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# Seasonal and diurnal variations of atmospheric PAHs and OCPs in a suburban paddy field, South China: Impacts of meteorological parameters and sources

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## ABSTRACT

The atmospheric contaminations of polycyclic aromatic hydrocarbons (PAHs), hexachlorocyclohexanes (HCHs), and DDTs have been extensively monitored for decades, but contaminations in agricultural paddy fields have rarely been reported. We measured the atmospheric PAH, HCH, and DDT constituents during different rice growth stages in a suburban paddy field in South China. Diurnal variations were found in the atmospheric concentrations of PAHs and HCHs, but not for DDTs. Additional nocturnal emissions and meteorological conditions, such as low nocturnal stable atmospheric boundary layers, may be mainly responsible for the higher PAH and HCH levels at night, respectively. Atmospheric con- centrations of PAH, HCH, and DDT constituents varied with rice growth stage, but no regular seasonal variation was found, suggesting that rice growth has no significant influence on the atmospheric con- centrations of these chemicals. A correlation analysis suggested that meteorological parameters, such as temperature, precipitation, mixing layer height, or wind speed, may directly or indirectly affect the air concentrations of PAHs, HCHs, and DDTs. Source apportionment showed that atmospheric PAHs, HCHs, and DDTs in the paddy field originated from mixed sources, and the contribution of each source varied with time. The isomer ratio of fluoranthene/(fluoranthene + pyrene) may result in an invalid diagnosis of PAHs.

## INTRODUCTION

The atmosphere is considered to be an efficient medium for the regional and global dissemination of persistent organic pollutants (POPs), such as polycyclic aromatic hydrocarbons

(PAHs), organo- chlorine pesticides (OCPs), and polychlorinated biphenyls (PCBs). POPs can undergo long-range atmospheric transport till their ultImate deposition. However, the observed atmospheric levels of POPs undergo significant seasonal and diurnal fluctuations. These variations are caused not only by changes in meteorological conditions (e.g. air temperature, humidity, wind speed, and wind direction) and various oxidants (e.g. ozone and hydroxyl radicals) but also by the presence of seasonal or diurnal emission sources (Ohura et al., 2013; Reisen and Arey, 2005; Tsapakis and Stephanou, 2003, 2007). It has been suggested that the temperature-mediated reversible airesurface exchange between the air and soil, water, or plant (Gouin et al., 2002), atmospheric photodegradation with hydroxyl radicals during daylight time (Mandalakis et al., 2003; Totten et al., 2002), or stable air conditions at night (Bidleman and Leone, 2004) can lead to diurnal variations in the atmospheric concentration of POPs.

Vegetation can influence the level of POPs in the atmosphere (Moeckel et al., 2009; Su et al., 2007). Airborne POPs can be efficiently captured by vegetation via partitioning with air on the extensive organic surface of leaves, especially during bud break in spring (Choi et al., 2008), or through the “filter effect” of foliage (Terzaghi et al., 2013). The effects of vegetation may to some extent modify the air concentrations and compositions of POPs. However, these effects have not been well characterized in agricultural fields. As one of the most widely cultivated crops, rice is grown on an area of ~163 million ha globally. China is the world's largest producer of rice, accounting for ~19% of the world's harvested area (FAOSTAT, 2013). The large growing area of rice may modify the concentrations and profiles of POPs in the air. Moreover, the unique flooding conditions and the dry-wet alternation during the cultivation of rice can also influence air-soil exchange processes (Wang et al., 2015), which may lead to fluctuations in the atmospheric concentrations of POPs. To date, few studies (Pozo et al., 2011) have focused on the environmental fate of POPs in the air above the distinctive paddy fields.

Both PAHs and OCPs are ubiquitous POPs in the environment, and have been studied for decades (Shen et al., 2005; Wu et al., 2005; Zhang et al., 2004). Despite years of study, many unresolved questions remain regarding the sources and factors influencing these POPs, especially in agricultural fields, such as rice paddy. PAHs originate from the incomplete combustion of fossil fuels or biomass, whereas the production and usage of OCPs are prohibited, and current environmental levels are mainly derived from historical usage. Understanding the various sources and the factors influencing those POPs in the air above paddy fields is critical for appropriate pollution management and food safety. The purpose of this study was: (i) to characterize the seasonal and diurnal concentrations of PAHs and OCPs in the ambient air of a suburban paddy field, (ii) to investigate the factors that influence the variations of atmospheric PAHs and OCPs, and (iii) to assess the potential sources of PAHs and OCPs in the air of a paddy field.

