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In situ determination of the depuration of three- and four-ringed polycyclic aromatic hydrocarbons co-adsorbed onto mangrove leaf surfaces

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ABSTRACT

A dual-wavelength fiber-optic fluorimetry for the *in situ* simultaneous determinations of fluorene (Flu), phenanthrene (Phe) and pyrene (Pyr) adsorbed onto the leaf surfaces of living *Avicennia marina* (*Am*) seedling were developed and used to study the depuration kinetics of the three PAHs, adsorbed individually or mixed together, onto living *Am* leaf surfaces. Limits of detection for the *in situ* measurements of adsorbed Flu, Phe and Pyr were 4.62, 2.75 and 1.38 ng spot^{-1}, respectively. The depuration kinetics of the three selected polycyclic aromatic hydrocarbons (PAHs) are divided into rapid and slow phases; both phases followed the same first-order kinetics with relative clearance rates of Flu > Phe > Pyr during the rapid phase, and a clearance rate order of Pyr > Flu > Phe during the slow phase. For the three PAHs co-adsorbed on living *Am* leaf surfaces, a significant synergistic effect was detected during the rapid phase clearance; conversely, an antagonistic effect was observed during the slow phase. However, the synergistic effect dominated during both phases of the depuration process, and the co-adsorption of PAHs promoted the clearance of all three compounds from the mangrove leaf surfaces. These findings demonstrate a novel analytical method for *in situ* characterization of multiple PAHs adsorbed onto the plant surfaces.

1. Introduction

Certain polycyclic aromatic hydrocarbons (PAHs) have been classified as persistent organic pollutants (POPs), which are ubiquitous in the environment. PAHs are primarily byproducts of the incomplete combustion of coal/petroleum and the pyrolysis of organic materials. Several PAHs have been reported as carcinogenic and/or mutagenic, and their persistence in the atmosphere presents a considerable public health hazard (Yu et al., 2015). Significant concerns throughout the world have prompted investigations into the routes by which these compounds are removed from the atmosphere (Su et al., 2006). Given the high surface coverage of vegetation (80% of the earth's terrestrial surface) and the presence of hydrophobic lipids and waxes in foliage (Chen et al., 2010), forests have a significant influence on the regional/global movement of PAHs and their ultimate environmental fates (Simonich and Hites, 1994). For instance, plant life can reduce concentrations of atmospheric PAHs by increasing their transference to the forest floor (McLachlan and Horstmann, 1998; Howsam et al., 2001; Choi et al., 2008). Secondly, forests have been identified as a very important terrestrial storage compartment of PAHs. Thirdly, PAHs are subject to photolytic degradation on plant surfaces or metabolism within the plant (Barber et al., 2004). In brief, it is vital to investigate these processes and provide more insight into relevant mechanisms (Nizzetto et al., 2014).

Previous reports have identified air-surface exchange as a key research point for increasing our understanding of the role of vegetation in filtering atmospheric PAHs (Nizzetto et al., 2008; Nizzetto and Perlinger, 2012). Certain investigations have primarily focused on depuration or clearance processes, rather than uptake experiments, because data of the former leads itself to easier

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interpretation (Sun et al., 2013a). Living plant cuticles have been described as high-efficiency natural sorbents and good potential reservoirs for PAHs, and as a result, the cuticles strongly influence the fate of PAHs (Chen et al., 2005; Wang et al., 2008a,b). Specifically, PAHs adsorbed onto the relatively impermeable cuticular surfaces may undergo photolysis and volatilization (Niu et al., 2003; Barber et al., 2004), or further diffuse into the cuticle and, ultimately, other lipid compartments deep in the leaf body (Li and Chen, 2014). Photolysis has been considered a significant route of depuration for PAHs accumulating on the surfaces of pine and spruce needles (Niu et al., 2003; Wang et al., 2005). However, there is variability among the species and chemicals involved in the depuration processes (Geisler et al., 2012), and more investigations regarding the depuration kinetics and their mechanisms are warranted.

Mangrove wetlands, serve as a buffer in estuaries, and act as a sink for atmospheric PAHs in coastal ecosystems (Lu et al., 2011, 2014; Wang et al., 2014a); the interactions between PAHs and mangroves are a potential key component in the global cycling of PAHs (Zhang et al., 2014). As reported in our previous studies, mangroves could accumulate PAHs from the atmosphere because of the thick waxy or lipidic layers on their leaf surfaces (Wang et al., 2008a,b); under the irradiation of a high pressure Hg lamp, photolysis was determined to be the main transformation pathway for PAHs adsorbed onto mangrove leaf surfaces, while the contribution from volatilization to the disappearance of adsorbed PAHs was negligible (Wang et al., 2014b). However, these conclusions can not completely explain the depuration of adsorbed PAHs from the mangrove leaf surfaces under natural conditions. Our recent study which conducted under natural conditions demonstrated that the depuration of adsorbed individual PAHs adsorbed on the living mangrove leaf surfaces included rapid and slow phases, and volatilization played a main role in the clearance of adsorbed individual PAHs during the rapid phase, while the combined effect of volatilization and photolysis was the dominant mechanism for the slow phase. Additionally, the individual contributions of volatilization and photolysis to the total loss of adsorbed PAHs were also determined in this work (Sun et al., 2013b). In real-world environments, PAHs often exist as a mixture, and the depuration kinetics when multiple PAHs are present on the leaf surfaces of living mangrove seedlings remain to be investigated.

