SPATIAL BIOMONITORING OF POLYCHLORINATED BIPHENYL AND POLYBROMINATED DIPHENYL ETHERS IN TIBETAN PLATEAU USING TIBETAN BUTTER

Yawei Wang, Ruiqiang Yang, Thanh Wang, Qinghua Zhang, Yingming Li, and Guibin Jiang
State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, E-mail: gbjiang@rcees.ac.cn

Abstract
In the present study, Tibetan butter samples were collected from different prefectures in Tibet Autonomous Region (TAR) to investigate the spatial distributions of polychlorinated biphenyl (PCBs) and polybrominated diphenyl ethers (PBDEs). $\sum_{25}$PCB concentrations ranged from 137.3 to 2518 pg g^{-1} with a mean value 518.5 pg g^{-1}, which were far lower than those in the butter from other worldwide regions. The average concentration of $\sum_{12}$PBDE was 124.6 pg g^{-1}, which was comparatively lower than PCBs. Back trajectory model and principal component analysis indicated the source of these two groups of persistent organic pollutants were mainly from the global long-range transport via to cold trap in this region.

Introduction

Many studies indicated that alpine mountains act as cold-trap or cold-condensation areas and play significant roles when POPs are transported from the lowlands to the high-altitude areas [1-3].
The study on the environmental behaviors of POPs in high altitude mountains can help us to understand the presence, transportation and transformation of these contaminants. Recently, the relationship between accumulation of POPs and altitudinal-temperature gradient, seasonal trends, was investigated in many alpine areas [4-6].
The Tibetan Plateau is considered as a potential cold trap for POPs and plays an important role in the global long-range transport of these compounds. Previous works have found that POPs and other contaminants might be particularly pronounced in the plateau due to the orographic cold-trapping effect [7-9]. However, the environmental behaviors of POPs in the region still remain unclear due to difficulties in obtaining the samples, complex climate conditions, vast regions etc.
The aim of the present study is using locally produced butters as biomonitors to assess the distribution, sources, and environmental fate of polychlorinated biphenyl (PCBs) and polybrominated diphenyl ethers (PBDEs). The results from this study were discussed to further understand the transport and cold-condensation of these contaminants.

Material and methods

The sample collection was carried out in 2006 and 2007. Parts of the samples were bought from local market and parts were directly obtained from local inhabitants. About 2 g of each sample was dissolved in 50 mL hexane and then the lipid was then removed by acid silica gel column (33%). The sample pretreatment, instrumental analysis, quality assurance and quality control, and quantification of the target analytes followed our previous methods [10]. 12 PBDE congeners (BDEs-17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, and 183) and 25 PCB congeners including 12 coplanar congeners (CBs-77, 81, 105, 114, 118, 123, 126, 156, 157, 167, and 169), six indicator congeners (CBs-28, 52, 101, 138, 153, and 180), and other congeners (CBs-3, 15, 19, 202, 205, 208, and 209) were analyzed. The recoveries of ^{13}C-labeled surrogate PBDEs and PCBs were in the range of 51.7-73.7% and 64.3-128.8%, respectively.

Results and discussions

PCBs PCB concentrations in Tibetan butters ranged from 137 to 1123 pg g^{-1} with a mean value of 460 pg g^{-1}. The major PCB homologues in the samples were tri-, penta-, and hexa-CBs, which accounted for 20.8%, 23.2%, and 46.1% of $\sum_{25}$ PCB, respectively. Comparison the concentrations of the non-ortho-PCB, the mono-ortho-PCB, and di-ortho-PCB in Tibetan butters to other regions in the world [11,12] indicated that concentrations of non-ortho-PCB in Tibetan butters are comparable to those in other regions, while the concentrations of the mono-ortho-PCB and di-ortho-PCB were one order magnitude lower than those from the worldwide area.

Relative higher value of $\sum_{25}$PCB was found in samples collected from the eastern and southern regions than those from western areas in the Tibetan Plateau. On the whole, PCB concentrations in the present work were lower than those found in most countries investigated by Kalantzi et al, only comparable to the concentrations from Australia, Japan, Sweden, Thailand, and United State of America[13].

PBDEs $\sum_{12}$PBDE concentrations were in the range of 18.0-955 pg g^{-1} with a mean value of 131 pg g^{-1}. Lowly brominated congeners BDE -17, 28, 47, and 66 were detected in more than 90% of the samples. BDE-47 was the most dominant congener, accounting for 26.9% of $\sum_{12}$PBDEs, and followed by BDE-28, 99, 153, which accounted for 15.1%, 12.4%, and 12.9%, respectively. Levels of PBDEs in butters are very scarce. Comparison to limited published data showed that the concentrations in this study were far lower than PBDEs in butter from Spanish commercial foodstuffs (1193 pg g^{-1}, fat weight) [14] and United States food (more than 500 pg g^{-1}, fat weight) [15].

