DETERMINATION OF THE ABSORPTION PATHWAYS AND DEPOSITION MECHANISM OF BROMINATED FLAME RETARDANTS (BFRS) TO WHEAT LEAVES

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Introduction

Brominated flame retardants (BFRs) are a group of compounds, which are incorporated into polyurethane foam, textile, furniture, expanded and extruded plastic, as well as electric and electronic equipment, etc., to make the products more fire-resistant by reducing the combustibility of the materials [1]. Emerging toxicological data show that some BFRs share the major characteristics of persistent organic pollutants (POPs), i.e., persistency, bioaccumulation, and long-range transport (LRT) potential [1], and pose various human health threats, i.e., endocrine disruption, neurotoxic effects, enzyme induction, immunotoxicity, and effect on sex hormones and reproduction [2-3]. For these reasons, penta-, octabromodiphenyl ether (PBDEs) and hexabromocyclododecanes (HBCDs) were added to the POPs list of the Stockholm Convention successively and they have been banned by most parties of the world [4].

Plant is an important media in terrestrial systems and a main pathway for human exposure. Based on the proposed qualitative frameworks for plant absorption and physicochemical parameters of BFRs [5], foliar uptake should be an important pathway for the accumulation of BFRs in plant aerial parts, which in turn increases the exposure risk to human health through food chain transfer. Despite its importance, research on the plant uptake of BFRs is insufficient, with no studies found regarding BFRs uptake by plant leaves from the atmosphere. McLachlan proposed a framework based on the octanol-air partition coefficient (K_{oa}) of chemicals to interpret the absorption of semivolatile organic compounds (SOCs) in plants. Depending on log K_{oa}, chemicals are absorbed by plant leaves via three processes, including gaseous partitioning equilibrium, kinetically limited gaseous deposition and particle-bound deposition, and the transitions from one process to another were at log K_{oa} of 8.5 and 11, respectively [6]. BFRs have a wide range of log K_{ow} (octanol-water partitioning coefficients) and log K_{oa}, which in the range 5−11 and 8−15, respectively. Such different physical properties and molecular structures of different BFRs may have different effects on the plant uptake behavior. Despite its importance, however, the mechanism of the plant uptake of different BFRs is poorly understood, especially in field study. Therefore, the uptake pathways of different BFRs to wheat leaves were studied under near natural conditions using a closed exposure chambers (ECs). Simultaneously, the deposition mechanisms for BFRs transfer into plant leaves from atmosphere were evaluated.

Materials and methods

Four identical ECs were prepared using synthetic glass, including one EC serving as the control group (A), and three ECs serving as the testing groups and were separately exposed to BFRs through contaminated air (B), air and soil (C), and air, soil and particulates (D). The BFRs studied in this study are: BDE-28, -47, -99, -100, -153, -154, -183, -197, -206, -209 and HBCDs. The measured concentrations of the targeted BFRs were in the ranges of 0.012-5.78 ng/m^3 in the air, 45.5-21,619 ng/g in particles, and 1.90-212 ng/g in soil, respectively. In this study, the designed BFR concentrations spiked in various environmental media match well with their concentrations around potential point sources in the environment and meet the requirements of the exposure experiment.

The 10 PBDE congeners were purchased from Wellington Laboratories (Guelph, ON, Canada). Surrogate standards (BDE77 and 166), internal standards (BDE118 and 128) were purchased from AccuStandards Inc. (New Heaven, US). Surrogate standard (^{13}C-BDE209) was purchased from Cambridge Isotope Laboratories (Andover, MA, US). Native and d_{18}-labeled HBCDs (α-, β-, and γ-HBCDs) were purchased from Cambridge Isotope Laboratories (Andover, MA, USA) and Wellington Laboratories (Guelph, ON, Canada), respectively. All solvents for sample processing were analytical grade (Anpel, Shanghai, China). Silica (3 mL, 500 mg) cartridges were obtained from CNW, Germany. Anhydrous sodium sulfate (Na_2SO_4), silica gel (100–200 mesh), and copper (< 63 μm) were purchased from Merck. The anhydrous Na_2SO_4 was treated before using by being soaked with hexane and then heated at 450 °C for 4 h. All glassware was washed with detergent, rinsed with water, dried at 100 °C, and rinsed with hexane prior to use.

Details of the description of the EC and analytical methodology has been described previously [7-8].

Results and discussion

Although a polyurethane foam (PUF) was installed in the inlet of the control EC (A), BFRs were detected in the air and wheat leaves in control EC. This may be caused by that indoor environment itself is an important source of BFRs. On average, the BFRs blank levels were < 2.14% of the sample collected from the test ECs, thus the control EC was not discussed further. As shown in Figure 1, the concentrations of BFRs in the same

wheat tissues collected from groups B, C and D arose by their turns. For example, the concentrations of BFRs in wheat inner leaf collected from group B, C and D were 1.28−374 ng/g, 2.06−393 ng/g and 4.26−1727 ng/g, respectively. Ideally, this differences in BFRs concentrations in the wheat tissues among the three test groups were assumed to be caused by the increasing in uptake pathways.

