

Spatial Distribution of Old and Emerging Flame Retardants in Chinese Forest Soils: Sources, Trends and Processes.

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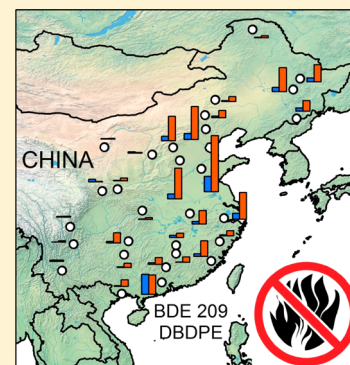
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S Supporting Information

ABSTRACT: The levels and distribution of polybrominated diphenylethers (PBDEs), novel brominated flame retardants (NBFRs) and Dechlorane Plus (DP) in soils and their dependence on environmental and anthropological factors were investigated in 159 soil samples from 30 background forested mountain sites across China. Decabromodiphenylethane (DBDPE) was the most abundant flame retardant (25–18 000 pg g⁻¹ and 5–13 000 pg g⁻¹ in O-horizon and A-horizon, respectively), followed by BDE 209 (nd-5900 pg g⁻¹ and nd-2400 pg g⁻¹ in O-horizon and A-horizon, respectively). FRs distributions were primarily controlled by source distribution. The distributions of most phasing-out PBDEs, DP isomers and TBPH were in fact correlated to a population density-based index used as proxy of areas with elevated usage and waste of FR containing products. High concentrations of some NBFRs were however observed in industrialized regions and FR manufacturing plants. Strongly positive correlations were observed between PBDEs and their replacement products suggesting similar emission pattern and environmental behavior. Exposure of mineral subsoils depended on precipitations driving leaching of FRs into the soil core. This was especially evident for some emerging BFRs (TBE, TBPH, and TBB etc.) possibly indicating potential for diffuse groundwater contamination.



1. INTRODUCTION

Flame retardants (FRs) are a class of chemicals used to reduce flammability in different kind of products. They are commonly added in construction materials, furniture, electronics, etc.¹ Brominated flame retardants (BFRs) and chlorinated flame retardants (CFRs) are among the most widely used.

BFRs are structurally heterogeneous.^{2,3} Among them, polybrominated diphenylethers (PBDEs) were historically marketed as three different commercial mixtures commonly referred to as penta-BDE, octa-BDE, and deca-BDE.¹ However, due to their persistence and bioaccumulative properties some tetra-BDE, penta-BDE, hexa-BDE, and octa-BDE were added to the list of banned Persistent Organic Pollutants (POPs) under the Stockholm Convention.⁴ Restrictions on the use of PBDE congeners have paved the way for the use of “novel” BFRs (NBFRs).^{5,6} Most commonly used NBFRs are 1,2-bis(pentabromodiphenyl)ethane (DBDPE), 1,2-bis(2,4,6-tribromophenoxy)ethane (TBE), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB), bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate (TBPH), hexabromobenzene (HBB), and pentabromoethylbenzene (PBEB).^{5,7} Despite the impelling demand for

avoiding compounds with POP characteristics, some NBFRs were shown to have potential for long-range atmospheric transport, persistence, and bioaccumulation.^{4,8,9}

Dechlorane plus (DP) belongs to the CFRs group and is common in electrical and electronic items such as wires and cables, as well as plastic roofing materials.^{10,11} DP has been shown to be bioavailable, bioaccumulative and potentially toxic.¹²

Soils represent a principal receptor and environmental reservoir for many persistent semivolatile organic contaminants.¹³ Forest soils, in particular have been pointed out as effective accumulators of several hydrophobic and persistent substances due to the forest canopy effect in enhancing atmospheric depositions, elevated soil organic carbon (OC) content (representing the bulk capacity for storing these contaminants), and relatively low level of disturbance, which

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could prevent remobilization.^{14–17} Research on soils as environmental reservoirs of semivolatile contaminants have mainly focused on legacy POPs.^{18,19} Forest soils may also be important reservoirs of airborne old and emerging FRs,^{20,21} and high persistence in soils has been described for some NBFRs (e.g., the half-lives of TBE and HBB in soil are reported to be 8600 h).²²

China has 134 million hectares of forested land including tropical, subtropical, temperate, and boreal biomes.²³ Main forested areas in China are prevalently far away from major conurbations and therefore possible primary sources. Contaminant levels and distribution in these soils can therefore be regarded as indicators of background environmental contamination expectedly reflecting the influence of major environmental drivers of distribution and distance from sources.²⁴ Meteorological conditions (temperature and precipitation patterns),²⁵ influence distribution of semivolatile contaminants over large geographical scales.²⁶ The large land area, climate variability, topographic complexity, ecosystem diversity, and expected elevated production, use and emissions of FRs make China an interesting case study and possibly an important region influencing global contamination and distribution pattern of these contaminants.²⁷

Research on NBFRs and DP have traditionally mainly focused on air, sediment, water, sewage sludge, and dust with very limited information on accumulation and levels in soils.^{5,8,28–31} The scope of this study was to (i) identify the levels and spatial distribution of target compounds in background forest soils along a range of environmental and anthropological gradients, (ii) explore colinearity between the distribution of the target compounds, and (iii) assess possible influences of environmental and geographical variables (namely: precipitation, altitude, soil OC content, and exposure to/distance from primary sources) on contaminant distribution.

2. EXPERIMENTAL SECTION

2.1. Monitoring Design. Thirty mountain sites across major accessible mountainous areas of China were chosen (shown in Supporting Information (SI) Figure S1). In each site 1–4 sampling locations were chosen along the same aspect on the altitudinal transect. In total, 159 forest-soil samples including O-horizon (77) and A-horizon (82) were collected at 82 locations between 16 May 2012 and 15 March 2013. Major transects included: latitude ranging from 21° to 53°; altitude ranging from 200 to 3800 m; the yearly mean temperature ranging from 6 to 21 °C and mean yearly precipitation ranging from 245 mm to 2129 mm. Georeferenced data sets of elevation, yearly mean temperature and precipitation (0.5' resolved) were obtained from WorldClim. Details on sampling location characteristics are presented in SI Table S2.

2.2. Sampling of Soil. In each sampling location, three small trenches located at about 5 m apart from each other were excavated. Vegetation litter was carefully removed and the soil layers were classified based on color and structure of the material present in each horizon. Samples from the O- (humus) and A- (topsoil) horizons were collected separately from each trench, folded in aluminum foil, placed in polyethylene zip-bags, cooled and transported to the laboratory. The samples were then freeze-dried and stored at –20 °C until chemical analysis began.

