The fractional patterns of polybrominated diphenyl ethers in the soil of the central Tibetan Plateau, China: The influence of soil components

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Sixteen soil samples were collected from the central Tibetan Plateau (CTP). The soil concentrations of polybrominated diphenyl ethers (PBDEs) in CTP were analyzed. The detected 42 congeners were divided into light, intermediate and heavy fractions. In addition to the various minerals, other soil properties were also characterized, including the content of soil organic carbon (SOC) and the particle size distribution. The clay content is positively related to the intermediate fraction of the PBDEs and negatively related to the light and heavy fractions. Similar correlations were observed for SOC and the fine-particle fraction (size < 2 μm). The coefficient of determination ($r^2$) associated with a linear regression indicated that the clays were more highly correlated with the fractional pattern of the PBDEs than with the other properties, such as SOC and the fine-particle fraction. The values of $r^2$ between clays and three fractions of PBDEs are 0.70, 0.69 and 0.58.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are anthropogenic chemicals that have been produced for industrial applications such as additive flame retardants (DiGangi et al., 2010). Due to persistence, bioaccumulation and toxicity, these PBDEs are considered persistent organic pollutants (POPs) (McDonald, 2002; Zhang et al., 2011). The study of the sorption and desorption behaviors of PBDEs on soils has recently attracted substantial interest (Liu et al., 2011; Olshansky et al., 2011).

Soil is an important sink and reservoir for POPs. In this context, surface soil is especially important because air-soil exchange typically occurs on the surface soil (Cousins et al., 1999; Li et al., 2010). The investigation of the soil concentration of POPs contributes to the understanding of the soil-air partition coefficients and fugacities of these pollutants (Demircioglu et al., 2011). The soil concentration represents an integration of input and loss processes.

The relationships between contaminant concentrations and soil properties (e.g., soil organic carbon (SOC)) were investigated. In most cases, SOC is considered to play a dominant role in adsorbing and immobilizing POPs in soil (Nam et al., 2008; Liu et al., 2010). Experimental data also appear to show that the sorption and desorption behaviors of PBDEs on soil are primarily affected by SOC (Liu et al., 2011; Olshansky et al., 2011), although the concentrations of PBDEs used in these experiments are several orders of magnitude higher than those in the field.

Surface minerals, especially clays, are potentially important for adsorption from the gas phase to the soil (Goss and Eisenreich, 1996; Ruiz et al., 1998). Furthermore, experimental studies found that if the content of SOC was less than the critical point of 1–2%, the principal dynamic for the sorption of contaminants originates from minerals rather than from the SOC in the soil (Nam et al., 1998; Li and Sun, 2006). Experimental research aids in understanding the mechanism underlying these results, but such results are not proved to be consistent with those observed in the field. If the concentration of SOC in the field is indeed sufficiently low, even less than 2%, we hypothesize that soil minerals, rather than SOC, are the primary determinants of the sorption and desorption behaviors of PBDEs in the soil due to large surface area of clays competing with SOC. In contrast, previous reports emphasized the role of SOC (Nam et al., 2008).

The Tibetan plateau is an ideal site for testing this hypothesis because sampling sites without direct human impacts can be selected and organic matter is not abundant. The Tibetan plateau, located in southwestern China, is the highest plateau in the world. It is also called “the third pole” because of its unique meteorological and geographic characteristics (Wang et al., 2010). Monitoring data on POPs from the Tibetan Plateau (Wang et al., 2006, 2007, 2008) suggest that the POPs may be impacted by air masses derived from the Indian subcontinent as well as by certain local sources.
Wang et al. (2010) have divided the plateau into the Monsoon region and the westerly region based on the air circulation. On the Central Tibetan Plateau (CTP), a part of the Monsoon region to which air masses bring the majority of the contaminants from the Indian subcontinent, several congeners of PBDEs were detected in the atmosphere and the soil (Wang et al., 2009, 2010).

In this study, the composition of the PBDE congeners and the soil properties were analyzed in detail in soil samples collected from the CTP to understand the relationship between the fractional pattern of PBDEs and soil properties (i.e., SOC and minerals).