## MATERIALS AND METHODS

### Sample collection

The sampling site was located in a large rice-growing area (~2.5 km$^2$) in the suburban area [23$^o$ 9’ 59’’ N, 113$^o$ 22’ 7’’ E] of Guangzhou City, South China. These paddy fields cultivated two rice crops annually and were surrounded by a highway, a small airport, a forest park, and a university campus (Fig. 1). Active air sampling was conducted inside this rice-growing area and 1 m next to the selected paddy field (~0.3 km$^2$). Air samples were collected between May 3 and December

13, 2012 during five separate growth stages: tillering, jointing, heading, mature, and idle (period after harvest), spanning two rice growing seasons (see Table S1 of the Supporting Information, SI).

The diurnal air samples were obtained using a high-volume active air sampler every 12 h (day: 6:00–18:00; night 18:00–6:00) for ~3 d. The air samples were drawn through glass fiber filters (GF/A 20.3 cm x 25.4 cm, prebaked at 450 $^{o}$ C for 4 h), and subsequently through polyurethane foam (PUF) plugs (6.5 cm diam. x 7.5 cm thickness, pre-cleaned by acetone and dichloro- methane) at a flow rate of 0.3 m3/min. All samples were wrapped with aluminum foil, placed into polythene zip-bags, and stored at -20 $^{o}$ C until analysis.

## Sample extraction and analysis

PUF samples were spiked with surrogate standards (naphthalene-$D_8$, acenaphthene-$D_{10}$, phenanthrene-$D_{10}$, chrysene-$D_{12}$, per- ylene-$D_{12}$, TCMX, PCB30, PCB198, and PCB209), and Soxhlet extracted with dichloromethane (DCM) and activated copper for 24 h. After solvent exchange with hexane, the extract was cleaned by a multilayer silica gel/alumina column containing anhydrous sodium sulfate, neutral silica gel (3% deactivated), and neutral alumina (3% deactivated) from top to bottom for PAH analysis, and then further purified by a column containing 50% (w/w) sulfuric acid-silica gel and neutral silica gel (3% deactivated) for OCP analysis.

We analyzed 12 PAHs, including acenaphthylene (ACY), ace- naphthene (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), using an Agilent 7890GC-5975MS equipped with a DB5-MS capillary column (30 m x 0.25 mm x 0.25 µm). 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) were also determined by using an Agilent 7890GC-7000A triple-quadrupole mass spectrometer equipped with a CP-Sil 8CB capillary column (50 m x 0.25 mm x 0.25 µm). Helium was used as the carrier gas at a flow of 1 mL/min. The initial oven temperature was set at 60 $^{o}$C for 1 min, and raised to 290 $^{o}$C at the rate of 4 $^{o}$ C/min for both PAHs and OCPs.

## QA/QC

Procedural and field blanks were run simultaneously with the PUF samples to assess potential contamination during deployment and analysis. No target compounds were detected in the blanks. The average recoveries of the surrogate NAP-$D_8$, ACE-$D_{10}$, PHE-$D_{10}$, CHR-$D_{12}$, perylene-$D_{12}$, TCMX, PCB30, PCB198, and PCB209 in the PUF samples were 64 ± 10%, 69 ± 12%, 89 ± 10%, 91 ± 15%, 105 ± 16%, 72 ± 17%, 79 ± 11%, 90 ± 16%, and 89 ± 19%, respectively. The reported results were not corrected by the surrogate recoveries.

## RESULTS AND DISCUSSION

### Diurnal variations of atmospheric PAHs and OCPs

#### PAHs

The total concentrations of 12 PAHs were in the range 40.9 - 333 ng/m$^3$ with an average of 88.3 ± 41.8 ng/m$^3$ and 194 ± 88.5 ng/m$^3$ during the daytime and at night, respectively. The highest concentrations of PAHs during the day and night were both found in the idle stage of the first growing season (Fig. 2a), when the burning of rice-straw occurred after rice harvesting. The air levels of PAHs in this area were comparable to those measured by previous studies (Bi et al., 2003; Yang et al., 2010).

