Direct determination of surfactant effects on the uptake of gaseous parent and alkylated PAHs by crop leaf surfaces

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ARTICLE INFO

ABSTRACT

The partitioning of atmospheric polycyclic aromatic hydrocarbons (PAHs) into crop systems raises concerns about their potential harm to ecosystem and human health. To assess parent and alkylated PAHs accumulation accurately, the uptake of individual 7-isopropyl-1-methylphenanthrene (Retene), 3-methyl-phenanthrene (3-MP) and phenanthrene (Phe) by living maize, soybean and potato leaf surfaces, as well as the effects of cationic cetyltrimethylammonium bromide (CTMAB) and anionic sodium dodecyl benzene sulfonate (SDBS), were examined *in situ* using fiber-optic fluorimetry. For each of three PAH chemicals, the uptake achieved equilibrium between the air and living crop leaf surfaces within the 120-h monitoring period. There is inter-chemical and inter-species variability in terms of both the time required reaching equilibrium, the equilibrated adsorption concentration (EAC) and the overall air-surfaces mass transfer coefficient (k_{AS}). The EAC of the three PAHs for each of the three crops' leaf surfaces increased with the number of alkyl substitutions on the aromatic ring. For any given PAHs, the EAC values followed the sequence of potato > soybean > maize, which was dominantly controlled by their leaf surface polarity index ($(O+N)/C$). The presence of CTMAB and SDBS increased the EAC of PAHs in the three crops' leaf surfaces by 6.5–17.1%, due to the plasticizing effect induced by the surface-sorbed surfactants, and the enhancement degree was closely associated with leaf-wax content and lg K_{OW} values of PAHs. In addition, the two surfactants promoted the k_{AS} values of the three chemicals by 7.7–23.3%. These results demonstrated that surfactants promoted the uptake of PAHs onto the crop leaf surfaces, potentially threatening the agricultural product safety.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), as a family member of ubiquitous persistent organic pollutants (POPs) in the environment, are mainly by-products of incomplete combustion of fossil fuels and biomass (Li et al., 2017). A number of atmospheric PAHs have potential to cause adverse effects to the mammals and human health due to their significant carcinogenic, mutagenic and toxic properties (Casal et al., 2014; Li et al., 2016; Lin et al., 2017). Alkylated PAHs are the predominant derivatives of PAHs and they are more plentiful, persistent and toxic than the parent PAHs (Hong et al., 2016; Cai et al., 2017). Cassandra and Tom (2016) reported that the detection frequency and level (0.2–35 ng/g) of alkylated PAHs were higher than corresponding PAH counterparts (0.2–4.7 ng/g) in Red Pine tree cores. Zhang et al. (2017) investigated the bioaccumulation and translocation of pyrene (Pyr) and 1-methylpyrene in maize seedlings, and the two chemicals were not only detected in maize roots, but also could be transferred to the edible parts of maize seedlings. Recently, numerous studies have

reported that the toxicity of alkylated PAHs to marine organisms was greater than those of corresponding parent PAHs (Fallahtafti et al., 2012; Mu et al., 2014), and their exchange between the air and other environmental media, such as soil (Wang et al., 2008a), water (Cheng et al., 2013), has attracted great attention. However, few studies have delved into the exchange behaviors of alkylated PAHs between the air and terrestrial vegetation.

As is well known, nearly three quarters of the earth's terrestrial surface is covered by vegetation, and the plant leaf can effectively accumulate PAHs from the air due to their richness in lipophilic waxes, lipids and other substances (Schreiber, 2006; Xiong et al., 2017). Therefore, the transfer of atmospheric PAHs occurring between the air and vegetation has a substantial impact on their contamination status in the atmosphere, environmental persistence and fates, and human health (Su et al., 2006; Li and Chen, 2014). Plant cuticle constitutes the most active and main component of plant tissues for adsorbing atmospheric PAHs, and it also provides the first barrier to PAHs penetrating farther into the plant (Stimler et al., 2006; Y.Q. Wang et al., 2008). To

date, some studies regarding the interaction between PAH chemicals and the isolated cuticle compositions, demonstrated that the soluble polymeric lipids serve as the main component to control affinity of bulk cuticle with PAHs (Chen et al., 2005; Tao et al., 2009; Li and Chen, 2009). However, the cuticles examined had been isolated from the living plant body using chemical solvents or enzymes, which commonly display different properties from the intact cuticle. Moreover, the analytical methods (*e.g.,* GC, HPLC and GC-MS) commonly used in these studies cannot realize *in situ* determination the uptake of gaseous PAHs by living plant leaf surfaces. We recently investigated the uptake kinetics of mixed phenanthrene (Phe), anthracene (Ant), Pyr and fluoranthene (Fla) by the living crop leaf surfaces using *in situ* multi-way models (Sun et al., 2016a). Nevertheless, the occurrence in a natural environment has not only parent PAHs but also has alkylated PAHs (Cassandra and Tom, 2016; Carlos et al., 2017). Furthermore, the accumulated PAHs on the plant leaf surfaces generally coexist with many other substances (*e.g.,* surfactants, abscisic acid) that can induce variation in the foliar microstructure (Tamura et al., 2001). Therefore, more studies concerning the effects of some of these typical chemicals on the uptake of parent and alkylated PAHs by the surfaces of living crop need to be conducted for better understanding agricultural product safety and human health.

