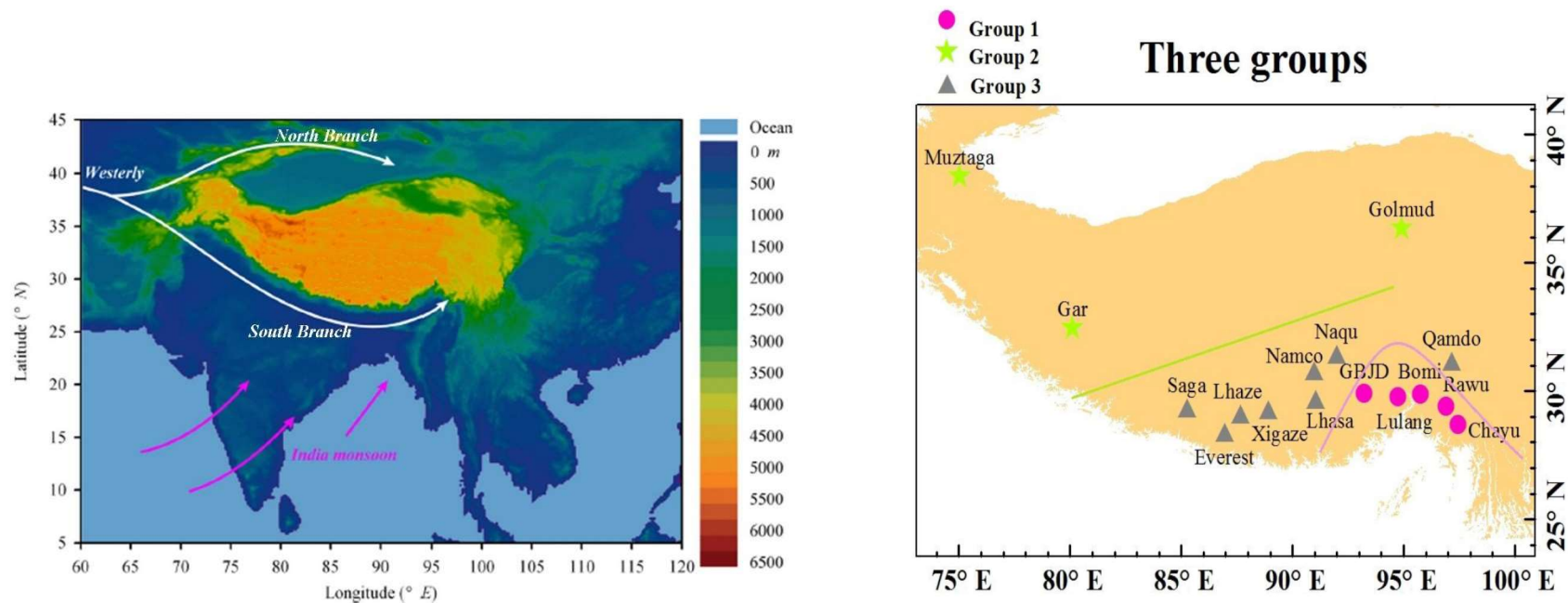


Figure S2 Schematic of the air circulation pattern over the Tibetan Plateau, group1: Monsoon region; group 2: Westerly region; group 3: transition region

Reference:

- Wang, X.; Ren, J.; Gong, P.; Wang, C.; Xue, Y.; Yao, T.; Lohmann, R. Spatial Distribution of the Persistent Organic Pollutants across the Tibetan Plateau and Its Linkage with the Climate Systems: Five Year Air Monitoring Study. *Atmospheric Chemistry and Physics* 2016, 16, 6901-6911.
- Wang, X.; Gong, P.; Yao, T., Jones, K.C. Passive air sampling of organochlorine pesticides, polychlorinated biphenyls, and polybrominated diphenyl ethers across the tibetan plateau. *Environ Sci Technol* 2010, 44, (8), 2988-93.

Table S10. P-values (one-way ANOVA) for significant variation in levels of different class of chemicals in different sites

Sampling site	8:2 FTO	Σ FTOH	Σ FOSA	Σ FOSE	Σ cVMS
Bomi	0.02	0.36	0.02	0.65	0.63
Rawu	0.04	0.02	0.01	0.39	0.01
Lunang	0.27	0.02	0.01	0.63	0.02
Qamdo	0.35	0.77	0.79	0.84	0.74
Chayu	0.29	0.03	0.02	0.74	0.01
Nam Co	0.37	0.45	0.86	0.38	0.56
GBJD	0.88	0.39	0.74	0.48	0.48
Lhasa	0.16	0.67	0.36	0.37	0.04
Lhaze	0.33	0.83	0.28	0.73	0.56
Xigaze	0.28	0.77	0.65	0.36	0.38
Mt. Everest	0.37	0.68	0.83	0.59	0.74
Saga	0.62	0.93	0.67	0.82	0.58
Golmud	0.44	0.87	0.37	0.39	0.03
Gaerze	0.56	0.68	0.55	0.58	0.52
Gar	0.87	0.05	0.47	0.44	0.46
Muztagata	0.43	0.03	0.74	0.76	0.48

Table S11 Ratios of 4:2/8:2 FTOH, 8:2/10:2 FTOH, 10:2/6:2FTOH in atmosphere of the TP			
ratio	4:2/8:2 FTOH	8:2/10:2 FTOH	10:2/6:2 FTOH
Monsoon region			
Bomi	1.1	9.03	1.09
Rawu	0.86	7.32	1.32
Lunang	0.67	11.2	1.36
Chayu	1.09	5.4	0.84
GBJD	0.76	8.9	1.28
Average		8.3	1.18
Transition region			
Qamdo	1.33	8.38	1.02
Nam Co	1.15	14.1	1.01
Lhaze	0.64	10.3	1.18
Xigaze	0.87	13.3	1.16
Mt. Everest	1.16	4.7	1.70
Saga	0.93	11.8	1.24
Naqu	0.59	12.0	1.18
Average		10.6	1.21
Westerly region			
Muztagata	1.28	7.26	0.92
Gar	0.41	10.4	1.06
Average		8.8	0.99
Cities			
Lhasa	0.61	2.43	1.72
Golmud	0.53	6.88	1.21

Table S12 Correlation (<i>r</i>) of individual VMS compounds among all the samples			
	D4	D5	D6
D3	0.69	0.79	0.38
D4		0.72	0.25
D5			0.13