There was a significant diurnal variation ($p < 0.01$) in the air concentrations of PAHs with minimum concentrations during the day and maximum concentrations at night. The relatively high concentration at night may be due to two reasons. First, atmospheric PAHs can be photodegraded by hydroxyl radicals or ozone in daylight (Mandalakis et al., 2003; Totten et al., 2002). Second, meteorological parameters related to atmospheric dispersion can also affect the diurnal variation of PAHs (van Drooge and Ballesta, 2009). The study area was generally under relatively high atmospheric stability with light winds and low nocturnal stable layers (Table S2, SI). The higher concentrations of PAHs at night may be due to temperature inversions, which can reduce atmospheric dispersion. As an indicator of the formation of temperature in- versions, the mixing layer heights (MLHs) were calculated (Table S2) using the HYSPLIT software from the National Oceanic and Atmospheric Administration Air Research Laboratory. MLHs were generally higher during daytime than at night, except for during the jointing and mature stages of the first growing season. Generally, the MLH steeply decreased after sunset, and increased again after sunrise. The low MLH at night can lead to a relatively high PAH concentration, assuming the input is constant. This hy- pothesis is supported by the significant negative correlations ($p < 0.05$) between MLHs and concentrations of PAH congeners, such as FLU, ANT, PYR, BaA, BaP, and total

PAHs (Table S3). More- over, the diurnal variation of air temperature affects the volatili- zation of PAHs as well as the airesurface exchange processes, which may also result in variations in the atmospheric concentration during the day. However, no significant correlation was found between the air temperature and individual PAH concentrations, except for ANT and BaA, which had a weak negative correlation ($0.01 < p < 0.05$) with air temperature. This suggests that the variation of air temperature was not the main factor responsible for the variations in atmospheric PAH concentrations. In addition, moderate inverse correlations ($p < 0.05$) were found between the wind speed and atmospheric concentrations of individual PAHs, except for ACE, ACY, PYR, and BaP (Table S3). The wind speeds were generally higher during the daytime, which assisted the atmospheric dispersion of PAHs. The dilution effect of wind suggests that PAHs originated mainly from local sources, because strong winds would sweep pollutants out of the study area, whereas light winds would allow pollution levels to increase (Hong et al., 2007). The relative humidity was also significantly negatively correlated with most PAH congeners (Table S3). However, we considered the correlation between humidity and PAH concentrations to be a spurious correlation. Because the relative humidity was inversely correlated with wind speed, it was the wind that was responsible for the diurnal variation of the PAH atmospheric concentrations. There may also have been additional sources at night that led to the higher PAH concentrations in the ambient air at night. As known, it is possible that some factories illegally and secretly discharge un-treated flue gas at night in China. The insignificant correlation ($p = 0.09$) between diurnal and nocturnal PAH concentrations in the air also implied that they originated from dissimilar sources.

Considering the significant higher PAH levels at night than during the daytime, we suggested that there were additional sources at night, such as secret illegal flue emission. Thus, we considered that additional emission and low nocturnal stable layers were both responsible for the higher PAH concentrations at night.

## HCHs

Fig. 2b shows that the total concentrations of HCHs were in the range 40.5e235 pg/m$^3$ with an average of 99.3 ± 39.8 pg/m$^3$ and 128 ± 48.0 pg/m$^3$ during the daytime and night, respectively. The highest concentrations of HCHs were found in the jointing stage of the first growing season.

Atmospheric HCH concentrations were also generally higher at night than during the daytime, but the difference was not statistically significant ($p > 0.05$). Photodegradation with hydroxyl radicals and the varied meteorological conditions may be responsible for the diurnal variations. Significant positive correlations were found between air temperature and β- ($p < 0.01$), δ- ($p < 0.01$), and γ-HCH ($p = 0.04$), whereas a-HCH levels were inversely correlated with wind speed ($p < 0.05$) and positively correlated with humidity ($p < 0.01$). This suggested that α-HCH might be of local fresh origin, while β -, γ -, or δ -HCH may be a mixture with both a local origin and a long-term atmospheric transport component. This was supported by the significant correlation between δ - and β -HCH ($p = 0.001$) or δ - and γ -HCH ($p < 0.001$), but no correlation between δ - and α -HCH ($p = 0.152$).

### DDTs

The total concentrations of 6 DDT constituents were 39.1 - 939 pg/m$^3$ with an average of 366 ± 221 pg/m$^3$ and 402 ± 213 pg/m$^3$ during the daytime and night, respectively. The highest concentrations of DDTs were found in the idle stage of the first growing season (Fig. 2c).

The concentrations of DDT constituents varied randomly be- tween night and day, and no significant diurnal variation ($p = 0.648$) was observed. It suggested that the input of DDTs into the atmosphere were randomly in this area. Instead, we found a significant correlation ($r = 0.882$, $p = 0.001$) between DDTs at night and during daytime, suggesting that there was no different input of DDT constituents during the night.