2.3. Chemical Analysis. In order to remove stones, each dry sample was sieved to exclude structures larger than 2 mm.

The samples were mixed by pooling together equivalent amounts of sample from the three trenches in order to create aggregated samples of the O-horizon and A-horizon (separately), reflecting average conditions of the sampling location. Sample extraction and preparation were consistent with those described in a previous study.³² Details are reported in the Supporting Information. Total organic carbon (TOC) in soil samples was determined with an elemental analyzer (CHNS Vario Ei III, Elementar) after removal of carbonates with HCl as described somewhere else.³³

2.4. QA/QC. Ten procedural blanks and 20 repeated analysis of an individual sample were included in the running list to assess potential laboratory derived contamination and ensure repeatability of analysis. The Instrument Detection Limit (IDL) ranged from 0.09 to 0.36 pg (injected) and Method Detection Limit (MDL) 1.1–28.6 pg g⁻¹, depending on substance (further details are reported in SI Text S1.2). 20 ng PCB 198 and PCB 209 recovery standards were added to each sample prior to extraction to monitor quantitative analysis performance. Obtained recoveries were respectively 82% ± 4.9% and 85% ± 3.7% (variance is expressed here as standard error). Results reported in the study are expressed on a dry weight basis (pg g⁻¹ dry wt) and not corrected for recovery results.

2.5. Atmospheric Back Trajectories Analysis and Index of Potential Source Influence. In a primary sources controlled scenario, FRs concentrations will be highest close to emission sources. Similarly to other parts of the world,³⁴ previous assessment of FRs (such as PBDEs) distribution in soils and other environmental compartments in China evidenced the existence of an urban-rural gradient with highly populated urban and industrial districts representing the areas with highest density atmospheric sources.^{35,36} In China, industrial and major urban clusters closely overlap.³⁷ For this reason population count is an adequate proxy for describing potential sources from FRs usage, wasting and manufacturing. A few important industrial plants manufacturing or processing NBFR can however be also found in areas with intermediate population density. In order to track the possible influence of use/related primary sources from high density urban areas on background soil contamination, air mass back trajectories (BT) and a numerical index of potential source influence (IPSI) in the regional domain were computed. We elaborated the concept of IPSI in a previous paper³⁸ (details are also reported in SI Text S2 of the present paper). In short, IPSI combines data on population density distribution (as proxy of source distribution) and BT density calculated for each sampling location considering a full year of simulations (twice a day). BT density is used by IPSI to weigh the influence of potential sources in a given area for an individual sampling location based on how often this area was upwind of the sampling point.

3. RESULTS AND DISCUSSION

3.1. Summary of FRs Concentration Results. All 16 selected compounds were analyzed in all the samples. SI Table S3 reports data of individual compounds in the O-horizon and A-horizon. The concentrations of target compounds in O-horizon were generally higher than those in A-horizon by an average factor of 5.4, possibly reflecting the more direct exposure to atmospheric deposition of the superficial O-horizon. (SI Table S3 reports details of soil characteristics).

The mean concentrations of the total PBDEs (\sum_8 PBDEs) in the O- and A-horizon samples were 920 pg g⁻¹ (3–6300 pg

g^{-1}) and 220 pg g^{-1} (not detected– 2500 pg g^{-1}), respectively. As expected from previous results, BDE 209 was the most abundant PBDE congener in these samples,^{33,39} accounting for more than 60% of \sum_8 PBDEs, followed by BDE 47 and BDE 99. The concentrations of BDE 209 were in the range of nd– 5900 pg g^{-1} and nd– 2400 pg g^{-1} in O and A-horizon, respectively. These values are much lower than those reported for agricultural soils in southern China (39.8 – 95.2 ng g^{-1})⁴⁰ and soils in proximity of e-waste recycling areas (28.8 – 468 ng g^{-1}).⁴¹ They are nevertheless much higher than forest soil concentrations measured in Sweden (15 – 750 pg g^{-1}).⁴² Such elevated values can be linked to the higher consumption of PBDEs in China ($30\,000 \text{ t}$ in 2005) which experienced a sharp increase during last several years.⁴³ The concentrations of other PBDEs (\sum_7 PBDEs excluding deca-BDE) in O- and A-horizon were 3 – 800 pg g^{-1} and nd– 320 pg g^{-1} , respectively. \sum_7 PBDEs in A-horizon was comparable to that observed in other locations in background soils, including Kuwait (24.7 – 296 pg g^{-1}),³⁴ UK (73.5 – 285 pg g^{-1}),⁴⁴ and Brazil (434 pg g^{-1}),³⁹ somehow lower compared to that found in mountain soils in Italy ($710 \pm 830 \text{ pg g}^{-1}$),⁴⁵ however higher than that in the Tibetan Plateau soils.^{20,21}

NBFRs and DP data sets of the soil compartment are very limited. DBDPE was the FR with the highest concentrations measured in this study. It ranged 25 – $18\,000 \text{ pg g}^{-1}$ (mean 2643 pg g^{-1}) and 5 – $13\,000 \text{ pg g}^{-1}$ (mean 660 pg g^{-1}) in O- and A-horizon, respectively. The present data are lower than data reported for agricultural soils in southern China (28.1 ng g^{-1}).⁴⁰ DBDPE predominance in environmental samples was also previously shown in air samples at a rural site of China.³⁶ Such a behavior can be related to the large success of this product in the market. DBDPE market is currently increasing at a yearly rate of 80% in China.⁵ Some studies however have reported DBDPE concentrations lower than BDE 209 in sewage sludge samples in Europe^{2,16} and air samples in Chinese e-waste area.³⁶ This discrepancy might be attributed to several factors including regional and temporal variability in FR usage and emissions and type of samples.

The remaining set of NBFRs was present at generally lower concentrations. TBB: nd– 1400 pg g^{-1} (mean 250.5 pg g^{-1}) and nd– 1600 pg g^{-1} (mean 184.0 pg g^{-1}), TBPH: 4.0 – 643.7 pg g^{-1} (mean 131.7 pg g^{-1}) and 5.5 – 526.4 pg g^{-1} (mean 68.9 pg g^{-1}), TBE: nd– 330 pg g^{-1} (mean 48.5 pg g^{-1}) and nd– 240 pg g^{-1} (mean 22.9 pg g^{-1}), HBB: nd– 340 pg g^{-1} (mean 46.0 pg g^{-1}) and nd– 42 pg g^{-1} (mean 7.2 pg g^{-1}), and PBEB showed the lowest concentrations in the range of nd– 92 pg g^{-1} (mean 6.8 pg g^{-1}) and nd– 70 pg g^{-1} (mean 9.0 pg g^{-1}) in O-horizon and A-horizon, respectively. The detection frequencies varied among different compounds (details are given in SI Table S3).

