

The effects of rice canopy on the air - soil exchange of polycyclic aromatic hydrocarbons and organochlorine pesticides using paired passive air samplers

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ABSTRACT

The rice canopy in paddy fields can influence the air - soil exchange of organic chemicals. We used paired passive air samplers to assess the exchange of polycyclic aromatic hydrocarbons (PAHs) and organo- chlorine pesticides (OCPs) in a paddy field, South China. Levels of OCPs and light PAHs were generally higher under the canopy than above it. We found that the rice canopy can physically obstruct the evaporation of most OCPs and light PAHs, and can also act as a barrier to the gaseous deposition of p,p'- DDT and heavy PAHs. Paddy fields can behave as a secondary source of OCPs and light PAHs. The homolog patterns of these two types of chemical varied slightly between the air below and above the rice canopy, implying contributions of different sources. Paired passive air samplers can be used effectively to assess the in situ air - soil exchange of PAHs and OCPs in subtropical paddy fields.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) are groups of semi-volatile organic compounds (SVOCs) which are of great environmental concern for their persistence, toxicity and bioaccumulation. Airborne SVOCs can participate in air-surface exchange with various matrices including soil, water and vegetation (Nizzetto et al., 2014), which may act as a sink or a reservoir for those compounds in the environment. Understanding these exchange processes is crucial for pollution control and risk management.

The environmental fate of SVOCs can be significantly influenced by vegetation via root exudate dissolution, root uptake, degradation, foliage adsorption and capture (Wania and McLachlan,

2001; Wegmann et al., 2004; Wang et al., 2014). Plant uptake and degradation of SVOCs have been well characterized, especially for vegetables (Mueller et al., 2006; Huang et al., 2010) and crops (Lin et al., 2007; Su and Zhu, 2008). Plants can also act as filters of atmospheric SVOCs due to the efficient capture of both the vapor and particle phases (Nizzetto et al., 2006; Su et al., 2007; Choi et al., 2008; Li et al., 2009; Moeckel et al., 2009b). However, this “filter effect” has been well characterized only in forest ecosystems (Terzaghi et al., 2013). First, forest canopies can absorb vapor-phase SVOCs through the partitioning with air due to the extensive organic surface of the leaves. Choi et al. (2008) observed the rapid uptake of gaseous PAHs by a forest canopy, especially during bud break in early spring. Second, forests can sequester particle-bound SVOCs via foliage capture, but, because only a small proportion of the low molecular weight SVOCs is particle-bound in the air, aerosol deposition onto the canopy is assumed to be negligible (Horstmann and McLachlan, 1998). Thus, gaseous partitioning is more important for the accumulation of SVOCs by vegetation. Plant leaves can also form a dense canopy, which may obstruct the convection and diffusion of SVOCs between the atmosphere and soil. However, there is still a lack of information regarding the physical obstruction of the air - soil exchange of SVOCs by the plant canopy, especially in farmland.

Rice is one of the most widely cultivated and highly produced crops in the world, and has attracted considerable attention for its food safety aspects (e.g., uptake of toxic elements and organic chemicals), as well as the effects of its unique flooding conditions on contaminant transformation (Wang et al., 2015). Compact canopies formed by the high density of rice leaves can impede the convection and diffusive exchange of SVOCs in paddy fields from the elongation

stage to the rice harvest. Very few studies have been conducted on the “blocking effect” of rice canopy, probably due to the lack of appropriate sampling methodologies.

Polyurethane foam passive air samplers (PUF-PAS) have been deployed at various geographic scales to assess the air concentration and distribution of SVOCs (Harner et al., 2004; Pozo et al., 2006; Hogarh et al., 2012). PUF-PAS can enable a power-free and cost-effective collection of seasonally integrated air sample, and thus, it can reveal the average concentrations and long-term trends of SVOCs in the atmosphere, which are useful for long-term air quality assessment. We deployed pairs of PASs below and above the rice canopy, respectively. The purpose of this research was to investigate the long-term influence of the rice canopy on the air - soil exchange of selected PAHs and OCPs using in situ paired passive samplers in a subtropical paddy field, and to improve our understanding of the effects of rice growth on the environmental fate of these organic compounds.