## Seasonal variations of atmospheric PAHs and OCPs

### PAHs

The assessment of seasonal variations revealed that the average atmospheric PAH concentrations varied widely between the stages of rice growth in the first growing season, whereas they maintain stable in the second growing season. Theoretically, meteorological parameters and proximity to sources are the two main factors that influence contaminant levels in the atmosphere. Although, the meteorological parameters varied distinctly between seasons, there was no significant seasonal trend, except for precipitation, which was considerably higher in the first growing season than in the second (Table S2). Rainfall can scavenge contaminants from the air through rain-out or wash-out, which may account for the relatively low atmospheric

PAH concentration in the first growing season. However, the dispersion of atmospheric PAHs is a complex process and can be affected by other meteorological conditions, such as air temperature, solar intensity, or wind speed. Previous study (Choi et al., 2008) suggested that atmospheric POPs could be efficiently captured by plants via air-foliage partitioning on the extensive foliage surface, especially in the bud break period. Moreover, relatively high concentrations of PAHs were also found in the rice leaves and grains in this area, which indicated that rice plants can adsorb or absorb PAHs from the atmosphere (Wang et al., 2015). However, no regular trend was found between air concentrations of PAHs and the stage of rice growth in this study, which implied that the influences of rice growth were not enough to alter the atmospheric PAH concentrations. Therefore, the air concentrations of PAHs were mainly determined by the source strength.

## HCHs

Atmospheric HCH concentrations during the different sampling periods also varied in a random fashion, especially for α-HCH and γ- HCH, but no regular seasonal trend was found, suggesting that the effects of rice growth were not sufficient to change the air levels of HCHs. The relatively high HCH concentrations in the tillering and jointing stages of the second growing season were due to high concentrations and compositions (Fig. 3b) of α-HCH during these periods, which may due to the accidental inputs such as input via atmospheric transport or local emission. The concentrations of γ- HCH were higher in the first growing season than in the second growing season, which suggested a higher input of γ-HCH in the first half of the year. The concentrations of β-HCH or δ-HCH were relatively stable during the whole sampling period, which suggested that there was no occasional input of β-HCH or δ-HCH into the atmosphere during the sampling time. Although, a significant positive correlation was found between γ -HCH and precipitation (p = 0.005), we assumed that either γ -HCH was transported by air masses or clouds from other areas or this was also a spurious correlation.

### DDTs

No regular pattern of seasonal variation was found for DDT constituents as well. The relatively high concentrations of DDTs, especially p,p’-DDT and p,p’-DDE in the air during the tillering and idle stages of the first season and the mature stage of the second season, may have been due to occasional fresh inputs, such as the use of technical DDT-based antifouling paints and/or dicofol (Li et al., 2007; Lin et al., 2009; Qiu et al., 2005). Therefore, with the exception of the correlation between o,p'-DDE and temperature (r = 0.525, p = 0.017), no significant correlation was found between DDT constituents and meteorological variables because of the random inputs of DDT constituents.

## Composition profiles of atmospheric PAHs and OCPs

The composition profiles of PAHs, HCHs, and DDTs in the air above the paddy field are shown in Fig. 3.

### PAHs

The composition of PAHs varied slightly with the stage of rice growth, but no regular seasonal trend was found (Fig. 3a). Generally, the concentration of low-molecular-weight (LMW) PAHs ($\leq$3 rings) was relatively higher in the first growing season, whereas the concentration of high-molecular-weight (HML) PAHs ($\geq$4 rings) was higher in the second season. This result was due to the higher concentrations of PYR in the second season, which implied that the sources of PAHs in the first and second seasons were slightly different. A slight diurnal variation was found in the composition of PAHs as well, which implied that the diurnal and nocturnal inputs of PAHs may originate from dissimilar sources for the possible illegal emissions at night.

### HCHs

A random variation of HCH profiles was observed in the air above the paddy field (Fig. 3b). Relatively high abundances of γ- HCH were found during the first season, whereas relatively high abundances of α-HCH were observed in the second season. The high abundances of γ - HCH in the jointing and heading stages of the first growing season were consistent with the relatively high concentrations of γ - HCH at these stages, which suggested the input of lindane during these periods. The relative abundances of β-HCH ($p = 0.031$) and δ-HCH ($p = 0.005$) were higher during the daytime than at night, while the relative abundances of α-HCH ($p = 0.004$) were higher at night. However, no significant diurnal variations were found for γ - HCH ($p = 0.282$), which indicated that γ - HCH might have random inputs, such as the use of lindane.

