Assessment of the Air−Soil Partitioning of Polycyclic Aromatic Hydrocarbons in a Paddy Field Using a Modified Fugacity Sampler

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ABSTRACT

Rice, one of the most widely cultivated crops, has received great attention in contaminant uptake from soil and air, especially for the special approaches used for its cultivation. The dry−wet alternation method can influence the air−soil partitioning of semivolatile organic compounds (SVOCs) in the paddy ecosystem. Here, we modified a fugacity sampler to investigate the air−surface in situ partitioning of ubiquitous polycyclic aromatic hydrocarbons (PAHs) at different growth stages in a suburban paddy field in South China. The canopy of rice can form a closed space, which acts like a chamber that can force the air under the canopy to equilibrate with the field surface. When we compared the fugacities calculated using a fugacity model of the partition coefficients to the measured fugacities, we observed similar trends in the variation, but significantly different values between different growing stages, especially during the flooding stages. However, the measured and calculated fugacity fractions were comparable when uncertainties in our calculations were considered, with the exception of the high molecular weight (HMW) PAHs. The measured fugacity fractions suggested that the HMW PAHs were also closed to equilibrium between the paddy field and atmosphere. The modified fugacity sampler provided a novel way of accurately determining the in situ air−soil partitioning of SVOCs in a wet paddy field.

INTRODUCTION

Determining the partitioning of ubiquitous semivolatile organic compounds (SVOCs), such as polycyclic aromatic hydro- carbons (PAHs), and tracing their environmental fate, has become an important addition to monitoring their concentrations because of their persistence, toxicity, and bioaccumulation. Due to the strong affinity of SVOCs for organic matter, soil becomes one of the major reservoirs and sinks.[1,2] However, the deposition of SVOCs to soil is not permanent because the SVOCs can revolatile into the atmosphere and recycle continuously among the atmosphere, hydrosphere, and terrestrial environment until final deposition.[3−6] Therefore, an understanding of the air−soil partitioning process is crucial for controlling the environmental fate of SVOCs at regional and global scales.[7,8]

The two main ways to monitor the air−surface exchange of SVOCs in the environment are as follows. The first method is based on a fugacity model to describe the equilibrium partitioning process between the environmental compartments.[9] The transfer of SVOCs has been estimated by calculating the fugacity quotients and mass transfer coefficients of different environmental matrices.[5,10−13] Because only the measured concentrations of compounds in air, soil (or water), and several soil physicochemical properties (e.g., soil density and organic carbon content) are needed, this assessment is easy to perform because it requires less field monitoring and relies more on calculation. This method is feasible for assessment of the instantaneous air−surface exchange trend of SVOCs in a stable system with less artificial disturbance or impact. However, this method also requires several physicochemical parameters of the studied compound, such as Henry's constant (H) and the octanol−air partition coefficient (K_{oa}). Thus, it is neither suitable for assessing the exchange trend of the "new" emerging organic pollutants, whose properties are unknown or varied in literatures, nor is it appropriate for unstable or complex systems with varied concentrations or environmental parameters (e.g., temperature or organic carbon content). The second method is based on a fugacity sampler, designed by Meijer et al.[7] and improved by Cabrerizo et al.[14] to determine the partitioning and fugacity gradients between compartments. To measure the soil fugacity, this method uses a fugacity sampler to collect the air very close to the soil surface (≤3 cm), in which compounds have been proved to equilibrate in situ with those in the surface soil. Because this method measures the in situ concentration in the air directly, it can reveal the air− soil partitioning during the sampling period, regardless of the variations in the environmental parameters. The method can obtain a more reliable result than using the fugacity model, especially for an unstable ecosystem, because the fugacity sampler takes most of the environmental variations into account. However, the fugacity samplers used to date were only designed for assessing the air−soil partitioning on dry land, and are not suitable for measuring the partitioning on wet land or agricultural fields with plant involved.

Globally, rice covers a large cultivation area and accounts for high production; and in China, as well as the rest of the world, considerable attention has been paid to the crop in relation to food security.[15,16] The paddy field needs to be continuously flooded before rice mature. The special flooding condition of rice may change the mass transfer coefficients between air and surface, and have a significant effect on the transport of SVOCs in the paddy field.[17,18] However, few studies have estimated the air−surface partitioning of PAHs in the paddy ecosystem due to the lack of appropriate methodologies for determining fugacity gradients in such complex fields, including soil, water, air, and plant. Liu et al.[19] used the fugacity model to assess the air−soil exchange of PAHs in paddy fields of the Pearl River Delta of South China, but not throughout the whole growing season of rice. This lack of data can directly lead to uncertainties in predictions of the environmental fate and risk of PAHs in rice paddy fields.