MATERIALS AND METHODS

Sample collection

The studied paddy field was located in a small farm in a sub-urban area of Guangzhou City [23°9'59" N, 113°22'27" E], Guangdong Province, South China, where two crops of rice, of different varieties, are cultivated annually. Pre-cleaned PUF disks (diameter, 14.0 cm; thickness, 1.30 cm; mass, 3.40 g; density, 0.0170 g/cm³) were spiked with depuration compounds (DCs, ¹³C-PCB28, 52, 101, 138, 153, 180 and 209) 3 days before deployment (Moeckel et al., 2009a; Wang et al., 2012). Paired passive air samplers were deployed simultaneously directly under and above the

rice canopy (Fig. 1), from the jointing stage until the rice harvest for both growing seasons (first season: May 29 to July 9, 2012; second season: September 25 to November 8, 2012). Within each growing season, three duplicated paired-samplers were deployed at an interval of >2 m to reduce random errors. After deployment, the PUF disks were wrapped in aluminum foil, placed in polyethylene Zip-lock bags and stored at -20 °C until analysis.

Sample extraction and analysis

PUF samples were spiked with surrogate standards (naphthalene-D₈, acenaphthene-D₁₀, phenanthrene-D₁₀, chrysene-D₁₂, perylene-D₁₂, TCMX, PCB30, PCB198 and PCB209) and then Soxhlet extracted with dichloromethane (DCM) and activated copper for 24 h. Following solvent exchange with hexane, the extract was first cleaned by passing through a multilayer silica gel/alumina column containing anhydrous sodium sulfate, neutral silica gel (3% deactivated) and neutral alumina (3% deactivated) from the top to the bottom using an eluent of 20 mL hexane/DCM (1:1, v/v) for PAH analysis. The extract was further purified on a column containing 50% (w/w) sulfuric acid silica gel and neutral silica gel (3% deactivated) using an eluent of 15-mL hexane/DCM (1:1, v/v) for PCB and OCP analysis.

An Agilent 7890GC-5975MS equipped with a DB5-MS capillary column (30 m x 0.25 mm x 0.25 µm) was used for the analysis of 13 PAHs, including naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF) and benzo[a]pyrene (BaP). An Agilent 7890GC-7000A triple-

quadrupole mass spectrometer equipped with a CP-Sil 8CB capillary column (30 m x 0.25 mm x 0.25 mm) was used for the determination of the seven ^{13}C labeled PCBs (DCs), five hexachlorocyclohexanes (HCHs, including α -HCH, β -HCH, γ -HCH, δ -HCH and ϵ -HCH) and six DDTs (including o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT and p,p'-DDT). Helium was used as the carrier gas at 1 mL/min. The initial oven temperature was set at 60 °C for 1 min, raised to 290 °C at the rate of 4 °C/min.

QA/QC

Procedural and field blanks were run with the PUF samples to assess potential contamination during deployment and analysis. Except NAP (8e10 ng/PUF), no target compounds were detected in the blanks. The average recoveries of the surrogate NAP-D₈, ACE-D₁₀, PHE-D₁₀, CHR-D₁₂, perylene-D₁₂, TCMX, PCB30, PCB198 and PCB209 in the PUF samples were 66 ± 17%, 75 ± 12%, 94 ± 7%, 102 ± 12%, 96 ± 18%, 71 ± 15%, 81 ± 9%, 101 ± 14% and 97 ± 16%, respectively. The reported results in this paper were corrected by the blanks, but not by the surrogate recoveries.

