ATMOSPHERIC NEW FLAME RETARDANTS IN LHASA CITY IN THE TIBETAN PLATEAU, CHINA

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Introduction

The Tibetan Plateau, known as "the Roof of the World" and "Third Pole on the Globe", is located on the eastern Eurasian continent and the north of Himalayas, covering approximately one-fourth of the land area of China. So the Tibetan Plateau is suggested to be an important indicator region to study the global long range atmospheric transport (LRAT) of persistent organic pollutants (POPs) [1]. Recently, much more attentions have been attracted for the study of POPs in the Tibetan Plateau for deeply understanding the LRAT and environmental fate of POPs [2]. Previous studies on POPs in the Tibetan Plateau focused on polybrominated diphenyl ethers, organochlorine pesticides, polycyclic aromatic hydrocarbons, and polychlorinated biphenyls [2-4]. And the influences of LRAT by the Indian Monsoon System and westerly winds on POPs in the Tibetan Plateau were deeply and clearly studied [3-4]. However, few studies were conducted on new contaminates in the Tibetan Plateau region, such as new flame retardants (NFRs). Recent studies clearly confirmed the wide occurrence of some NFRs in the Tibetan Plateau, such as 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), 2-ethyl-1-hexyl 2,3,4,5-tetrabromobenzoate (EHTBB) and bis(2-ethyl-1-hexyl)tetrabromophthalate (BEHTBP) in the atmosphere [5], and hexabromocyclododecanes (HBCDs) in the aquatic ecosystems [6].

The objective of this study was to comprehensively screen the occurrence of NFRs in the atmosphere in Lhasa, the most densely populated city in the Tibetan Plateau. Furthermore, this study aims to verify the influences of LRAT (air mass) on atmospheric NFRs in the Tibetan Plateau region.

2. Materials and Methods

2.1. Sampling

Lhasa is the capital city of the Tibet Autonomous Region in China, which is one of the highest cities in the world (3650 m above sea level). The sampling site (latitude 29.64 ºN, longitude 91.18 ºE) is situated on a roof of a building in the campus of Tibet University (about 12 m high). A modified high-volume air sampler was used to collect gas and particle phases air samples by polyurethane foam (PUF) and glass fiber filter (GFF), respectively. 48 pairs of gas and particle phase samples were collected from August 5, 2008 to July 13, 2009 on weekly base.

2.2. Treatment and analysis

GFF and PUF samples were Soxhlet extracted with dichloromethane, mixture of acetone:hexane (1:1, v/v) for 24 h, respectively. Extracts were cleaned-up by silica gel column. 22 brominated NFRs [ATE (Allyl 2, 4, 6-tribromophenyl ether), p-TBX (2, 3, 5, 6-tetrabromo-p-xylene), BATE (2-bromoallyl 2, 4, 6- tribromophenyl ether), PBBZ (1, 2, 3, 4, 5-Pentabromobenzene), TBCT (tetrabromo- o-chlorotoluene), PBT (pentabromotoluene), PBEB (petabromoethylbenzene), DPTE (2, 3-dibromopropyl 2, 4, 6-tribromophenyl ether), HBBZ (hexabromobenzene), PBBA (pentabromobenzyl acrylate), OBIND (octabromotrimethylphenylindane), DBDPE (decabromodiphenylethane), α, β-TBECH (α, β-tetrabromoethylcyclohexane), α, β-TBCO (α, β-1, 2, 5, 6-tetrabromocyclooctane), HCDBCO (hexachlorocyclopentenyl- dibromocyclooctane), T23BPIC (tris (2,

3-dibromopropyl) isocyanurate), EHTBB, BEHTBP, BTBPE and γ-HBCD] and 2 chlorinated NFRs [syn-dechlorane plus (*syn*-DP) and anti-dechlorane plus (*anti*-DP)] were analyzed by Agilent 6890-5975B gas chromatography-mass spectrometry.

2.3 QA/QC

Field blanks and method blanks were performed during the sampling and sample treatment to check any background contaminations. Only PBT was detected with trace amount in blanks, and all the reported results were blank corrected. CB-155 was used as the recovery standard (surrogate) to check the performance of the applied method. The mean recovery of CB-155 was higher than 80% for all samples, and all the reported results were corrected with surrogate recovery. The instrumental limit of detection (LOD) was calculated as 3 times the signal to noise (S/N) ratio, which gave a range from 0.017 pg/m^3 (p-TBX) to 2.9 pg/m^3 (γ-HBCD).

3. Results and Discussion

3.1 Concentration

In order to get the representative results, only compounds with detection rate > 30% were considered in this study. The concentrations (pg/m^3) of NFRs are summarized in **Table 1**. Generally, only 6 compounds and 8 compounds were detected with detection rate > 30% in gas phase and particle phase, respectively. For gas phase, α-TBECH was the most abundant compound, followed by β-TBECH, PBBZ and PBT. The total concentration of the 6 compounds ranged from 0.30 to 14.55 pg/m^3, with a mean and median value of 4.61 and 4.16 pg/m^3, respectively. For particle phase, DBDPE was the most abundant compound, followed by γ-HBCD, EHTBB, and BEHTBP. The total concentration of the 8 compounds ranged from below detection limit (BDL) level to 48.83 pg/m^3, with a mean and median value of 12.99 and 7.78 pg/m^3, respectively.

