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Characterization of the exchange of PBDEs in a subtropical paddy field of China: A significant inputs of PBDEs via air–foliage exchange

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A B S T R A C T

Rice and the distinctive cultivation practices employed in rice growth can significantly influence the environmental fate of polybrominated diphenyl ethers (PBDEs) in a paddy field. We studied variations in PBDE concentrations in multiple compartments of a paddy field in the suburban area of Guangzhou, South China, including air, soil, water, and rice tissues. The input/output fluxes of air–surface and air–foliage exchange, atmospheric deposition and water input during different rice growth stages were measured simultaneously. Air–foliage and air–water diffusion exchanges were the key processes controlling inputs and outputs of PBDEs in paddy fields, respectively, whereas atmospheric deposition dominated inputs of higher brominated PBDEs. The high input of PBDEs via air–foliage exchange suggested that vegetation can significantly increase the air-to-field transport of PBDEs in ecosystems. The annual input of PBDEs in all paddy fields in Guangdong Province was estimated to be 22.1 kg.

1. Introduction

The environmental fate of semivolatile persistent organic pollutants (POPs) is significantly influenced by exchange between the atmosphere and the surface of the terrestrial ecosystems. Soil is considered one of the main reservoirs or sinks for POPs (Meijer et al., 2003), and vegetation is also a large reservoir since it is an important compartment of the terrestrial environment and covers ~80% of the Earth's land surface (Cousins and Mackay, 2001). Plants play important roles in trapping and transferring airborne POPs into terrestrial ecosystems and affecting their global transport (Tian et al., 2012). Air–foliage diffusional exchange is regarded as a significant sink for atmospheric POPs, which may distinctly impact the environmental fate of those pollutants (Horstmann and McLachlan, 1998). Plant leaves present a large interface for diffusional exchange with air, and also have specialized tissues and organs (e.g. spongy mesophyll and stomata) which favor air–foliage exchange of POPs. However, variations in environmental conditions (e.g. climate change, season variation and land use type) may principally cause re-emission of organic chemicals to the atmosphere (Nizzetto and Perlinger, 2012). Therefore, it is crucial to quantify the flux and equilibrium of absorption and clearance processes between foliage and gaseous POPs (Mackay et al., 2006), if we try to understand and modify their fates in the terrestrial ecosystem. Air–foliage exchange is also significantly influenced by different types of vegetation (e.g. trees, crops and grasses). Previous studies (Wania and McLachlan, 2001; Wei et al., 2008; Nizzetto and Perlinger, 2012) have estimated the flux or long-term fate of POPs exchanged between air and plants. However, there is still a lack of information on air–foliage exchange of POPs, especially in the agricultural ecosystems. Besides the diffusion exchange, the air deposition and irrigation are also important processes involved in the transport of POPs to agricultural field.

Rice is widely cultivated in the world and has drawn considerable attention for its distinctive flooding patterns and its importance in maintaining food safety (Wang et al., 2015). The dry/wet alternations characteristic of paddy fields may significantly influence the environmental fate of POPs, including air–field exchange, air–rice exchange and root enhanced biodegradation. Moreover, the high density of rice leaves, which have large organic surfaces, can affect atmospheric exchange and deposition of POPs in a paddy field, but lack of field studies.

Although there are several models which estimate the environmental fate of POPs in paddy fields (Inao, 2003; Inao et al., 2008;

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Wei et al., 2008), few studies have assessed the *in situ* exchange fluxes and net inputs of POPs using simultaneous field measurements in multiple environmental compartments. In particular, polybrominated diphenyl ethers (PBDEs), of which commercial penta– and octa–PBDEs have been banned for only 5 years, have not been investigated extensively. The purpose of the present study was 2-fold: (i) to assess the different exchange processes of PBDEs and their short-term variability during different rice growing stages based on simultaneous measurements and (ii) to estimate the inputs/outputs of PBDEs during rice growing period in a subtropical paddy field.

2. Materials and methods

2.1. Sampling

Sampling was conducted in a paddy field (Area: 0.01 km^2) of a suburban area of Guangzhou City [23° 9′ 59″ N, 113° 22′ 7″ E], South China. The study field, located in the subtropical monsoon climate zone, cultivates two annual rice crops, consisting of different rice varietals. Six rice plants (*Oryza sativa* L.) and eight surface soils (0–10 cm) were collected during four separate growth stages: jointing (the elongation period), heading (the flowering and grain filling period), mature (the mature period) and idle (the period after harvest). Plant samples were separated into root, stem (internode), leaf (sheath and blade) and seed (grain and hull, if any). Totally, four irrigation and four field water samples were collected during the flooded jointing and heading stages as well. Irrigation was undertaken every 5–10 days using water from a nearby river until the rice matured. Each plant, soil and water sample consisted of five subsamples randomly collected at five sites within the study area.