2. Materials and methods

2.1. Sampling

All samples were collected during August 2010. The sample sites are shown in Fig. 1, and detailed information is shown in Table S1 (Supplementary Materials). The samples were collected on a hillside near the original sources (rocks hill) to ensure that the contents of SOC and minerals in the soil were representative. Sixteen surface soil samples were collected at a depth of 0–5 cm. All samples are collected far from the main road and cities in the CTP to avoid direct human impact. At each site, multiple soil samples were collected with a stainless steel spade and mixed. The samples were sealed in a clean black box (purchased from New Landmark Soil Equipment Co., China), transported to the lab and stored in frozen form until extraction.

2.2. Chemicals

A standard solution of 39 PBDE congeners (EPA method 1614 standard solution) (Accustandard, New Haven, CT, USA) was used to quantify the following congeners: mono-BDEs 1, 2, and 3; di-BDEs 7, 8, 10, 11, 12, 13, and 15; tri-BDEs 17, 25, 28, 30, 32, 33, 35, and 37; tetra-BDEs 47, 49, 66, 71, 75, and 77; penta-BDEs 85, 99, 100, 116, 118, 119, and 126; hexa-BDEs 138, 153, 154, 155, and 166; and hepta-BDEs 181, 183, and 190. The analytical standard of BDE-205 and 206 was purchased from Supelco (Bellefonte, PA, USA). Another standard solution of PBDE congeners (EO-5278) (Cambridge Isotope Laboratories, USA) was used for the quantization of BDE-209. This standard solution contained BDE-28, 47, 99, 100, 153, 154, 183, and 209. 13C-labeled BDE-209 (Cambridge Isotope Laboratories) was used as an internal surrogate standard. The laboratory glassware was washed with detergents and dichromate acid cleaning solution, rinsed with tap water and distilled water, and then rinsed with methanol (analytical grade, Beijing Chemical Factory, China), dichloromethane (analytical grade, Beijing Chemical Factory, China) and acetone (analytical grade, Beijing Chemical Factory, China). The pre-cleaning procedure with each solvent was repeated six times, using fresh solvent, to clean the laboratory glassware prior to use. The other solvents used were pesticide grade (J. T. Baker, Phillipsburg, NJ, USA).

2.3. PBDEs extraction and cleanup

The pre-treatment procedure used for the sample and the analytical method used are described in a previous report (Mai et al., 2005). Ten grams of each soil sample was ground with anhydrous sodium sulfate to produce a free-flowing powder. Before extraction, surrogate standards (13C-labeled BDE-209) were spiked to each sample in a centrifuge tube, vortexed and then left to equilibrate overnight. Each sample was extracted with 30 mL of hexane/dichloromethane (1:1, vol/vol) by ultrasonication for 4 min and then centrifuged at 3000 × g. This process was repeated three times, and the extracts were combined. The concentrated extracts were evaporated to 1 mL in a Kuderna–Danish concentrator under a gentle N2 stream for cleanup.

The concentrated extracts were then cleaned on a 15-mm i.d. column packed from the bottom to the top with 2 g of silver nitrate silica (10%, w/w), 1 g of activated silica gel, 4 g of acid silica gel (44% concentrated sulfuric acid, w/w), 4 g of acid silica gel (22% concentrated sulfuric acid, w/w), 1 g of activated silica gel and 1 cm of anhydrous sodium sulfate. The first fraction was eluted with 100 mL of hexane, and the PBDE fraction was then eluted with 70 mL of hexane/dichloromethane (1:1, v/v). The elution was evaporated with a rotary evaporator and then reduced to 20 μL under a gentle N2 stream for analysis. Throughout the extraction, cleanup and analysis procedure, the analytes were protected from light. The containers were wrapped with aluminum foil, or amber glassware was used.

2.4. Analysis

PBDEs were measured with an Agilent 6890 series gas chromatogaph (GC) coupled with an Agilent 5973 high resolution mass spectrometer using a negative chemical ionization source with the selected-ion monitoring mode (SIM). The 1 μL injection was injected in the pulse splitless mode onto a DB-5 MS (15 m × 0.25 mm i.d., 0.25 μm film thickness) fused silica capillary column with helium as the carrier gas at a constant flow rate of 1 mL/min. The ion source and interface temperatures were set to 150 °C and 300 °C, respectively. The GC oven temperature program was conducted as follows: Initially 80 °C, held for 1 min, increased to 200 °C at 10 °C/min and then to 300 °C at 20 °C/min, and held for 20 min. Ion fragments m/z 79 and 81 were monitored for mono- to nona-BDE congeners, m/z 488.6, 486.6 for BDE-209 and 492.6, 494.6 for 13C-labeled BDE-209.