By computation and comparison, the contributions of three uptake pathway, including root uptake, gaseous and particle-bound deposition, for the accumulation of BFRs in wheat leaves were 0.343−18.7%, 0.747−56.5%, and 37.3−98.9%, respectively. Apparently, soil-related pathways did not measurably influence the substance levels in the wheat leaves, and the major portion of the BFRs in the leaves is directly absorbed from the air via gaseous and particle-bound deposition. A similar result was presented by Lin et al., where approximately 49.5−95.0% of the polycyclic aromatic hydrocarbons in the leaves of the tea plant were uptake from the atmosphere [9]. Along with the increase in number of bromine atoms of the targeted compounds, the contributions of gaseous deposition for the accumulation of BFRs in wheat leaves rapidly decreased, while the case for particle-bound deposition was opposite. Especially for BDE-209, almost all came from particle-bound deposition (98.9%). Welsch-Pausch et al. found that dry gaseous deposition was the principal pathway of Cl_4−Cl_6 DD/F (polychlorinated dibenzo-p-dioxins and dibenzofurans) to the grass leaves and the deposition of large particles was an important pathway for the uptake of $C1_7$DD and Cl_8DD [10].

The interpretive framework of McLachlan has been often used to identify the mechanism dominating the plant uptake of SOCs [6]. The log of the ratio of the concentration in vegetation (C_v) to that in the gaseous phase (C_g) was plotted against log K_{oa} for BFRs present in the gaseous phase. Likewise, the log of the ratio of the plant concentration to the particle-bound concentration (C_p) was plotted against the log C_p/C_g for BFRs present in the particle phase. The plots showed linear increases of log C_v/C_g with log K_{oa} between 12 and 16, indicating a particle-bound deposition. There was a very slight flat trend at log K_{oa} between 9 and 12, which are attributed to a kinetically limited gaseous deposition. The plots of log C_v/C_p vs log C_p/C_g began with a linear decreasing trend (indicating kinetically limited gaseous deposition) in the present study and followed by a flat trend (indicating particle-bound deposition) according to the interpretive framework. On the whole, the uptake of most less-brominated BFRs (tri- through hexa-BFRs) was controlled primarily by kinetically limited gaseous deposition, and the uptake of higher-brominated BFRs (hepta- through deca-BFRs) was controlled primarily by particle-bound deposition. A similar yet slightly different result has also been observed for BFRs previously by Tian et al. [11].

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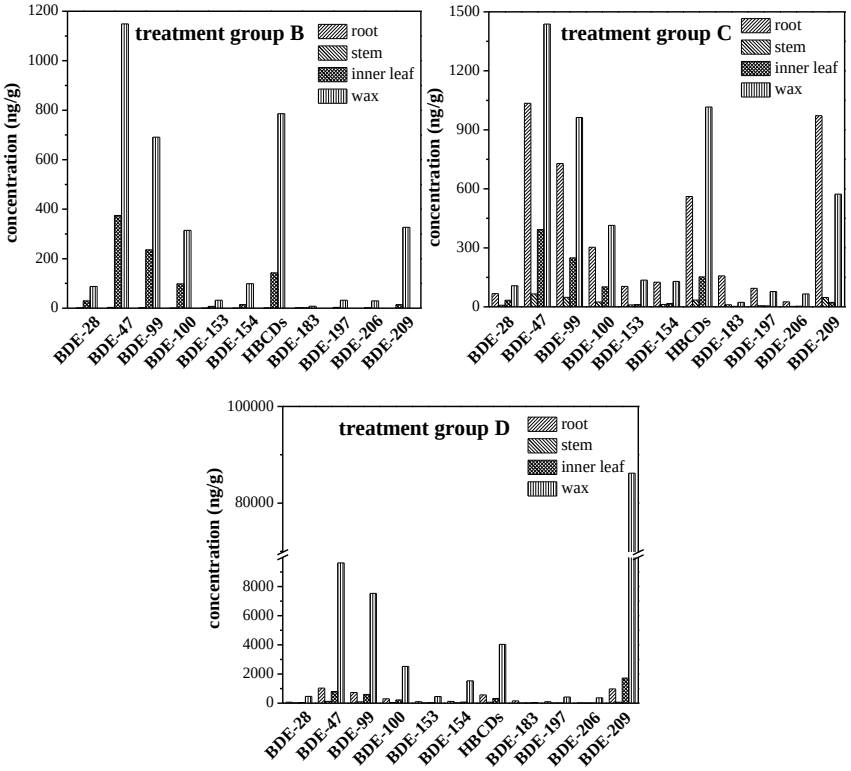

Figure 1 The concentrations of BFRs in wheat tissues among different experimental treatments (B, C, and D represents exposure to air, air+ soil, and air+soil+particles)

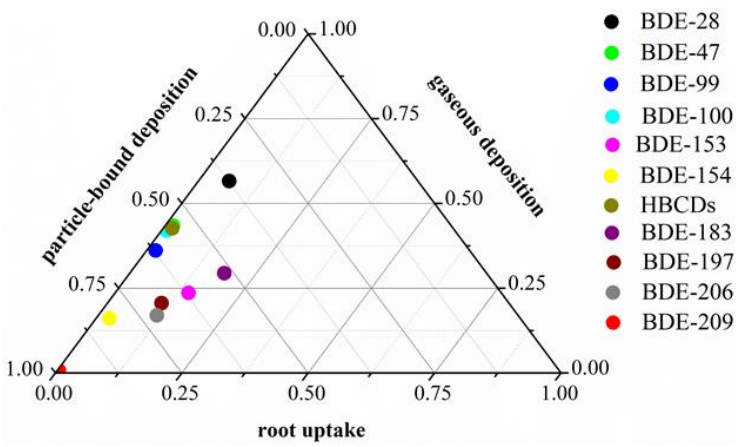

Figure 2 The contribution of three uptake pathway, including root uptake, gaseous and particulate deposition for the accumulation of BFRs in wheat leaves