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Concentrations and distribution of novel brominated flame retardants in the atmosphere and soil of Ny-Ålesund and London Island, Svalbard, Arctic

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ABSTRACT

Novel brominated flame retardants (NBFRs) were investigated in Arctic air and soil samples collected from Ny-Ålesund and London Island, Svalbard, during Chinese scientific research expeditions to the Arctic during 2014–2015. The concentrations of Σ_9 NBFRs in the Arctic air and soil were 4.9–8.7 pg/m³ (average 6.8 pg/m³) and 101–201 pg/g dw (average 150 pg/g dw), respectively. The atmospheric concentration of hexabromobenzene (HBB) was significantly correlated with that of pentabromotoluene (PBT) and pentabromobenzene (PBBz), suggesting similar source and environmental fate in the Arctic air. No significant spatial difference was observed among the different sampling sites, both for air and soil samples, indicating that the effects of the scientific research stations on the occurrence of NBFRs in the Arctic were minor. The fugacities from soil to air of pentabromoethylbenzene (PBEB), 2,3-dibromopropyl 2,4,6-tribromophenyl ether (DPTE), and decabromodiphenylethane 1,2-bis (pentabromophenyl) ethane (DBDPE) were lower than the equilibrium value, indicating a nonequilibrium state of these compounds between air and soil, the dominant impact of deposition and the net transport from air to soil. The correlation analysis between the measured and predicted soil-atmosphere coefficients based on the absorption model showed that the impact of the soil organic matter on the distribution of NBFRs in the Arctic region was minor. To the best of our knowledge, this work is one of the limited reports on atmospheric NBFRs in the Arctic and the first study to investigate the occurrence and fate of NBFRs in the Arctic soil.

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Introduction

Most brominated flame retardants (BFRs) are commercially produced to restrict the flammability of various consump-

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tion products, such as textures, building materials, and electronic equipment (Sun et al., 2018). By 2008, more than 75 different types (Alaee et al., 2003) and 410,000 tons of BFRs were produced (Fink et al., 2008). Notable BFRs, such as polybrominated diphenyl ethers (PBDEs), have stimulated great attention due to their properties of environmental persistence, bioaccumulation, and high toxicity and their potential to be transported from emission sources to remote regions through atmosphere (de Wit, 2002, 2006; Birnbaum and Staskal, 2004). Considering the adverse impacts of these compounds on the environment and biota, products that contain PBDEs were regulated through the Stockholm Convention on Persistent Organic Pollutants (POPs) (Covaci et al., 2011; Zhang et al., 2016; NICNAS, 2007; USEPA, 2010), which directly resulted in the use of novel BFRs (NBFRs) as alternatives to meet the market requirement of flame retardants (FRs) (Betts, 2008). Several NBFRs were only developed recently as the substitutes of the banned Deca-, Octa-, and Penta-BDEs (Arias, 2001; Renner, 2004), such as 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB), 1,2-bis (2,4,6-tribromophenoxy) ethane (BTBPE), and decabromodiphenylethane 1,2-bis (pentabromophenyl) ethane (DBDPE). Other NBFRs, such as hexabromobenzene (HBB) and pentabromotoluene (PBT), were produced early before the 1990s and were traditionally used as alternative BFRs for several decades (Arp et al., 2011).