2.5. Quality control

All analytical procedures were monitored using strict quality assurance and control measures. The field blanks consisted of pre-cleaned soil taken to the sampling site. A total of 2 field blanks were extracted and analyzed in the same way as the samples. The target compounds were not detected when the field blank samples were analyzed. A solvent blank, a procedural blank and a standard mixture were run per 6 samples to check for contamination, peak identification and quantification. The target compounds were not detected in the solvent blanks and the procedural blanks. Duplicate samples in the laboratory were analyzed along with regular samples to determine repeatability and reproducibility for additional quality-control assessment to ensure valid results. The instrument stability and relative response factor variance were determined by analyzing the calibration standard solutions in each sample batch.

The PBDEs were quantified using an external-standard method. Three quality-control criteria were used to ensure the correct identification of the target compounds: (1) GC retention times matched those of the standard compounds within 0.05 min; (2) the signal-to-noise ratio was greater than 3:1; and (3) each...
The SRM sample (NIST-2585) was analyzed to validate the analytical method. The recovery of the surrogate standards of 13C-labeled BDE-209 averaged 80 ± 10% in the soil. The matrix spike recoveries of the PBDE congeners (including certain low-level brominated DEs) were within 0.5%–110%, with a 10% standard deviation. The SRM sample (NIST-2585) was analyzed to validate the analytical method employed. The results were satisfactory, with a z-score of ≤ 1 for all congeners (range: 0.3–0.9 for the PBDEs, p > 0.05). The recovery of the 13C-labeled BDE-209 surrogate was 85% with the NIST-2585 sample.

2.6. Analysis of minerals and other properties of soil

The process for sample preparation was conducted according to Chinese Standard SY/T 6210-1996. The analysis of the minerals in the soil was performed with an X-ray diffractometer (Rigaku D/MAX 2500) by PetroChina Exploration & Development Research Institute. The qualitative and quantitative analysis of the minerals, including the clays, was also based on this standard. The soil organic carbon (SOC) contents were analyzed on an SOC Analyzer (SHIMADZU TOC-V CPH). The samples were weighed and loaded into a combustion cup packed with quartz wool. The contents were analyzed on an SOC Analyzer (SHIMADZU TOC-V CPH). The samples were heated and cooled until the vapor pressure was low enough for the PBDEs to be detected. The SOC values in all sixteen soil samples were determined. The SOC values ranged from 0.03 to 0.43 ng g⁻¹ for dry soil shown in Table S2 in Supplementary Materials) for mono- to nona-BDEs and 0.1 ng g⁻¹ for BDE-209. Simultaneously, the ongoing precision was determined. The recoveries of the surrogate standards of 13C-labeled BDE-209 averaged 80 ± 10% in the soil. The matrix spike recoveries of the PBDE congeners (including certain coeluting PBDE congeners) were within 75%–110%, with a 10% standard deviation. The SRM sample (NIST-2585) was analyzed to validate the analytical method employed. The results were satisfactory, with a z-score of ≤ 1 for all congeners (range: 0.3–0.9 for the PBDEs, p > 0.05). The recovery of the 13C-labeled BDE-209 surrogate was 85% with the NIST-2585 sample.

3. Results

3.1. Soil concentration and fractional patterns

Table S2 (Supplementary Materials) shows the minimum, maximum and mean concentrations of the 42 congeners detected in the central Tibetan Plateau. BDE-3 was the most abundant congener, followed by BDE-2 and BDE-1. The maximum concentration of BDE-3 is 64.0 ng/kg and the mean of it is 14.74 ng/kg. A wide variety of other congeners were also detected. The congeners detected included BDE-209. The average concentration of this congener was 1.25 ng/kg. This value was determined but was not included in a previous report (Wang et al., 2009). The soil concentration of PBDEs ranged from 17.03 to 298.29 ng/kg, with a mean value of 80.39 ng/kg (Fig. 2). The maximum value in the soil area was found at the highest-elevation site, 4824 m. The results are similar to those of another study conducted in this area (Wang et al., 2009) but slightly lower than those obtained for the Loess plateau in China (Meng et al., 2011).