### DDTs

Only slight variations were observed in the profiles of DDTs in the air above the paddy field with p,p'-DDT being the dominant congener throughout the whole sampling period (Fig. 3c). No obvious seasonal or diurnal variations were found in the DDT constituent profiles, suggesting that the sources of DDTs were stable and continuous. However, relatively higher percentages of p,p'-DDT were found during the idle stages of the two growing seasons, when the rice plants were harvested, implying that in addition to random inputs, rice plants may also modify the atmospheric concentrations of DDTs as well as other POPs, to some extent, during their growth. This was consistent with the hypothesis that gaseous POPs can be captured by plants via air-foliage partitioning (Choi et al., 2008).

## Source apportionment of atmospheric PAHs and OCPs

### PAHs

Paired isomer ratios are usually used as markers for the source diagnostics of PAHs, assuming that the isomers are diluted to a similar extent during atmospheric transport (Yunker et al., 2002), although there are many criticisms of this method (Katsoyiannis et al., 2011). ANT/(ANT + PHE), FLA/(FLA + PYR), and BaA/(BaA + CHR) are three commonly used isomer ratios for source identification (Shen et al., 2013). An ANT/(ANT + PHE) ratio of 0.1 is used to distinguish petrogenic (<0.1) and pyrogenic (>0.1) sources. A FLA/(FLA + PYR) ratio of 0.5 is used to distinguish petroleum (<0.5) and combustion (>0.5) sources, while a FLA/(FLA + PYR) ratio 0.4 - 0.5 is more characteristic of petroleum combustion. A BaA/(BaA + CHR) ratio <0.2 is indicative of petrogenic origins,

>0.35 is indicative of combustion origins, while 0.2 - 0.35 suggests mixed origins (Yunker et al., 2002). The PAH isomer ratios in the air above the paddy field are shown in Fig. 4 and Fig. S1. The source diagnostics of the ANT/(ANT + PHE) and BaA/(BaA + CHR) ratios were similar (Fig. 4a). Most of the air samples from the first growing season were located in the lower left corner of Fig. 4a, suggesting a higher contribution from petrogenic origins in the first season; whereas most of the air samples in the second season were located in the center or the upper right corner of Fig. 4a, suggesting a relatively higher contribution from combustion sources, such as biomass burning. However, the FLA/(FLA + PYR) ratio implied that atmospheric PAHs in the first growing season mainly originated from the combustion sources, while in the second season they were from mixed sources (Fig. S1), which contradicted the diagnostics of the ANT/(ANT + PHE) and BaA/(BaA + CHR) ratios, especially for the atmospheric PAHs in the first season. Fig. 4b also showed that the seasonal trends of the ANT/(ANT + PHE) and BaA/(BaA + CHR) ratios contradicted those of the FLA/(FLA + PYR) ratio, which implied that the FLA/(FLA + PYR) ratio may be invalid and would produce an inaccurate diagnosis. Similar observations with different seasonal trends between the BaA/(BaA + CHR) and FLA/ (FLA + PYR) ratios were also found by Dvorska et al. (Dvorska et al., 2011) in the air of Kosetice, Czech Republic. Katsoyiannis et al. (2011) also confirmed that isomer ratios, such as ANT/ (ANT + PHE), FLA/(FLA + PYR), and BaA/(BaA + CHR), gave mixed and contradictory messages about site/source differences, which suggested they are not valid signatures of known differences in source categories. We considered that the varied gas/particle phase partitioning of the different PAH congeners could definitely affect their fate and the diagnostic ratios. However, these ratios can still exhibit temporal or seasonal differences in PAH sources. The clear difference in the PAH ratios between the first and second growing seasons

suggested different PAH sources between the two seasons (Fig. 4). This could be attributed to the relatively low precipitation and frequent occurrence of biomass burning during the second season. Considering the large contribution of biomass combustion in the second season, we preferred to use ANT/(ANT + PHE) and BaA/(BaA + CHR) as the source diagnostic ratios (Fig. 4a), although the efficiency of the ANT/(ANT + PHE) ratio has also been questioned (Braendli et al., 2007). The results indicated that atmospheric PAHs during the daytime mainly originated from a mixture of sources, including petrogenic origins, traffic, or fuel/coal/biomass combustion, whereas atmospheric PAHs at night were mostly derived from petrogenic sources in the first growing season and combustion in the second season.