The purpose of this study was 2-fold: to validate a modified fugacity sampler for the in situ determination of the air−surface partitioning of PAHs between the field surface (i.e., soil or water) and gas phase in the paddy ecosystem, and to obtain a better understanding of the influence of rice cultivation on the environmental fate and implication of PAHs.

MATERIALS AND METHODS

Sampling

The paddy field under study was located in a small area of farmland in the suburban environment of Guangzhou City [23°9′59″ N, 113°22′7″ E], South China, where two crops of rice (*Oryza sativa* L.) are cultivated annually. The farmland, covering an area of ∼2 km^2, is surrounded by a highway, a small airport, a forest park, and a university campus (Figure S1, Supporting Information). The surface soil (0−5 cm, 8), field water (4), and fugacity samples (16) were collected simultaneously from the different growth stages of the two growing season: the jointing, heading, mature, and idle (after harvesting) stages between May 3 and December 13, 2012. Each soil or water sample consisted of 5 subsamples randomly collected within the study area. Details are shown in Figure S1, Table S1, and S1.1 of the Supporting Information.

Modification of the Fugacity Sampler

The soil fugacity (f_s) of PAHs can be measured by analyzing the concentrations of PAHs in air that has equilibrated in situ with the soil surface using the fugacity sampler designed by Cabrerizo et al.[14] This sampler uses a chamber that forces air to have a laminated flow parallel to the soil surface.

However, the sampler is unsuitable for measuring the soil or water fugacity (f_w) of wet land. In addition, it cannot measure the fugacity of complex agricultural fields covered with crops, for which the equilibrium may involve not only soil (or water) and air but also plant matrix. The high planting density of rice can form a “canopy”, which acts like a closed chamber and can obstruct the major exchange of the air below this canopy with the air outside the canopy (Figure 1). Therefore, the air below the rice canopy can be equilibrated with the surface soil or water after sufficient time, and can be used to calculate the fugacity. The modified sampler collected the air in the canopy chamber formed by the rice leaves, and assumed that this air (gaseous phase) has become equilibrated with the surface soil or water. The Teflon pipeline used to collect the equilibrated air consisted of 5 branch pipes covering an area of ∼4 m^2. The pipeline was deployed in the field at least 15 d before the canopy was formed to minimize the disturbance during the sampling. The pipe holes used for air sampling were located at a height of 12 cm above the soil surface to prevent field water from entering the pipeline (i.e., ∼2−4 cm above the water surface for a water depth ranged from ∼8 to 10 cm; Figure 1). Air was first pumped through a glass fiber filter (GF/A, 47 mm diam.) and then through a polyurethane foam (PUF) plug, which was connected to a low-volume air pump at a flow rate of 6−8 L/min. Because the Teflon pipeline had 10 holes, the sampling rate for each hole was reduced to 0.6−0.8 L/min to ensure the minimal disturbance. The residence time of air under the canopy was ∼150−200 min calculated using the chamber volume (4 m^2 × 0.3 m) divided by the sampling rate (6−8 L/min). The relatively high residence time can ensure the occurrence of the air−surface equilibrium under the canopy. The fugacity sampler was conducted for 48 h, and obtained a sampling volume of ∼20−24 m^3. The air fugacity was calculated by measuring the ambient air concentrations at a height of 1.5 m using an identical low volume sampler. Each of our sampling time was in the middle of the each rice growth stage to ensure that the air we collected was equilibrated with the surface soil or water.

Sample Analysis

All samples were analyzed for 10 PAHs: 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). After Soxhlet (soil or PUF) or liquid−liquid extraction (water), all samples were purified and analyzed by Agilent 7890GC-5975MS. The details of the sample analysis and QA/ QC are given in S1 of the Supporting Information.