Low-level brominated BDEs evaporate more readily due to their higher vapor pressure and therefore have a greater potential to undergo long-range air transport (LRAT). As shown in Fig. 2, the fraction of BDEs from mono- to hexa-BDEs contributes approximately 90% of the ∑PBDEs, and the sum of the low-level brominated congeners (mono-, di-, and tri-BDEs) contributes ca. 50% of the ∑PBDEs. In contrast, the heavier (hepta-, octa-, nona-, and deca-BDEs) congeners are more stable and contributed 4.4% of the ∑PBDEs on average. The contribution of the other congeners (tetra-, penta-, hexa-BDEs) was ca. 45%. All of these congeners are major components of commercial penta-BDEs. In the present study, the general pattern of BDE concentrations showed the following order: low > middle > high-brominated BDEs.

It is understandable that the low-brominated DEs (mono-, di- and tri-BDEs) result primarily from degradation in nature. Commercial penta-BDE was composed primarily of tetra- (40%), penta- (45%), and hexa-BDEs (6%) (Zhang et al., 2009). High-brominated DEs, such as hepta-, octa-, nona- and deca-BDEs, are the main components of commercial octa-BDEs and deca-BDEs.

Based on the octanol-air partition coefficient (Koa) and supercooled liquid vapor pressure, Shoeb et al. (Shoeb et al., 2004) have found that the light fraction of BDEs occurred in the gas phase, whereas the heavier fraction occurred in the particle phase. In this study, the percentages of mono- and tetra-BDEs are higher than the other BDEs that were mainly transported into CTP in the gas or particle phase by LRAT (Chen et al., 2008; Wang et al., 2010). High-brominated DEs are transported near their sources in the CTP and the similar properties of BDE congeners, the BDEs may be tentatively classified. Here we use the categorization in terms of the following three fractions: light (mono-, di- and tri-BDEs); intermediate (tetra-, penta- and hexa-BDEs); and heavy (hepta-, octa-, nona- and deca-BDEs).

3.2. SOC and its correlation with PBDE fractions

Table S3 (Supplementary Materials) shows the content of soil organic carbon (SOC) in all sixteen soil samples. The SOC values in all samples are less than 2%. This value seems to characteristic of the Tibetan plateau due to the special environment of the area. Most previous reports considered SOC the primary dynamic factor responsible for the sorption of POPs, including PBDEs, in soil (Sweetman et al., 2005; Nam et al., 2008; Liu et al., 2010). The soil concentration of the PBDEs shows little correlation with the content of SOC. Note, however, that the percentages of the three PBDE fractions show linear relationships with the SOC content which is suggested by correlation analysis (Table S4 in Supplementary Materials). As shown in Fig. 3, the light fraction and heavy fraction are negatively correlated with SOC, whereas the intermediate fraction is positively correlated with it. In theory, the affinity of SOC to BDEs changes gradually with changes in molecular weight if there is no other competing factors. In this study, the lack of such a gradual trend among the three fractions suggests that the pattern of the PBDE fractions is poorly correlated with the content of SOC.

3.3. Soil minerals and their correlation with three fractions

Minerals are basic components of the soil and play a critical role in its physical and chemical properties. Table S5 (Supplementary Materials) shows the results of the analysis of the content of various
minerals in the soil samples, and clays ranged from 9.3 to 18.9%. Although soil concentration of PBDEs shows little correlation with content of clays (Table S4 in Supplementary Materials), the clays showed a significant linear relationship with the proportion of each fraction of the PBDEs (Fig. 4). Note that the intermediate fraction shows a correlation, the sign of which is opposite to that found for correlations with the light and heavy fractions. This result is similar to that obtained for SOC. Note also that the coefficient of determination, $r^2$, is higher for the clays than for SOC. A regression analysis was also applied to the other minerals, such as quartz, orthoclase and plagioclase, in relation to the proportions of the three PBDE fractions. No significant linear relationships were found. This result indicates that clays play a more important role in adsorbing contaminants than other minerals (Ahn et al., 2006; Yuan et al., 2011). Our results also confirmed the previous conclusion (Nam et al., 1998; Li and Sun, 2006) that the clays directly control the sorption and desorption of POPs if the content of SOC in the soil is less than the critical value.