Air was collected by pumping through a glass fiber filter (GF/A, 47-mm diam.) and polyurethane foam (PUF, 10-cm length × 2-cm diam.) plug at a height of 1.5 m and a low flow rate of ~8 L/min for 48 h. Atmospheric deposition samples (both dry and wet, 14–35 d) were obtained using three duplicate glass funnels (20-cm diam.) deployed over the rice canopy at a height of 1.2 m. The funnel was connected to an amber glass bottle using a Teflon pipe. Air samples (8) and deposition samples (7) were also collected for all of the four growth stages in each of the two growing seasons. Sampling was conducted between May 31 and December 13, 2012, spanning two growing seasons. The details of sampling information are shown in Table S1 of the Supporting Information and our previous studies (Wang et al., 2015).

2.2. Sample extraction and analysis

Sampling preparation, extraction, analysis and QA/QC were shown in S1 and S2 of Supporting Information, respectively. Totally, 8 PBDE congeners, including BDE28, 47, 99, 100, 153, 154, 183 and 209, were analyzed using a GC–ECNI–MS.

2.3. Calculation of the fugacity fraction, exchange fluxes and inputs of PBDEs

The key input processes include air-to-surface transport (i.e. water, soil and rice plant surfaces), atmospheric deposition and irrigation, while the key output processes include emission, drainage, leaching and harvesting. The fugacity fractions of air-water, air-soil and air-rice, the exchange fluxes between the air and the paddy field surface and the net inputs of PBDEs were calculated based on the measurements in multiple compartments of the paddy field. The details of these calculations are listed in the S3–S6 of Supporting Information.

3. Results and discussion

3.1. PBDEs in soil, water, air and rice tissues in the paddy field

Concentrations of PBDEs in soil, water, air, air deposition and rice tissues at different growth stages of two growing seasons are shown in Fig. 1 and Fig. S1. All of the concentrations in soil and plant samples reported in the study are expressed on a dry weight basis (ng/g dry wt.). Briefly, the total concentrations of 7 PBDEs (Σ_7PBDE except for BDE209) in the field water for the jointing and heading stages were 0.27 and 0.69 ng/L and 1.14 and 0.55 ng/L in the first and second growing seasons, respectively; while the concentrations of BDE209 in the field water for the jointing and heading stages were 3.97 and 31.5 ng/L and 18.3 and 57.9 ng/L in the first and second seasons, respectively. The total 7 PBDE concentrations in irrigation water for the two seasons were 0.45–0.57 ng/L and 0.33–0.46 ng/L, respectively; whereas BDE209 concentrations were 3.14–4.87 ng/L and 5.37–13.4 ng/L, respectively. Generally, PBDEs in the field water were higher than those in the irrigation water, which implied that irrigation was not the main source of PBDEs in the paddy field. The PBDE concentrations in the irrigation and field water were about 10 times higher than these detected in water of the Pearl River Estuary (Guan et al., 2007; Chen et al., 2011), which suggested a relatively high pollution of PBDEs in this study area.

Σ_7PBDE measurements in soils ranged between 0.24 and 0.36 ng/g and 0.25–0.37 ng/g for the first and second seasons, respectively; while BDE209 in soils ranged between 40.4 and 71.2 ng/g and 75.4–133 ng/g for the first and second seasons, respectively. Generally, PBDE concentrations in surface soils decreased with increasing rice growth time, especially for low brominated congeners, because of the rice enhanced emission, runoff, leaching, or root adsorption. However, PBDE concentrations in soil sampled during the jointing stage of the second growing season were higher than those from the idle stage of the first growing season, which may be due to some additional PBDE inputs during the idle stage, such as sewage irrigation, straw burning (Chang et al., 2014), which have all been identified as significant sources of POPs in paddy fields (Chen et al., 2008; Chang et al., 2014; Wang et al., 2015). Moreover, the adhered PBDEs in soils can be released by root exudates of rice, which may also increase the detected PBDE concentrations in the soil of the jointing stages.

