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In situ investigation into surfactant effects on the clearance of polycyclic aromatic hydrocarbons adsorbed onto soybean leaf surfaces[☆]

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ABSTRACT

The partitioning of polycyclic aromatic hydrocarbons (PAHs) in agricultural crop leaves, contributes to the exposure of organisms to these chemicals through the dietary pathway. To precisely predict the fate of PAHs and crop safety, the clearance of three-ringed phenanthrene (Phe) and four-ringed pyrene (Pyr) adsorbed individually onto living soybean leaf surfaces, as well as the effects of two surfactants, namely, an ionic surfactant (sodium dodecylbenzene sulfonate, SDBS) and a non-ionic surfactant (polyoxyethyleneglycol dodecyl ether, Brij35), were investigated *in situ* using the laser-induced nanosecond time-resolved fluorescence (LITRF) method. The effects varied significantly with surfactant types primarily in terms of the elimination rates and the final residues of PAH chemicals. With increasing SDBS and Brij35 concentrations, volatilization rate constants (k_C) of both Phe and Pyr initially decreased at fast rates and then at more moderate rates later on, resulting from the plasticizing effect of surfactants adsorbed on leaf surfaces. In addition, the photolysis rate constants (k_P) decreased with the presence of SDBS but increased with the presence of Brij35. Overall, the total clearance rates of PAHs (k_T) adsorbed onto living soybean leaf surfaces were inhibited by the presence of SDBS but promoted by the presence of Brij35. These observations show that surfactants may significantly alter the clearance of PAHs in agricultural systems, and the potential impact of surfactants on crop safety is closely related to surfactant types in natural environments.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are common atmospheric pollutants that are emitted primarily from the incomplete combustion of biomass or fossil fuels (Jia et al., 2015). Most PAHs, some of which persist in the atmosphere, are considered to be a health risk because they are toxic, mutagenic, and carcinogenic to mammals, and they present a considerable public health hazard (Amarillo et al., 2014; Choi et al., 2015). As primary food producers, plant life provides an exposure route to higher trophic levels; therefore, the transfer of atmospheric PAHs, and its biological effects on plants constitutes a key step which must be investigated when looking at the transfer of PAHs via the terrestrial food chain (Desalme et al., 2013). Clearly, an increased understanding of the actions of PAHs between the air and vegetation has significant implications for crop safety and risk assessments.

The epicuticular wax (ECW) has been described as a determinant penetration barrier of living plant leaves, as well as being a highly efficient natural sorbent and a good potential reservoir for PAHs, all of which strongly influence the fates of PAHs (Moeckel et al., 2008; Wang et al., 2008a). Specifically, PAHs that are adsorbed onto the relatively impermeable cuticular skin are prone to photolysis and volatilization, but the amount of chemicals penetrating through the cuticle skin is not significant (Niu et al., 2003; Wang et al., 2005; Sun et al., 2016). Our previous study, which was conducted under natural conditions, demonstrated that the

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clearance of single PAHs adsorbed onto living mangrove leaf skin included both rapid and slow phases, and that volatilization played a major role in the disappearance of adsorbed PAHs over the rapid phase, whereas the combined effects of volatilization and photolysis were the dominant mechanism for the slow phase (Sun et al., 2013a). However, the question of whether these conclusions can sufficiently explain the clearance of PAHs adsorbed onto the cuticle skin of other species remains to be investigated. Moreover, under natural conditions, PAHs that are adsorbed onto crop leaf surfaces commonly coexist with many other substances (e.g., abscisic acid, surfactants) that can induce variation of the foliar structure (Tamura et al., 2001; Barber et al., 2002). However, little is known about how some of these typical substances affect the clearance of PAHs that are adsorbed onto plant leaf surfaces.

The ECW's transport-limiting barrier to PAH chemicals, which was mentioned above, also limits the efficient performance of foliar-applied agrochemical molecules, including pesticides, fruit chemical thinning, and growth regulators (Petracek et al., 1998; Kirkwood, 1999; Schreiber, 2006). To enhance the efficacy of foliar-applied agrochemicals, the application of surfactants in spray solutions is a common way to increase the solubility of the active ingredient, to improve wettability of the plant cuticle, and to increase cuticular penetration (Petracek et al., 1998). Annually, approximately 230,000 tonnes of surfactants are used in agrochemical products. These products typically contain 1–10% of one or more surfactants (Caroline, 2007). As a plasticizer, surfactants enable the softening of the crystalline ECW and thus increase the mobility of the agrochemicals across the cuticular membrane (Schonherr et al., 2000; Popp et al., 2005). As reported by Li et al. (2009), all of anionic sodium dodecylbenzene sulfonate (SDBS), cationic cetyltrimethylammonium bromide (CTMAB), and nonionic polyoxyethylene (20) sorbitan monolaurate (Tween 20) increase the intrinsic sorption coefficients of 1-naphthol and naphthalene by both isolated tomato and apple cuticles, which is attributed to the cuticle-sorbed surfactant's plasticizing effect. However, by far, the effects of surfactants coexisting with these chemicals on the clearance of PAHs adsorbed onto the living plant leaf surfaces have not been well understood.