Surfactants, as a kind of amphiphilic compounds, are widely used in spray solutions to enhance the efficiency of foliar-applied agrochemicals (*e.g.,* fruit chemical thinning, ripening agent, and pesticides), since their specific properties, such as emulsification, dispersion and wetting, enable them to improve the solubility of the active ingredients, and increase the wettability and permeability of the plant cuticle (Petracek et al., 1998; Zhang et al., 2017). Surfactant usage in agrochemical products reaches up to 230,000 t annually, to enhanced crop production by 1–10% (Caroline, 2007). More important, foliar-sorbed surfactants can promote the mobility of the agrochemicals across the cuticular interface *via* softening the crystal structure of epicuticular wax, thereby serving as effective plasticizer (Schonherr et al., 2000; Tamura et al., 2001; Popp et al., 2005). In this work, we selected the cetyl-trimethylammonium bromide (CTMAB) and sodium dodecyl benzene sulfonate (SDBS) as the representative surfactants owing to their widespread usage in agrochemicals and high detection frequency in crop leaf (Li et al., 2009). More important , the effects of the above surfactants to crop cuticles have received special attention (Petracek et al., 1998; Knoche and Bukovac, 2004; Sun et al., 2016b). For example, a study regarding the effects of surfactants on the affinity of plant cuticle with organic pollutants in aqueous solution has shown that the addition of surfactants enhances the intrinsic sorption coefficients (Li et al., 2009). However, in a real environment, the surfactants used in agrochemical products tend to accumulate on the cuticle after spraying, and the organic pollutants adsorbed by living plant surfaces mainly come from the atmosphere. To date, the impact of surfactants on the uptake of gas-phase parent and alkylated PAHs by living crop leaf surfaces remain unclear.

Recently, we developed a fiber-optic fluorimetry approach for the *in situ* determination of PAHs adsorbed onto the living crop surfaces (Sun et al., 2016a). Nevertheless, the feasibility of this approach in the *in situ* quantification of PAHs together with surfactants co-adsorbed onto living crop leaf surfaces remains unclear. Meanwhile, studies are limited concerning the effects of surfactant on the uptake of gas-phase parent and alkylated PAHs by the cuticle surfaces of living crop seedlings. Thus in this work, Phe, 7-isopropyl-1-methylphenanthrene (Retene), and 3-methy-phenanthrene (3-MP) were selected as model components of parent and alkylated PAHs. The fiber-optic fluorimetry method was employed for the *in situ* investigation of surfactant effects on the uptake of the three chemicals by the leaf surfaces of living maize, soybean and potato seedlings.

2. Materials and methods

2.1. Apparatus and reagents

All the fluorescence spectra were obtained using a Cary Eclipse fluorescence spectrophotometer equipped with fiber optic accessories with the length of 2 m (Agilent, USA). Phe, 3-MP and Retene (purity > 98%) were purchased from Sigma Aldrich Chemical Co., Ltd, USA. All other organic compounds (A.R.), including CTMAB and SDBS, were obtained from Shanghai Trustin Chemical Co. Ltd., China. Stock and working solutions of PAHs and surfactants were prepared according to the method reported in our previous studies (Chen et al., 2010; Sun et al., 2013a, 2016b).

2.2. Preparation and pretreatment of living crop seedlings

In this study, maize, soybean and potato were chosen as representative crop species due to their intimate relationship with human life. These three crops were cultivated in a controlled climate chamber (MGC-450HP, Shanghai Yiheng Science Instruments Co. Ltd., China) programmed for a 16 h light (22 °C)/8 h dark (20 °C) cycle for 21 days, with light intensity of 20000 lx at daytime and relative humidity of 35% and continuous air circulation systems for ventilation. These crop seedlings of approximately the same heights (maize, 26 ± 0.4 cm; soybean, 19 ± 0.3 cm; potato, 12 ± 0.2 cm), leaf surface areas (maize, 47 ± 0.6 cm²; soybean, 14 ± 0.2 cm²; potato, 21 ± 0.5 cm²) and fresh weights (maize, 1.3 ± 0.05 g; soybean, 0.5 ± 0.02 g; potato, 0.8 ± 0.03 g) were selected for the following experiments. Next, all of the chosen leaves were cleaned up using tap water and Milli-Q water three times to remove the silts adhered onto the leaf surfaces. According to our previous studies (Sun et al., 2013a, 2016a), the determination areas were produced on the leaf surfaces by using a large round end of 5 mL pipette. The area of the circle was defined as a unit of 'spot' which had the same size area (0.28 cm², r ≈ 0.30 cm) as the fiber optical probe. For each crop species, three of leaves from three different seedlings were selected, and for each leaf, three detection spots that distributed over front, middle and nether parts were made (n = 9).

2.3. Determination of PAHs on the leaf surfaces of living maize, soybean and potato

To figure out the surfactant effects on the spectra of adsorbed Phe, 3-MP and Retene was the necessary prerequisite for the accurate quantification of PAHs using the fiber-optic fluorimetry. Firstly, the surfactant solutions were introduced onto the 'detection spots' to produce the maximum dosages of CTMAB (300 ng/spot) and SDBS (200 ng/spot), respectively. After 12 h, the working solutions of individual Phe, 3-MP and Retene were introduced onto these 'detection spots' interacted with surfactants, and the concentration of 400 ng/spot was selected as model content for the three chemicals (Sun et al., 2016b). Then, fluorescence spectra of individual chemical adsorbed onto the living crop leaf surfaces were scanned using the fiber-optic fluorimetry method.