Table 1 Summary of NFRs concentrations (pg/m^3) in air in Lhasa City, China

	Compounds	**Min**	**5th**	**Median**	**95th**	**Max**	**Mean**	**SD**	**DR (%)**
Gas Phase	α-TBECH	BDL	BDL	1.20	3.41	4.84	1.28	1.36	56
	β-TBECH	BDL	BDL	0.84	3.54	5.60	1.19	1.47	52
	PBBZ	BDL	0.24	0.94	2.54	2.77	1.07	0.75	98
	PBT	BDL	0.05	0.61	2.14	3.67	0.82	0.75	98
	PBEB	BDL	BDL	0.10	0.30	0.37	0.10	0.11	56
	HBBZ	BDL	BDL	0.11	0.50	0.53	0.14	0.15	69
	Sum	0.30	0.51	4.16	10.42	14.55	4.61	3.58	-
Particle Phase	DPTE	BDL	BDL	BDL	0.77	1.02	0.15	0.26	35
	EHTBB	BDL	BDL	1.23	6.96	14.88	2.07	2.80	79
	γ-HBCD	BDL	BDL	2.60	7.66	11.98	2.68	2.81	63
	BTBPE	BDL	BDL	0.02	0.31	0.47	0.08	0.12	50
	BEHTBP	BDL	BDL	0.36	8.55	28.04	1.77	4.80	60
	syn-DP	BDL	BDL	BDL	0.14	0.27	0.04	0.06	40
	anti-DP	BDL	BDL	0.15	0.80	1.56	0.22	0.30	63
	DBDPE	BDL	BDL	BDL	23.03	28.57	6.40	9.02	40
	Sum	BDL	0.57	7.78	39.11	48.83	12.99	13.06	-

There are very limited data on the NFRs concentrations in atmosphere in the Tibetan Plateau. In an early study,

atmospheric concentrations of BTBPE, EHTBB and BEHTBP at Nam Co Lake in the Tibetan Plateau were reported for the first time, with the mean values of 3.1, 0.54 and 0.38 pg/m^3, respectively [5]. The concentration of BTBPE was much higher than the result in the present study (0.08 pg/m^3). However, for EHTBB and BEHTBP, the two major components in Firemaster 550 (a replacement for PBDEs), our monitoring results (2.07 and 1.77 pg/m^3) were one order magnitude than the previous study [5]. On the global scale of remote areas, the levels of EHTBB and BEHTBP in the present study were also higher than those at Alert in the Canadian High Arctic (0.74 and 0.80 pg/m^3) [5] and that in East Greenland Sea of the European Arctic (< 0.08 pg/m^3 for BEHTBP) [7].

The concentration of PBT in Lhasa City was much higher than those in Artic atmosphere [5,7]. In contrast, lower concentrations of HBBZ, DPTE, *syn*-DP and *anti*-DP were lower than those in Artic atmosphere [5,7]. For other compounds (DBDPE and PBEB), no information was available for the atmospheric concentration in remote areas. When compared with the Great Lakes and the Taihu Lake in China, the atmospheric concentrations in this present study were lower, which is expected since these compounds are frequently used in developed areas [8, 9].

3.2 Monthly variation

In order to study the monthly variation of atmospheric concentrations of NFRs in Lhasa City, the total concentration of NFRs in gas and particle phases were calculated and discussed separately. **Fig. 1** shows the monthly variation of the atmospheric concentrations of NFRs. For particle phase, the concentration in April to June was much higher than other months. For gas phase, the similar monthly variation was also observed, with higher concentration in April to September. In an early study, higher atmospheric concentrations of other POPs, such as HCHs and DDTs, were also observed in the same months in the Tibetan Plateau [1]. The India monsoon season occurs between May and September in the Tibetan Plateau, which is also called the summer monsoon season [10]. During monsoon season, the air masses across the Indian subcontinent and Bay of Bengal lift toward the north, and reach the hinterland of the Tibetan Plateau [3]. So it can be concluded that the monthly variation of atmospheric NFRs concentrations was significantly influenced by the Monsoon System.