The commonly used analytical methods (e.g., GC, GC-MS and HPLC) of related studies are generally destructive techniques (Kobayashi et al., 2007; Kuang et al., 2015) that are incapable of monitoring the interactions between PAHs and mangrove leaf surfaces *in situ*. In our previous studies, a solid-surface fluorimetry realizes the *in situ* determination of PAHs adsorbed on detached mangrove leaf surfaces (Wang et al., 2008a,b), but not the PAHs adsorbed on living plant surfaces. A laser-induced nanosecond time-resolved fluorescence (LITRF) method enables the *in situ* determination of single PAHs adsorbed onto living mangrove leaf surfaces with relatively higher sensitivity (Yang et al., 2013; Sun et al., 2013a, 2013b), but insufficient in differentiating a single component spectrum from multi-component spectra due to the limitation of a single excitation wavelength (266 nm). Although an established synchronous solid surface fluorimetry helps us to achieve the *in situ* analysis of binary mixtures of PAHs adsorbed onto living mangrove leaf surfaces (Wang et al., 2014b), but is less than ideal for the *in situ* analysis of ternary mixtures or more. A method of fiber-optic fluorimetry can be used to *in situ* determine ternary PAHs adsorbed on living mangrove leaf surfaces, but the multiple target analytes are restricted to only those PAHs with non-interfering spectra (Chen et al., 2010; Wang et al., 2014a). Chen et al. (2008) used a dual-wavelength fluorimeter for the simultaneous determination of three dissolved PAHs. Thus, the combination of fiber-optics with dual-wavelength fluorimetry would most likely serve as a good foundation for an approach capable of *in situ* determinations of multiple PAHs adsorbed onto leaf surfaces without being hindered by spectral overlap.

In this work, fluorene (Flu), phenanthrene (Phe) and pyrene (Pyr) were selected as model component of PAHs due to their prevalence in both mangrove leaves and gas phase. A novel established dual-wavelength fiber-optic fluorimetric method was developed and employed for the *in situ* investigation of the kinetics behind the depuration of the three adsorbed PAHs, either individually or as a mixture, from the leaf surfaces of living *Avicennia marina* (*Am*) seedlings.

2. Materials and methods

2.1. Apparatus and reagents

All the fluorescence spectra were obtained by using a Cary Eclipse fluorescence spectrophotometer equipped with 150 W Xenon flash lamp and fiber optic accessories with the length of 2 m (Varian, Harbor City, California), and the schematic diagram of this device has been shown in Fig. S1. The large circular ends of a 5 mL pipette and a 10 μL flat head micro-injector were adopted for these experiments, and have been previously illustrated in the references (Chen et al., 2011; Sun et al., 2013a). Stock and working solutions of Flu, Phe and Pyr (Aldrich, purity > 99%, USA) were prepared according to our published method (Chen et al., 2010).

2.2. Sample preparation

Mature viviparous propagules of *Am* were collected from Cao Putou village, Longhai city, China (east longitude: 117°29′–118°14′; north latitude: 24°11′–24°36′; altitude: 0 m above sea level), and *Am* hypocotyls of approximately the same size and maturity were rapidly transported to a laboratory for a 15 month cultivation in a sand bed. Next, *Am* seedlings of approximately the same height (35 ± 0.5 cm), and leaves with similar surface area (11 ± 0.2 cm^2) and fresh weight were selected for the following depuration experiments.

2.3. Pretreatment of Am seedlings for the experiment

Six living *Am* seedlings were chosen for the depuration experiment; six leaves (one per seedling) of approximately the same size were chosen for the experiments. Next, according to a method documented in the literature (Chen et al., 2010), the silt on all of the selected leaf surfaces was removed. After air-drying, a 'spot' with a diameter of 0.6 cm was produced using the method reported by our laboratory (Chen et al., 2011), which was used as the determination location. Working solutions of the three PAHs, individually and in combination, were dissolved in acetone and deposited onto these 'spots' with a 10 μL flat head micro-injector.

2.4. Determination of PAHs adsorbed onto the leaf surfaces of living Am seedlings

The amounts of PAHs adsorbed onto the leaf surfaces of living *Am* seedlings were determined *in situ* using a Cary Eclipse fluorescence spectrophotometer equipped with fiber optic accessories. Living *Am* seedlings, with leaf surfaces contaminated by PAHs, were placed under the optical fiber probe with an angle of 45° (between the probe and the tested leaf) to avoid interference from the scattered light. A dual-wavelength fiber-optic fluorimetric method, used for *in situ* determination of Flu, Phe and Pyr, either individually or as a mixture, adsorbed onto the living *Am* leaf surfaces was