Σ_7PBDEs in ambient air (gaseous phase) ranged from 35.8 to 171 ng/m^3 and from 33.1 to 51.9 ng/m^3 for the first and second seasons, respectively; whereas BDE209 in air (gaseous phase) ranged from 159 to 705 ng/m^3 and from 21.6 to 130 ng/m^3, respectively. The air concentrations of PBDEs varied widely with sampling time, but no regular trend was found, which suggested that air concentrations of PBDEs cannot be significantly impacted by the rice growth. Σ_7PBDE concentrations in atmospheric deposition lay within the ranges of 0.80–5.24 $ng/m^2/d$ and 0.70–2.47 $ng/m^2/d$ in the first and second seasons, respectively; while BDE209 in atmospheric deposition lay within the ranges of 33.7–1360 $ng/m^2/d$ and 55.6–595 $ng/m^2/d$, respectively. The atmospheric depositions of PBDEs increased with rice growing time in the first season, but decreased with rice growing time in the second season. The variation of air deposition of PBDEs was consistent with that of temperature, which implied that high temperature may cause more emission of particle bounded PBDEs into the atmosphere and more air deposition of PBDEs into the soil.

Σ_7PBDEs in rice tissues for each of the two seasons were measured at concentrations in the range 0.09–1.55 ng/g and 0.05–1.05 ng/g, respectively; whereas BDE209 in the range 1.60–32.6 ng/g and 1.48–32.0 ng/g, respectively. The highest concentrations were found in rice leaves, followed by roots, stems and seeds. Generally, PBDE concentrations in rice shoots increased with