Principal component analysis (PCA) Based on PCA, higher concentrations of PCBs and PBDEs existed in Tibetan butters from south and east of Qinghai-Tibet Plateau, such as Changdu and Lhasa, which were in accord with the distributions of total organic carbon in soil. The square of the correlation coefficient between $\sum_{12}$PBDEs and $\sum_{25}$PCBs were up to 0.94.

Using the congener-specific air to milk transfer factor ($TF_{A:M}$) calculated by Thomas et al [16], the prediction of air concentrations of CBs-28, 101, 118, 138, and 180 ranged from 0.3 to 10.9 pg m^{-3}.

Back trajectory model calculations revealed that atmospheric transport and deposition of organic pollutants in the Qinghai-Tibetan Plateau are mainly influenced by tropical monsoon from south Asia during winter and spring.

Acknowledgements This work was jointly supported by National Basic Research Program of China (2009CB421605) and Natural Science Foundation of China (40601101, 40873078).

Reference

1. Wania, F., Mackay, D. Global fractionation and cold condensation of low volatility organochlorine compounds in polar regions. Ambio, 1993, 22, 10-18.
2. Daly, G.L., Wania, F. Organic contaminants in mountains. Environ. Sci. Technol. 2005, 39, 385-398.
3. Davidson, D.A., Wilkinson, A.C., Blais, J.M. Orographic cold-trapping of persistent organic pollutants by vegetation in mountains of western Canada. Environ. Sci. Technol. 2003, 37, 209-215.
4. Nizzetto, L., Pastore, C., Liu, X., Camporini, P., Stroppiana, D., Herbert, B., Boschetti, M., Zhang, G., Brivio, P.A., Jones, K.C., Guardo, A.D. Accumulation parameters and seasonal trends for PCBs in temperate and boreal forest plant species. Environ. Sci. Technol. 2008, 42, 5911-5916.
5. Chen, D.Z., Liu, W.J., Liu, X.D., Westgate, J.N., Wania, F. Cold-trapping of persistent organic pollutants in the mountain soils of western Sichuan, China. Environ. Sci. Technol. 2008, 42, 9086-9091.
6. Shen, H.Q., Henkelmann, B., Levy, W., Zsolnay, A., Weiss, P., Jakobi, G., Kirchner, M., Moche, W., Braun, K., Schramm, K.W. Altitudinal and chiral signature of persistent organochlorine pesticides in air, soil, and spruce needles (Picea abies) of the Alps. Environ. Sci. Technol. 2009, 43, 2450-2455.
7. Yang, R.Q., Yao, T.D., Xu, B.Q., Jiang, G.B., Zheng, X.Y. Distribution of organochlorine pesticides (OCPs) in conifer needles in the southeast Tibetan Plateau. Environ. Pollut. 2008, 153, 92-100.
8. Loewen, M., Kang, S.C., Armstrong, D., Zhang, Q.G., Tomy, G., Wang, F.Y. Atmospheric transport of mercury to the Tibetan Plateau. Environ. Sci. Technol. 2007, 41, 7632-7638.
9. Wang, X.P., Yao, T.D., Cong, Z.Y., Yan, X.L., Kang, S.C., Zhang, Y. Gradient distribution of persistent organic contaminants along northern slope of central-Himalayas, China. Sci. Total Environ. 2006, 372, 193-202.
10. Wang, Y.W., Li, X.M., Li, A., Wang, T., Zhang, Q.H., Wang, P., Fu, J.J., Jiang, G.B. Effect of Municipal Sewage Treatment Plant Effluent on Bioaccumulation of Polychlorinated Biphenyls and Polybrominated Diphenyl Ethers in the Recipient Water. Environ. Sci. Technol. 2007, 41, 6026-6032.
11. Weiss, J., Päpke, O., Bergman, Å. A worldwide survey of polychlorinated dibenzo-p-dioxins, dibenzofurans, and related contaminants in butter. Royal Swedish Acad. Sci. 2005, 34, 589-597.
12. Malisch, R., Dilara, P. PCDD/Fs and PCBs in butter samples from new Eurpoean Union member states and a candidate country: Analitical quality control, results and certain PCB-specific aspects. Chemosphere, 2007, 67, S79-S89.
13. Kalantzi, O.I., Alcock, R.E., Johnston, P.A., Santillo, D., Stringer, R.L., Thomas, G.O., Jones, K.C. The global distribution of PCBs and organochlorine pesticide in butter. Environ. Sci. Technol. 2001, 35, 1013-1018.
14. Gŏmara B., Herrero, L., Gonzălez, M.J. Survey of polybrominated diphenyl ether levels in Spanish commercial foodstuffs. Environ. Sci. Technol. 2006, 40, 7541-7547.
15. Schecter, A., Păpke, O., Tung, K.C., Staskal, D., Birnbaum, L. Polybrominated diphenyl ethers contamination of United States food. Environ. Sci. Technol. 2004, 38, 5306-5311.
16. Thomas G.O., Sweetman A.J., Lohmann R., Jones K.C. Derivation and field testing of air-milk and feed-milk transfer factors for PCBs. Environ. Sci. Technol. 1998, 32, 3522-3528.