Sampling volume calculation

Calculation of sampling rate (R) and effective sampling volume (V_{eff}) was conducted according to the method established by Moeckel et al. (2009a), using a stable DC_{Stable}, that can barely volatilize from the PUF to correct for the recoveries of DCs:

$$R = \frac{-\ln(\epsilon') \cdot K_{PUF-A} \cdot \rho_{PUF} \cdot V_{PUF}}{t} \quad (1)$$

$$\begin{aligned} V_{eff} &= K_{PUF-A} \cdot \rho_{PUF} \cdot V_{PUF} \cdot \left(1 - \exp \left[\frac{-R \cdot t}{K_{PUF-A} \cdot \rho_{PUF} \cdot V_{PUF}} \right] \right) \\ &= K_{PUF-A} \cdot \rho_{PUF} \cdot V_{PUF} \cdot (1 - \epsilon') \end{aligned} \quad (2)$$

$$\epsilon' = \left(\frac{C_{DC}}{C_{DC,0}} \right) / \left(\frac{C_{CD-Stable}}{C_{CD-Stable,0}} \right) \quad (3)$$

$$K_{PUF-A} = 10^{0.6366 \log K_{OA} - 3.1774} \quad (4)$$

where $C_{DC, 0}$ and C_{DC} are the original and residual amounts of DC (ng/sample) before and after deployment, respectively. ϵ' is the corrected recovery of DC by the recovery (ϵ) of stable DC^{Stable} . ρ_{PUF} is the density of PUF (g/m³), V_{PUF} is the volume of PUF (m³) and t is the deployment time (d). K_{PUF-A} is the PUF-air partition coefficient (m³/g), which was calculated according to Shoeib and Harner (2002). The K_{OA} was calculated from the relationship in Harner and Bidleman (1996). Only a loss of DC within 20% - 80% can be used in the calculation of sampling volume (Huckins et al., 2002). In our study, the losses of ¹³C-PCB28 and most of ¹³C-PCB52 met this requirement (Table S1 of the Supporting Information, SI). The sampling volume used in our study was the average effective volume of ¹³C-PCB28 and 52 (Fig. S1 of the SI).

RESULTS AND DISCUSSION

Air concentrations of PAHs and OCPs above and below the rice Canopy

PAHs

The total concentrations of 13 PAHs measured in the air above and below the rice canopy were $44.2 \pm 3.9 \text{ ng/m}^3$ and $45.4 \pm 4.2 \text{ ng/m}^3$ for the first growing season, and $57.0 \pm 5.0 \text{ ng/m}^3$ and $66.2 \pm 5.4 \text{ ng/m}^3$ for the second season, respectively (Fig. 2a). The total PAH concentrations were slightly higher in the air below the canopy than those above the canopy. However, the trends were inconsistent among all PAH congeners. The concentrations of the low-molecular-weight (LMW, ≤ 3 rings) PAHs were higher under the canopy, whereas the concentrations of the high-molecular-weight (HMW, ≥ 4 rings) PAHs were higher over the canopy. This suggests that the paddy field may act as a secondary source of LMW PAHs, which tended to escape from the soil into the air, during the rice growing period. There are two possible explanations for why HMW PAHs were higher above the canopy: first, since the paddy soil mostly consists of clay, HMW PAHs in the soil or field water are strongly adsorbed to fine soil particles, and relatively difficult to volatilize into the air under the canopy. Second, the rice leaves can capture the air particles, which results in a lower concentration of particles in the air below the canopy than above the canopy. HMW PAHs were apt to adsorb to atmospheric particles. Because the PUF samplers can capture the fine particles and their bound compounds (Klanova et al., 2008; Chaemfa et al., 2009), the HMW PAHs were, therefore, higher over the rice canopy. The concentrations of PAHs in the air of the second growing season were generally higher than those in the first season, especially for FLA, PYR and CHR, which may be due to new inputs of PAHs, such as biomass burning. Besides the different sources, the relatively low concentrations in the first season may also be due to the higher precipitation, which washed out the gaseous and particle PAHs and other chemicals in the atmosphere.