Calculation of Fugacity

Fugacity, a measure of the chemical potential of a particular compound to escape from one matrix to another,[9] can be calculated using the fugacity capacities and the measured concentrations in the matri- ces.[5,7,20,21] The air (f_a), water (f_w), and soil (f_s) fugacities (Pa) of the PAHs were calculated as follows[9,21]

$$f_a = C_a RT \quad (1)$$

$$f_w = C_w H \quad (2)$$

$$f_s = C_s RT / K_{sa} = C_s RT / (0.411 \rho_s \varphi_{soc} K_{oa}) \quad (3)$$

where C_a, C_w, and C_s are the PAH concentrations in the air, water, and soil (mol/m^3), respectively, R is gas constant (8.314 Pa m^3/mol/K), T is the average absolute air temperature (K), H is the Henry’s constant (Pa) according to Bamford et al.[22] and Ten Hulscher et al.,[23] ρ_s is the soil density (assumed to be 2.5 kg/L), ϕ_{soc} is the organic carbon fraction in the soil, K_{sa} is the soil−air partition coefficient of congener, and K_{oa} is the octanol−air partition coefficient of congener according to Ma et al.[24] Research has showed that a coefficient of 0.411 can improve the correlation between K_{sa} and K_{oa}.[7,25] Air, water, and soil properties used in the calculations are listed in Table S2 of the Supporting Information.

The water fugacity (f_{fw}) and soil fugacity (f_{fs}) measured by the fugacity sampler were calculated as follows

$$f_{fw} = C_{wa}RT \tag{4}$$

$$f_{fs} = C_{sa}RT \tag{5}$$

where C_{wa} and C_{sa} are the PAH concentrations in the air equilibrated in situ with the water and soil surface, respectively. The fugacity fraction (ff) has been used as an indication of the net direction of air−surface exchange. The ff is defined as the ratio of water (or soil) fugacity to the sum of the water (or soil) fugacity and the air fugacity as follows

$$\mathrm{ff}_w = f_w/(f_w + f_a) = C_w H/(C_w H + C_a RT) \tag{6}$$

$$\mathrm{ff}_s = f_s/(f_s + f_a) = C_s/(C_s + 0.411\rho_s\varphi_{soc}K_{oa}C_a) \tag{7}$$

$$\mathrm{ff}_{fw} = f_{fw}/(f_{fw} + f_a) = C_{wa}/(C_{wa} + C_a) \tag{8}$$

$$\mathrm{ff}_{fs} = f_{fs}/(f_{fs} + f_a) = C_{sa}/(C_{sa} + C_a) \tag{9}$$

where ff_W and ff_s are the fugacity fractions calculated using the fugacity capacities and PAH concentrations in water or soil, respectively, and air. Whereas, fff_W and fff_s are the fugacity fractions estimated using the PAH concentrations in the fugacity air samples equilibrated with the water or soil surface. Theoretically, ff = 0.5 indicates equilibrium, ff > 0.5 indicates net emission into the air, and ff < 0.5 indicates net transport from the air to the soil or water.

Because of the uncertainties, an ff of 0.25−0.75 was considered to indicate equilibrium (S2.1, Supporting Information), whereas an ff_f of 0.33−0.67 was considered to indicate equilibrium (S2.2, Supporting Information).

RESULT AND DISCUSSION

PAHs in Paddy Soil, Water, and Ambient Air.

The PAH concentrations and profiles in soil, water, and air are presented in Figures S2, S3, and S4 of the Supporting Information. The variation in PAHs in paddy soil and water have been reported elsewhere.[26] Briefly, the total concentrations of PAHs in soil lay within a range of 456−598 ng/g and 503−747 ng/g for the first and second growing seasons, respectively. PAHs in the field water at the jointing and heading stages were 732 and 1490 ng/L and 164 and 58.9 ng/L for the first and second seasons, respectively. PAHs with molecular weights higher than CHR were not detected in the water of the first season and were reported as contributing to half of the detection limit (0.1 ng/L). The ambient air concentrations of PAHs, collected at a height of 1.5 m, lay in the range of 257−364 ng/m^3 and 166−272 ng/m^3 for the first and second seasons, respectively. The concentrations of PAHs in air and paddy soil were in consistent with the previous study nearby.[19] Generally, the PAH concentrations in the ambient air decreased with advancing rice growing period. The significant variation in the PAH concentrations in the air may be due to the varied PAH sources, such as occasional biomass burning or industrial/ traffic discharge from nearby locations. PHE dominated in the PAH profiles of all samples. Similar PAH profiles were found in soils in Europe[27] and Tibetan Plateau, China.[28] The PAH concentrations and profiles in the surface air equilibrated with the paddy field surface are shown in Figure S5 (Supporting Information). The total PAH concentrations in the surface air varied with growth stages, and were in the range of 177−420 ng/m^3 and 96.7−303 ng/m^3 for the first and second growing seasons, respectively.