The key parameters for instrumental settings were shown as follows: excitation and emission slits were set at 10 nm; scan speed was 600 nm/min; PMT voltage was 600 V. During the measurement, the living contaminated crop leaves were put under the optical fiber probe which was kept at 45° to avoid interference from the scattered light. The spectra of individual PAHs adsorbed onto the leaf surfaces were acquired under the optimized maximum excitation and emission wavelengths. Each chemical with five concentration gradients ranging from 100 to 1000 ng/spot were evenly introduced onto the 'detection spots' on the leaf surfaces using a 10 μL flat head micro-injector (Shanghai Medical Laser Instrument Plant, China), respectively, and the amounts were *in situ* determined after evaporation of acetone. Moreover, to verify the accuracy of the established analytical approach, recovery

experiments were performed based on our reported method (Chen et al., 2010; Sun et al., 2016a).

2.4. Uptake experiment

In real environment, the concentrations of CTMAB and SDBS in crop leaves were in the range of 0–70 µg/g and 0–50 µg/g (wt), respectively (Sun et al., 2016b). It was assumed that the surfactant was evenly distributed on the leaf surfaces, thus CTMAB and SDBS have an ambient background concentration range of 0–328 ng/spot and 0–234 ng/spot, respectively. Therefore, the initial concentrations of CTMAB (0, 100, 200, 300 ng/spot) and SDBS (0, 50, 100, 200 ng/spot) were chosen in the uptake experiments. There were one control and two treatment groups: "crop without surfactants", "crop + CTMAB", "crop + SDBS". For each treatment, three replicate seedlings and three replicate leaves (one per seedling) were selected for the uptake experiment. The different dosages of surfactant were introduced firstly onto the 'detection spots' on the leaf surfaces of the three living crop seedlings, respectively. Then, all of the selected seedlings with and without surfactants were placed into the exposure chamber along with the pots that had been covered with aluminum foil to avoid the uptake of gaseous chemicals by the cultural medium (Fig. S1).

The key parameters of the controlled exposure chamber with volume of 125 L were as follows: light/dark regime: 16/8 h; temperature: $(22 \pm 2)°C$; relative humidity: $(35 \pm 3)\%$; illumination intensity: 20000 lx (Yang et al., 2007; Sun et al., 2016a). The contaminated air was produced based on our previously reported method (Sun et al., 2016a): approximately 60 mg of each chemical (Phe, 3-MP and Retene) were dissolved in 10 mL of acetone in a 100 mL brown bottle with an inlet and an outlet; then, a constant air flow passed through each bottle from the inlet to accelerate the PAH vaporization and the chemicals were introduced into the chamber from the outlet of the bottle. Because the PAHs were prone to reside on the wall of the bottle after the acetone vaporized, only gaseous PAHs could enter the chamber. A 12 V fan inside each chamber mixed the air to ensure a homogenous distribution of gaseous PAHs and a stable and elevated concentration (1250 ng/m³) of gaseous PAHs were produced in the chamber. Then, fluorescence intensity of parent and alkylated Phe adsorbed onto the living crop leaf surfaces was *in situ* determined at the setting time points of 0, 2, 5, 12, 24, 30, 48, 72, 96 and 120 h.

2.5. Characteristics of leaf-wax

The leaf-wax was extracted from the selected three crop species and the leaf-wax contents were quantified based on the method reported by D.G. Wang et al. (2008), Y.Q. Wang et al. (2008) and P. Wang et al. (2008). The leaf-wax samples were analyzed using GC-MS and the compounds were identified by comparing their mass spectra with published data and authentic standards. Wax compounds were quantified using GC-FID to analyze the leaf-wax mixtures. Wax compound peak areas were compared against the internal standard (Szafranek and Synak, 2006; Guo and Jetter, 2017). In addition, the elemental compositions of leaf surfaces of the three-crop species were acquired by XPS (Li et al., 2016).

2.6. Statistical analysis

The determination of PAHs adsorbed onto the crop leaf surfaces and the uptake experiments were all performed nine times, and the average values of the nine measurements were used as the final results. Statistical analyses for the variations in the fluorescence intensities obtained *via* the fiber-optic fluorimetry method were performed using SPSS 19.0 for Windows. The statistically significant differences of the results were identified using an analysis of variance post hoc test (ANOVA, Tukey's test) at the 95% confidence level ($P < 0.05$).
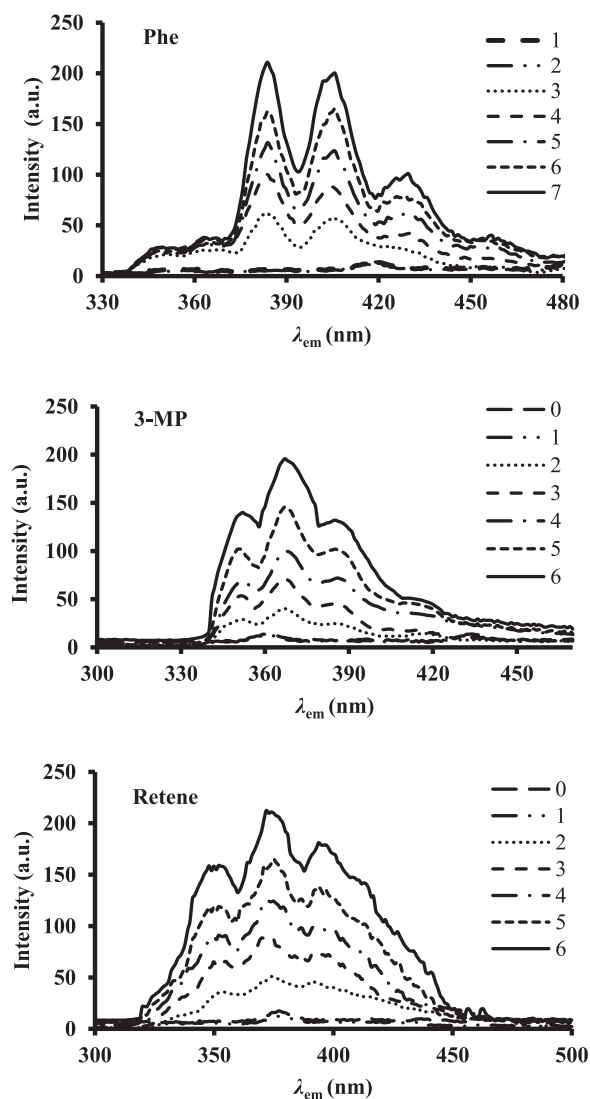

