Assessment of polychlorinated biphenyls and polybrominated diphenyl ethers in Tibetan butter

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The Tibetan plateau is considered a potential cold trap for persistent organic pollutants (POPs) and plays an important role in the global long-range transport of these compounds. This present work surveyed the concentrations of polychlorinated biphenyl (PCBs) and polybrominated diphenyl ethers (PBDEs) in Tibetan butter samples collected from different prefectures in Tibet autonomous region (TAR). \( \sum \)PCBs concentrations ranged from 137 to 2518 pg g\(^{-1} \) with a mean value 519 pg g\(^{-1} \), which were far lower than those in the butter from other regions in the world. The highest level was found in butter from Sichuan province, which is located to the east of the Tibetan plateau and the lowest value was in samples from southeast TAR. The average concentration of \( \sum \)PBDE was 125 pg g\(^{-1} \). The sample with highest and lowest \( \sum \)PBDE concentration (955 and 18.0 pg g\(^{-1} \)) was from the south and southeast part of the plateau, respectively. Back trajectory model implied that the sources of these two groups of POPs were by atmospheric deposition in south, whereas the western plateau was mainly influenced by the tropical monsoon from south Asia. Air currents from Sichuan and Gansu province are further responsible for the atmospheric transport of PCBs and PBDEs to the eastern and northern side of the plateau. Local air concentrations of \( \sum \)PCBs predicted using air–milk transfer factor were at the lower end of published global levels.

1. Introduction

Persistent organic pollutants (POPs) and other semivolatile organic compounds can undergo long-range transport (LRT) and temperature-dependent air-surface exchange where high-altitude areas are considered important for the global transport of these contaminants (Blais et al., 1998; Simonich and Hites, 1995). Alpine regions play significant roles when POPs are transported from the lowlands to the high-altitude areas (Daly and Wanja, 2005; Shen et al., 2009). In general, concentrations of pollutants tend to decrease with altitude since the upper reaches of high mountains are more remote away from pollution sources than lower areas (LeNoir et al., 1999). However, increasing number of studies have revealed that high mountains can act as cold-trapping or cold-condensation areas (Davidson et al., 2003), where cooler temperatures lead to enhance concentrations of POPs at high altitudes. This is a similar process to that occurring in high latitude areas such as the Arctic, although the mechanisms are maybe different (Wania and Mackay, 1993; Wania and Westgate, 2008). Estellano et al. (2008) found that endosulfans and HCH concentrations increased with altitude on the east side of the Andean mountain range in Bolivia using polyurethane foam disk passive air samplers.

Recently, Chen and his co-workers (2008) discussed the mountain cold-trapping mechanism based on the temperature dependence of precipitation scavenging. Their results revealed that soil concentration for all analytes increased significantly and exponentially with altitude.

The sources of POPs in alpine regions are quite easy to identify. Because high altitude mountains are usually far away from industrial sources and have minimal human activities, POPs tend to reach these areas by atmospheric transport and deposition. Mountain ecosystems take part in the global LRT of POPs depending on the extent of air-surface exchange, including dry/wet deposition, emission, etc. (Fernandez et al., 1999). The study of different environmental behavior of POPs in high altitude mountains can help us to further understand the presence, transportation and transformation of these contaminants. Potential adverse impacts on drinking and agricultural water supplies are also important to assess since mountain regions serve as fresh water supply. Recently, a relationship between accumulation of POPs and altitudinal-temperature gradient has been found in an alpine forest in the Italian Alps (Nizzetto et al., 2006), seasonal trends for POPs have been investigated in temperate and boreal alpine valley forest plants (Lys Valley, Aosta, Italy) (Nizzetto et al., 2008), and accumulation of organochlorine compounds in fish from high mountain lakes (Vives and Grimalt, 2004) have been investigated. These studies have contributed to the understanding of POPs in mountainous...
areas with respect to the influence of seasonal trends, composition of POPs in alpine regions, the influence of various environmental behavior and the effects of remote pollution sources.

Often called the roof of the world (with an average altitude of 4000 m above sea level), the Tibetan plateau lies north of the Himalayas and it is one the coldest and most remote regions in the world. Previous works have found that POPs might be particularly pronounced in the plateau due to the orographic cold-trapping effect (Hindman and Upadhyay, 2002; Li et al., 2006; Wang et al., 2006, 2008a; Loewen et al., 2007; Yang et al., 2008). The atmospheric circulation is considered to be responsible for the deposition of POPs which are transported from the source regions to the Tibetan plateau by the Indian monsoon and westerly winds. However, due to difficulties in obtaining the samples, the complex climate conditions, the vastness of the region, and the diversity of vegetation, the environmental behaviors of POPs in the plateau still remain unclear.