We calculated the air−water ($K_{aw} = C_{wa}/C_w$) and soil−air ($K_{sa} = C_s/C_{sa}$) partition coefficients of PAHs using the measured concentrations in the water, soil, and surface air and assumed as measured K_{aw} and K_{sa}. We also calculated the predicted Kaw (Kaw = H/RT) and K_{sa} (eq 3). The predicted and measured K_{sa} are compared in Figure 2. Results showed that the measured K_{aw} or K_{sa} using our sampler were comparable to the predicted ones for low molecular weight (LMW) PAHs, suggesting the modified sampler is suitable to determine real soil−air or air−water partition coefficients of those compounds in paddy fields. However, for the HMW PAHs, the method using the measured concentrations overestimated K_{aw} and underestimated K_{sa}. Assuming that the measured HMW PAH concentrations in the surface air were accurate, the results indicated that using the measured concentrations may underestimate the amount of exchangeable HMW PAHs in soil and water, which meant that some nonextractable HMW PAHs in soil or water may be also involved in the air−surface partitioning process.

Calculated Air, Water, and Soil Fugacities of PAHs

Traditionally, the air, water, and soil fugacities of SVOCs have been estimated using the air, water, and soil concentrations, the gas constant, and the Henry's constant or the octanol−air partition constant [eqs 1−3]. The calculated fugacities of PAHs in air, water, and soil are shown in Figure 3. As expected, PHE exhibited the highest fugacity in every matrix, followed by FLU and ANT, with their high concentrations, high Henry's constant, and low K_{ow}, whereas the fugacities of BbF, BkF, and BaP were very low. The high fugacity of PHE and low fugacities of BbF, BkF, and BaP, independent of sampling site and season, were also reported by Cabrerizo et al.[27] Identical to the trend in total PAH concentration, the fugacities of PAHs in air and soil also generally decreased with increasing time after rice planting. This result was consistent with the assumption that rice growth can enhance the dissipation of PAHs in soil, as well as in the ambient air. Increased microbial species and communities, and mineraliza- tion by plant growth can stimulate microbial degradation, root uptake, volatilization, or leaching of PAHs and other SVOCs in soil.[18,29] The fugacities of LMW PAHs in air were comparable with those in soil, whereas the fugacities of LMW PAHs in water were 5−10 times higher than those in air and soil. The dramatic variation in the PAH fugacities in water at different sampling times may be a result of additional input by wastewater irrigation, which suggests that irrigation was one of the main sources of PAHs in the paddy field study site. Since the paddy field was covered with water during the jointing and heading periods, the fugacities of PAHs in air and soil during these two wet periods were generally higher than those during the mature and idle periods (Figure 3a,c), especially for LMW PAHs (e.g., PHE and FLU). This result indicates that the PAH fugacities were increased by the flooding water in the field during the jointing and heading stages. Because the fugacity measures the escape potential of compound from one matrix to another, an increased fugacity suggests the emission of target compound from the matrix was enhanced. The diffusivity, partition coefficient, convective mass transfer coefficient, initial concentration, and factors that affect these parameters can impact the emission of SVOCs. During the flooding period, the increased soil moisture content may influence the mass transfer rate within soil, and lead to a higher escape of compounds from the soil. Soil sorption can also be influenced by soil water content.[7,25,30] High soil water content can decrease the sorption capacity of soil and increase the escape of the compound.[7] Previous studies have shown that soil relative humidity and soil water content have a strong influence on the air−soil partitioning of SVOCs.[8,30] High water content and relative humidity in soil may increase the emission of SVOCs from the soil.

The fugacity calculated using the traditional method is easy to perform, requiring less equipment and field monitoring. It is convenient for calculating the instantaneous fugacity in a relatively stable system. However, this calculated method also has some disadvantages: First, when the matrix fugacity is calculated, the concentration should be the homogeneous concentration in the matrix directly involved in the partitioning process between the different matrices. For instance, the compound concentration in soil used for calculating the soil fugacity should be the amount of compound in surface soil (0− 5 cm), instead of bulk soil (0−20 cm), because the compound in deeper soil does not participate in the soil−water or soil−air partitioning process. Because the concentration usually varies with the soil depth, using the concentration in bulk soil instead of surface soil to calculate the fugacity may give rise to a systemic error. However, the surface soil involved in the partitioning process is not easy to distinguish and collect, especially for soils covered with plants. The scenario for water is similar, and the water−soil or water−air partitioning should use the concentration in the boundary layer of water. Second, besides the soil organic carbon fraction, soil density, and ambient air temperature, this method also requires the physicochemical properties of the compound (e.g., H or K_{oa}). Some of those parameters are not available for the newly emerging organic contaminants. Even for the "old" organic pollutants, such as PAHs, the physicochemical properties also vary in the literature.[24,31] Moreover, because these parameters are also temperature-dependent, the variation in ambient temperature can lead to a calculation error. Third, because both the exchangeable and nonexchangeable forms of