Detectable NBFRs were observed in various environment media and biota (McGrath et al., 2018; Malliari and Olga, 2017). Similar to PBDEs, atmospheric NBFRs might be emitted from potential sources (i.e., manufacturing, open e-waste combustion, and other industrial processes) and reach remote sites through atmospheric transport (McGrath et al., 2017; Matsukami et al., 2017). The Arctic has been one of the most remote and pristine regions in the world due to its lack of industrial sources and anthropogenic activities. However, recent studies have reported the occurrence of various NBFRs in the Arctic biota and atmosphere, confirming the bioaccumulation and long-range atmospheric transport (LRAT) of NBFRs (de Wit et al., 2010). For example, 2,3-dibromopropyl 2,4,6-tribromophenyl ether (DPTE) was observed to be abundant and dominant both in abiotic and biotic samples from polar regions (Vorkamp and Riget, 2014). The study of ice cores from the Svalbard (the Arctic) confirm the LRAT of pentabromomethylbenzene (PBEB), BTBPE, and DBDPE (Hermanson et al., 2010). Although several studies have been carried out to detect atmospheric NBFRs in the Arctic, conclusive data regarding spatial distribution and diffusive behavior of the NBFRs in the Arctic is still scarce. Further studies on NBFRs in the Arctic are needed to understand the fate of these POPs candidates in the environment (Covaci et al., 2011). Atmospheric NBFRs could reach to the land through net deposition, and some NBFRs have been detected in the soil samples collected from various regions (Newton et al., 2014; Shi et al., 2009). Owing to the lipophilic properties of NBFRs, they could bind to organic matter of soil, leading them to persist in soil for many years (Andrade et al., 2010). Hence, an investigation of NBFRs in the soil could help evaluate their persistence and transport potential (McGrath et al., 2017).

In this study, selected NBFRs were investigated in Arctic air and soil samples collected from the Ny-Ålesund and London Island, Svalbard, during Chinese scientific research expeditions to the Arctic during 2014–2015. The main aim is to (1) investigate the concentrations, compound profiles, and spatial distribution of NBFRs in Arctic atmosphere and soil; and (2) estimate the soil-atmosphere exchange and partitioning of NBFRs and assess the impact of total organic carbon (TOC) on the distribution of NBFRs in the remote Arctic region.

1. Materials and methods

1.1. Sampling sites

All the samples were collected in the Ny-Ålesund and London Island, Svalbard, Norway, during the Chinese scientific research expeditions to the Arctic from August 2014 to August 2015. Five air samples were collected at different sites (S1–S5) using XAD-2 resin (Supelco, U.S.A.) based passive air samplers (XAD-PAS) (Wania et al., 2003). Due to the advantage of high sorption capacity of POPs in the gas phase and the lower cost compared with active air sampling (Okeme et al., 2018), XAD-PAS is used to collect air samples in the Arctic region annually. Sites S1, S2, and S3 were located on the Ny-Ålesund Island while S4 and S5 were located on the London Island. In addition, Site S1 was close to the leading edge of glacier while Site S3 was close to the Chinese Arctic Yellow River Station. Before the air sampling, XAD-2 resin was cleaned to remove the impurities with hexane and dichloromethane (1:1, V/V) using Soxhlet extraction for 24 hr. Ten soil samples were collected in the vicinity of Site S1–S5 and the other 5 sites (A1–A4 and P). The Sites A1–A4 were located at different distances from the same glacier margins, with the distances of 29.3, 35.7, 58, and 106 m, respectively. All air and soil samples were wrapped with clean aluminum foil and stored at -20°C before chemical analysis.

1.2. Detection of TOC of soil samples

The TOC values in the soil samples were calculated by the difference between the total carbon and inorganic carbon values, which were determined by the Carbon Analyzer (SHIMADZU, SSM-5000A, Japan). In brief, the soil sample, which was freeze-dried, sieved and homogenized, was divided into two parts. One part was used for the detection of total carbon, which was calculated by the capture of CO₂ produced through the combustion of organic matters at high temperature. The other part was used for the inorganic carbon, which was calculated by the capture of CO₂ produced in the reaction between carbon and phosphoric acid.

1.3. Sample analysis

Chemical analysis of target NBFRs has been described in our previous studies (Wang et al., 2019; Zhang et al., 2019). In brief, all the samples were spiked with 1 ng of surrogate standards of BDE-77 and BDE-128 before sample extraction. The air samples were then extracted using Soxhlet extraction for 24 hr with 500 mL hexane and dichloromethane (1:1, V/V). Soil samples were extracted using accelerated solvent extraction (ASE 300, Dionex, USA) with hexane and dichloromethane (1:1, V/V) at 100°C and 1500 psi (10.3 MPa). All the extracts were evaporated, then added to the precleaned Florisil SPE cartridges (1 g, 6 mL) (Supelco, Bellefonte, PA, U.S.A.), and eluted with 20 mL hexane. After all the eluents were concentrated to ~20 µL, injection standards of 1 ng BDE-138 were spiked into the samples prior to instrumental analysis.