Fig. 1. Emission spectra of Phe, 3-MP and Retene adsorbed onto maize leaf surfaces. (Phe: λ_{ex} = 256 nm; 3-MP: λ_{ex} = 255 nm; Retene: λ_{ex} = 257 nm). Concentrations of the adsorbed Phe, 3-MP and Retene were: 0: Blank; 1: Blank + acetone ; 2–6: 200, 300, 500, 700, 900 (ng/spot). Each emission spectrum is the mean of nine replicates.

3. Results and discussion

3.1. Quantification of PAHs on the crop leaf surfaces

First, the excitation wavelength (λ_{ex}) and emission wavelength (λ_{em}) of Phe, 3-MP and Retene adsorbed onto the three living crop leaf surfaces were optimized. The results show that $\lambda_{ex}/\lambda_{em}$ for *in situ* measurement of adsorbed Phe, 3-MP and Retene were as follows: 256/406 nm, 255/368 nm and 257/388 nm for maize; 256/406 nm 255/368 nm and 258/370 nm for soybean; 256/406 nm, 255/368 nm and 257/388 nm for potato. From Fig. 1, the fluorescence spectra of blanks (uncontaminated leaf) and leaf with acetone did not interfere with the *in situ* determination of parent and alkylated Phe on the maize leaf surfaces. Similar results were also observed for soybean and potato species. Moreover, to ensure the effects of surfactant occurrence on the determination of adsorbed parent and alkylated Phe, the fluorescence emission spectra of the three compounds adsorbed onto the living crop leaf surfaces with the addition of CTMAB and SDBS were determined. As shown in Fig. S2, there were no significant changes either in intensity or shapes of the fluorescence emission spectra for adsorbed Phe, 3-MP and Retene onto the living soybean leaf surfaces. Similar results

Table 1

Analytical merits of the established method (n = 9).

Crop	PAHs	Calibration curves	Linear ranges (ng/spot)	Correlation coefficients	Detection limits[c] (ng/spot)	RSD[d] (%)
Maize	Phe	$y^b = 0.26x^a + 0.9$	2.4–1200	0.9868	0.2	4.9
	3-MP	$y = 0.27\times + 0.6$	1.3–1000	0.9889	0.2	5.3
	Retene	$y = 0.28\times + 5.2$	2.6–985	0.9919	0.3	4.4
Soybean	Phe	$y = 0.21\times + 1.6$	3.5–1000	0.9922	0.6	4.6
	3-MP	$y = 0.22\times + 7.1$	1.1–1100	0.9943	0.4	5.1
	Retene	$y = 0.23\times + 8.6$	3.7–925	0.9881	0.3	4.6
Potato	Phe	$y = 0.17\times + 4.2$	1.5–1050	0.9952	0.5	4.8
	3-MP	$y = 0.19\times + 1.6$	3.6–975	0.9899	0.2	5.4
	Retene	$y = 0.20\times + 6.4$	2.8–1000	0.9887	0.3	5.2

[a] x represents the concentration of PAHs.

[b] y represents the relative intensity of PAHs adsorbed onto living crop leaf surfaces.

[c] Detection limit of the Fiber-optic fluorimetry method which was calculated by $3S_B/m$, where 'S_B' is the standard deviation of the blank (n = 9), and 'm' is the slope of the calibration curve.

[d] RSD represents the relative standard deviation of the established method.

were also observed for maize and potato (data not shown). All of the above results suggest that the fiber-optic fluorimetry is suitable for the *in situ* determination of Phe, 3-MP and Retene adsorbed onto the living crop leaf surfaces.

The amounts of parent and alkylated PAHs adsorbed onto the living crop leaf surfaces were quite low in the natural environment, so the accurate measurement of the amount of Phe, 3-MP and Retene adsorbed onto the leaf surfaces of three living crops was a prerequisite for the subsequent uptake experiment. In this study, calibration curves of the adsorbed three chemicals were obtained using the established

method (Table 1). The results show that a good linear relationship was found between the content (x) and fluorescence intensity (y) of the adsorbed parent and alkylated Phe within a certain range. The detection limits were in the range of 0.2–0.6 ng/spot. Meanwhile, the relative standard deviation (RSD) lies within the range of 4.4–5.4%. Additionally, to confirm the feasibility and accuracy of the established method, the recovery experiment was carried out and the recoveries ranged from 83.3% to 107.7%. These results clearly confirmed the feasibility of the fiber-optic fluorimetry for the *in situ* determination of adsorbed parent and alkylated Phe in the following uptake experiments.