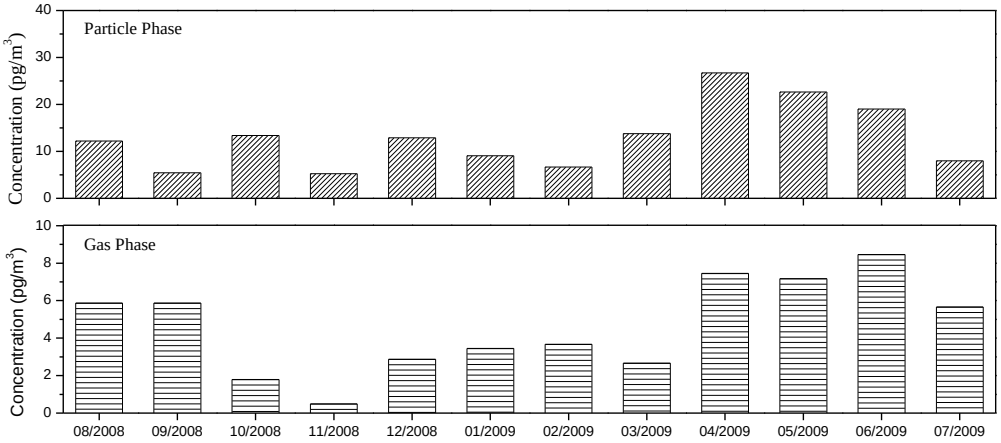

Fig. 1. Monthly variation of atmospheric NFRs in Lhasa City, China

3.3 Air mass influences

In order to assess the influences of air mass on atmospheric concentrations of NFRs in Lhasa City, the HYSPLIT model developed by the National Oceanic and Atmospheric Administration Air Resource Laboratory was applied. As shown in **Fig. 2**, 4 types of source regions were identified according to their pathway of the air mass transport obtained from the HYSPLIT model, such as type A: air mass originated from China; type B: air mass originated from India; type C: air mass originated from Southeast Asia; type D: air mass originated from West Asia. As

presented in **Fig. 2**, the air mass reaching Lhasa City was mostly originated from other countries and regions other than China, with the ratio of 45:3. It is interesting to note that the compositional profiles of NFRs with type B, type C and type D were similar for both particle and gas phases. However, significant difference was found with the compositional profiles between type A and other types. The results indicated the different sources of NFRs between China and other Asia countries. Furthermore, for both particle and gas phases, lower concentration of NFRs was observed with type A than other types. All these findings suggested the significant potential for long-range atmospheric transport of NFRs in the Tibetan Plateau.

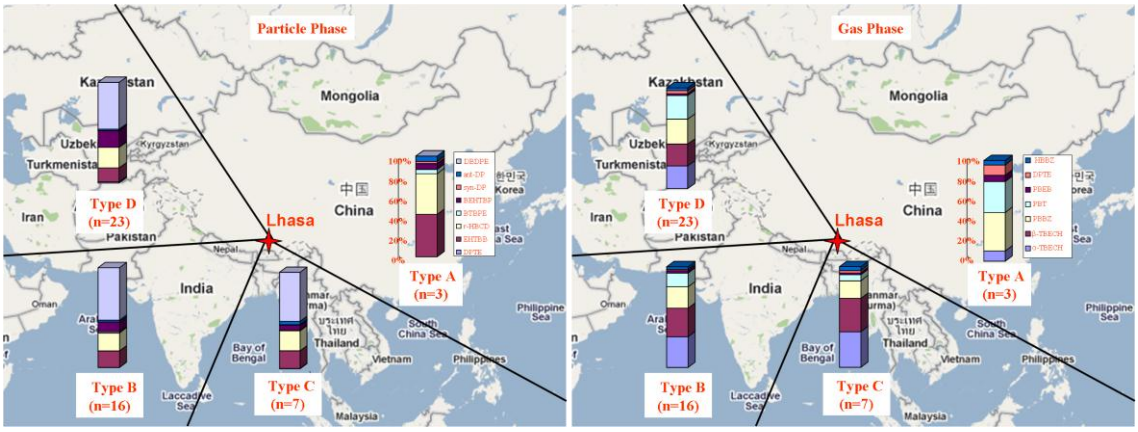

Fig. 2. Compositional profiles of NFRs with the four types air masses

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References:

1. Sheng J, Wang X, Gong P, Joswiak DR, Tian L, Yao T, Jones KC. (2013); *Environ Sci Technol.* 47(7): 3199-208
2. Gong P, Wang X, Sheng J, Yao T. (2010); *Atmos Environ.* 44(21): 2518-23
3. Wang X, Gong P, Yao T, Jones K. (2010); *Environ Sci Technol.* 44(8): 2988-93
4. Liu W, Chen D, Liu X, Zheng X, Yang W, Westgate JN, Wania F. (2010); *Environ Sci Technol.* 44(5): 1559-65
5. Xiao H, Shen L, Su Y, Barresi E, DeJong M, Hung H, Lei YD, Wania F, Reiner EJ, Sverko E. Kang SC. (2012); *Environ Poll.* 161: 154-61
6. Zhu N, Fu J, Gao Y, Ssebugere P, Wang Y, Jiang G. (2013); *Environ Pollut.* 181: 7-13
7. Möller A, Xie Z, Sturm R, Ebinghaus R. (2011); *EnvironPollut.* 159(6): 1577-83
8. Salamova A, Hites RA. (2011); *Environ Sci Technol.* 45(20): 8698-706
9. Qiu X, Zhu T, Hu J. (2010); *Chemosphere.* 80(10): 1207-12
10. Kang J, Choi S, Park H, Baek S, Hong S, Chang Y. (2009); *Sci Total Environ.* 408(1): 57-63