The gas chromatography coupled with a negative ion chemical ionization mass spectrometer (GC-NCI-MS, SHIMADZU 2010 Ultra, Japan) was used for the analysis of nine selected NBFRs which included pentabromobenzene (PBEB), PBT, PBEB, DPTE, HBB, EHTBB, BTBPE, bis (2-ethyl-1-hexyl) tetrabromophthalate (BEHTEBP), and DBDPE. These analysis methods have been developed and validated in our laboratory, and detailed information can be found in our previous reports (Wang et al., 2019; Zhang et al., 2019).

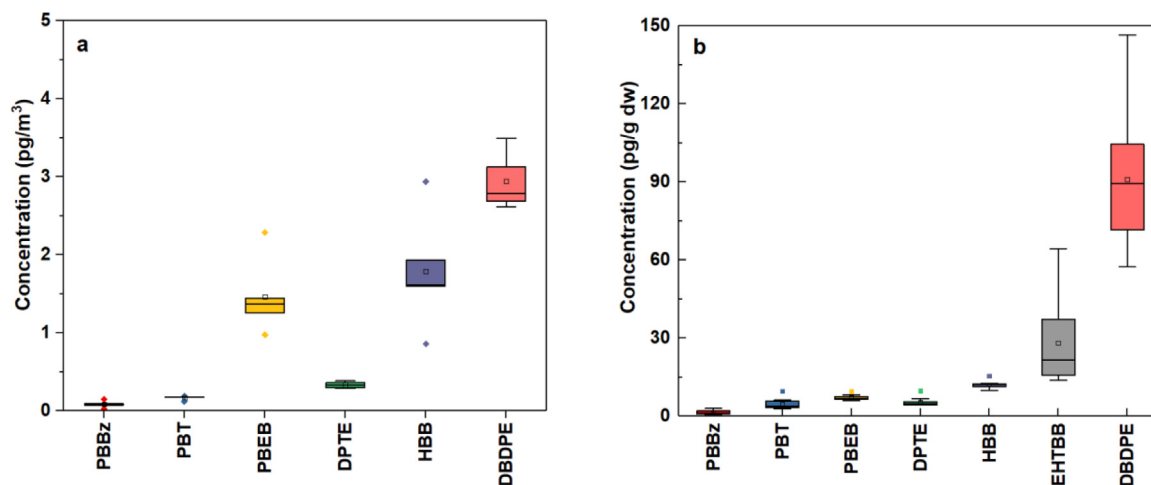


Fig. 1 – Concentrations of novel brominated flame retardants (NBFRs) in the Arctic atmosphere (a) and soil (b).

1.4. Quality assurance and quality control (QA/QC)

The surrogate standards and injection standards were added to each sample for quality control. The sample recoveries of internal standards ranged from 68.6% to 107.2%. The limits of detections (LODs), defined by the signal-to-noise ratio of three, were in the ranges of 0.01–12.4 pg/sample for the nine NBFRs in all samples. Laboratory blanks and field blanks were processed to prevent possible contamination from sampling and chemical analysis. No target compounds were detected in blanks, except DBDPE, whose concentrations were lower than 5% of the levels in the Arctic samples. Therefore, the values of detected concentrations of both air and soil samples were not corrected by the blank.

2. Results and discussion

2.1. NBFRs in the arctic atmosphere

The atmospheric concentrations of nine NBFRs in the Arctic from August 2014 to August 2015 are shown in Fig. 1a. The XAD-PAS was confirmed to be efficient in the sampling of NBFRs in previous studies (Okeme et al., 2016, 2018). The sampling rate of 0.52 m³/day, which has been used in the field of Canadian High Arctic (Wania et al., 2003), was used in this study to calculate the atmospheric concentrations of NBFRs. Among the nine selected NBFRs, EHTBB, BTBPE, and BEHTEBP were not detected in all the air samples in this study. The DBDPE (2.6–3.5 pg/m³, average: 2.9 pg/m³) was the predominant compound among the nine NBFRs in this study. The atmospheric concentrations of PBBz (0.02–0.1 pg/m³, mean value: 0.1 pg/m³), PBT (0.1–0.2 pg/m³, 0.2 pg/m³), and DPTE (0.3–0.4 pg/m³, 0.3 pg/m³) were observed in comparable levels in the Arctic, which were lower than the concentrations of PBEB (1.0–2.3 pg/m³, 1.5 pg/m³) and HBB (0.9–2.9 pg/m³, 1.8 pg/m³).