3.2. Uptake of parent and alkylated Phe on leaf surfaces

3.2.1. The time needed to achieve adsorption equilibrium

The uptake of Phe, 3-MP and Retene with or without surfactant by the living maize, soybean and potato leaf surfaces are presented in Fig. 2. All of the three compounds reached adsorption equilibrium over the 120-h monitoring period. However, the time required to reach adsorption equilibrium varied between different chemicals and plant species. Within the same plant species, Retene spent the longest time achieving equilibrium, followed by 3-MP, and Phe (Table S1). Due to the

domination of kinetically limited gaseous deposition, the chemicals with relatively lower lg K_{OA} values (octanol-air partition coefficient) will more readily achieve adsorption equilibrium (McLachlan, 1999; Sun et al., 2016b). In this work, the lg K_{OA} values of the three chemicals follow the order of Retene (8.70) > 3-MP (7.50) > Phe (7.22); hence, the times to achieve the adsorption equilibrium followed the sequence of Retene > 3-MP > Phe. In addition, for the same PAHs, the time needed to achieve the adsorption equilibrium was different between the three selected crop species with the decreasing order of soybean > potato > maize ($P < 0.05$). The variability can be explained by the fact that leaf-wax content followed the sequence of soybean (3.4 ± 0.3 mg/g) > potato (2.8 ± 0.3 mg/g) > maize (1.3 ± 0.2 mg/g). Our earlier study reported that vegetation with higher leaf-wax content possesses more adsorption capacity and it would take longer time for PAHs to achieve adsorption equilibrium (Sun et al., 2016b). Meanwhile, this observation might be associated with other plant parameters, such as lipid content,

leaf surfaces roughness, *etc.* (Franzaring and van der Eerden, 2000). From Table S1, it is noted that neither of the two surfactants have any effects on the time required to achieving adsorption equilibrium ($P > 0.05$).

3.2.2. The adsorption capacity for PAHs without surfactant on leaf surfaces

As seen from Fig. 2, significant variability existed in the equilibrated adsorption concentration (EAC) among the three compounds with values in the order of Retene > 3-MP > Phe, irrespective of crop species ($P < 0.05$). The result indicates that, within the same plant species, the leaf surfaces had the highest affinity for Retene, followed by 3-MP, then by Phe. The K_{OA}-dependent nature of organic contaminants adsorption capacity has been reported previously (Yang et al., 2007). Moreover, one of our studies demonstrated that the sorbed content of parent PAHs on mangrove leaf surfaces escalates with the increasing lg K_{OA} values (Sun et al., 2013b). Similarly, a positive correlation was observed between the EAC and lg K_{OA} of four parent PAHs (Sun et al., 2016a). These observations are in general agreement with our work, where Retene with the highest K_{OA} values had the maximum adsorbed amount, 3-MP medium, and Phe least, indicating that the adsorption capacity of crop leaf surfaces for the three compounds displayed a K_{OA}-dependent response as well. Meanwhile, it is noted that the chemical with relatively higher lg K_{OA} values not only took longer time to reach the adsorption equilibrium, but had stronger adsorption capacity.

For the same chemical, the EAC varied with different crop species with the decreasing order of potato > soybean > maize. Generally, the adsorption capacity of plant to PAHs escalated with the increment of leaf-wax content (Sun et al., 2013a; Li et al., 2017). As mentioned above, the order of leaf-wax content among the three studied crop species was soybean (3.4 ± 0.3 mg/g) > potato (2.9 ± 0.2 mg/g) > maize (1.3 ± 0.2 mg/g), which is not completely consistent with the sequence of EAC values reported above. Soybean and potato, with higher leaf-wax content could accumulate gaseous PAHs effectively, while maize with much lower leaf-wax content had obviously low adsorption of PAHs. Meanwhile, Li et al. (2017) reported that plant leaves with more hairs were prone to accumulate more PAH compounds than hairless leaves were. Soybean and potato leaf surfaces have salt glands and more hairs than maize, leading to the greater roughness of leaf surfaces of the former two relative to the latter, which might account for the higher EAC values for soybean and potato as well. As noted above, soybean leaf had more wax content than potato, but potato had the greater EAC than soybean. Clearly, in addition to leaf-wax content, there are additional factors affecting the affinity of plant leaf surfaces for PAHs.