The aim of the present study is to investigate the distribution of polychlorinated biphenyl (PCBs) and polybrominated diphenyl ethers (PBDEs) in Tibetan butter that is part of the dairy food for local inhabitants. Butter can also be considered a sampling medium, which provides an integrated surrogate for ambient air concentrations (Kalantzi et al., 2001). The results from this study on PCB and PBDE concentrations are discussed to further understand the source, the transport and cold-condensation of these contaminants on the Tibetan plateau.

2. Materials and methods

2.1. Sampling collection

The sampling sites are shown in Fig. 1. Tibetan butter samples \( (n = 32) \) produced from yak milk, were collected in 2006 and 2007 from seven prefectures in the prefectures of Tibet autonomous region (TAR): Lhasa, Naqu (Nagqu), Changdu (Qamdo), Shannan, Rikaze (Xigaze), Ali (Ngari), and Linzhi (Nyingchi). Some samples were bought from local market and some were directly obtained from local inhabitants. Three samples from the areas with Tibetans residents live in the provinces of Sichuan, Gansu, and Qinghai were also collected for comparison and a total of 35 samples were collected. After collection, the samples were immediately put into an ice box, then transported to the laboratory and stored in a freezer at \(-20^\circ\text{C}\) until analysis.

2.2. Sample analysis

About 2 g of each sample was dissolved in 50 mL hexane, then \(^{13}\text{C}\) labeled standard of PCBs and PBDEs were spiked for recovery assessment. The lipid was removed by acid silica gel column. The sample pretreatment, instrumental analysis, quality assurance and quality control, and quantification of the target analytes followed previously published methods (Wang et al., 2007). Thirteen PBDE congeners (BDEs-17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, and 190) and 25 PCB congeners including 12 coplanar congeners (CBs-77, 81, 105, 114, 118, 123, 126, 156, 157, 167, and 180), and other congeners (CBs-3, 15, 19, 202, 205, 208, and 209) were analyzed. The quantification was performed on an Agilent 6890 gas chromatography coupled with high-resolution mass spectrometer (HRMS) (Waters Micromass, Manchester, UK) with an electron impact (EI) ion source. The HRMS operated in SIM mode with resolution >10,000. 1 mL extract was injected with a CTC PAL autosampler in splitless mode. DB-5 (30 m × 250 \(\mu\text{m}\) i.d. × 0.1 \(\mu\text{m}\) film thickness for PBDEs and 60 m × 250 \(\mu\text{m}\) i.d. × 0.25 \(\mu\text{m}\) for PCBs) capillary column was used for separation. Helium was used as carrier gas with flow rate of 1.2 mL min\(^{-1}\). For PBDEs, the oven temperature program was the following: the initial oven temperature was 100 \(^\circ\text{C}\) held for 2 min. It was then increased to 210 \(^\circ\text{C}\) at 25 \(^\circ\text{C}\) min\(^{-1}\), held for 1 min, increased to 275 \(^\circ\text{C}\) at 10 \(^\circ\text{C}\) min\(^{-1}\) held for 10 min, finally to 330 \(^\circ\text{C}\) at 25 \(^\circ\text{C}\) min\(^{-1}\) and held for 10 min. For
PCBs, the initial oven temperature was 120 °C, which was held for 1 min. It was increased to 150 °C at 30 °C min⁻¹, and then increased to 300 °C at 2.5 °C min⁻¹ and held for 1 min.

The recoveries of 13C-labeled surrogate BDE congeners 47, 99, and 153 were in the range of 51.7–73.7%. The mean recoveries for 13C-labeled surrogate PCBs were 64.3–128.8%.

2.3. Data analysis

Statistical analysis was performed with SPSS 13.0 for Windows release (SPSS Inc., 1989–2006). Principal component analysis (PCA) was used to extract the visual representation of the main characteristics of PCB and PBDE congeners in Tibetan butter. Principal components (PCs) were obtained if their eigenvalues were >1. The combination of loading and score plots can present useful information to identify groups of samples with similar behavior and visualize relationships among the different variables.

3. Results and discussion

The lipid content in Tibetan butter was found to reach as high as 90%. Therefore, the concentrations in this study are reported on lipid weighted basis. Table 1 summarizes the statistical results of indicators PCB congeners and selected main PBDE congeners in Tibetan butter collected from different areas of Tibet. Fig. 2 illustrates the frequency distributions of selected concentrations of PCB and PBDE congeners.