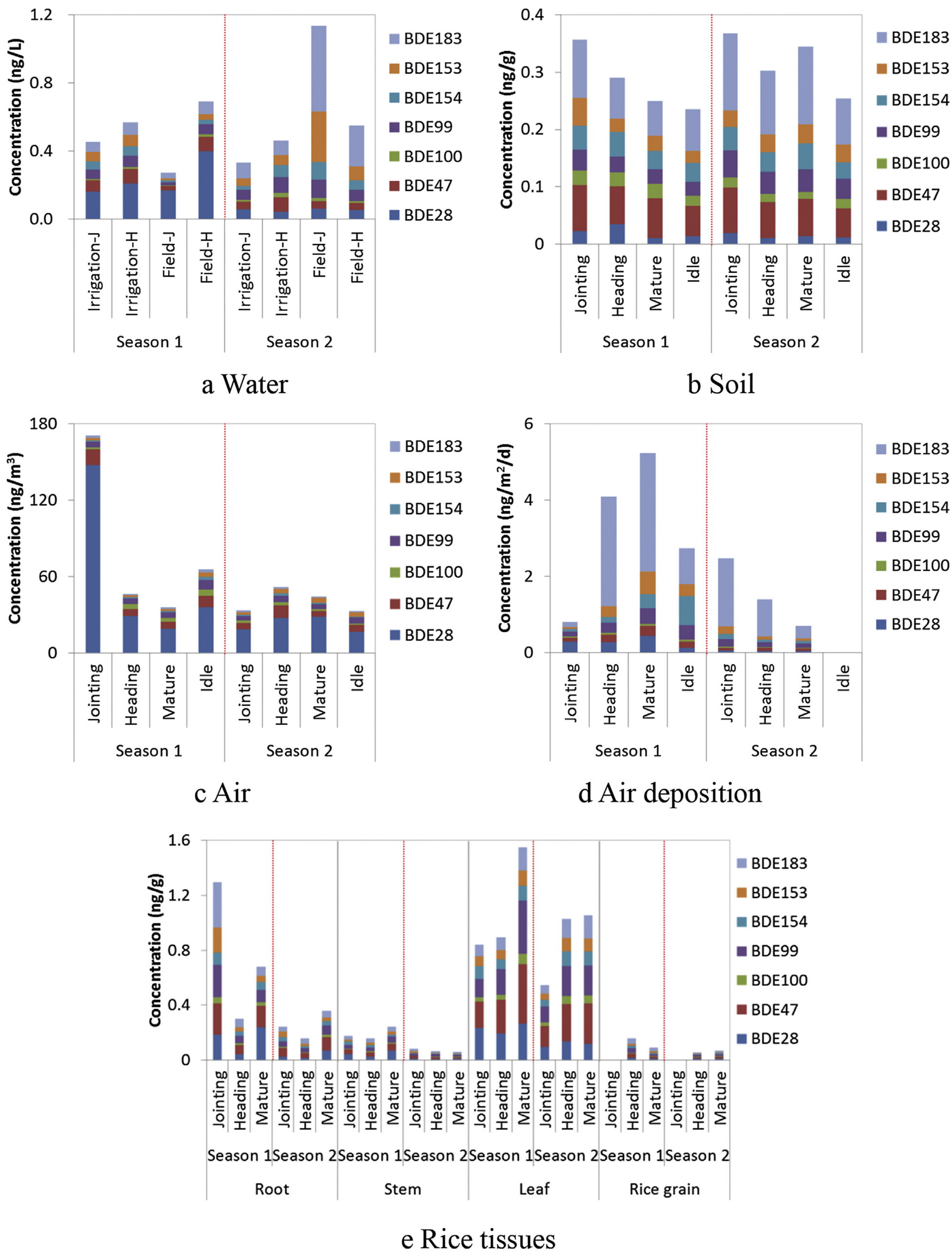

Fig. 1. The concentrations of PBDEs in water, soil, air, air deposition and rice tissues during different growth stages of two growing seasons. (J means jointing stage, while H means heading stage. Field means field water.)

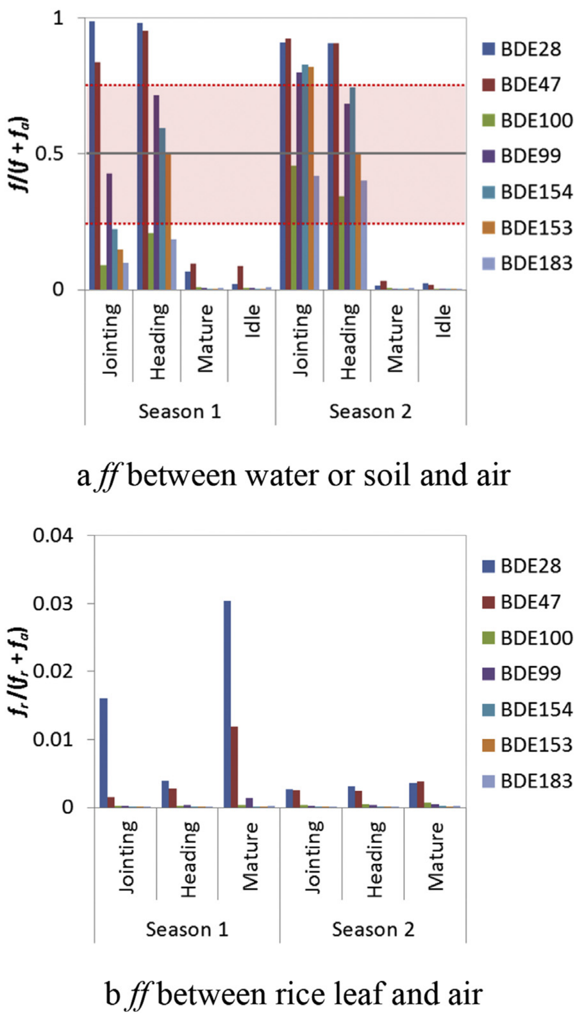

Fig. 2. The fugacity fractions (*ff*) of PBDEs between water, soil, rice plant and air during different rice growth stages of two growing seasons. (The *ff* during jointing or heading stage is between water and air, while the *ff* during mature or idle stage is between soil and air. For the uncertainty, *ff* between 0.25 and 0.75 (two dotted lines) is considered as equilibrium.).

increasing growing time, especially in rice leaves, which suggested that rice plant can, to some extent, accumulate PBDEs in its tissues. The accumulations of PBDEs in roots may dominated by a passive uptake followed by an apoplastic pathway transport (Chow et al., 2015). However, the transport of PBDEs from root to shoot is usually considered to be unlikely, whereas PBDEs in shoot mainly come from atmospheric deposition (Su et al., 2007; Li et al., 2015) or directly absorb from atmosphere (Tian et al., 2012). PBDE concentrations in rice grains from the study area were slightly lower than those in rice hulls (0.34–3.18 ng/g) sampled at an e–waste dismantling site elsewhere in China (Fu et al., 2012).

3.2. The transport of PBDEs between water, soil, plant and air

The fugacity fraction (*ff*) can be used to identify the direction of air–surface diffusional exchange. The calculated *ff* of PBDEs between water (or soil) and air are shown in Fig. 2a. The *ff* values of BDE209 were not estimated for the lack of necessary physico-chemical parameters. *ff* varied with rice growing time with higher values found during the flooded jointing and heading stages than during the mature and idle stages, suggesting the flooding significant increased the emission of PBDEs from the paddy field. Results showed that BDE28 and BDE47 tended to escape from water into air during the jointing and heading stages, while the other five PBDEs generally tended to be in equilibrium during the flooding periods, except for the jointing stage of the first season. However, all PBDE congeners tended to deposit from air into soil during the dry mature and idle stages. The results imply that the distinctive flooding patterns in rice paddies significantly influence the environmental fate of PBDEs in paddy fields. Firstly, high concentrations of PBDEs in field water indicated that flooding condition can significantly increase the emission of PBDEs in the paddy field. Secondly, the strong depositional trend during dry periods indicated high air-to-soil deposition fluxes for gaseous PBDEs in this area.