Both *anti*-isomer and *syn*-isomer of DP were detected in 100% of the samples, demonstrating the currently broad distribution of this FRs in the Chinese markets. The concentrations of *anti*-isomer and *syn*-isomer were 5 – 680 pg g^{-1} and 4 – 390 pg g^{-1} in O-horizon and 3 – 220 pg g^{-1} and 2 – 170 pg g^{-1} in A-horizon, respectively. Concentrations measured in the selected forest soils were lower than those previously measured in urban, rural, and remote surface soils of Northern China (nd– 8.45 ng g^{-1} and nd– 3.76 ng g^{-1} for *anti*-DP and *syn*-DP, respectively).²⁸

3.2. Spatial Trends in Superficial Soils. High spatial variability of FR concentrations was observed during this survey. For DBDPE, the differences between the highest and lowest concentrations were up to a factor of 2300. In contrast,

PBEB and the major components of PBDE congeners (i.e., BDE 28, BDE 153, and BDE 183) showed a considerably lower variability, due to the lower usage volume or possibly current regulation. Figure 1 shows the spatial variations of target

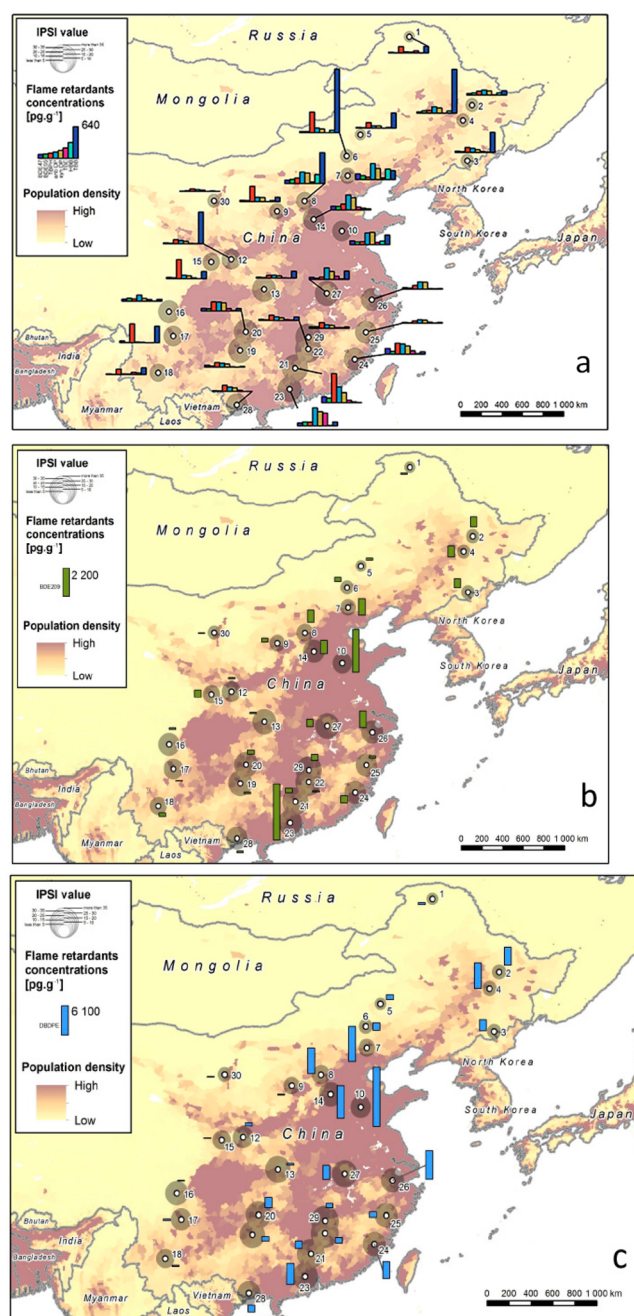


Figure 1. Spatial distribution of selected FRs in organic (O-horizon) soil samples. (a: BDE47, BDE99, *anti*-DP, *syn*-DP, TBPH, TBB, HBB and TBE; b: BDE 209; c: DBDPE).

compounds in O-horizons. Overall, high levels of many FRs were mainly found in the Southeast China. For instance, the highest average concentrations of BDE 47, BDE 99, and TBPH were measured in site 21; whereas, *anti*-DP, *syn*-DP, BDE 209, and TBE showed peaking concentrations in site 23. Sites 21 and 23 are both in the Guangdong province, already reported as one of the important e-waste recycling and the most urbanized/industrialized regions in South China.^{36,41,46} Some

interesting and informative outliers were found too. DBDPE displayed the highest average concentration in site 10 (Figure 1c) in Shandong Province, due to important DBDPE production facilities are located in this area,^{5,8} while two outliers for TBB and HBB were located in site 6 and 7 (Figure 1a) in Hebei province, also an important industrial area. In China, 600 tons/year of HBB are produced in Shandong province,⁵ and as expected high concentration could be found in site 10. Unfortunately, there is no production or usage information publically disclosed for TBB.^{5,8} As far as we know, TBB combined with TBPH was used in Firemaster BZ-54, Firemaster 550 (in a 4:1 ratio) and DP-45 (91% TBPH together with 2–6% TBB by weight).⁴⁷ The ratios of TBB to TBPH in samples in Northern China averaged 5.2 (in contrast with diagnostic ratios observed in the Southern part averaging 0.55), indicating different sources or fate in these subregions as well as the northern samples probably been more affected by proximity to manufacture related sources. The high consumption of Firemaster 550 in Northern China, especially in Hebei province appears to be related to the peculiar type of manufacturing district present here which includes oil, coal, metallurgical, mechanical, and electronics industry. The considerably lower ratio value found in Southern China suggests that manufacturers in this area may have used different FR formulations (such as DP-45, neoprene and polyvinyl chloride (PVC)³¹) with a relatively higher level of TBPH. Moreover, TBB has been reported to be more vulnerable to photodegradation with a half-life twice shorter than TBPH.^{47,48} Warmer climate and higher solar radiation in Southern China might accelerate degradation and result in lower ratios observed in the soils of this region. In general, the presence of these outliers highlights the strong influence of local production point sources for the exposure of background mountain soils. These data indicate that the current emission control measures applied during industrial production and processing in China may be insufficient to prevent off-site exposure to FRs at the subregional level.