We used one-way ANOVA to test for statistical significance at the 0.05 level for the air concentrations of the same congener (Fig. 2a). Significant differences ($p < 0.05$) between the air concentrations measured above and below the rice canopy were found in the two growing seasons for NAP, ACE, ACY, PYR, CHR and BaP, respectively. Additionally, the differences were significant only in the first growing season for FLA, BaA, BbF and BkF, and only in the second season for FLU and ANT. There was no significant difference, however, between the air concentrations of PHE above and below the rice canopy. The statistical significance also indicates that the rice canopy can markedly influence the convection and diffusion of PAHs in the paddy field.

HCHs

The total concentrations of HCHs in the air above and below the rice canopy were 39.3 ± 2.3 $\mu\text{g}/\text{m}^3$ and 52.1 ± 3.9 $\mu\text{g}/\text{m}^3$ for the first season, and 42.2 ± 5.3 $\mu\text{g}/\text{m}^3$ and 68.9 ± 6.5 $\mu\text{g}/\text{m}^3$ for the second season (Fig. 2b), respectively. The total HCH concentrations were higher below the canopy than those above the canopy ($p < 0.05$). This trend was consistent for each HCH congener, but was statistically significant only for β -HCH (both seasons), α -HCH (second season) and γ -HCH (second season). The higher levels of HCHs under the rice canopy also suggested that there is a net flux of HCHs from the soil surface to the atmosphere in the paddy field. The relatively high concentrations of HCHs in the second season compared to the first season were attributed to the additional input of α -HCH from the surrounding environment. The concentrations were similar in both seasons for other HCH congeners.

DDTs

The air concentrations of total DDTs above and below the canopy were $299 \pm 11.7 \text{ pg/m}^3$ and $348 \pm 35.3 \text{ pg/m}^3$ for the first season, and $475 \pm 46.1 \text{ pg/m}^3$ and $496 \pm 72.7 \text{ pg/m}^3$ for the second season (Fig. 2c), respectively. Similar to the PAHs and HCHs, the total DDT levels were also higher under the rice canopy, although the difference was insignificant ($p > 0.1$). The concentrations of p,p'-DDE and o,p'-DDD were significantly higher under the canopy than those above the canopy for both seasons, whereas that of p,p'-DDT was significantly higher above the canopy in only the second season. No significant differences were found between the concentrations measured above and below the canopy for o,p'-DDE, p,p'-DDD and o,p'-DDT. These results imply that the paddy field may be a secondary source of only p,p'-DDE and o,p'-DDD. The higher p,p'-DDT in the air samples from above the canopy suggest a new input of p,p'-DDT during the sampling period. The concentrations of p,p'-DDT increased in the second season compared to the first season, which also suggests an additional input of p,p'-DDT in the second season.

Congener profiles of PAHs and OCPs above and below the rice

PAHs

The congener profiles of PAHs (Fig. 3a) show that PHE was the most dominant congener, followed by FLA and PYR. Similar to the concentrations, the profiles of PAHs collected above and below the rice canopy were different. The relative abundance of HMW PAHs (≥ 4 rings) was reduced under the canopy (25% - 33%) compared to that above the rice canopy (42% - 45%). There are two possible explanations: first, the filter effect of the rice leaves led to the relatively low

concentration of particles and associated HMW PAHs below the canopy compared to that above the canopy; second, the PAH profiles in the air under the canopy were similar to those in the field water (Wang et al., 2015), which suggests that the PAHs in the air under the canopy generally originated from the field water.