The atmospheric concentrations of NBFRs in the Arctic were two to three orders of magnitude lower than that in e-waste sites of Pakistan (Iqbal et al., 2017). The air concentrations of PBBz (not detected (ND)–4.3 pg/m³), PBT (ND–2.8 pg/m³), DPTE (ND–2.3 pg/m³), and HBB (0.12–26 pg/m³) observed in the marine atmosphere across the cruise from the East Indian Archipelago to the Southern Ocean (Möller et al., 2012) were higher than those detected in the Arctic air in this study, which might be attributed to the influence of continental emissions (Gauthier et al., 2007; Covaci et al., 2011).

However, no significant spatial differences ($p > 0.05$, Kruskal-Wallis H Test) in atmospheric concentrations and composition profiles for NBFRs were observed (Figs. 2 and 3) between S3 (close to the Chinese Arctic Yellow River Station) and the other sites, indicating that the influence of the station on the distribution of atmospheric NBFRs was minor. Comparable atmospheric concentrations of PBBz (0.09–2 pg/m³), PBT (0.1–4.5 pg/m³), DPTE (0.1–2.5 pg/m³), and HBB (0.10–5.9 pg/m³) were observed throughout the cruise from the East China Sea to the high Arctic (Möller et al., 2011a). Similar to the results detected in this study, BTBPE was also undetectable in the atmosphere near northeastern Greenland (Vorkamp et al., 2015), whereas HBB was detectable in this study and in all the air samples collected from the Atlantic Ocean (Xie et al., 2011) to the East Greenland Sea (Möller et al., 2011b). This phenomenon can be explained by the longer half-life of HBB (11,000 hr) than that of BTBPE (8.6 hr) in the air (Xiao et al., 2012) and the fact that atmospheric HBB was dominated by the LRAT (Möller et al., 2012).

DBDPE, used as the alternative of Deca-BDE (Covaci et al., 2011), was reported to be detectable in ice cores from the Arctic (Hermanson et al., 2010). The atmospheric concentrations of DBDPE in the European Arctic (0.04–2.2 pg/m³) (Salamova et al., 2014) were observed to be comparable to those in this study, which were all lower than those in the Great Lakes (0.5–35 pg/m³) (Venier and Hites, 2008) and the eastern Tibetan Plateau (ND–171 pg/m³) (Liu et al., 2018).

PBBz, PBT, and HBB might be formed from the degradation of highly brominated compounds, such as DBDPE, and the debromination reaction converting HBB to PBBz (Möller et al., 2011a). According to the result of Spearman's rank correlation coefficient analysis among PBBz, PBT, HBB, and DBDPE, HBB was significantly and positively correlated with the PBT ($R = 0.9$, $p < 0.05$) and PBBz ($R = 0.9$, $p < 0.05$), whereas no significant relationships ($p > 0.05$) were observed between DBDPE and the other three compounds, indicating similar sources and environmental fates of HBB and PBT, which was different compared to DBDPE.

2.2. NBFRs in arctic soil

The concentrations of Σ_9 NBFRs in Arctic soil were 101–201 pg/g dw with an average of 150 pg/g dw in this study (Fig. 1b). DBDPE was the dominant compound in the Arctic soil with the concentrations of 57.3–147 pg/g dw (average: 91.0 pg/g dw). However, relatively low concentrations were observed for PBBz, PBT, PBEB, and DPTE, which showed levels of 0.4–2.9 pg/g