In summary, spatial distribution of flame retardants in background soils in China appears to be dependent on source distribution and sensitive to the typology of sources (e.g., e-waste facilities and manufacturing facilities as well as highly populated areas where the majority of FR containing products are used).⁴⁹

In order to provide a more quantitative assessment of this hypothesis, we statistically explored the interaction between concentrations of FRs in the O-horizon and the results for IPSI. IPSI values for different sampling sites ranged between 1 and 37 following a slightly negatively skewed distribution, with most frequently observed values around 25 (Figure 1). Consistently, the highest IPSI values are observed in the Southeast (in particular sites 21–23). Most of the target compounds in the O-horizon showed high levels in locations with a high IPSI. Nearly all the FRs (with the exception of PBEB, HBB, and TBB) showed positive correlation with IPSI with correlation coefficients (Spearman) typically ranging between 0.1 and 0.5 (with exception of BDE 28: $r = 0.08$ and BDE 209: $r = 0.06$) (SI Table S6). These relationships were statistically significant ($p < 0.05$) for most of the PBDE congeners (BDE 47, BDE 100, BDE 153, BDE 154, and BDE 183), DP-isomers and TBPH (Figure 2 and SI Table S6a). We can only speculate on the reasons behind the higher sensitivity of these PBDEs on use-related source distribution, compared to other FR which did not display a clear dependence on IPSI. From a regulatory

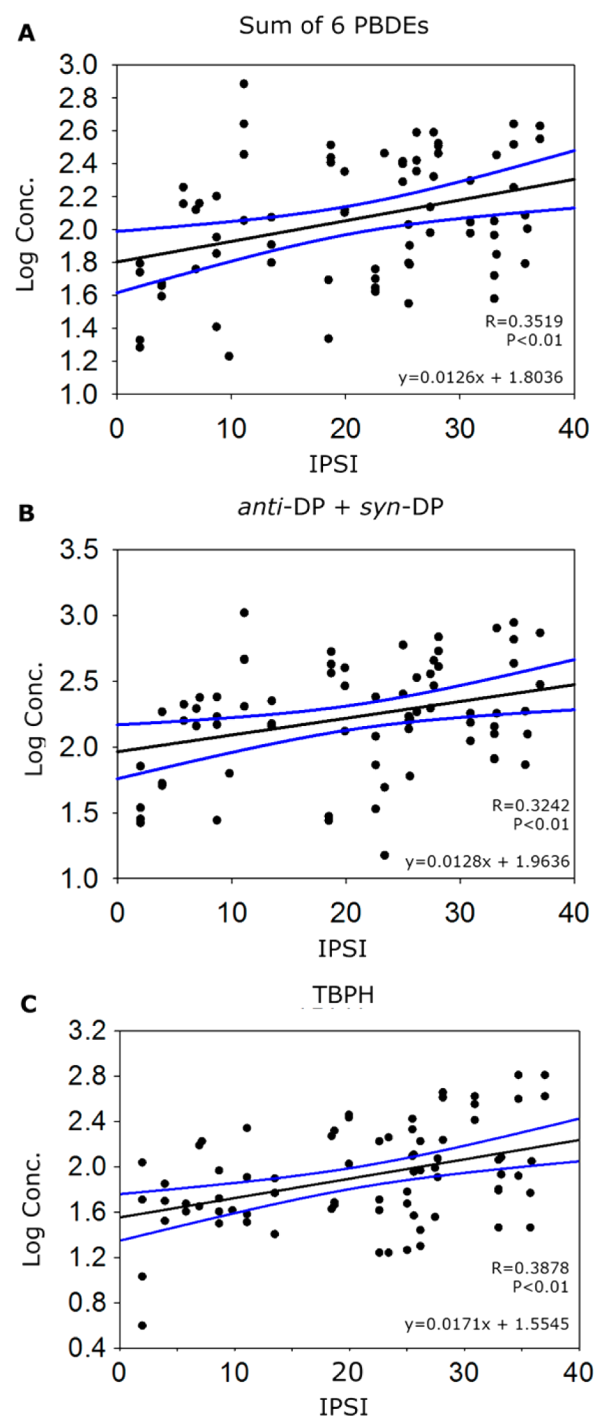


Figure 2. Correlation between selected FR concentrations and IPSI values.

point of view, penta-BDE and octa-BDE technical mixtures are currently undergoing phasing out, therefore primary emissions are continuing mostly from consumer products still in use or inadequate waste management. These types of sources are obviously associated with the use of FR rather than manufacturing. Hence use-related sources are a function of population density which in turn is a key for IPSI calculation. In contrast, BDE 209 is still produced and largely used in China. Similarly to emerging FRs, emissions from production and processing plants is expected to lower the dependence on IPSI. As an example, the extremely high level of BDE 209 observed at

site 10 (Shandong province, in spite of the relatively low IPSI score) is likely associated with the documented presence of production plants in this area.⁵⁰ As for DPs and TBPH (displaying dependence on IPSI), may already follow a consolidated distribution in the market and their usage- and disposal-related sources. In contrast, the distribution of some more abundant NBFRs in soils appeared to be influenced by production plant/processing location and did not display dependence on IPSI. This trend is in general agreement with previous studies that had shown that the signal of FR sources from manufacturing locations can be detected in air and other media on the local scale range.^{8,51} The present results expand this paradigm showing that emission point sources can possibly affect soil concentrations even at subregional level.

3.3. Co-Linearity between Compound Distributions.

The large-scale data set of both discontinued and current use flame retardants presented here provides a unique opportunity to explore how market shifts may have affected environmental levels and distribution patterns. For example a mixture of TBPH and TBB, TBE and DBDPE are used as alternatives for penta-BDE, octa-BDE, and deca-BDE formulation, respectively.^{5,7,31,52,53} Hence, a spatial distribution pattern with PBDEs levels being negatively correlated to NBFR levels could be hypothesized as a result of growing emissions of NBFR and simultaneously declining emissions and ongoing degradation of the environmental burden of PBDEs. In contrast to this hypothesis, levels of PBDEs and NBFRs were strongly positively correlated, suggesting similar drivers controlling their spatial distribution. A summary of the correlation analysis results are reported in SI Table S4. Significantly positive relationships between BDE 209 and DBDPE were observed in both O- and A-horizon, such a behavior was previously observed by Ma et al. in the Great Lakes atmosphere.⁷ Similarly, BDE 183 and TBE (TBE being a replacement for octa-BDE) were strongly positively correlated in both O- and A- soil horizons (SI Table S4). TBPH was significantly correlated to the penta-BDE mixtures (sum of BDE 47, 99, 100, 153, and 154) in both O- and A-horizons, despite this novel FR is used as a substitute of banned PBDEs. This result indicates that emission patterns and environmental behavior of old and emerging FRs are, to a certain extent, similar. In addition, there is evidence here that the reduced emissions of PBDEs following the international ban are not yet reflected in background soil samples over the large spatial scale. Kawai et al. proposed half-lives of brominated organic compounds in soil (e.g., BDE 35 and BDE 99 in the order of 17 000 and 55 000 h, respectively).⁵⁴ These values reflect the elevated persistence of PBDEs in soil. Hence it is unlikely that management actions to reduce emissions can be reflected in changes of soil contamination in the short term. In addition, the observed correlation between the behavior of old and emerging flame retardants shed (at least from the environmental exposure point of view) a critical light on the effectiveness of the substitution strategy adopted in recent years by the FRs industry.