Fig. 2b shows the fugacity fractions of PBDEs between rice leaves and ambient air during the different rice growth stages of two growing seasons. Although *ff* values between rice leaf and air varied with rice growth time, PBDEs intensively tended to transfer from air to rice leaves, demonstrating that rice plants act as an adsorbent for PBDEs in the environment. The relatively low *ff* values between air and rice leaves compared to that of air–soil or air–water suggested that the diffusional exchange of air-foliage was more significant.

3.3. Exchange fluxes of PBDEs in paddy field

The calculated diffusional fluxes, atmospheric deposition fluxes, irrigation input fluxes and net exchange fluxes of PBDEs (ng/m^2/d) in the paddy field are listed in Table 1. These fluxes varied widely with rice growth time, especially for diffusion processes. The diffusional fluxes between the field surface (water or soil) and air were usually higher during flooding stages than during dry stages, which suggested that rice cultivation patterns can influence the exchange flux and environmental fate of PBDEs. The exchange fluxes between rice leaves and air (18.3–45.7 ng/m^2/d for total PBDEs) also varied with rice growth stage with higher fluxes during the jointing and heading stages than during the mature stage. This result also suggested that different land use types (e.g. farmland, wasteland, etc.) may lead to dissimilar exchange conditions, since plant variety and vegetation coverage can significantly influence diffusion fluxes. Irrigation and drainage ((−1.22)–6.08 ng/m^2/d) were also found to be a significant exchange input/output processes of PBDEs in the study area. However, the input/output occurred only during the flooded periods. Atmospheric deposition of PBDEs was in the range 0.70–5.24 ng/m^2/d, and was one of the key processes controlling the input of higher brominated PBDEs (e.g. BDE183) to this paddy field.

The direction of net transport of PBDEs was dominated mostly by input into the paddy ecosystem, except for lower brominated PBDEs (BDE28 and BDE47) in the flooding stages of the first growing season. Net inputs of total PBDEs were higher during the mature stage, since the field was dry and outputs were limited. Among the input processes, air–surface (soil, water or leaf) exchange was the dominant process, showing the highest exchange flux, followed by irrigation and atmospheric deposition. The results suggested that air–surface diffusional exchange was the main process dominating inputs and outputs of PBDEs in the paddy field, especially air–water and air–foliage exchange processes. Vegetation, especially foliage, can provide a large, carbon–rich interface for interaction with POPs (Gouin et al., 2002; Nizzetto et al., 2008), and can accumulate compounds with log $K_{oa} > 6$ efficiently from the atmosphere (McLachlan, 1999; Nizzetto et al., 2008). Thus, air–foliage exchange is believed to be the primary route of plant uptake for semi-volatile organic compounds (SVOCs). This suggests that air–surface exchange of PBDEs can not only harm the paddy field ecosystem directly, but may also pose a potential risk to local

Table 1
The exchange fluxes of PBDEs in paddy field during different growth stages of two growing seasons. (Positive means input; while negative means output in the paddy field system.)