PAHs are considered, the traditional method using the detected PAH concentration to calculate the fugacity can overestimate the soil or water fugacity.[27] Only the exchangeable PAHs, which can escape from the soil or water and participate in the surface−air exchange process, should be involved; whereas the remaining nonexchangeable PAHs could not contribute to the soil or water fugacity of the PAHs, since they are strongly attached to organic matter. However, the exchangeable PAHs are not equal to the extractable PAHs we measured. Fourth, it is difficult to perform if there are more than two compartments, especially when vegetation is involved. The equilibrium near the agricultural field surface is more likely air−vegetation−surface equilibrium rather than air−surface equilibrium. Finally, the variation in soil water content, atmosphere temperature, and other environmental parameters can also cause unavoidable errors in calculating the fugacity. Because of the systematic error caused by the parameters, the calculated fugacity may not reveal the actual or exact situation. Therefore, an in situ fugacity sampler was necessary, especially for the unstable and complex paddy fields.

Measured Water and Soil Fugacities of PAHs.

The modified fugacity sampler was used to obtain relatively accurate fugacities of PAHs in the paddy field (Figure 1). We assumed that PAHs in the air collected near field surface had approximately equilibrated with these in the surface soil or water for the two growing reasons: first, the canopy formed by rice leaves can ensure that there is enough time for the air under the canopy to equilibrate with the surface soil or water; second, the sampling rate is very slow which can hardly disturb the equilibrium between air and soil or water surface. The measured water and soil fugacities of PAHs using this sampler [using eqs 4 and 5] are shown in Figure 4.

When comparing similar trend in the variation was found, especially for PHE. However, the values were significantly different between measured and calculated fugacities, particularly during the flooding (jointing and heading) stages. Because the paddy field was a very complex system, including the air, plant, water, and soil compartments, the traditional calculated fugacities cannot reveal the relatively accurate fugacities in this area. For the LMW PAHs, the calculated fugacities were ~1 order of magnitude higher than the measured fugacities, especially during the flooding period of the first season (Figure S6, Supporting Information), whereas the calculated and measured fugacities of LMW PAHs were comparable for the rest time. The variation during the flooding time may be the result of frequent irrigation. This also suggested that using the fugacity model and the water concentrations can overestimate the water fugacity of LMW PAHs. Because rice is a semiaquatic plant, the paddy field must be continuously flooded up to maturation of the rice grain, which requires frequent irrigation with freshwater. If the calculation is based on the fresh field water, in which not enough time for equilibration with the air occurs, the fugacity value can be over- or underestimate. Moreover, the extractable compounds in the water phase may not be able to escape from the water because of the strong binding capacity of the dissolved organic matter and fine particles. On the contrary, the calculated fugacities for the HMW PAHs (BbF, BkF, and BaP) were ~2−3 orders of magnitude lower than the measured fugacities, which imply that the calculated fugacities can underestimate the transfer trends of HMW PAHs. The result also suggests that even though the HMW PAHs that have bound to organic matters and particles, they may still have the capability to desorb and be involved in the air−surface equilibration process. In summary, the measured fugacity using the fugacity sampler can obtain more accurate values than the calculated fugacity, especially for an unstable and complex ecosystem like paddy fields. However, this method also has some disadvantages. The fugacity sampler has a relatively low temporal resolution (the minimum resolution is ~24 h). To optimize the detection of compounds at such a low sampling rate, 24 h of continuous sampling must be conducted, which then provides an average fugacity over the sampling period instead of instantaneous fugacities. In addition, the water height in the paddy filed, as well as the concentration of the compound in the water, varied slightly with time. Therefore, in reality, an approximate dynamic equilibrium of the compound among soil, water, and air occurred. Meanwhile, as the rice grows, this may change the volume of rice "chamber" and cause a systematic error in the calculations. The conditions, after the rice straw harvest, are not suitable for measuring the fugacity of the soil as well. Although this sampler has some limitations, it still provides a novel and appropriate approach for assessing the fugacity gradients of SVOCs in such agricultural fields. Table S3 (Supporting Information) shows the advantages and disadvantages of the two calculation methods using traditional fugacity model and using modified fugacity sampler in the present study.