TBB and TBPH distribution were negatively correlated in soil samples despite these substances are used together (yet with varying proportions) in FR commercial formulations. The ratio of $c_{\text{TBB}}/c_{\text{(TBPH+TBB)}}$ in these soil samples ranged from 0 to 0.97 (mean 0.48) and 0 to 0.99 (mean 0.45) in O-horizon and A-horizon respectively (shown in SI Table S5). A wide range of $c_{\text{TBB}}/c_{\text{TBPH}}$ (0.05–50) was also previously reported in another study focusing on the analysis of dust samples.³¹ Differences in sources (e.g., commercial formulations) and physical chemical

properties controlling environmental fate of the different ingredients have to be considered among the most likely causes, as also discussed in section 3.2 of this paper.

In spite of the great variation in DP levels across different forest sites, *anti*- and *syn*-isomers showed extremely strong relationship ($R^2 = 0.96$, $p < 0.01$ and $R^2 = 0.92$, $p < 0.01$ in O-horizon and A-horizon, respectively) (SI Figure S2). This is consistent with other reports focusing on different matrices (e.g., soil of Huai'an City ($R^2 = 0.98$)⁵⁵ and ambient air around Shanghai ($R^2 = 0.93$).⁵⁶ The ratio between *anti*- or *syn*- isomer has widely been used as a proxy of remoteness (in space and time) of the contamination following their different environmental behavior.^{55,56} In this study, f_{anti} is defined as the ratio of $c_{\text{anti-DP}}/c_{\text{(anti-DP+syn-DP)}}$ (SI Table S5). f_{anti} ranged 0.43 to 0.72 (mean 0.56) in O-horizon and 0.41 to 0.79 (mean 0.58) in A-horizon. Possibly because of the large spatial scale covered in our survey, these ranges are larger and their mean values are lower than those reported by Wang et al. (0.67–0.85),⁵⁵ Hoh et al.⁵⁷ and Qiu et al. (0.75–0.80),^{57,58} but similar to those reported in a case study in Lake Ontario (0.53).⁵⁹ Lower f_{anti} values (<0.5) were also observed in Great Lakes air and sediment samples, which were collected in distal sites from production facilities.⁵⁷ The forested sites selected in the present study are classified as semiremote areas. f_{anti} values lower than 0.5 measured here can also be discussed as a result of different environmental behavior of the two isomers (including stereoselective degradation) and remoteness from sources.

3.4. Influence of Environmental Parameters. Biogeochemical Control. The spatial trends of FRs in the A-horizons were often poorly consistent with those observed in O-horizons. The O-horizon is directly exposed to atmospheric depositions, while the presence of flame retardants in the “aged” A-horizon has to be related to the effects of a range of processes driving to their downward vertical transport in the soil column. These processes, in particular, are water driven leaching, vertical diffusion and, up to a minor extent, bioturbation. The generally higher measured levels and detection frequency of TBE (66%) in A-horizon compared to its “predecessor” BDE 183 (29%) suggested that mobility in soils might be significantly higher for TBE. Levels of TBE and other NBFRs (TBPH and TBB, etc. (SI Table S3)) in the A-horizon were in some cases similar to those observed in the O-horizon, confirming rapid vertical translocation of these contaminants in soils. In soil ecotoxicology, the concepts of mobility and “availability” (including bioavailability) are strictly related.⁶⁰ High leaching rates are also associated with higher potential for groundwater contamination. The fact that many NBFRs are found in mineral soils at similar levels as observed in superficial soil, after relatively short time from their introduction is of some concern. Interestingly, NBFRs were more frequently detected in the A-horizon of forested sites of the subtropical part of China, where precipitation is more intense and turnover of organic matter in O-horizon is faster. In conclusion, the climatic and ecological conditions of this region may configure an increased risk for leaching.⁶¹

Total Organic Carbon (TOC) in Soil. Soil OC is a key parameter controlling distribution of hydrophobic persistent contaminants (including POPs) at the global scale. The relationship between concentration of POPs and soil OC is underpinned by the large affinity of these compounds to the organic matter and their persistence.^{24,38,62} In contrast, the present assessment shows that among the PBDE congeners only BDE 47 had a significantly positive correlation with soil

OC in both O- and A-horizon (SI Table S6). Only PBEB was significantly and positively correlated with OC in A-horizon. Some compounds were negatively related to OC either in O-horizon or A-horizon (TBE in O-horizon ($r = -0.14$; $p > 0.05$); BDE 183 in A-horizon ($r = -0.05$; $p > 0.05$)). These negative correlations have to be regarded as spurious and essentially due to the contingent inverse (nonsignificant) relationship between source distribution (as described by IPSI) and soil TOC.

The majority of the target compounds did not display any dependence on TOC. This is an important result supporting the hypothesis that source distribution (rather than environmental factors) is pivotal for controlling distribution of both “old” and novel FRs in background soils.

Precipitation, Temperature and Latitude. Precipitation and temperature influence deposition, degradation and reemission processes of many POPs,²⁵ possibly resulting in a general dependence of concentration (or pattern) on latitude.⁶³ In the O-horizon, more than 80% of the FRs did not display any dependence on precipitation and latitude (SI Table S6a). The situation was totally different in the A-horizon in which 75% of contaminants had significant positive correlations with precipitation and negative correlations with latitude (SI Table S6b). Heavy precipitation in Southern China accelerates leaching, enhancing exposure of mineral soil layers in this region. Negative correlations between environmental levels and latitude in A-horizon (SI Table S6b) have therefore simply to be interpreted as the result of the influence of areas with higher source density in the rainy Southern China, as described above. Similarly, spurious correlations between the levels of many compounds and temperature were observed in both O- and A-horizon owing to colinearity between source distribution and temperature.