3.4. Particle size distribution and correlation with three fractions

Particle size is an important factor influencing the content of contaminants in soil and sediments. Due to their large surface area, fine particles tend to adsorb contaminants (Yuan et al., 2011). The distribution of particle sizes detailed in this study is shown in Table S6 (Supplementary Materials). Although the concentration of PBDEs in the soils was not directly correlated with that of each size fraction (Table S4 in Supplementary Materials), the proportion of the fine-particle fraction (grain size less than 2 μm) showed a certain degree of linear correlations with the proportions of the three PBDE fractions (Fig. 5). Note that the light and heavy fractions of PBDEs are also negatively correlated with the proportion of the fine-particle fraction, whereas the correlation between the fine-particle fraction and the intermediate fraction of PBDEs is positive. Although the regressions between the other particle fractions (grain size >2 μm) and each PBDE fraction are not shown here, the trends found were similar to those found for the fine-particle fraction. The fraction with grain size >200 μm did not show a significant linear correlation. The coefficient of determination, $r^2$, was highest for the fine-particle fraction in the regressions with the light, intermediate and heavy PBDEs. This result suggests that the fine-particle fraction, especially the fraction with grain size <2 μm, correlates well with sorption and the pattern of the PBDE fractions in the soil.

4. Discussion

4.1. Comparing coefficients

The values of the coefficient of determination, $r^2$, in the linear regression analyses presented above express the quantification of the correlation between the soil properties and the three PBDE
fractions. In a certain sense, they also represent the strength of the effect of different soil properties on each fraction. The results of a comparison of these coefficients of determination are shown in Fig. 6. For all the PBDE fractions, the clays show the best linear correlation and the highest $r^2$ value. Although SOC and the fine particles ($<2\mu m$) did not show values of $r^2$ as high as those found for the clays, they still showed a relationship with the three PBDE fractions. Based on the quantification of the correlation represented by $r^2$ in the linear regressions, it could be inferred that the effect of the clays on the pattern of PBDE fractions in the CTP area was greater than the effect of SOC or the effect of fine particles. Although the coefficients of determination differed, the correlations of these three properties with each of the three PBDE fractions showed the same trend.

4.2. Relationships among soil properties

In this study, all samples were collected on the hillside near the original rocks to ensure that the contents of SOC and minerals in the soil were representative. Fig. 7 shows the linear regression between the clay content of the soil and SOC. The figure clearly shows a good linear correlation. The high value of $r^2$ in the regression analysis indicated that the content of SOC in the soil was associated with the content of clay in the soil. The regression analyses of the other soil minerals showed no significant correlations. It is possible that the clay content of the soil affected the content of SOC due to larger surface area of the clay particles.

Fig. 8A shows the linear regression of the content of SOC and the fraction of particles with grain size $<2\mu m$ in the soil. Fig. 8B shows the correlation coefficients between SOC and the different particle fractions. The coefficient of the fraction of size $<2\mu m$ is clearly the highest. The coefficients decreased as the particle size increased. The coefficient for the coarse fraction (size $>200\mu m$) was even negative. These results showed that fine particles were more effective at adsorbing organic matter in the soil than coarse particles. The content of fine particles affects the content of SOC more strongly than does the content of the coarse fraction. The content of the fine-particle fraction is correlated with the content of SOC, at least in part, because SOC tended to be absorbed on the surface of the fine particles.

According to the above discussion, the fine particles, composed primarily of clay minerals, determined the concentration of SOC in the central Tibetan Plateau. Although the complex of SOC and clays functions to adsorb PBDEs, the principal dynamic effect may be caused by the clays because SOC may lose its dominant role if its content is less than the critical value (Ruiz et al., 1998; Nam et al., 1998; Li and Sun, 2006). The positive correlations between clays, SOC and fine particles explain the finding that the correlations of these variables with each PBDE fraction show the same trend. As shown in Section 4.1, the clays exhibited a positive correlation with the intermediate fraction of the PBDEs and negative correlations with the light and heavy fractions. Similar trends were observed for SOC and for the fine particles. The $r^2$ values indicated that the influence of the clays on the patterns of the PBDE fractions in the CTP area was more important than the influence of SOC or of the fine particles. The different trends found for the correlation of SOC
and the fine particles with the three PBDE fractions allow a simplified discussion of the relationship between the clays and the PBDEs. The proportion of the intermediate fraction of the PBDEs increased as the content of the clays increased, whereas the proportions of the light and heavy fractions of the PBDEs decreased as the content of the clays increased.