### HCHs

Technical HCH consists of 60e70% α-HCH, 5 -12% β-HCH, 10 - 15% γ-HCH, δ - 10% γ-HCH, and 3 - 4% ε-HCH, while commercial lindane consists of >90% γ-HCH. Therefore, a relatively high ratio of α/γ (>4) indicates that the primary origin was the recent use of technical HCH, while a low α/γ ratio (<4) indicates mixed sources of both technical HCH and lindane (Kalantzi et al., 2001). The α/γ ratios in the air above the paddy field were all <3 (Fig. S2), suggesting that air HCHs originated from the emission of both technical HCH and lindane. The seasonal variation in the α/γ ratio, with the average value in the second season (1.89) higher than in the first season (1.18), indicated a relatively higher contribution of lindane in the first season. A significant diurnal variation of the α/γ ratio (p = 0.049) was found in the ambient air, which was similar to that of the α-HCH concentration, but the opposite of that for wind speed, implying that HCH concentrations were mainly governed by local sources.

## DDTs

A high ratio of DDE/DDT indicates the input of aged DDT con-stituents, while a high ratio of DDT/(DDE + DDD) indicates the input of fresh DDTs (Hitch and Day, 1992; Zheng et al., 2010). The ratios of DDT/(DDE + DDD) and DDE/DDT in the air above the paddy field are shown in Fig. S3. Points located in the lower right corner suggest a fresh input of DDTs, while points located in the top left corner suggest an emission of historical DDTs. The air samples were generally located in close proximity to each other, with the exception of the samples collected in the mature and idle stages of the second growing season. This implies that there were fresh in- puts of DDTs during these stages.

## CONCLUSION

The atmospheric concentrations and compositions of PAHs, HCHs, and DDTs in a suburban paddy field of South China varied with the stage of rice growth. However, no significant diurnal variations were found for HCHs and DDTs. Meteorological parameters can affect the air concentrations of PAHs, HCHs, and DDTs, but their influence may not be direct or independent. The variation in the atmospheric concentrations of these chemicals may be the result of the combined impact of various meteorological conditions and their sources. The lack of a regular pattern of seasonal variability for PAHs, HCHs, and DDTs suggested that rice growth did not have a strong influence on the levels or profiles of these chemicals in ambient air. PAHs, HCHs, and DDTs in the air above the paddy field originated from mixed sources, both historical and recent, especially for PAHs and DDTs. However, the exact contribution of each source remained unclear. Compared with other isomer ratios, the FLA/(FLA + PYR) ratio may reveal an invalid or inaccurate diagnosis of PAHs, which needs to be confirmed by further studies. Because of the relatively high and continuous inputs, the levels and environmental fate of PAHs and OCPs in the paddy field should be closely monitored for reasons of food safety.

## ACKNOWLEDGMENTS

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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.atmosenv.2015.04.047.

## FIGURES

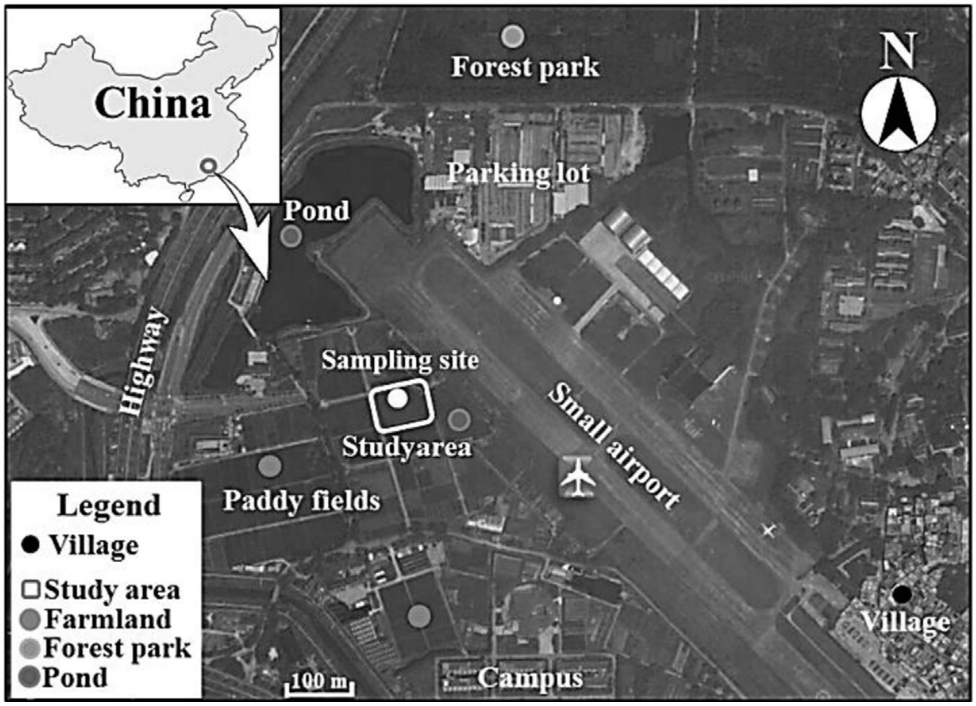
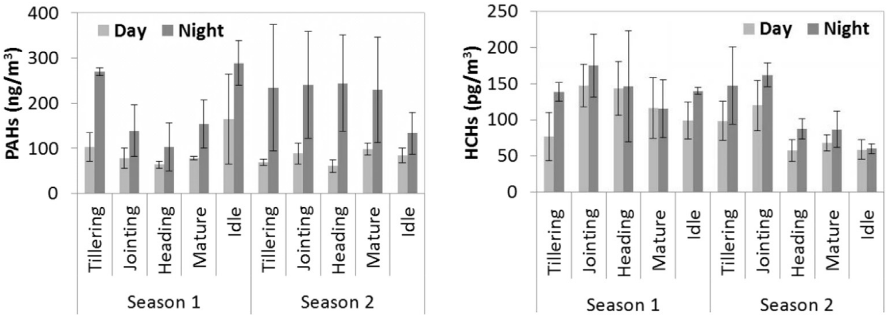
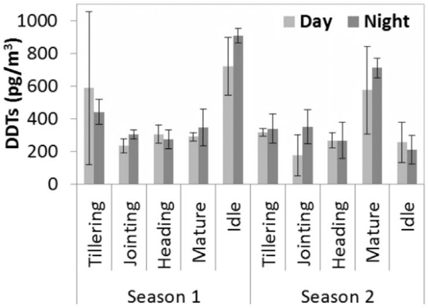