The present study highlighted the importance of source location in controlling distribution of both old and emerging FRs in soils of background mountain environments across a large regional scale. The contribution of local sources dominated over the possible influence of environmental factors and soil biogeochemical processes affecting contaminants fate. The only exception is the exposure of mineral subsoils that appeared to be controlled by the amount of precipitation. Colinearity between the distribution of PBDEs and NBFRs (used as their substitute) suggests still high emission of phasing-out substances and similar environmental behavior of phasing-in ones.

■ ASSOCIATED CONTENT

■ Supporting Information

Details on chemical analysis methodology, the full experimental data set of concentrations and environmental/anthropogenic variables and results of statistical analysis are reported. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Stapleton, H. M.; Misenheimer, J.; Hoffman, K.; Webster, T. F. Flame retardant associations between children’s handwipes and house dust. *Chemosphere* **2014**, *116*, 54–60.
- (2) Gorga, M.; Martinez, E.; Ginebreda, A.; Eljarrat, E.; Barcelo, D. Determination of PBDEs, HBB, PBEB, DBDPE, HBCD, TBBPA and related compounds in sewage sludge from Catalonia (Spain). *Sci. Total Environ.* **2013**, *444*, 51–59.
- (3) WHO (1997) *Environmental Health Criteria; Flame Retardants: A General Introduction*; World Health Organization: Geneva, Switzerland, <http://www.inchem.org/documents/ehc/ehc/ehc192.htm>.
- (4) Ma, Y.; Venier, M.; Hites, R. A. 2-Ethylhexyl tetrabromobenzoate and bis(2-ethylhexyl) tetrabromophthalate flame retardants in the Great Lakes atmosphere. *Environ. Sci. Technol.* **2012**, *46* (1), 204–208.
- (5) Covaci, A.; Harrad, S.; Abdallah, M. A. E.; Ali, N.; Law, R. J.; Herzke, D.; de Wit, C. A. Novel brominated flame retardants: A review of their analysis, environmental fate and behaviour. *Environ. Int.* **2011**, *37* (2), 532–556.
- (6) Betts, K. New flame retardants detected in indoor and outdoor environments. *Environ. Sci. Technol.* **2008**, *42* (18), 6778–6778.
- (7) Ma, Y.; Salamova, A.; Venier, M.; Hites, R. A. Has the phase-out of PBDEs affected their atmospheric levels? Trends of PBDEs and their replacements in the Great Lakes atmosphere. *Environ. Sci. Technol.* **2013**, *47* (20), 11457–11464.
- (8) de Wit, C.; Kierkegaard, A.; Ricklund, N.; Sellström, U. Emerging brominated flame retardants in the environment. In *Brominated Flame Retardants*; Springer: Berlin Heidelberg, 2010; pp 241–286.
- (9) de Wit, C. A. An overview of brominated flame retardants in the environment. *Chemosphere* **2002**, *46* (5), 583–624.
- (10) Xiang, N.; Chen, L.; Meng, X.-Z.; Li, Y.-L.; Liu, Z.; Wu, B.; Dai, L.; Dai, X. Polybrominated diphenyl ethers (PBDEs) and dechlorane plus (DP) in a conventional wastewater treatment plant (WWTP) in Shanghai: Seasonal variations and potential sources. *Sci. Total Environ.* **2014**, *487*, 342–349.
- (11) Sverko, E.; Tomy, G. T.; Reiner, E. J.; Li, Y.-F.; McCarty, B. E.; Arnot, J. A.; Law, R. J.; Hites, R. A. Dechlorane Plus and related compounds in the environment: A review. *Environ. Sci. Technol.* **2011**, *45* (12), 5088–5098.
- (12) Yu, Z.; Lu, S.; Gao, S.; Wang, J.; Li, H.; Zeng, X.; Sheng, G.; Fu, J. Levels and isomer profiles of Dechlorane Plus in the surface soils from e-waste recycling areas and industrial areas in South China. *Environ. Pollut.* **2010**, *158* (9), 2920–2925.
- (13) Wang, Y.; Cheng, Z.; Li, J.; Luo, C.; Xu, Y.; Li, Q.; Liu, X.; Zhang, G. Polychlorinated naphthalenes (PCNs) in the surface soils of the Pearl River Delta, South China: Distribution, sources, and air-soil exchange. *Environ. Pollut.* **2012**, *170*, 1–7.
- (14) Moeckel, C.; Nizzetto, L.; Strandberg, B.; Lindroth, A.; Jones, K. C. Air-boreal forest transfer and processing of polychlorinated biphenyls. *Environ. Sci. Technol.* **2009**, *43* (14), 5282–5289.
- (15) Nizzetto, L.; Cassani, C.; Di Guardo, A. Deposition of PCBs in mountains: The forest filter effect of different forest ecosystem types. *Ecotoxicol. Environ. Saf.* **2006**, *63* (1), 75–83.