PAH isomer ratios can be used as signatures for source diagnostics assuming that the paired isomers are diluted to a similar extent and remain constant during transport from the sources to receptors (Yunker et al., 2002; Katsoyiannis et al., 2011). Commonly used isomer ratios for the source diagnostics are $\text{ANT}/(\text{ANT} + \text{PHE})$, $\text{FLA}/(\text{FLA} + \text{PYR})$, and $\text{BaA}/(\text{BaA} + \text{CHR})$ (Shen et al., 2013). An $\text{ANT}/(\text{ANT} + \text{PHE})$ ratio of 0.1 is used to distinguish petrogenic (<0.1) and pyrogenic (>0.1) sources. The $\text{ANT}/(\text{ANT} + \text{PHE})$ ratios in the air collected above and below the canopy were all below 0.07, suggesting petrogenic origins (petroleum inputs) of the PAHs. A $\text{FLA}/(\text{FLA} + \text{PYR})$ ratio of 0.5 is usually defined as the petroleum (<0.5) and combustion (>0.5) transition point, and a $\text{FLA}/(\text{FLA} + \text{PYR})$ ratio between 0.4 and 0.5 is more characteristic of petroleum combustion (Yunker et al., 2002). A $\text{BaA}/(\text{BaA} + \text{CHR})$ ratio < 0.2 is indicative of petrogenic origin PAHs, a ratio > 0.35 is indicative of combustion origin PAHs, while a ratio between these two critical values implies mixed origin (Yunker et al., 2002; Ping et al., 2007). The PAH isomer ratios of the passive air samples collected above and below the canopy are shown in Fig. S2. The PAH sources in the air of the studied paddy field may be mainly of combustion origin. This result is in consistent with the frequent burning of straw and other biomass in this area. Additionally, a slight difference was found between the sources of air above and below the rice canopy, although they may originate from similar sources. Besides the coal and biomass combustion sources, petroleum combustion (such as vehicle exhaust) may also contribute, although to a very limited extent, to the PAH

sources in the air above the rice canopy, since it is located closer to the mixed sources compared to the air below the canopy (Fig. S2). However, it was suggested by Katsoyiannis et al. (2011) that even PAH molecular diagnostic ratios can exhibit seasonal differences, but they are not valid markers of known differences in source categories and types.

HCHs

As shown in Fig. 3b, α -HCH dominated in the HCH profiles, followed by γ -HCH and β -HCH. Technical HCH consists principally of 60% - 70% α -HCH, 5% - 12% β -HCH, 10% - 15% γ -HCH, 6% - 10% δ -HCH and 3% - 4% ϵ -HCH (Kutz et al., 1991). Among the HCHs, γ -HCH is the only conformer with insecticidal properties and has been commercially produced as Lindane (γ -HCH > 90%). Therefore, a high α/γ ratio (>4) indicates a source of technical HCH, while a low α/γ ratio (<4) indicates a mixed source of both technical HCH and Lindane (Kalantzi et al., 2001). The average α/γ ratios in the air above and below the canopy were 1.9 and 2.0 for the first season, and 2.5 and 2.9 for the second season; hence, the HCHs in the air of the study area originated from the emission of both technical HCH and Lindane, which may be used quite a while ago. The relatively high α/γ ratios in the air under the canopy indicate that the contribution of historical technical HCH may be larger for the air under the canopy.

DDTs

The DDT profiles showed that p,p'-DDT was the dominant congener, followed by p,p'-DDE. DDE and DDD are the dehydro- chlorinated products under aerobic and anaerobic conditions, respectively. High concentrations of p,p'-DDE compared to p,p'- DDD indicate that aerobic degradation was more favorable in the paddy field, regardless of the long period of field flooding. A high ratio of DDT/(DDE + DDD) suggests fresh inputs of DDTs (Hitch and Day,1992), whereas a high ratio of p,p'-DDE/p,p'-DDT indicates aged DDTs (Zheng et al., 2010). The ratios of DDT/(DDE + DDD) in the air above the canopy were higher than those below the canopy, while the ratios of p,p'-DDE/p,p'-DDT were lower above the canopy, suggesting more fresh inputs of DDTs in the ambient air via atmospheric transport (Fig. S3, SI). Moreover, the relatively high ratios of p,p'-DDE/p,p'-DDT may also be due to the degradation of historical used DDT in the paddy soil.