### 4.3. Potential factors affecting correlation trend

Wang et al. (2010) suggested that the contaminants on the CTP originated primarily from the Indian subcontinent and were transported over the Himalayas by LRAT. To a lesser extent, these contaminants could also originate from local sources. This conclusion is consistent with our finding that the proportions of the light and intermediate fractions were dominant, with the heavy fraction occurring in proportions of less than 10% (Fig. 2). The heavy fraction, such as BDE-205, 206 and 209, could originate from local sources. The LRAT potentials (Wania and Dugani, 2003) of them determine that it is impossible for them to be transported over the Himalayas.

Fig. 9 shows the PBDEs percentage of three fractions, content of clay, and content of SOC in 16 samples. There is no special site showing abnormal values for soil properties or PBDEs. Nevertheless, the proportion of intermediate fraction of PBDEs is higher than that of light fraction at sites (T1–T16) near to the two biggest cities in Tibet, Lhasa and Shigatse. However, at other sites (T1–T16) a little far from two cities, the proportion of the intermediate fraction of PBDEs is lower than that of light fraction. It is reasonable that PBDEs were originated from the two cities and transported from valley to mountain by air. It is also reasonable that heavy PBDEs are difficult to be transported by air. As the result, intermediate fraction is higher than light fraction at sites near to city sources, and the proportion of heavy fraction is very small in all sites.

After clearing the sources, the physical and chemical properties of BDEs also affect their behaviors in soil. The smaller the PBDE, the more volatile and the more mobile it is. The larger the PBDE, the more transport mediated by sorption to particles (Wania and Westgate, 2008). Among larger BDE, intermediate PBDEs are apt to penetrate into soil and adsorbed by clays while heavy PBDEs are adsorbed by surface particles. Due to heavy windy flow, there are little clays in surface of soil.

Although more detailed research is required to reveal the relationship between the content of clays and the proportion of each fraction, the trends in the correlations between the clays and each fraction of the PBDEs could be determined in rudimentary form. The congeners of the intermediate fraction are apt to be adsorbed by fine particles (or clays) and penetrated in the soil. As a result, the content of clays showed a positive relationship with the proportion of the intermediate fraction of PBDEs. Because the light fraction tended to evaporate, it showed a negative relationship with the clays. The transport of the heavy fraction to far location by the air particles would appear to be difficult, and to be adsorbed by surface particles rather than clays. Accordingly, the heavy fraction also showed a negative relationship with the clays.

### 5. Conclusions

The occurrence of PBDEs on the CTP was investigated by determining the concentrations of 42 congeners. These congeners were divided into light, intermediate and heavy fractions. A regression analysis was applied to the relationship between the proportion of each PBDE fraction and selected soil properties. Of
these properties, the content of clays, the SOC and the proportion of particles of size <2 μm showed relatively good linear correlations with each fraction. The clays are positively correlated with the intermediate fraction of the PBDEs and negatively correlated with the light and heavy fractions. Similar trends were observed for the correlations with SOC and the fine-particle fraction <2 μm. These trends were well explained by the correlation between the three properties (clays, SOC and the fine-particle fraction). The coefficient of determination, $r^2$, indicated that the clays were relatively strongly correlated with the pattern of the PBDE fractions and that the SOC and the fine-particle fraction were less strongly correlated with this pattern. It was concluded that the impact of the clays on the pattern of PBDE fractions was greater than that of the other two factors. It is possible that the proportion of the intermediate fraction of the PBDEs increased as the content of clays increased and the proportions of the light and heavy fractions decreased as the content of clays increased because two potential sources of PBDEs were available and because physical and chemical properties affect behaviors of PBDEs in soil of the CTP area.

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Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.envpol.2012.07.011.

References