Fig. 1. Sampling site.



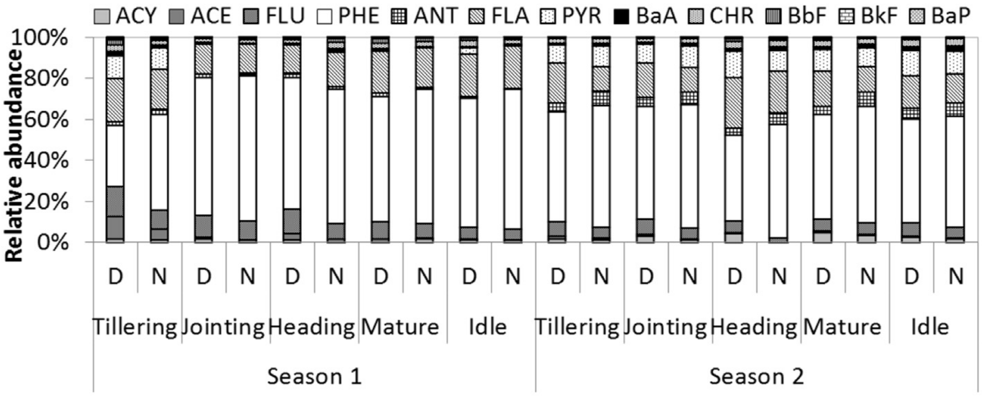
a PAHs

b HCHs

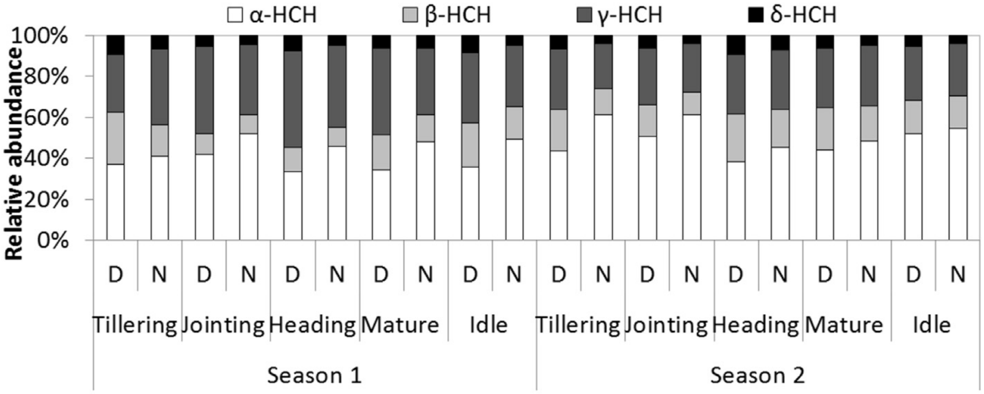


c DDTs

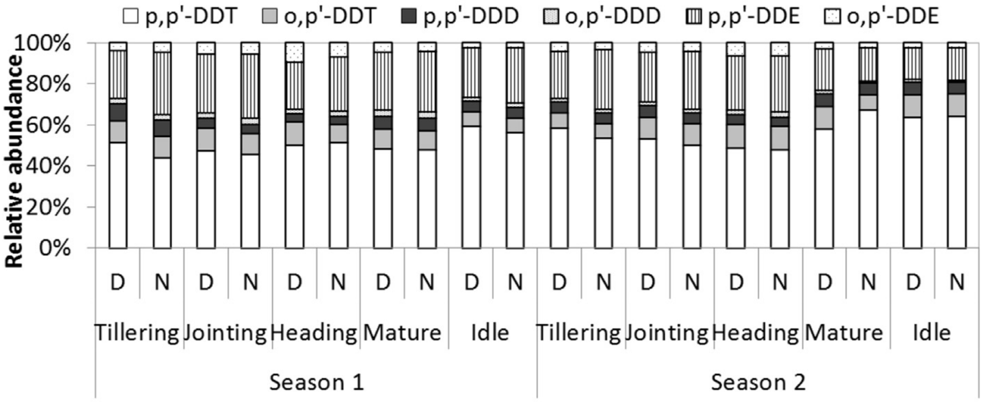
Fig. 2. Diurnal and seasonal variations of PAHs, HCHs, and DDTs in the air above the paddy field.



a PAHs

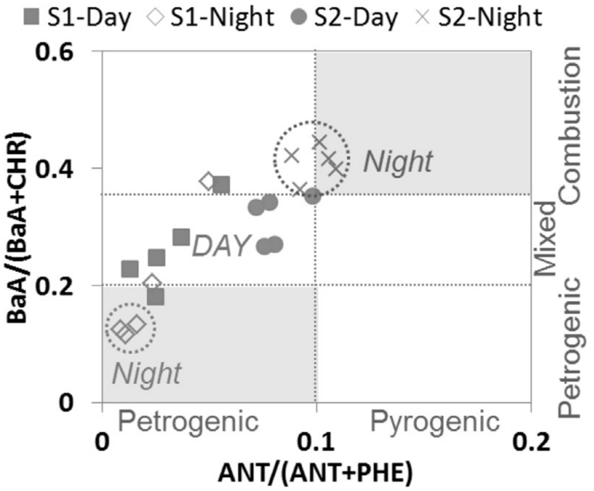


b HCHs

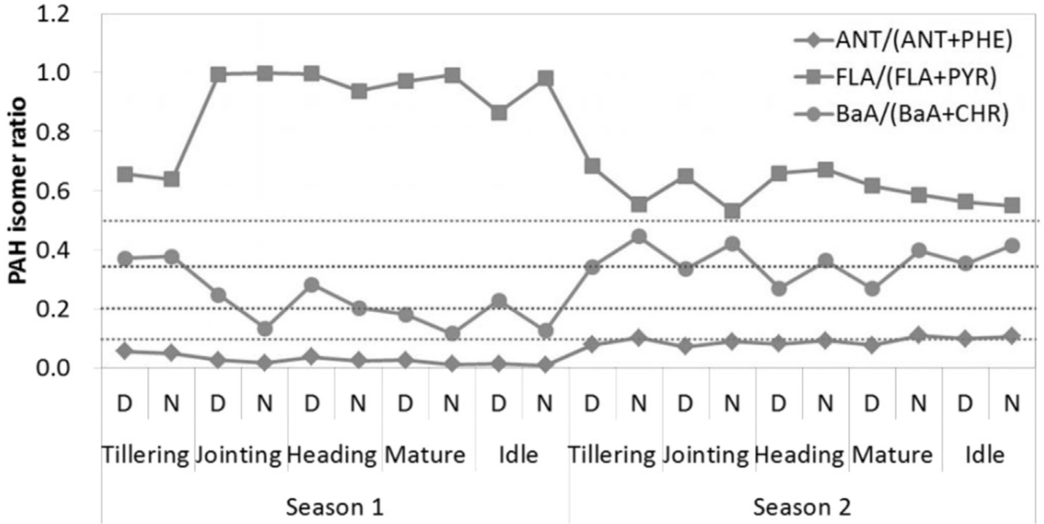


c DDTs

Fig. 3. Compositions of PAHs, HCHs, and DDTs in the air above the paddy field. (D means day, while N means night.)



a ANT/(ANT+PHE) and BaA/(BaA+CHR)



b Diurnal and seasonal variations of PAH isomer ratios

Fig. 4. The atmospheric PAH isomer ratios during different rice growing seasons. (S1 means the first growing season, while S2 means the second growing season. D means day, while N means night.)

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