Influence of the rice canopy on the convection and diffusion of PAHs and OCPs

The key mechanism of air - soil exchange of gaseous SVOCs is partitioning, a process governed by the thermodynamics of diffusion and hydrophobic interactions between the chemicals and environmental matrices (Nizzetto et al., 2014). SVOCs in the air below the canopy tend to equilibrate with those in the surface soil or water, while SVOCs in the air above the rice canopy are homogenous with those in the ambient air (Fig. 1). We calculated the ratios of $C_{\text{under}}/(C_{\text{under}} + C_{\text{cover}})$ using the air concentrations measured over and under the rice canopy to assess the exchange trends of PAHs and OCPs in the paddy field (Fig. 4). A ratio of >0.5 indicates that the air concentration below the canopy is higher than that above the canopy, implying that the rice canopy may be obstructing emission from the soil to air. Otherwise, a ratio of <0.5 indicates that

the rice canopy may be obstructing gaseous air-to-soil transport. In our study, the ratio was >0.5 for the LMW PAHs, and <0.5 for the HMW PAHs. This suggests that the rice canopy may weaken the volatilization of LMW PAHs into the air and the deposition of gaseous HMW PAHs into the soil. Generally, the ratios of HCHs and DDTs were also higher than 0.5, suggesting that the paddy field was a secondary source of these OCPs. The one exception with a ratio lower than 0.5 was p,p'-DDT, which implies new continued inputs of DDT into the ambient air. However, if we take uncertainties into account (SI, S1), only Nap, ACY, ACE and FLU were found to exhibit net volatilization in the second season, whereas only CHR, BkF, BbF and BaP were found to exhibit net deposition in the first season. In general, our results suggest that the rice canopy can influence the air-soil exchange of PAHs, HCHs and DDTs in the paddy field.

CONCLUSION

Rice growth can affect the air-soil exchange of SVOCs through physical obstruction or filter effect of foliage. Our results suggest that the paddy field acted as a secondary source for p,p'-DDE, o,p'-DDD and LMW PAHs, and a temporary reservoir for HMW PAHs and p,p'-DDT. Additionally, there were new inputs of technical DDT via atmospheric transport. The dense rice canopy, however, blocked the evaporation of most OCPs and LMW PAHs, while it also blocked the deposition of vapor-phase HMW PAHs and p,p'-DDT. The "blocking effect" of the rice canopy may potentially increase the entrance of SVOCs into the rice plant and pose a potential risk to food safety. Our results demonstrate the effectiveness of paired passive air samplers to assess the air-soil

exchange of PAHs and OCPs in paddy fields, which provides a novel methodology for the in situ assessment of the long-term air-surface exchange of SVOCs in such environments.

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APPENDIX 1. SUPPLEMENTARY DATA

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2015.01.037>.

FIGURES

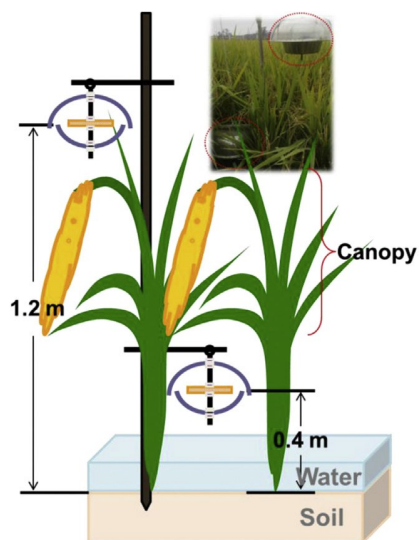
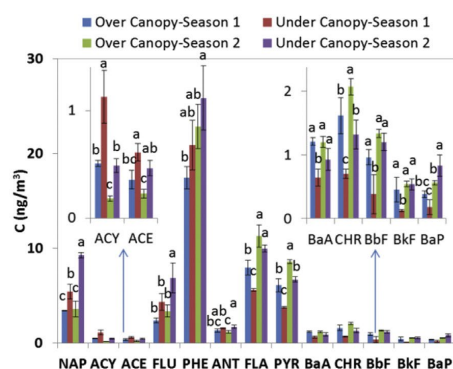
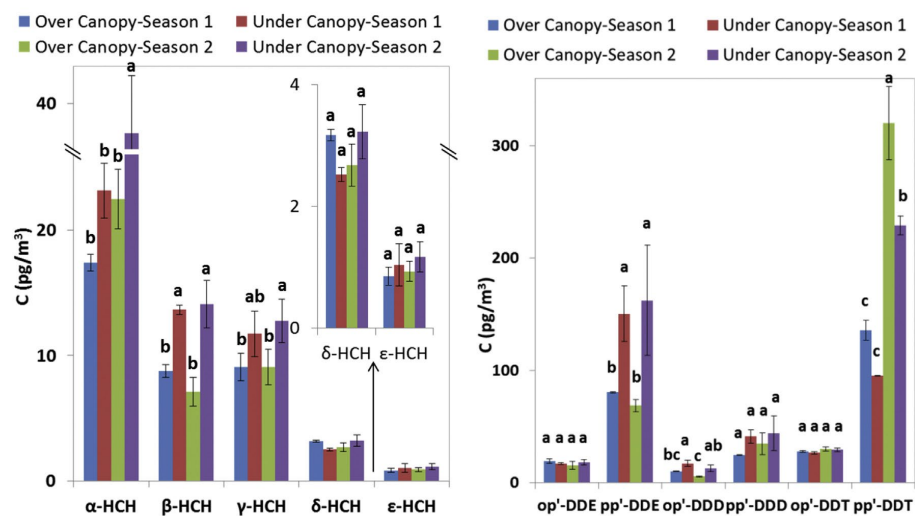