3.1. General comments on PCB congener profiles

\[ \sum_{25} \text{PCB} \] concentrations in Tibetan butters ranged from 137 to 1123 pg g⁻¹ with a mean value of 460 pg g⁻¹, which were lower than that from Sichuan province (2518 pg g⁻¹), but comparable to butter from Qinghai (611 pg g⁻¹) and Gansu province (411 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 \( \sum_{25} \text{PCB} \), respectively. As expected, the sum of six indicator PCB congeners (CBs-28, 52, 101, 138, 153, and 180) represented 79.1% of \( \sum_{25} \text{PCB} \). A very strong linear relationship was found between sum of indicator PCB congeners and \( \sum_{25} \text{PCB} \) with a coefficient \( R^2 = 0.98 \) (\( P < 0.05 \)). This means that indicator PCB concentrations could be selected to represent \( \sum_{25} \text{PCB} \) if analytical difficulties would be an obstacle to study the PCB behavior in butter from this region. Among the six indicator congeners, CB-52 (3.7% for \( \sum_{25} \text{PCB} \)) and 101 (5.5%) concentrations were lower than CB-138 (23.8%) and 153 (20.5%), which might be due to the fact that the congeners containing 4,4'-chlorine are more resistant to metabolism in mammalian systems (McLachlan, 1993; Thomas et al., 1998). A global investigation on the distribution of PCBs and organochlorine pesticides (OCPs) in butter indicated that CB-28 were detected only close to the limit of detection in butter from different countries, which could reflect the result of fast metabolism in cows (McLachlan, 1993; Thomas et al., 1998). In our work however, CB-28 was detected at relative high levels (Fig. 2) with concentrations close to those of other indicator congeners, accounting for 19.7% of \( \sum_{25} \text{PCB} \). It was also interesting that although CB-209 has poor long-range transport capability, it could be detected in most samples. We also compared the concentrations of the non-ortho-PCBs, the mono-ortho-PCBs, and di-ortho-PCBs in Tibetan butters with those reported for butter from other regions in the world (Fig. 3) (Weiss et al., 2005; Malisch and Dilara, 2007). The 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 in butters in the present region are comparable to those in other regions.
work were one order magnitude lower, especially far lower than those collected from Europe. Relative higher values of $\sum_{25}$PCB were found in butter from Changdu and Shannan with concentration of 1123 and 627 pg g$^{-1}$, respectively. Samples collected from the eastern and southern regions showed higher concentrations of PCBs than those from western areas on the Tibetan Plateau. On the whole, PCB concentrations in Tibetan butter were lower than those found in most countries investigated by Kalantzi et al., only comparable to the concentrations in butter from Australia, Japan, Sweden, Thailand, and USA (Kalantzi et al., 2001).

Jafari et al. (2008) used produced butter to investigate the spatial distribution of POPs in Iran. In their study, the concentrations of PCBs in produced butter from Iran (mean, 4320 pg g$^{-1}$ with a range of 350 and 57,400 pg g$^{-1}$) were higher than the global average and considerably higher than the results in our study. They also pointed out that PCBs in butter originate from atmospheric deposition since Iran is not known for widespread PCB usage. Indicator congeners (CBs-28, 52, 138, 153, and 180) also accounted for a majority of $\sum_{25}$PCB except for CB-101, which was not detected in their work.

3.2. General comments on PBDE congener profiles

$\sum_{12}$PBDE concentrations in Tibetan butters were in the range of 18.0–955 pg g$^{-1}$ with a mean value of 131 pg g$^{-1}$, and were far lower than those of PCB concentrations. Higher concentrations of PBDEs were also found in butter collected from Shannan prefecture. Different from the result for PCBs, $\sum_{12}$PBDEs concentrations in Tibetan from TAR were higher than those from Sichuan, Gansu, and Qinghai. Levels of PBDEs in butters are generally 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) (Gomara et al., 2006) and from United States (above 500 pg g$^{-1}$, fat weight) (Schecter et al., 2004).
The concentrations of BDE-85 and 138 were below the detection limits in more than 50% of the samples. Lowly brominated congeners such as BDE-17, 28, 47, 66 were detected in more than 90% of the samples. BDE-47 was the most dominant congener, which accounted for 26.9% of $\sum_{12}$PBDEs, followed by BDE-28, 99, 153, which accounted for 15.1%, 12.4%, and 12.9%, respectively.

### 3.3 Multivariate statistical analysis for PCBs and PBDEs

Principal component analysis (PCA) was performed to extract valuable information from the chemical analysis of PCB and PBDE congeners in Tibetan butter.