To further determine the mechanism for PAH adsorption, we analyzed the leaf-wax mixtures of the three-crop species and the wax compositions according to the methods reported by Guo and Jetter (2017), and the results are presented in Fig. S3. Generally, the proportions of components followed the sequence of n-alkanes > 2-
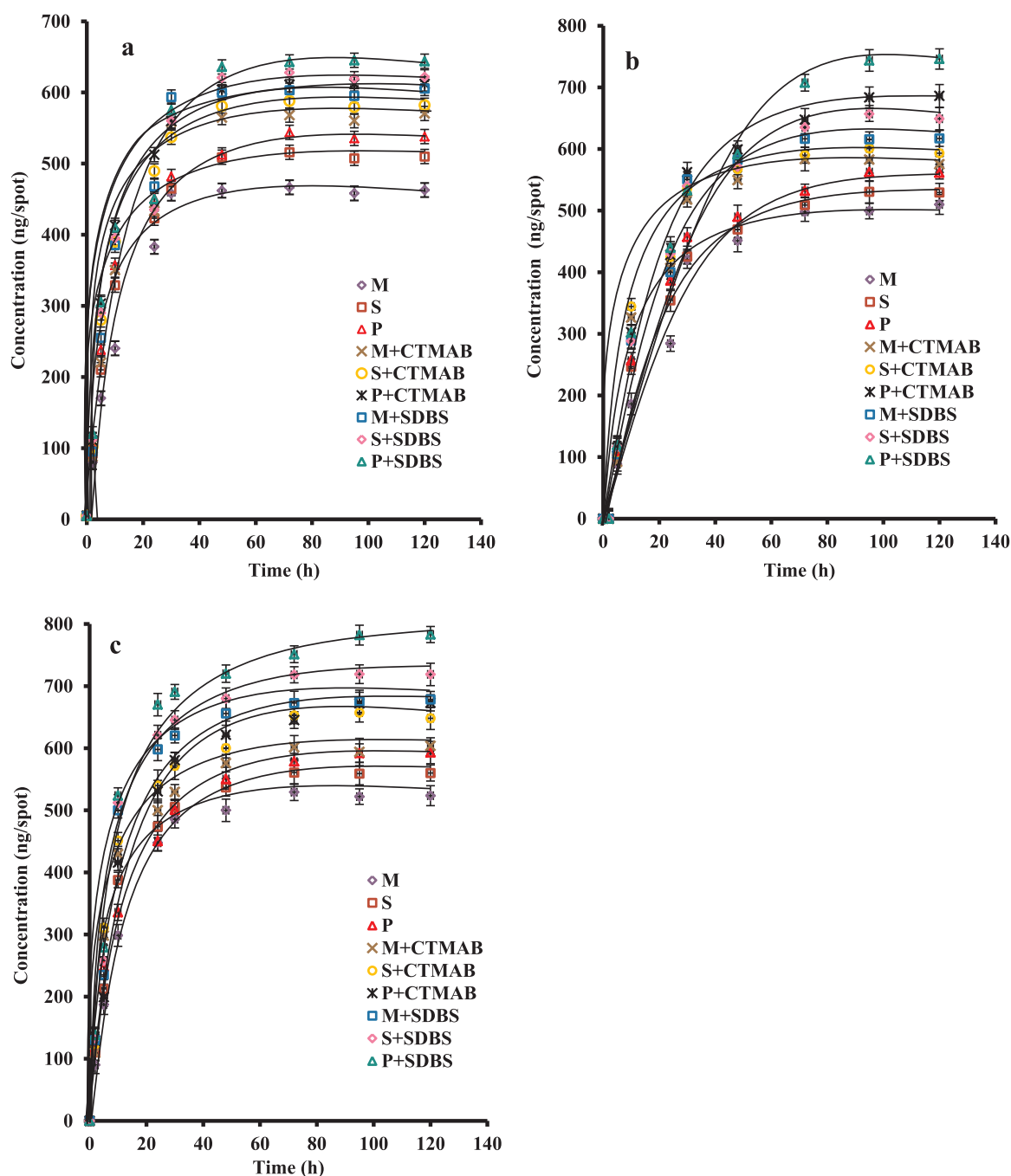
Fig. 2. Uptake of (a) Phe, (b) 3-MP and (c) Retene by the living crop leaf surfaces with or without CTMAB (200 ng/spot) and SDBS (200 ng/spot). Results are all shown as means ± SD (n = 9). M: maize; S: soybean; P: potato.

methylalkanes > primary alcohols > fatty acids > esters > secondary alcohols > not identified; meanwhile, significant difference existed in the proportions of components

among the three species ($P < 0.05$). And, the percentages of total organic carbon (TOC) on the leaf surfaces were 67.5% for soybean, 60.2% for potato, and 64.2% for maize, respectively. Clearly, no good correlation was found between the TOC of leaf-wax and the EAC of three PAHs as well. This divergent observation reveals that it is of great necessity to probe the leaf-surface polarity using a commonly polar index of (O + N)/C and the EAC of parent and alkylated Phe (Li et al., 2017). The average polar index varied following the sequence of 0.33 for maize > 0.30 for soybean > 0.26 for potato. Interestingly, the EAC of the three chemicals showed a close negative correlation with the leaf-surface polarity of the three-crop species (Fig. S4a), indicating that the

surface polarity of leaf-wax dominated the retention of gaseous parent and alkylated Phe. Moreover, a previous study investigating the compositions of cuticular waxes from potato leaves observed appreciable quantities of phenyl-containing compounds, such as benzoic acid esters and phenylethyl esters (Szafranek and Synak, 2006), which might have a certain contribution to the higher affinity of potato for parent and alkylated PAHs.

