Environmental Pollution 205 (2015) 1–7

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

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

Yan Wang [a, b], Shaorui Wang [b], Yue Xu [c], Chunling Luo [b, *], Jun Li [b], Gan Zhang [b]

[a] Key Laboratory of Industrial Ecology and Environmental Engineering (MOE), School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China
[b] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[c] State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China

ARTICLE INFO

*Article history:*
Received 29 March 2015
Received in revised form
8 May 2015
Accepted 11 May 2015
Available online xxx

*Keywords:*
Paddy field
PBDEs
Fugacity fraction
Exchange flux
Net input

ABSTRACT

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;

* Corresponding author.
*E-mail address:* clluo@gig.ac.cn (C. Luo).

http://dx.doi.org/10.1016/j.envpol.2015.05.016
0269-7491/

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 ($\Sigma_7$PBDE 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.

$\Sigma_7$PBDE 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.

$\Sigma_7$PBDEs 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. $\Sigma_7$PBDE 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.

$\Sigma_7$PBDEs 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