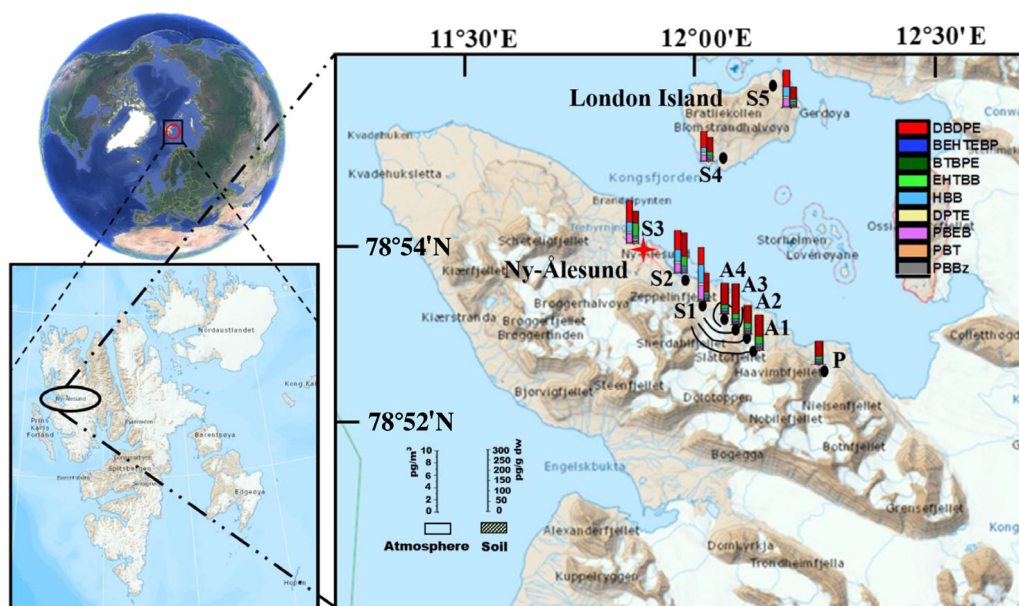


Fig. 2 – Spatial distribution of NBFRs in the Arctic atmosphere and soil (S1-S5, A1-A4 and P represent the sampling sites).

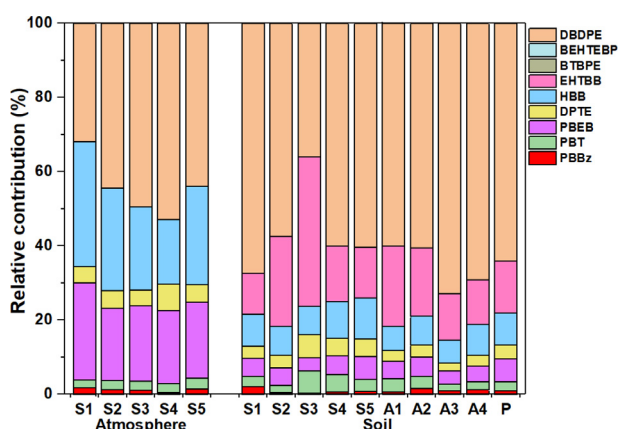


Fig. 3 – Composition profile of NBFRs in the Arctic atmosphere and soil.

dw (average 1.4 pg/g dw), 2.8–9.6 pg/g dw (average 4.6 pg/g dw), 5.9–9.5 pg/g dw (average 7.1 pg/g dw), and 4.3–9.8 pg/g dw (average 5.3 pg/g dw), respectively. Unlike EHTBB, which was undetectable in the Arctic air in this study, measurable levels of EHTBB were observed in all Arctic soil samples with the concentrations of 13.8–64.4 pg/g dw (average 28.1 pg/g dw).

The investigation of measurable NBFRs in the soil of remote polar regions is still scarce. To the best of our knowledge, this is the first report to investigate the occurrence and composition profile of NBFRs in the Arctic soil. Compared with NBFRs levels in soil of BFRs-manufacturing and E-waste processing regions, concentrations of NBFRs in this study were extremely low, by at least two orders of magnitude (McGrath et al., 2017). The concentrations of HBB observed in the soil collected from the eastern Tibetan Plateau (ND-4.5 pg/g dw) were lower than that observed in this study (HBB: 9.8–15.4 pg/g dw), whereas the result of DBDPE was opposite. DBDPE levels of ND-1450 pg/g dw was observed in eastern Tibetan Plateau (Liu et al., 2018), and 57.3–147 pg/g dw was observed in this study. Although detectable DBDPE were observed in the Arctic soil, their concentrations were still

