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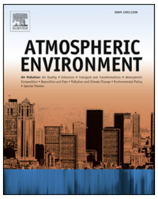

Seasonal and diurnal variations of atmospheric PAHs and OCPs in a suburban paddy field, South China: Impacts of meteorological parameters and sources

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HIGHLIGHTS

- Diurnal and seasonal variations of air PAHs and OCPs in a paddy field were measured.
- Illegal nocturnal emissions may be responsible for the high PAH levels at night.
- Rice growth has no significant influence on the ambient air levels of PAHs or OCPs.
- The fluoranthene/(fluoranthene + pyrene) ratio may lead to an invalid PAH diagnosis.

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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 concentrations 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 concentrations 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.

1. 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), organochlorine 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)

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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 air–surface 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.

2. Materials and methods

2.1. Sample collection

The sampling site was located in a large rice-growing area (~2.5 km^2) in the suburban area [23° 9′ 59″ N, 113° 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 × 25.4 cm, prebaked at 450 °C for 4 h), and subsequently through polyurethane foam (PUF) plugs (6.5 cm diam. × 7.5 cm thickness, pre-cleaned by acetone and dichloromethane) at a flow rate of 0.3 m^3/min. All samples were wrapped with aluminum foil, placed into polythene zip-bags, and stored at −20 °C until analysis.

2.2. Sample extraction and analysis

PUF samples were spiked with surrogate standards (naphthalene-D$_8$, acenaphthene-D$_{10}$, phenanthrene-D$_{10}$, chrysene-D$_{12}$, perylene-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), 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), using an Agilent 7890GC-5975MS equipped with a DB5-MS capillary column (30 m × 0.25 mm × 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 × 0.25 mm × 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 °C for 1 min, and raised to 290 °C at the rate of 4 °C/min for both PAHs and OCPs.

2.3. 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.

3. Results and discussion

3.1. Diurnal variations of atmospheric PAHs and OCPs

3.1.1. 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