Fugacity Fractions of PAHs

The calculated (ff) and measured (ff_f) fugacity fractions of PAHs [eqs 6−9] at different rice growth stages are shown in Figure 5. The uncertainty in the calculated ff is greater than that of the measured ff_f (S2.1 and S2.2, Supporting Information), which suggests that using the calculation method may result in a greater uncertainty. The calculated ff showed that most of the LMW PAHs were closer to equilibrium, whereas the HMW PAHs (especially BbF, BkF, and BaP) were close to net deposition from the air at the sampling time (Figure 5a). The ff varied with the rice growth stage, particularly when the paddy filed was flooded. The LMW PAHs revealed a net volatilization during the first flooding stage, whereas they were close to equilibrium during the second flooding stage. This was because of the relatively high PAH concentrations in field water of the first season compared to those of the second season (Figure S3, Supporting Information). Our previous study[26] showed that the concentrations of PAHs in the irrigation water of the first season were also much higher than those of the second season, and wastewater irrigation was one of the main inputs of PAHs in the study area. It suggested that the high emission trend of LMW PAHs may be due to the input of PAHs from wastewater irrigation. For the measured ff$_f$, most of the PAHs were in equilibrium at different time of sampling, even for the HMW PAHs. The relatively low emission trends of LMW PAHs compared to those of Cabrerizo et al.[27] may be due to the high concentrations of PAHs in the air of our study area (Figure S4, Supporting Information). Moreover, the large area of rice crops may also justify the air profile of PAHs and cause the low volatilization of LMW PAHs. When the uncertainties were considered, the measured ff$_f$ was generally comparable with the calculated ff for the LMW PAHs, which supports the suitability of the modified fugacity sampler for assessing the air−surface partitioning of PAHs in paddy fields. The HWM PAHs exhibited the largest differences between the calculated and measured fugacity fractions. The traditional calculated method may underestimate the emission trend of HMW PAHs. Two possible explanations for this include first, the traditional method cannot identify and determine the exact quantity of PAHs involved in the air−surface partition process, especially for the HMW PAHs, and second, HMW PAHs tend to adsorb to particles; however, this adsorption is at dynamic equilibrium, which means that the adsorbed PAHs can desorb from particles and participate in the partitioning process. This adsorption−desorption process is more likely to occur in the paddy field under the flooding conditions. Cabrerizo et al.[27] also showed that the gradients between the soil and air fugacities of HMW PAHs with 4−5 aromatic rings were smaller or close to unity. The authors suggested that the HMW PAHs were close to air− soil equilibrium for soils in transition between being a sink and a source.

Environmental Implications of Rice Growth on the Transport of PAHs

As shown in Figure 5, the more volatile FLU tended to escape from the paddy field into the air, especially during the mature or idle stages in summer, which implies that the flooding of rice fields may hinder the transport of FLU. Other PAHs with 3−4 rings were close to equilibrium between the paddy field and the air, although the ff values also varied with the rice growing time, especially when the field changed its characteristics from wet to dry land. This suggests that the rice growth may change the soil fugacities of PAHs, but is insufficient to alter their fugacity fractions and transport trends. However, the growth of rice may result in a rapid equilibration of PAHs between the paddy field and ambient air, because water in the flooded rice field can enhance the mass transfer rates of PAHs among soil, water, and air.[8] For PAH congeners with >5 rings, the results of the fugacity sampler also suggest that these HMW PAHs were close to equilibrium. HMW PAHs tend to be adsorbed to particle surfaces for their more hydrophobic properties. Thus, the emission or transfer tendencies of HMW PAHs are much lower than those of LMW congeners. The results of the traditional calculated method indicate that HMW PAHs have a strong tendency to be deposited from air to soil (Figure 5a). However, the results of the fugacity sampler in our study suggest that HMW PAHs are close to equilibrium between the paddy field and air, no matter how low the volatilization is. This finding challenges the traditional viewpoint that the less volatile HMW PAHs have difficulty in reaching equilibrium and tend to be deposited from the air. The result also implies that HMW PAHs in soil may come from particles associated transport via irrigation or atmospheric particle deposition instead of gaseous exchange. Because rice farming patterns may increase the emission and environmental risks of SVOCs, the transfer of those compounds in paddy fields should be continuously monitored to ensure food safety, especially in relatively contaminated locations.