3.2.3. The effects of surfactant on EAC

From Fig. 2, the EAC of individual Phe, 3-MP and Retene by each of the three crop leaf surfaces increased rapidly initially as CTMAB and SDBS dosages increased to relatively lower levels, and then increased at a decreasing rate with dosages up to higher levels. The observation suggests that the adsorption capacity of leaf surfaces for the three

gaseous chemicals increased when the surfactants introduced on the leaf surfaces of the three living crop seedlings, which could be explained by the plasticizing effects of the leaf-adsorbed surfactants. As reported, the plasticizing effect can promote the accessibility of vegetation cuticle to organic compounds and provide more adsorption sites as well as specific interactions on the outer leaf surfaces, *via* decreasing the leaf-wax's viscosity and tortuosity, and increasing the porosity of the cuticle (Chen and Xing, 2005; Li et al., 2009). Specifically, cuticle was proven to be a potential reservoir for POPs as well as an impermeable structure for the diffusion of POPs owing to the existence of a crystalline wax layer (Moeckel et al., 2008). However, the introduction of surfactants would dissolve the epicuticular wax to some degree, thereby increasing the accessibility of the three chemicals to internal lipid that possesses higher adsorption capability for PAHs. Li et al. (2009) reported that, the inclusion of SDBS, CTMAB and Tween 20 with their content below the critical micelle concentration (CMC) enhanced the intrinsic sorption capacity of 1-naphthol and naphthalene to the isolated cuticles from tomato and apple, while the surfactants with the dosages above CMC have solubilization-dominated effects on the organic compounds, thereby reducing their partitioning into the cuticle from the aqueous solution. In this work, no solubilization effect was observed because the accumulated parent and alkylated PAHs came from the air.

Notably, the effects varied with the types of surfactant and chemical, as well as plant species. Within the same chemical and crop species, SDBS induced greater enhancement of PAHs adsorption than CTMAB, when the two surfactants had the identical initial concentration (Table 2). For maize, as CTMAB and SDBS concentrations each increased up to 100 ng/spot, the EAC values increased by 9.0% *versus* 14.6% for Phe, 9.4% *versus* 15.6% for 3-MP, and 10.3% *versus* 17.1% for Retene, respectively. The different increasing extent of EAC values suggests that the induced-plasticizing effects varied with the surfactant. This should be attributed to the distinct hydrophilic lipophilic balance (HLB) values between the two surfactants. The HLB value is a key factor determining the lipophilicity of surfactant, and generally, lower HLB value favors higher lipophilicity. The HLB value of SDBS (10.6) was smaller than that of CTMAB (15.8), indicating that SDBS had greater affinity for and plasticizing effects on the epicuticular wax. In addition, for the same PAHs and surfactant with unchanged initial contents, the enhancement of EAC were different among the three-crop species with the decreasing order of maize > potato > soybean. As mentioned above, the leaf-wax content followed the sequence of soybean > potato > maize. It is reasonable to explain the inverse relationship that the surfactant's plasticizing effects on the crop leaf surfaces with lower wax content was more apparent than that with higher wax amount. Finally, within the same crop species and surfactant with unchanged initial dosage, inter-chemical variability in the enhancement of the EAC was observed with the decreasing order of Retene > 3-MP > Phe ($P < 0.05$). Under this kind of treatment, the plasticizing effect induced by

surface-sorbed surfactant would remain invariant. In other words, the variation in enhancement degrees should be associated with certain physicochemical properties of the chemicals. As shown in Fig. S4b, the enhancement degree exhibited a good positive correlation with the lg K_{OW} values of the three chemicals for maize (CTMAB: $R^2 = 0.87$; SDBS: $R^2 = 0.80$). For the other two crops, the correlation coefficients between the enhancement degree of EAC and the lg K_{OW} values of the three chemicals are 0.84/0.79 (CTMAB/SDBS) for soybean, 0.91/0.82 for potato, respectively. The results demonstrate that the leaf surfaces with surfactants' plasticizing effects would interact more strongly with PAHs owning to greater lg K_{OW}.

3.3. Model interpretation of PAHs adsorption

Mathematical models are a common way to be used for describing the exchange of PAHs between the air and vegetation. In this work, the adsorption experiment data were fitted using the following three adsorption models.

pseudo-first-order model:

$$C_S(t) = C_A[1 - \exp(-k_{AS}t)] \tag{1}$$

pseudo-second-order model:

$$\frac{t}{C_s(t)} = \frac{t}{C_A} + \frac{1}{k_{AS}C_A^2} \tag{2}$$

one-compartment model:

$$\frac{dC_S}{d_t} = k_{AS}a_{AS}(C_A - \frac{C_L}{BCF}) \tag{3}$$

where C_s is the concentration of PAHs on the leaf surfaces of living crop seedlings (ng /m^3), t is time (h), k_{AS} represents the overall air-surfaces mass transfer coefficient referenced to the air (m/h), a_{AS} is the crop leaf surfaces area normalized to leaf volume (m^2/m^3) and considered to be invariable since the crop leaves used in the experiment are almost identical. BCF represents the surface/air bio-concentration factor ((ng/m^3)/(ng/m^3)). The fitting coefficients to the pseudo-first-order model, pseudo-second-order model and one-compartment model were obtained using Origin 8.0 and the values were in the range of 0.50–0.75, 0.43–0.66 and 0.81–0.89, respectively, indicating that the one-compartment model was the most applicable to the uptake of parent and alkylated PAHs by the crop leaf surfaces.