Fig. 1. The details of the paired passive air samplers.



a PAHs



b HCHs

c DDTs

Fig. 2. The air concentrations of PAHs, HCHs and DDTs collected over and under the rice canopy. (The different lowercase letters mean that the difference is statistical significance at the 0.05 level.)

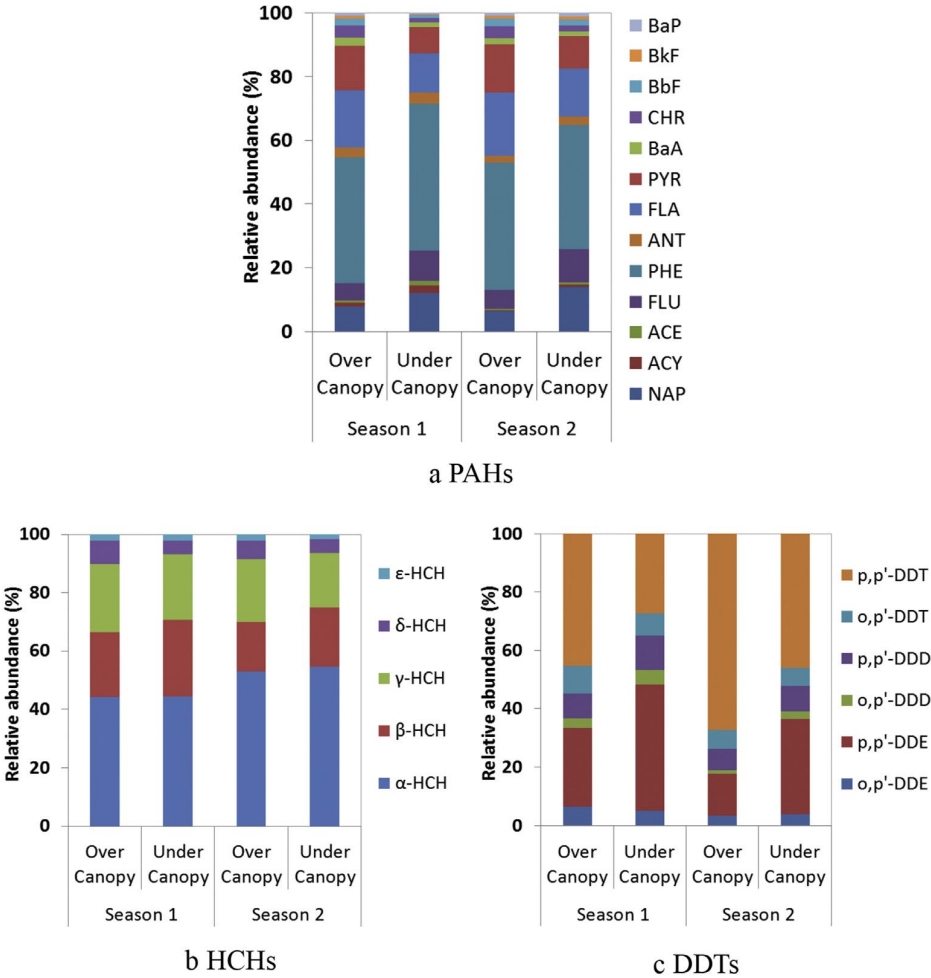
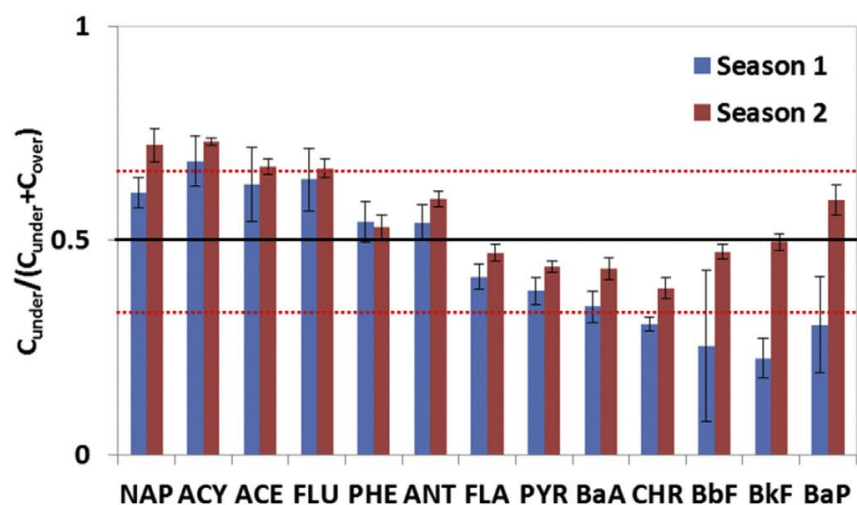
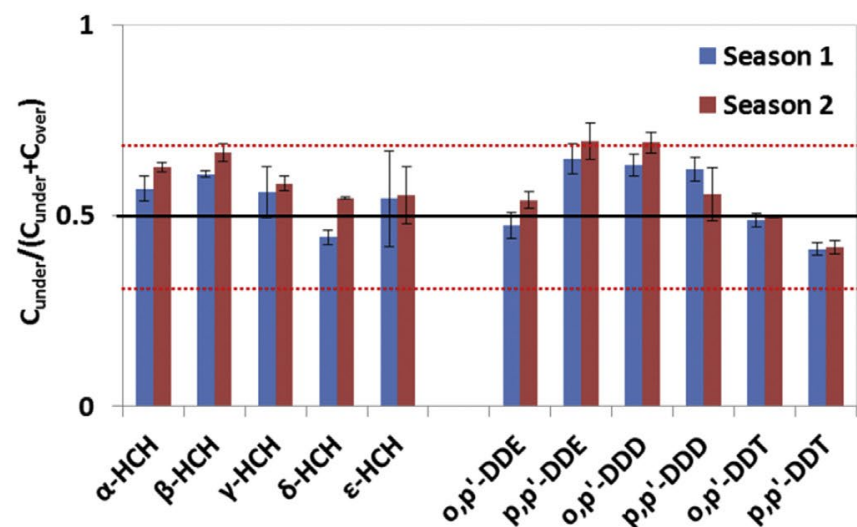


Fig. 3. The congener profiles of PAHs, HCHs and DDTs collected over and under the rice canopy.



a PAHs



b OCPs

Fig. 4. The exchange trends of PAHs, HCHs and DDTs in the paddy field during two growing seasons. (The dotted lines show the uncertainty of fugacity fraction. According to the uncertainty, the ratio between 0.33 and 0.67 is considered as equilibrium.)

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