ASSOCIATED CONTENT

Details of the sampling, sample analysis, QA/QC, and uncertainty calculation. Tables of the sampling information, air, water, and soil properties, and the advantages and disadvantages of two fugacity calculation methods using model or sampler. Figures of the sampling site, PAH concentrations and profiles in the soil, water, air, and surface air, and ratios of the calculated PAH fugacities to the measured PAH fugacities. This material is available free of charge via the Internet at http://pubs.acs.org.

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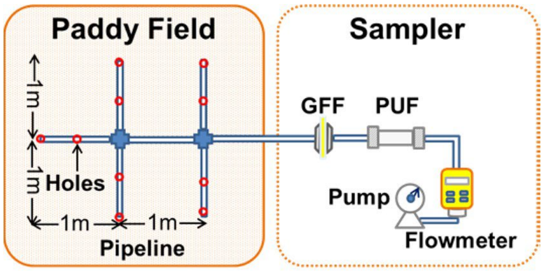
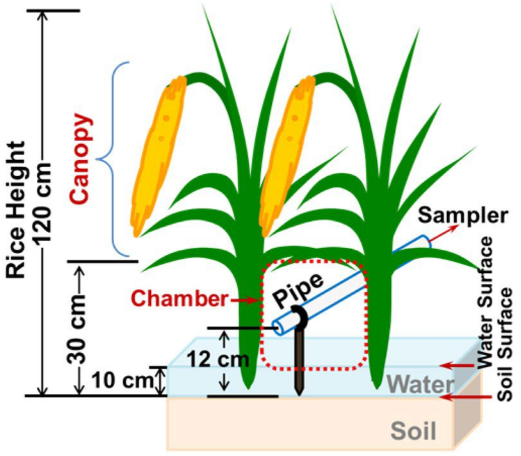
FIGURES

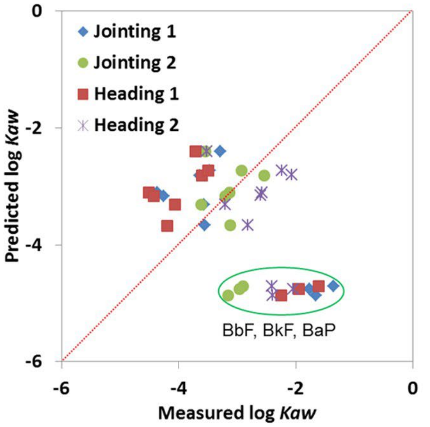


a Scheme of the improved fugacity sampler

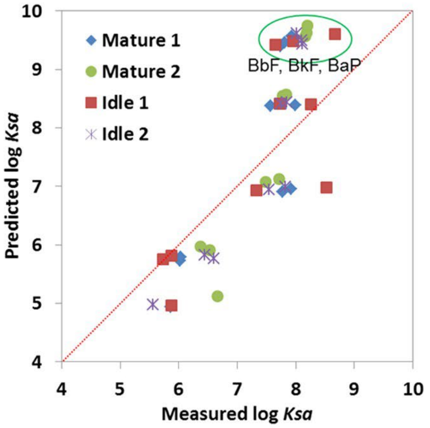


b Location of the sampling pipes

Figure 1. Details of the improved fugacity sampler.