For PCBs, the first two principal components accounted for 78.2% of the total variance. Fig. 4 represents the loading and score plots from the results of PCA for PCB data. As can be seen, higher concentrations of PCBs were found in Tibetan butters collected from southern and eastern part of Qinghai-Tibet plateau, such as Changdu (S20), Huangniu1 (S13), Langkazi (S6, S7) and Lhasa (S1). For PBDEs, the first two components of PCA accounted for 61.08% and 16.04% of the total variance, respectively (Fig. 5). The butter samples from Langkazi (S7, S9), Huangniu (S13), and Namucuo (S31–33) contained higher concentrations of PBDEs compared to other Tibetan sites. High square of the correlation coefficient (0.94) were found between $\sum_{12}$PBDEs and $\sum_{25}$PCBs.

Previous work on the distribution characteristics of soil organic carbon on the plateau has shown that soil organic materials decrease from southeast to northwest, similar to the decreasing trend in precipitation (Tian et al., 2008). PCA results indicated that the concentrations of PCBs and PBDEs in Tibetan butters collected from south and east areas are higher than those in west and north sampling sites, which were in accord with the distributions of TOC in soil. A previous work from in our group on the altitude dependence of PCBs and PBDEs in surface soil from the Tibetan plateau also found that PCBs and lower brominated BDE congeners in surface soil have significant linear relationship with TOC in soil (Wang et al., 2009). These distribution trends might imply that these two groups of POPs are introduced by atmospheric deposition brought into soil or adsorbed/absorbed by grass and other plants, which then can be transferred to yak milk through intake and finally concentrated in butter. Other studies also found that the atmospheric deposition of pollutants such as OCPs, polycyclic aromatic hydrocarbons (PAHs) and mercury varied with the season and source changes in the adjacent region (Wang et al., 2008b).

Air butter exchanges for semivolatile lipophilic chemicals including PCBs have been studied to discuss their accumulation, elimination rate and equilibrium partition, etc. (Schramm and Hutzinger, 1989). Thomas et al. (1998) discussed the derivation of air–milk transfer factors for PCBs. In their work, they found that congenerspecific air to milk transfer factors (TF$_{A,M}$) provides an excellent tool to predict milk concentrations of PCBs from average air concentrations at the regional scale. Using TF$_{A,M}$ value for CBs-28, 101, 118, 138, and 180 (3.2, 11, 400, 380, and 540 m$^3$ air g$^{-1}$ fat, respectively) derived from Thomas et al. and the assumption that yak and cow share similar metabolism for these compounds, air concentrations of the five selected PCB congeners ($\sum_5$PCBs) were estimated at the local region and the predicted $\sum_5$PCBs ranged from 5.84 to 218 pg m$^{-3}$.

Back trajectory analysis was carried out to assess the origin of the air masses passing through the plateau and to apportion the potential source of PCBs and PBDEs by long-range atmospheric transport from the adjacent regions. The back-trajectories were calculated with NOAA HYSPLIT using GDAS1 data (www.arl.noaa.gov/ready/hysplit4.html). Five sampling sites including Changdu (31.13°N, 97.15°E, Changdu prefecture), Langkazi (28.90°N, 90.70°E, Shannan prefecture), Gaize (32.20°N, 84.60°E, Ali prefecture), Anduo (32.17°N, 91.41°E, Naqu prefecture), and Lhasa prefecture (29.10°N, 91.02°E) were selected to roughly represent the western, southern, western, northern, and central part of the TAR. Two day back trajectories at the 500 m level were computed using the wind field in the first week of every month during 2006 (Supplementary material).

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. In summer and autumn, besides the influence of southern winds, there are also southwesterly wind passing over the west of the plateau and reach the sites investigated in this study. At the east and north side of the plateau, release and emission of PCBs from adjacent provinces can also be regarded as potential sources by atmospheric transport. This is also in accord with previous report regarding the Indian summer monsoon (Loewen et al., 2007).

### 4 Conclusions

The variation in concentrations of PCBs and PBDEs in Tibetan butters within TAR shows the complexity of environmental behaviors influencing the distribution of these two groups of contaminants. Back trajectory analysis indicated that the potential air...
transport of these POPs in TAR would mainly be influenced by the tropical monsoon arriving from south Asia. As one of the coldest and most remote regions in the world, other works about POPs in the plateau also hint that the sources of contaminants are mainly from atmospheric depositions. Further work about POPs in this region is warranted to better understand the long-range atmospheric transport of POPs at a global scale.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2009.09.069.

References