The k_{AS} values were calculated at the initial phase of the uptake experiment, thus C_S/BCF in Eq. (3) is negligible. Eq. (3) can be simplified by the following equation:

$$\frac{dC_S}{d_t} = k_{AS}a_{AS}C_A \tag{4}$$

From Table 3, the calculated k_{AS} values of gas-phase Phe, 3-MP and Retene adsorbed onto the crop leaf surfaces in the presence and absence of surfactants ranged from 3.0 m/h to 5.1 m/h. The inter-species and

Table 2
The effects of surfactants on the retained quantity (ng/spot) of the three selected PAHs on living crop leaf surfaces.

Surfactant	Concentration of surfactant (ng/spot)	Maize			Soybean			Potato		
		Phe	3-MP	Retene	Phe	3-MP	Retene	Phe	3-MP	Retene
	0	461.5 ± 13[a]	503.1 ± 18[a]	525.0 ± 14[a]	510.0 ± 19[a]	524.4 ± 15[a]	557.4 ± 13[a]	539.0 ± 17[a]	559.4 ± 21[a]	592.6 ± 19[a]
CTMAB	100	503.2 ± 16[b]	550.2 ± 12[b]	579.0 ± 17[b]	543.0 ± 15[a]	565.4 ± 19[b]	605.8 ± 20[b]	582.1 ± 25[b]	605.3 ± 14[b]	646.5 ± 22[b]
	200	536.9 ± 14[b]	589.8 ± 17[c]	623.1 ± 11[c]	582.5 ± 21[b]	606.2 ± 20[c]	648.5 ± 23[c]	625.1 ± 18[c]	650.3 ± 23[c]	697.6 ± 26[c]
	300	570.9 ± 18[c]	627.0 ± 19[d]	657.6 ± 23[d]	608.4 ± 28[c]	635.0 ± 23[d]	682.7 ± 28[d]	653.8 ± 21[c]	686.9 ± 26[d]	729.3 ± 23[c]
SDBS	50	497.3 ± 19[a]	546.0 ± 14[b]	572.7 ± 19[b]	536.8 ± 20[a]	559.6 ± 19[b]	599.9 ± 21[b]	576.2 ± 15[b]	599.4 ± 17[b]	642.6 ± 15[b]
	100	528.7 ± 13[b]	581.6 ± 16[c]	615.0 ± 25[c]	574.6 ± 16[b]	599.3 ± 22[c]	645.6 ± 17[c]	609.8 ± 20[c]	641.4 ± 18[c]	688.9 ± 13[c]
	200	564.8 ± 16[c]	621.7 ± 20[d]	660.1 ± 17[d]	609.5 ± 18[c]	641.5 ± 27[d]	689.4 ± 20[d]	652.9 ± 22[d]	688.2 ± 24[d]	736.9 ± 17[d]

The results are shown as the means ± SD of nine replicates for each treatment. For each treatment, means superscripted by the different lower-case letters in a column indicate significant differences ($P < 0.05$) between the treatments based on the determination by Tukey's test.

Table 3
The calculated overall air-surfaces mass transfer coefficient referenced to the air (k_{AS}, m/h).

Crop	Surfactant	Phe	3-MP	Retene
Maize	Blank	3.0 ± 0.1^a	3.5 ± 0.2^a	3.9 ± 0.2^a
	CTMAB	3.3 ± 0.3^b	3.8 ± 0.1^b	4.2 ± 0.2^b
	SDBS	3.7 ± 0.2^c	4.0 ± 0.3^b	4.7 ± 0.3^c
Soybean	Blank	3.2 ± 0.2^a	3.7 ± 0.2^a	4.2 ± 0.1^a
	CTMAB	3.5 ± 0.4^b	4.3 ± 0.1^b	4.6 ± 0.3^b
	SDBS	3.7 ± 0.2^b	4.5 ± 0.2^b	4.9 ± 0.3^c
Potato	Blank	3.5 ± 0.1^a	3.9 ± 0.2^a	4.5 ± 0.2^a
	CTMAB	3.8 ± 0.3^b	4.4 ± 0.3^b	4.9 ± 0.2^b
	SDBS	4.0 ± 0.3^b	4.7 ± 0.2^c	5.1 ± 0.4^b

The results are shown as the mean ± SD of nine replicates. For each treatment, means superscripted by the different lower-case letters in a column indicate significant differences ($P < 0.05$) among the treatments based on the determination by Tukey's test.

inter-chemical variability was observed in k_{AS} values. For each of the three-crop species, the k_{AS} values followed the order of Retene > 3-MP > Phe. In comparison to PAHs without surfactants, the observed k_{AS} values increased by 7.7–23.3% for those with CTMAB or SDBS, indicating that the presence of surfactants promoted the uptake rates of Phe, 3-MP and Retene onto the living crop leaf surfaces.

4. Conclusions

In this work, we successfully investigated the uptake of gaseous Phe, 3-MP and Retene by living crop leaf surfaces, as well as the effects of surfactants using fiber-optic fluorimetry. The results provided new insights into the mechanism for

producing the differences in PAHs' EAC on crop leaf surfaces. In addition, the usage of surfactants had a significant impact on the uptake of PAHs by the living crop leaf surfaces, mainly in terms of EAC and k_{AS}. Above all, the presence of surfactants increased both the EAC and k_{AS} values, posing an adverse effect on agricultural product safety. These findings have significance to an understanding of the environmental behaviors of alkylated PAHs in crop systems and will enable us to evaluate more precisely the crop safety. Furthermore, the interactions of PAHs with coexisting substances such as surfactants that will likely alter the behavior, fate and risk in crop system are a valuable and pertinent subject.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ecoenv.2018.02.045.

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