- (16) Su, Y. S.; Wania, F. Does the forest filter effect prevent semivolatile organic compounds from reaching the Arctic? *Environ. Sci. Technol.* **2005**, *39* (18), 7185–7193.
- (17) Wania, F.; Mackay, D. Global fractionation and cold condensation of low volatility organochlorine compounds in polar-regions. *Ambio* **1993**, *22* (1), 10–18.
- (18) Bergknut, M.; Wiberg, K.; Klaminder, J. Vertical and lateral redistribution of POPs in soils developed along a hydrological gradient. *Environ. Sci. Technol.* **2011**, *45* (24), 10378–10384.
- (19) Aichner, B.; Bussian, B.; Lehnik-Habrink, P.; Hein, S. Levels and spatial distribution of persistent organic pollutants in the environment: A case study of German forest soils. *Environ. Sci. Technol.* **2013**, *47* (22), 12703–12714.
- (20) Yuan, G.-L.; Xie, W.; Che, X.-C.; Han, P.; Liu, C.; Wang, G.-H. The fractional patterns of polybrominated diphenyl ethers in the soil of the central Tibetan Plateau, China: The influence of soil components. *Environ. Pollut.* **2012**, *170*, 183–189.
- (21) Zheng, X.; Liu, X.; Jiang, G.; Wang, Y.; Zhang, Q.; Cai, Y.; Cong, Z. Distribution of PCBs and PBDEs in soils along the altitudinal gradients of Balang Mountain, the east edge of the Tibetan Plateau. *Environ. Pollut.* **2012**, *161*, 101–106.
- (22) Xiao, H.; Shen, L.; Su, Y.; Barresi, E.; DeJong, M.; Hung, H.; Lei, Y.-D.; Wania, F.; Reiner, E. J.; Sverko, E.; Kang, S.-C. Atmospheric concentrations of halogenated flame retardants at two remote locations: The Canadian High Arctic and the Tibetan Plateau. *Environ. Pollut.* **2012**, *161*, 154–161.
- (23) Fang, J. Y.; Chen, A. P.; Peng, C. H.; Zhao, S. Q.; Ci, L. Changes in forest biomass carbon storage in China between 1949 and 1998. *Science* **2001**, *292* (5525), 2320–2322.
- (24) Meijer, S. N.; Ockenden, W. A.; Sweetman, A.; Breivik, K.; Grimalt, J. O.; Jones, K. C. Global distribution and budget of PCBs and HCB in background surface soils: Implications or sources and environmental processes. *Environ. Sci. Technol.* **2003**, *37* (4), 667–672.
- (25) Xu, Y.; Tian, C.; Zhang, G.; Ming, L.; Wang, Y.; Chen, Y.; Tang, J.; Li, J.; Luo, C. Influence of monsoon system on α -HCH fate in Asia: A model study from 1948 to 2008. *Journal of Geophys. Res.: Atmos.* **2013**, *118* (12), 6764–6770.
- (26) Kirchner, M.; Faus-Kessler, T.; Jakobi, G.; Levy, W.; Henkelmann, B.; Bernhoeft, S.; Kotalik, J.; Zsolnay, A.; Bassan, R.; Belis, C.; Kraeuchi, N.; Moche, W.; Simoncic, P.; Uhl, M.; Weiss, P.; Schramm, K. W. Vertical distribution of organochlorine pesticides in humus along Alpine altitudinal profiles in relation to ambient parameters. *Environ. Pollut.* **2009**, *157* (12), 3238–3247.
- (27) Jiang, H.; Apps, M. J.; Zhang, Y. L.; Peng, C. H.; Woodard, P. M. Modelling the spatial pattern of net primary productivity in Chinese forests. *Ecol. Modell.* **1999**, *122* (3), 275–288.
- (28) Ma, J.; Qiu, X.; Liu, D.; Zhao, Y.; Yang, Q.; Fang, D. Dechlorane Plus in surface soil of North China: Levels, isomer profiles, and spatial distribution. *Environ. Sci. Pollut. Res. Int.* **2014**, *21* (14), 8870–7.
- (29) Hoh, E.; Hites, R. A. Brominated flame retardants in the atmosphere of the east-central United States. *Environ. Sci. Technol.* **2005**, *39* (20), 7794–7802.
- (30) Gouteux, B.; Alae, M.; Mabury, S. A.; Pacepavicius, G.; Muir, D. C. G. Polymeric brominated flame Retardants: Are they a relevant source of emerging brominated aromatic compounds in the environment? *Environ. Sci. Technol.* **2008**, *42* (24), 9039–9044.
- (31) Stapleton, H. M.; Allen, J. G.; Kelly, S. M.; Konstantinov, A.; Klosterhaus, S.; Watkins, D.; McClean, M. D.; Webster, T. F. Alternate and new brominated flame retardants detected in U.S. house dust. *Environ. Sci. Technol.* **2008**, *42* (18), 6910–6916.
- (32) Wang, Y.; Luo, C.; Li, J.; Yin, H.; Zhang, G. Influence of plants on the distribution and composition of PBDEs in soils of an e-waste dismantling area: Evidence of the effect of the rhizosphere and selective bioaccumulation. *Environ. Pollut.* **2014**, *186*, 104–109.
- (33) Mai, B. X.; Chen, S. J.; Luo, X. J.; Chen, L. G.; Yang, Q. S.; Sheng, G. Y.; Peng, P. G.; Fu, J. M.; Zeng, E. Y. Distribution of polybrominated diphenyl ethers in sediments of the Pearl River Delta and adjacent South China Sea. *Environ. Sci. Technol.* **2005**, *39* (10), 3521–3527.
- (34) Gevao, B.; Ghadban, A. N.; Uddin, S.; Jaward, F. M.; Bahloul, M.; Zafar, J. Polybrominated diphenyl ethers (PBDEs) in soils along a rural-urban-rural transect: Sources, concentration gradients, and profiles. *Environ. Pollut.* **2011**, *159* (12), 3666–3672.
- (35) Jaward, T. M.; Zhang, G.; Nam, J. J.; Sweetman, A. J.; Obbard, J. P.; Kobara, Y.; Jones, K. C. Passive air sampling of polychlorinated biphenyls, organochlorine compounds, and polybrominated diphenyl ethers across Asia. *Environ. Sci. Technol.* **2005**, *39* (22), 8638–8645.
- (36) Tian, M.; Chen, S.-J.; Wang, J.; Zheng, X.-B.; Luo, X.-J.; Mai, B.-X. Brominated flame retardants in the atmosphere of e-waste and rural sites in southern China: Seasonal variation, temperature dependence, and gas-particle partitioning. *Environ. Sci. Technol.* **2011**, *45* (20), 8819–8825.
- (37) Xing, X.; Lu, Y. L.; Dawson, R. W.; Shi, Y. J.; Zhang, H.; Wang, T. Y.; Liu, W. B.; Ren, H. C. A spatial temporal assessment of pollution from PCBs in China. *Chemosphere* **2005**, *60* (6), 731–739.
- (38) Zheng, Q.; Nizzetto, L.; Mulder, M. D.; Ondřej, Sáníka; Lammel, G.; Li, J.; Bing, H.; Liu, X.; Jiang, Y.; Luo, C.; Zhang, G. Does an analysis of polychlorinated biphenyl (PCB) distribution in mountain soils across China reveal a latitudinal fractionation paradox? *Environ. Pollut.* **2014**, *195*, 115–122.
- (39) Thorenz, U. R.; Bandowe, B. A. M.; Sobocka, J.; Wilcke, W. Method optimization to measure polybrominated diphenyl ether (PBDE) concentrations in soils of Bratislava, Slovakia. *Environ. Pollut.* **2010**, *158* (6), 2208–2217.
- (40) Shi, T.; Chen, S.-J.; Luo, X.-J.; Zhang, X.-L.; Tang, C.-M.; Luo, Y.; Ma, Y.-J.; Wu, J.-P.; Peng, X.-Z.; Mai, B.-X. Occurrence of brominated flame retardants other than polybrominated diphenyl ethers in environmental and biota samples from southern China. *Chemosphere* **2009**, *74* (7), 910–916.
- (41) Cheng, Z.; Wang, Y.; Wang, S.; Luo, C.; Li, J.; Chaemfa, C.; Jiang, H.; Zhang, G. The influence of land use on the concentration and vertical distribution of PBDEs in soils of an e-waste recycling region of South China. *Environ. Pollut.* **2014**, *191*, 126–31.
- (42) Ejarrat, E.; Marsh, G.; Labandeira, A.; Barcelo, D. Effect of sewage sludges contaminated with polybrominated diphenylethers on agricultural soils. *Chemosphere* **2008**, *71* (6), 1079–1086.
- (43) Zou, M.-Y.; Ran, Y.; Gong, J.; Maw, B.-X.; Zeng, E. Y. Polybrominated diphenyl ethers in watershed soils of the Pearl River Delta, China: Occurrence, inventory, and fate. *Environ. Sci. Technol.* **2007**, *41* (24), 8262–8267.
- (44) Harrad, S.; Hunter, S. Concentrations of polybrominated diphenyl ethers in air and soil on a rural-urban transect across a major UK conurbation. *Environ. Sci. Technol.* **2006**, *40* (15), 4548–4553.
- (45) Parolini, M.; Guazzoni, N.; Binelli, A.; Tremolada, P. Polybrominated diphenyl ether contamination in soil, vegetation, and cow milk from a high-mountain pasture in the Italian Alps. *Arch. Environ. Contam. Toxicol.* **2012**, *63* (1), 29–44.
- (46) Wang, Y.; Jiang, G.; Lam, P. K. S.; Li, A. Polybrominated diphenyl ether in the East Asian environment: A critical review. *Environ. Int.* **2007**, *33* (7), 963–973.
- (47) La Guardia, M. J.; Hale, R. C.; Harvey, E.; Mainor, T. M.; Ciparis, S. In situ accumulation of HBCD, PBDEs, and several alternative flame-retardants in the bivalve (*Corbicula fluminea*) and gastropod (*Elimia proxima*). *Environ. Sci. Technol.* **2012**, *46* (11), 5798–5805.
- (48) Davis, E. F.; Stapleton, H. M. Photodegradation pathways of nonabrominated diphenyl ethers, 2-ethylhexyltetrabromobenzoate and di(2-ethylhexyl)tetrabromophthalate: Identifying potential markers of photodegradation. *Environ. Sci. Technol.* **2009**, *43* (15), 5739–5746.
- (49) She, J.; She, Y.; Song, W. Comparison of PBDE congener profiles and concentration levels in human specimens from China and the US and identification of human exposure sources. *Sci. China-Chem.* **2010**, *53* (5), 995–1002.
- (50) XUE Zheng-ran, L. H.-j. The productive mechanism and technology research of new highly efficiency flame retardant of decabromodiphehyl ether. *Shandong Chem. Ind.* **2002**, *04*, 31–32.