N	Jointing					Heading					Mature					Idle				
ng/m²/d	N_{wa}	N_{ra}	N_{ad}	$N_i - N_{dw}$	N_{net}	N_{wa}	N_{ra}	N_{ad}	$N_i - N_{dw}$	N_{net}	N_{sa}	N_{ra}	N_{ad}	$N_i - N_{dw}$	N_{net}	N_{sa}	N_{ra}	N_{ad}	$N_i - N_{dw}$	N_{net}
Season 1																				
BDE28	−27.9	7.52	0.28	−0.07	−20.2	−65.6	29.7	0.28	−1.90	−37.5	0.65	5.73	0.44	0	6.82	4.09	0	0.13	0	4.22
BDE47	−1.88	5.54	0.11	0.38	4.14	−6.93	4.49	0.18	0.00	−2.26	0.25	2.21	0.26	0	2.72	0.31	0	0.16	0	0.47
BDE100	0.17	1.58	0.03	0.05	1.83	0.19	2.14	0.06	−0.02	2.37	0.33	2.65	0.06	0	3.04	0.56	0	0.05	0	0.61
BDE99	0.12	4.22	0.14	0.37	4.84	−0.66	3.75	0.27	0.09	3.45	0.33	2.65	0.40	0	3.38	0.40	0	0.38	0	0.78
BDE154	0.46	5.55	0.05	0.39	6.45	−0.14	2.56	0.14	0.29	2.85	0.19	1.52	0.37	0	2.09	0.31	0	0.76	0	1.07
BDE153	0.25	2.52	0.05	0.47	3.30	0.00	1.54	0.29	0.31	2.13	0.25	2.03	0.59	0	2.88	0.15	0	0.31	0	0.47
BDE183	0.16	1.46	0.14	0.23	1.98	0.14	1.48	2.87	0.01	4.51	0.18	1.47	3.11	0	4.76	0.15	0	0.93	0	1.08
PBDEs	−28.6	28.4	0.80	1.81	2.37	−73.0	45.7	4.09	−1.22	−24.5	2.18	18.3	5.24	0	25.7	5.97	0	2.73	0	8.70
Season 2																				
BDE28	−9.52	24.0	0.06	0.15	14.7	−8.08	21.5	0.05	0.09	13.5	1.78	14.8	0.04	0	16.6	0.77	0	/	0	0.77
BDE47	−3.33	3.68	0.07	−0.40	0.03	−3.13	4.43	0.07	−0.12	1.26	0.31	2.53	0.06	0	2.90	0.33	0	/	0	0.33
BDE100	0.02	1.17	0.03	−0.14	1.08	0.07	1.21	0.02	0.08	1.37	0.08	0.60	0.02	0	0.70	0.27	0	/	0	0.27
BDE99	−1.42	4.09	0.20	−0.37	2.50	−0.66	4.83	0.14	0.38	4.69	0.30	2.42	0.12	0	2.84	1.34	0	/	0	1.34
BDE154	−1.50	3.35	0.13	−0.45	1.53	−0.63	2.89	0.06	0.51	2.82	0.07	0.58	0.06	0	0.71	0.31	0	/	0	0.31
BDE153	−1.22	2.80	0.20	−0.14	1.63	−0.01	3.46	0.08	2.14	5.68	0.29	2.31	0.07	0	2.67	0.93	0	/	0	0.93
BDE183	0.11	3.23	1.78	0.06	5.18	0.07	1.67	0.98	2.99	5.71	0.14	1.11	0.33	0	1.58	0.23	0	/	0	0.23
PBDEs	−16.9	42.3	2.47	−1.28	26.7	−12.4	39.9	1.40	6.08	35.0	2.96	24.3	0.70	0	28.0	4.18	0	/	0	4.18

/ means that atmospheric deposition fluxes of PBDEs in the idle stage of the second season was not collected.

human populations or wildlife through the food chain.

The air–soil exchange fluxes of PBDEs in the study field (2.18–5.97 ng/m^2/d) were comparable to those (3.2–23.4 ng/m^2/d) measured in Izmir, Turkey (Cetin and Odabasi, 2007); whereas the atmospheric deposition fluxes (0.70–5.24 ng/m^2/d) were considerably lower than those found (67.6–129 ng/m^2/d) in Izmir, Turkey (Cetin and Odabasi, 2007).