markedly lower than the levels detected in farmland (17,600–35,800 pg/g) (Shi et al., 2009) and forested areas (5–13,000 pg/g) (Zheng et al., 2015) in China, rural-urban transect in England (22–990 pg/g) (Drage et al., 2016), and urban transect in Sweden (200–160,000 pg/g) (Newton et al., 2015). The concentrations of PBEB in the Arctic soil were only observed to be comparable to that in rural regions of China (ND-2.0 pg/g) (Wang et al., 2009).

With regard to the spatial distribution of NBFRs in Arctic soil (Fig. 2), no significant difference ($p > 0.05$, Kruskal-Wallis H Test) was observed among different sampling sites, indicating that the influence of point source in the vicinity of sampling sites could be negligible. Owing to the global climate warming, the ice cap in the Arctic has been gradually melting (Dowdeswell et al., 1995). Interestingly, the concentrations of the NBFRs (except DBDPE) in soils collected from the Sites A1–A4 were observed to be decreasing with increasing distance from the glacier margin, indicating the influence of glacier melting on the distribution of NBFRs.

The TOC contents (%) in the Arctic soil were 0.07%–16.8% (mean value 3.8%), which were comparable to those observed in a previous study on three Arctic ecosystems (1.3%–15.8% in Truelove Lowland, Simpson Lake and Ross Point) (Banerjee et al., 2011). The correlation analysis was used to investigate the relationship between the NBFRs in the Arctic soil and the TOC contents. The results showed that none of the selected compounds was related with TOC ($p > 0.05$), suggesting that the impact of TOC contents on the distribution of NBFRs in the Arctic soil was minor. However, a significantly and positively correlated relationship was observed between PBEB and DBDPE ($R=0.7$, $p<0.05$), indicating that the emission sources of PBEB and DBDPE were similar, but different from the source of the other compounds, which is similar to observations from research on soil from Nepal (Yadav et al., 2018).

2.3. Soil-atmosphere exchange and partitioning

The pattern of soil-atmosphere exchange can be described by the fugacity fraction (F), which has been previously widely used (Aliyeva et al., 2012; Devi et al., 2014). F is the ratio of the soil fugacity (F_s) to the sum of both soil and air fugacity (F_a) and can be calculated from the following Eq. (1). The F_a and F_s can be calculated by the Eqs. (2) and (3), respectively. Hence,

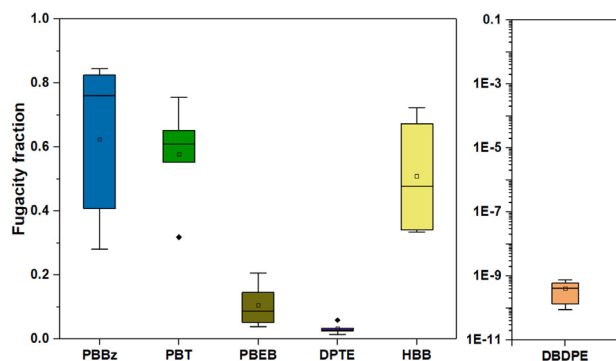


Fig. 4 – Box-whisker plot showing fugacity fraction of NBFRs in the Arctic.

the F value can be calculated by the Eq. (4).

$$F = F_s / (F_a + F_s) \quad (1)$$

$$F_a = 1 \times 10^{-9} C_a RT / MW \quad (2)$$

$$F_s = 1 \times 10^{-9} C_s RT / 0.411 \phi_{om} K_{OA} MW \quad (3)$$

$$F = C_s / (C_s + C_a \times 0.411 \phi_{om} K_{OA} / 1.5 \times 10^6) \quad (4)$$