(51) Qiu, X.; Hites, R. A. Dechlorane plus and other flame retardants in tree bark from the Northeastern United States. *Environ. Sci. Technol.* **2008**, *42* (1), 31–36.

(52) Renner, R. In U.S., flame retardants will be voluntarily phased out. *Environ. Sci. Technol.* **2004**, *38* (1), 14A–14A.

(53) Hoh, E.; Zhu, L. Y.; Hites, R. A. Novel flame retardants, 1,2-bis(2,4,6-tribromophenoxy)ethane and 2,3,4,5,6-pentabromoethylbenzene, in United States' environmental samples. *Environ. Sci. Technol.* **2005**, *39* (8), 2472–2477.

(54) Kawai, T.; Jagiello, K.; Sosnowska, A.; Odziomek, K.; Gajewicz, A.; Handoh, I. C.; Puzyn, T.; Suzuki, N. A new metric for long-range transport potential of chemicals. *Environ. Sci. Technol.* **2014**, *48* (6), 3245–3252.

(55) Wang, B.; Iino, F.; Huang, J.; Lu, Y.; Yu, G.; Morita, M. Dechlorane Plus pollution and inventory in soil of Huai'an City, China. *Chemosphere* **2010**, *80* (11), 1285–1290.

(56) Yu, Z.; Liao, R. e.; Li, H.; Mo, L.; Zeng, X.; Sheng, G.; Fu, J. Particle-bound Dechlorane Plus and polybrominated diphenyl ethers in ambient air around Shanghai, China. *Environ. Pollut.* **2011**, *159* (10), 2982–2988.

(57) Hoh, E.; Zhu, L. Y.; Hites, R. A. Dechlorane plus, a chlorinated flame retardant, in the Great Lakes. *Environ. Sci. Technol.* **2006**, *40* (4), 1184–1189.

(58) Qiu, X.; Marvin, C. H.; Hites, R. A. Dechlorane plus and other flame retardants in a sediment core from Lake Ontario. *Environ. Sci. Technol.* **2007**, *41* (17), 6014–6019.

(59) Tomy, G. T.; Pleskach, K.; Ismail, N.; Whittle, D. M.; Helm, P. A.; Sverko, E.; Zaruk, D.; Marvin, C. H. Isomers of dechlorane plus in Lake Winnipeg and Lake Ontario food webs. *Environ. Sci. Technol.* **2007**, *41* (7), 2249–2254.

(60) Riding, M. J.; Doick, K. J.; Martin, F. L.; Jones, K. C.; Semple, K. T. Chemical measures of bioavailability/bioaccessibility of PAHs in soil: Fundamentals to application. *J. Hazard. Mater.* **2013**, *261*, 687–700.

(61) Bearn, J.; Stapleton, H.; Mitchelmore, C. Accumulation and DNA damage in fat-head minnows (*Pimephales promelas*) exposed to 2 brominated flame-retardant mixtures, firemaster 550 and firemaster BZ-54. *Environ. Toxicol. Chem.* **2012**, *29* (3), 722–729.

(62) Hassanin, A.; Breivik, K.; Meijer, S. N.; Steinnes, E.; Thomas, G. O.; Jones, K. C. PBDEs in European background soils: Levels and factors controlling their distribution. *Environ. Sci. Technol.* **2004**, *38* (3), 738–745.

(63) Grimalt, J. O.; Borghini, F.; Sanchez-Hernandez, J. C.; Barra, R.; Garcia, C. J. T.; Focardi, S. Temperature dependence of the distribution of organochlorine compounds in the mosses of the Andean mountains. *Environ. Sci. Technol.* **2004**, *38* (20), 5386–5392.