Vertical distribution of PBDEs in farm soils irrigated by river wastewater

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Introduction

Polybrominated diphenyl ethers (PBDEs) are widely used as flame retardants in various products and once released; can be persistent in the environment, can travel over long distances, are able to bioaccumulate through the food web and are toxic. Intensive research has been conducted in recent years, but deficiencies still exist on the understanding of the environmental fate of this group of POPs. For example, the extent and significance of the soil compartment to act as a repository and/or sink to the global cycling of PBDEs is still unclear. In order to facilitate the assessment on regional and global fate of POPs, researchers have developed mathematical models based on experimentally derived physical-chemical properties and observed environmental behaviors of these chemicals. Most simple models assume a uniform distribution of POPs in the soil compartment, although more recent ones incorporate a concentration gradient through the vertical profile (Hollander et al., 2007). However, field studies on the depth distribution of PBDEs in soils are still scarce and research is thus warranted in order to validate model predictions. As most studies on the vertical distribution of POPs focus on undisturbed background areas such as montane forest soils (Moeckel et al., 2008), we were interested in how PBDEs behave in agricultural soils which is frequently disturbed by plowing at the surface.

Materials and Methods

Soil core samples (S1, S2, S3) were collected in Tongzhou district in Beijing, China where some farms utilize wastewater to irrigate their farmland. Custom built soil probes (1 m in length, 15 cm diameter) were used to collect soil cores at around 70 cm depth, and each soil core was sectioned into 2 or 4 cm layers. The actual length of each soil layer was estimated by correction for soil compression that occurred during the core probing. Determination of the PBDE analytes were based on an isotope dilution method modified from the US EPA 1614 protocol, and have been described in our previous works (e.g. Wang et al., 2007). Quantitative analysis for 13 PBDEs (BDE17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183 and 190) congeners was performed using a gas chromatograph coupled with high-resolution mass spectrometer (30 m column) with an electron impact (EI) ion source. Decabromodiphenyl ether (BDE209) was analyzed separately using an Agilent 7890A GC (15 m column) coupled with Agilent 7000A MS operated at EI mode. All samples were blank corrected and presented on a dry weight basis.

Results and Discussion

The general trend is that levels declined exponentially immediately after the plowed-subsoil interface (~20-30 cm), after which the concentrations remained somewhat constant at the lowest layers (Figure 1). Highest levels could be found for BDE209, which generally accounted >90% of the total PBDE levels and were in the range of 68.0-11400 pg/g dw for soil core S1, 274-18200 pg/g dw (S2) and

1330-64100 pg/g dw (S3). This corresponds well to the fact that DecaBDE is the most abundantly used technical PBDE mixture in China. The range for∑13BDEs (excl BDE209) were about one to two orders of magnitude lower and varied between 8.0-848 pg/g dw among the cores.

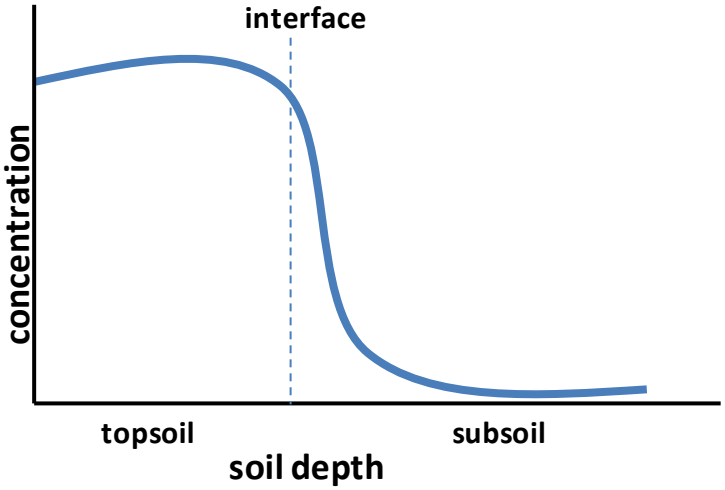

Figure 1. Illustration of general vertical trend for PBDE concentrations in farm soil.

Site S1 has not been irrigated by wastewater, and the levels were consequently also lower than soil cores at S2 and S3, indicating the wastewater river as a potential source for PBDE contamination. The most predominant congeners among the thirteen BDEs were BDE47, 99, 153 and 183, although not necessarily in the given order for the latter three congeners amongst the different cores.

No significant change in relative composition profile was observed between the different depths for all three soil cores. This was similar to the findings by Zou and coworkers (2007) which found a general decrease in PBDE levels with depth in agricultural soils sampled near the Pearl River Delta in southern China, and also found no significant change in composition pattern between the three crude soil layers (surface, subsurface and deep soil). This suggests that the depth distribution of PBDEs is not congener specific in the studied sites.

The levels of ∑13BDEs and BDE209 regressed quite well with the soil organic content (SOC). The coefficient of determination (R2) value was >0.8 for S3 suggesting strong correlation with %TOC. Strong correlation was also found for ∑13BDEs in S1, but was moderate for BDE209 (R2=0.5). Moderate correlations were also found at S2 for ∑13BDEs (R2=0.4) and BDE209 (R2=0.3). The results suggested that is soil organic content (SOC) is an important environmental factor for the vertical distribution of PBDEs in farm soil.

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