3.4. *Inputs of PBDEs to the paddy field during the rice growth period*

We calculated the PBDE inputs and outputs to/from the paddy field based on monitoring results (Table 2 and Fig. 3). Fig. 3 indicated that air–foliage and air–water exchange were the dominant input and output processes, respectively. Since some PBDE congeners, such as BDE28, BDE47 and BDE99, were exported from the paddy field through their higher volatility during the wet jointing and heading stages, the air–water exchange of total PBDEs demonstrated a net output during these wet stages; −2.55 μg/m^2 and −0.73 μg/m^2 for the first and second growing seasons, respectively. The diffusional exchange of PBDEs between rice leaves and atmosphere totally imported ~2.30 μg/m^2 and ~2.67 μg/m^2, which accounted for 87.7% and 89.7% of the PBDE inputs for the first and second growing seasons (75 d), respectively. Such high percentage of input via air–foliage exchange implied that vegetation can significantly increase the input of PBDEs in the ecosystem, as well as their potential risks. The input of PBDEs through air–soil exchange during each mature stage was 0.05 μg/m^2 and 0.07 μg/m^2 for the first and second seasons, respectively, demonstrating absolute values much lower than those measured during the wet stages. The diffusion inputs varied widely in different rice growth stages, especially for lower brominated PBDE congeners. PBDE input to the paddy field through irrigation also varied with sampling time, most likely because of variations in PBDE concentration in irrigation water. However, irrigation was intermittent and mostly conducted before the mature stage. Atmospheric deposition, in contrast, is a continuous input process to the paddy field. The inputs of PBDEs through air deposition accounted for 9.6% (0.25 μg/m^2) and 3.8% (0.11 μg/m^2) of the input for the first and second seasons, respectively. Moreover, rice harvesting can also reduce PBDE concentrations in the paddy field. Given that straw return and straw burning takes place *in situ*, the harvest of rice grain was only considered as the harvesting output from the paddy field. PBDE outputs via rice harvesting were −0.08 μg/m^2 and −0.06 μg/m^2 for the first and second seasons, accounting for 3.1% and 7.9% of the total PBDE outputs for the two seasons, respectively (Fig. 3). However, the output via harvesting may represent an input into human populations through the food chain. Net PBDE inputs throughout the entire growing season were calculated and found to be 0.01 μg/m^2 and 2.18 μg/m^2 for the two seasons, respectively. The net input of total PBDEs was considerably lower in the first season than in the second, which may be attributed to the high volatilization of BDE28 through air–water diffusion in the first season (−2.34 μg/m^2). Net inputs of 6 PBDEs excluding BDE28 were comparable (1.29 and 1.07 μg/m^2) for the two seasons. This suggests that the exchange of less volatile PBDE congeners remains almost constant annually, while the exchange of more volatile congeners (e.g. BDE28) varies widely with rice growing season, because the relatively volatile congeners were easier to revolatile into the air. Among the seven PBDE congeners, BDE183 showed the largest annual input to the paddy field, followed by BDE99 and BDE153, which was mainly attributed to high atmospheric deposition.

Table 2
The inputs and outputs of PBDEs in paddy field during different growth stages of two growing seasons. (Positive means input; while negative means output in the paddy field system.)

m	Jointing (25 d)					Heading (25 d)					Mature (25 d)					m_h	m_{net} (75 d)
μg/m^2	m_{wa}	m_{ra}	m_{ad}	$m_i - m_{dw}$	m'_{net}	m_{wa}	m_{ra}	m_{ad}	$m_i - m_{dw}$	m'_{net}	m_{sa}	m_{ra}	m_{ad}	$m_i - m_{dw}$	m'_{net}		
Season 1																	
BDE28	−0.698	0.188	0.007	−0.002	−0.504	−1.64	0.744	0.007	−0.048	−0.938	0.016	0.143	0.011	0	0.170	−0.010	−1.28
BDE47	−0.047	0.138	0.003	0.009	0.104	−0.173	0.112	0.005	<0.001	−0.056	0.006	0.055	0.007	0	0.068	−0.012	0.103
BDE100	0.004	0.040	0.001	0.001	0.046	0.005	0.054	0.001	<0.001	0.059	0.008	0.066	0.001	0	0.076	−0.004	0.177
BDE99	0.003	0.105	0.003	0.009	0.121	−0.016	0.094	0.007	0.002	0.086	0.008	0.066	0.010	0	0.085	−0.012	0.280
BDE154	0.011	0.139	0.001	0.010	0.161	−0.003	0.064	0.004	0.007	0.071	0.005	0.038	0.009	0	0.052	−0.009	0.276
BDE153	0.006	0.063	0.001	0.012	0.082	<0.001	0.038	0.007	0.008	0.053	0.006	0.051	0.015	0	0.072	−0.010	0.198
BDE183	0.004	0.036	0.003	0.006	0.050	0.004	0.037	0.072	<0.001	0.113	0.005	0.037	0.078	0	0.119	−0.026	0.256
PBDEs	−0.715	0.710	0.020	0.045	0.059	−1.83	1.14	0.102	−0.031	−0.611	0.054	0.457	0.131	0	0.642	−0.082	0.008
Season 2																	
BDE28	−0.238	0.601	0.001	0.004	0.368	−0.202	0.536	0.001	0.002	0.338	0.045	0.369	0.001	0	0.415	−0.008	1.11
BDE47	−0.083	0.092	0.002	−0.010	0.001	−0.078	0.111	0.002	−0.003	0.031	0.008	0.063	0.001	0	0.072	−0.014	0.090
BDE100	0.001	0.029	0.001	−0.004	0.027	0.002	0.030	<0.001	0.002	0.034	0.002	0.015	0.001	0	0.017	−0.003	0.075
BDE99	−0.036	0.102	0.005	−0.009	0.063	−0.016	0.121	0.004	0.009	0.117	0.008	0.060	0.003	0	0.071	−0.013	0.238
BDE154	−0.037	0.084	0.003	−0.011	0.038	−0.016	0.072	0.001	0.013	0.071	0.002	0.014	0.002	0	0.018	−0.006	0.120
BDE153	−0.031	0.070	0.005	−0.003	0.041	<0.001	0.087	0.002	0.054	0.142	0.007	0.058	0.002	0	0.067	−0.005	0.245
BDE183	0.003	0.081	0.045	0.002	0.130	0.002	0.042	0.025	0.075	0.143	0.003	0.028	0.008	0	0.040	−0.013	0.299
PBDEs	−0.422	1.06	0.062	−0.032	0.667	−0.309	0.998	0.035	0.152	0.876	0.074	0.608	0.017	0	0.700	−0.063	2.18