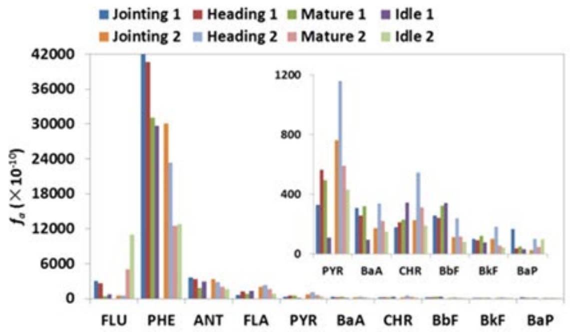


a logK_{aw}

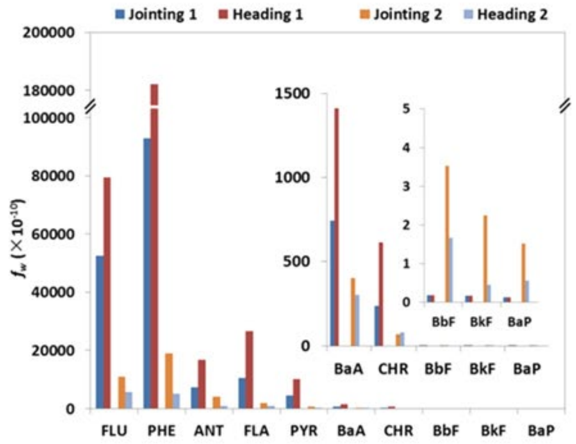


b logK_{sa}

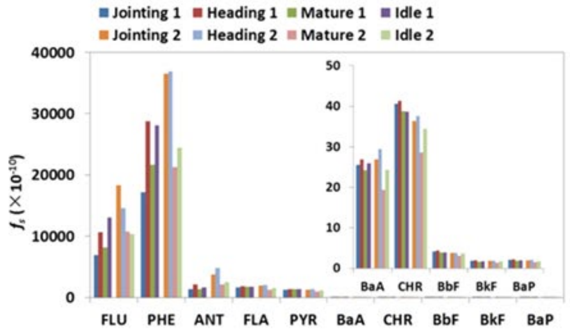
Figure 2. Measured log K_{aw} (or log K_{sa}) versus predicted log K_{aw} (or log K_{sa}) for PAHs of different stages during the two growing seasons (a, log K_{aw}; b, log K_{sa}).



a air fugacity



b water fugacity



c soil fugacity

Figure 3. Calculated air, water, and soil fugacities of PAHs during different rice growth stages. (No. 1 means the first growing season, whereas No. 2 means the second growing season.)

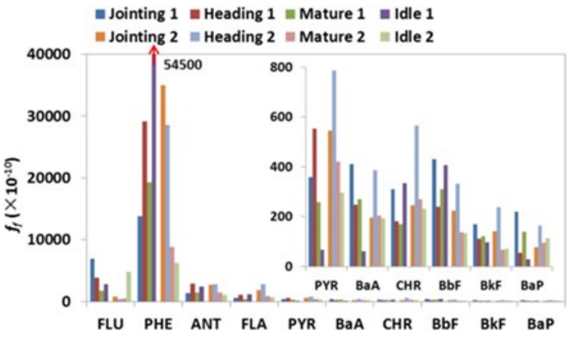
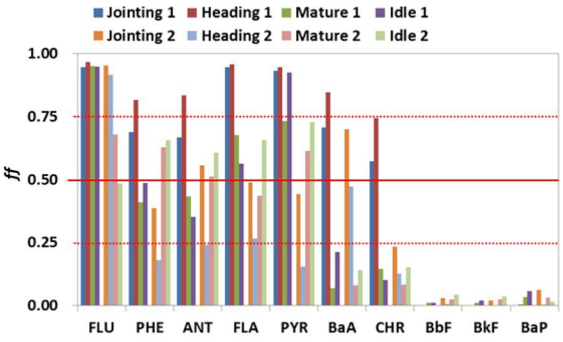
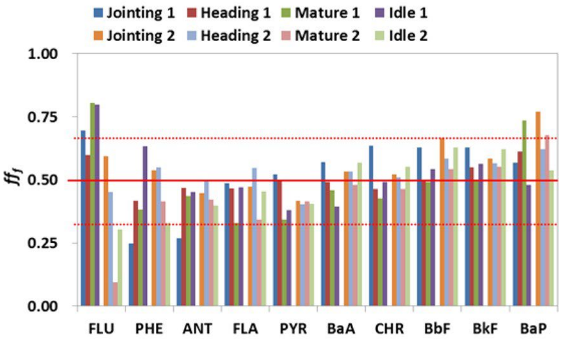


Figure 4. Measured water or soil fugacities of PAHs during different rice growth stages. (No. 1 means the first growing season, whereas No. 2 means the second growing season. It is measured water fugacity (f_{fw}) during jointing and heading stages, whereas it is measured soil fugacity (f_{fs}) during mature and idle stages.)



a Calculated fugacity fractions (*ff*)



b Measured fugacity fractions (ff_f)

Figure 5. Calculated and measured fugacity fractions of PAHs during different rice growth stages. (The dotted lines show the uncertainty of fugacity fraction. According to the uncertainty, the calculated fugacity fraction between 0.25 and 0.75 is considered as equilibrium, whereas the measured fugacity fraction between 0.33 and 0.67 is considered as equilibrium.)

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