The commonly used analytical methods (e.g., GC, GC–MS and HPLC) of related studies are generally destructive techniques (Kobayashi et al., 2007; Sojinu et al., 2010; Wang et al., 2013) that are incapable of an *in situ* determination of PAHs adsorbed onto living plant leaf surfaces. Recently, we developed a laser-induced nanosecond time-resolved fluorescence (LITRF) method for the *in situ* determination of PAHs that are adsorbed onto living mangrove leaf and root surfaces, with a detection limit up to 10^{-2} ng spot^{-1} (Sun et al., 2013b; Yang et al., 2013; Li et al., 2015). Therefore, this technique provides a potential way for the *in situ* investigation into the effects of surfactants on the clearance of PAHs from the cuticle skin of living plant seedlings. In this work, phenanthrene (Phe) and pyrene (Pyr) were selected as the model components of PAHs owing to their prevalence in both soybean leaves and the atmosphere, and the established LITRF method was employed to *in situ* investigate effects of the surfactants on the clearance of the two PAHs adsorbed individually onto the leaf surfaces of living soybean seedlings.

2. Materials and methods

2.1. Apparatus and reagents

LITRF system equipped with fiber optic accessories with a length of 5 m (Laser Laboratorium Göttingen, Germany) (Fig. 1), which has been given a detailed description in our previous study (Sun et al., 2013b), was employed to obtain all of the fluorescence spectra in this study. Moreover, the schematic setup of the UV-Laser and sensor head has been provided in Fig. S1 to visually display this determination technique. From the figure, the observation area of sensor head is approximately 0.28 cm^2, which is the basis for making detection 'spot' on soybean leaf surfaces mentioned in Section 2.2.

The organic compounds (A.R.) and two surfactants used in this study were all purchased from Shanghai Trustin Chemical Co., Ltd, China, and were used without further treatment. Stock solutions of the two surfactants at a concentration of 1 g L^{-1} were prepared by dissolving 0.1000 g SDBS and polyoxyethyleneglycol dodecyl ether (Brij35) in 100 mL acetone, respectively. Stock solutions of Phe and Pyr, purity >99% (Sigma, USA), were prepared based on the method recorded in our previous studies (Chen et al., 2011; Wang et al., 2014). The samples (solute solutions with surfactants) were obtained by mixing their stock solutions in set points first and then diluting the mixing solutions using acetone, whereas controls (solute solutions without surfactants) were prepared by diluting solute stock solutions alone with acetone.

2.2. Preparation of living soybean seedlings

Soybean seeds were cultivated in pots and allowed to grow for 6 weeks prior to being used for the following clearance experiment. For each sample or control mentioned in Section 2.2, six living soybean seedlings of approximately the same height (28 ± 0.5 cm) were selected, and then six leaves (one per seedling) of approximately the same size (13 ± 0.2 cm^2) and fresh weight (approximately 0.5 g per leaf) were chosen for the experiment. Next, the silt that was sorbed on the selected leaf surfaces was removed according to the method reported in our previous studies (Chen et al., 2011; Wang et al., 2014). After air-drying, a 'spot' with area of approximately 0.28 cm^2 ($r = 0.3$ cm) was produced by using the large round end of a 5 mL pipette (Shanghai Medical Laser Instrument Plant, China) (Sun et al., 2013b; Yang et al., 2013), which was used as the determination location. For a leaf, there were nine detection spots that distributed evenly over the front, middle and nether parts of the leaf, which was the same as that done with mangrove leaf in our previous study (Chen et al., 2011). The samples (solute solution with surfactants) and controls (solute solution without surfactants) were introduced onto these 'spots' slowly and evenly using a 10 μL flat micropipettes (Shanghai Medical Laser Instrument Plant, China), and this kind of pollution pattern was same as that reported in our previous studies (Chen et al., 2011; Sun et al., 2013a, 2016, 2013b).

2.3. Quantification of PAHs adsorbed onto living soybean leaf surfaces

The quantification of PAHs that were adsorbed onto the leaf surfaces of living soybean seedlings was accomplished by using the LITRF method (Fig. 1), and the key instrumental parameters were as follows: laser excitation wavelength, 266 nm; time slice, 100; time shift, 2 ns; channels, 674; laser energy, 38 μL; cooler temperature, −6 °C. Detailed operation procedures were the same as those reported in our previous study (Sun et al., 2013b). To verify the precision and accuracy of the LITRF method, interference and recovery experiments were performed based on the approach documented in our previous reports (Chen et al., 2011). For a fixed concentration of either Phe or Pyr, the increase of SDBS and Brij35 concentrations did not significantly influence the fluorescence signal of PAHs (Table S1). The recovery percentages of the added PAHs were in the range of 87.4%–95.9%, confirming the reliability of the analytical method in this work (Table S2). Additionally, the relative standard deviation (RSD) for the *in situ* determination of