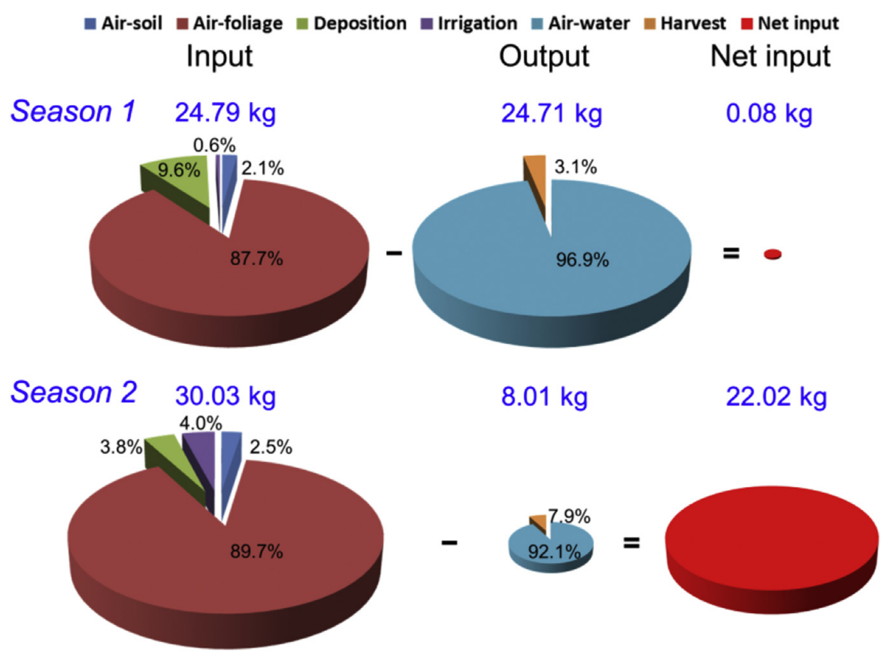

Fig. 3. The composition of PBDE input/output processes in paddy fields of Guangdong Province, South China.

3.5. *Estimated inputs of PBDEs in all paddy fields of Guangdong Province*

Due to the similar cultivation patterns, it is possible for us to estimate the general PBDE inputs to all paddy fields in Guangdong Province in South China based on our results (Table 3 and Fig. 3). The sown areas of early and late season rice in Guangdong Province were 9.42×10^3 and 1.01×10^4 km^2 respectively based on the Guangdong Statistical Yearbook of 2013. The total inputs of seven PBDEs into the paddy fields of Guangdong Province were calculated to be 0.08 and 22.0 kg for early and late rice respectively; while inputs of six PBDEs (excluding BDE28) were 12.2 and 10.8 kg for early and late rice, respectively. Meanwhile, ~0.77 kg and ~0.63 kg of PBDEs could directly enter the food chain through dietary intake

Table 3
The estimated input and output amounts of PBDEs in paddy fields of Guangdong Provence.

kg	Sown area ($\times 10^9$ m^2)	BDE28	BDE47	BDE100	BDE99	BDE154	BDE153	BDE183	Σ$_7$PBDEs	Σ$_6$PBDEs[a]
Early rice	9.42	−12.1	0.97	1.67	2.63	2.60	1.87	2.41	0.08	12.2
Late rice	10.1	11.2	0.91	0.76	2.40	1.21	2.47	3.02	22.0	10.8
Annual		−0.90	1.88	2.43	5.03	3.81	4.34	5.43	22.1	23.0

[a] Six PBDEs except for BDE28.

of early and late rice produced in Guangdong Province. Although, the assessment based on the results in this study has some limitations and uncertainties, it can still reveal the possible input level of PBDEs into the paddy field in Guangdong Province. These high inputs of prohibited PBDEs during the rice growing period, especially for the higher brominated PBDEs, may pose a potential risk to paddy ecosystems and human health through the food chain even 5 years after their prohibition by the Stockholm Convention, and require significant attention.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2015.05.016.

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