where, C_a (pg/m^3) and C_s (pg/g) represent the concentrations of individual compounds in air and soil, respectively. The soil bulk density of $1.5 \times 10^6 \text{ g/m}^3$ was used to convert the soil residues from a mass-to-volume concentration (Devi et al., 2014). R ($8.314 \text{ (Pa} \cdot \text{m}^3)/(\text{mol} \cdot \text{K})$) and T ($253\text{--}258 \text{ K}$ in Arctic) symbolize the universal gas constant and average temperature, respectively. MW (g/mol) is the molecular weights of the compounds. ϕ_{om} denotes the soil organic matter, which could be calculated by 1.5 times of TOC (Yadav et al., 2018). K_{OA} is the octanol-air partition coefficient of individual target compounds and was acquired from previous reports (Wang et al., 2008; Li et al., 2016) and from the estimation using the US Environmental Protection Agency KOAWIN model (EPIWEB 4.1). The value of 0.411 is the relationship coefficient constant between K_{SA} and K_{OA} , where K_{SA} is the soil-atmosphere coefficient of individual target compounds.

To the best of our knowledge, this is the first soil-atmosphere exchange study of NBFRs in the Arctic. According to the previous reports (Harner et al., 2001; Devi et al., 2014), the equilibrium state can be reached only when the F values equal 0.5. F value greater than 0.5 indicates volatilization and a net outflow of target compounds from soil to air, whereas the accumulation and net transport from air to soil would be suggested if the F value is lower than 0.5. As shown in Fig. 4, the soil to air fugacity for PBEB, DPTE, and DBDPE in this study was lower than the equilibrium value of 0.5, indicating nonequilibrium state of these compounds between air and soil, the dominant impact of deposition and the net transport from air to soil. Additionally, DBDPE in this study showed extremely low fugacity fractions (Fig. 4), which is attributed to its high K_{OA} (Gevao et al., 2010). However, the F values for PBBz, PBT, and HBB varied with different sampling sites, implying that the distribution of these compounds might be influenced not only by the soil-atmosphere exchange but also by other impact factors, which requires further investigations.

The soil-atmosphere coefficient (K_{SA}) is commonly used to describe the diffusive behavior of organic compounds between soil and air, which is essential to predict their fate in

the environment. The measured K_{SA} could be calculated by Eq. (5) (Cabrerizo et al., 2009). The dissemination of NBFRs might be influenced by the TOC content in the soil. Therefore, the predicted K_{SA} values were based on the TOC contents and were estimated by the absorption model expressed in Eq. (6) (Finizio et al., 1997).

$$\text{Measured } K_{SA} = 1 \times 10^9 C_s / C_a \quad (5)$$

$$\text{Predicted } K_{SA} = 1.5 (F_{\text{TOC}} / \delta_{\text{OCT}}) K_{OA} \quad (6)$$

where, the C_s , C_a , and K_{OA} are same as those in Eq. (4), F_{TOC} (g/g dw) is the TOC value, and δ_{OCT} is the octanol density (0.858 kg/L at -20°C).

To the best of our knowledge, this is the first study to estimate the K_{SA} in the Arctic according to the absorption model using the K_{OA} . No significant correlation ($p > 0.05$) was observed between $\log K_{OA}$ and $\log K_{SA}$. Additionally, comparison was analyzed between the measured K_{SA} and predicted K_{SA} , which was based on the absorption model using the behavior of target compounds as a function. No significant correlation ($p > 0.05$) was observed between measured K_{SA} and predicted K_{SA} , indicating that the impact of soil organic matter on the soil-atmosphere partitioning was minor (Yadav et al., 2018).

3. Conclusions

To investigate the occurrence and the environmental behavior of NBFRs in the Arctic, the concentrations and soil-atmosphere partitioning of these compounds were analyzed. Although detectable levels of NBFRs were observed in the Arctic air and soil, these compounds were still present at low levels compared with most urban areas in many countries. Similar sources and environmental fates of PBBz, PBT, and HBB were suggested by the correlation analysis. The fugacity fraction was used to describe the soil-atmosphere exchange of the target compounds, suggesting the nonequilibrium state for PBEB, DPTE, and DBDPE, the dominant impact of deposition and the net transport from air to soil on the distribution of these compounds. The results of soil-atmosphere partitioning showed that the impact of the soil organic matter on the distribution of various NBFRs in the Arctic region was minor.

Declaration of Competing Interest

The authors declared that we have no conflicts of interest to this work. We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted

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