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In situ visualization and quantitative investigation of the distribution of polycyclic aromatic hydrocarbons in the micro-zones of mangrove sediment☆

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The distribution of polycyclic aromatic hydrocarbons (PAHs) in the micro-zones of mangrove sediment is a predominant factors determining PAH bioavailability. In this study, a novel method for the *in situ* visualization (via microscope) and quantitative investigation of the PAH distribution in the micro-zones of mangrove sediment was established using microscopic fluorescence spectral analysis combined with derivative synchronous fluorescence spectroscopy (MFSA-DSFS). The MFSA-DSFS method significantly suppressed the background fluorescence signal of the sediment (the S/N values increased by over two orders of magnitude). The proportion of the nonpolar organic carbon content in the particulate organic matter (POM) rather than its content in the total organic matter (TOM) showed a significantly positive correlation with the uneven PAH distribution (Relative DC-M values) evaluated using the established method ($p < 0.05$). The extent of the uneven PAH distribution in the micro-zones of aged sediment was higher than that in the spiked sediment. Moreover, the distribution pattern of the PAHs within the mangrove sediment changed to become more homogeneous in the presence of low-molecular-weight organic acids (LMWOAs), which primarily contribute to increasing the POM content.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of persistent organic pollutants (POPs) that are ubiquitous in the environment. These compounds are of particular concern due to their carcinogenicity, mutagenicity, and toxicity to biota. It has been reported that over 90% of PAHs exist in soil or sediment (Shen et al., 2013; Wild and Jones, 1995). However, previous reports concluded that the exposure and effects of PAHs on biota are not directly related to their bulk concentration in soil/sediment (Cui et al., 2013). The amount of freely dissolved PAHs in pore water is controlled by the sorption/desorption and distribution of these compounds in the soil or sediment; the dissolved PAHs comprise the majority of the bioavailable PAHs (Oleszczuk et al., 2016; Zielinska and Oleszczuk, 2016). Therefore, improving the understanding of the sorption and distribution of PAHs in soil/sediment is critical to accurately evaluate their potential harmful effects.

Extensive studies have focused on probing the sorption and the subsequent distribution of PAHs in soil or sediment, as well as the associated mechanisms (Olu-Owolabi et al., 2012; Marquez-Bravo et al., 2016). The sorption of organic chemicals to soil and sediments is primarily attributed to the soil organic matter (SOM), and this process can be described using a “dual-mode sorption” model that includes the nonlinear adsorption of carbonaceous geosorbents (CG) and the linear absorption of amorphous organic matter (AOM) (Cornelissen et al., 2005). The former sorption capacity ($K_{F,CG}$) generally exceeds the latter by a factor of 10–100. With the application of solid-state ^{13}C nuclear magnetic resonance spectroscopy (^{13}C NMR) and X-ray photoelectron spectroscopy (XPS), the role played by the chemical composition of soil/sediment, SOM, AOM and CG in the sorption and distribution of PAHs was further explored (Chefetz and Xing, 2009). Wang et al. reported that the sorption of phenanthrene is dependent on the surface and bulk alkyl carbon contents of humic substances from peat soil, rather than being dependent on the aromatic carbon content

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(Wang et al., 2011). In addition to the chemical composition of organic matter, its physical conformation, including its crystalline structure and the spatial arrangement in the SOM domain, has been confirmed to be an important factor affecting its sorption capacity for PAHs, as well as the inaccessibility of the interior sorption domain (Yang et al., 2011).

However, the feature of organic matter and mineral (elemental compositions, functionalities, and physical conformation) that are directly responsible for the diverse molecular interactions of PAHs and soil/sediment at the macroscopic scale are significantly different from those at the microscopic scale (Falsone et al., 2014; Totsche et al., 2010). For example, the O/C value of amorphous black organic matter from the Harwood Forest in Northumberland (UK) can reach a maximum of 0.61 at the microscopic scale with a × 500 magnification, which is much higher than the macroscopic value of 0.34 Wilson et al., 2013. Therefore, the mechanisms of PAH sorption or distribution at the macroscopic scale cannot be fully applied to explain the primary reasons for the uneven PAH distribution in the micro-zones of soil/sediment.

The lack of an appropriate method for the visualization and quantitative analysis of PAH distribution in soil/sediment has been an important factor that has limited this area of study. Highly sensitive and selective chromatographic methods (GC, LC and HPLC) have been widely used to analyze PAHs in soil/sediment. However, due to the pre-treatment procedures, these methods were unable to detect the PAH distribution in the micro-zones of mangrove sediment (Chen and Sidisky, 2014; Sforzini et al., 2015). Similar to the mentioned chromatographic methods, the newly established two-step laser desorption/laser ionization mass spectrometry (L^2MS) method destroyed the original forms of the PAHs on sorbents in the process of changing the PAHs to the gas phase prior to ionization before time-of-flight mass spectrometric analysis (Faccinetto et al., 2015).

In situ microscopy techniques, including synchrotron-based soft X-ray spectromicroscopy, scanning electronic microscopy X-ray photoelectron spectroscopy (SEM-XPS), scanning transmission X-ray microscopy-near edge X-ray absorption fine structure spectroscopy (STXM-NEXAFS), and light microscopy, were used to locate and quantitatively determine the chemical species at the sub-particle scale of solid samples (Chen et al., 2014; Gomez-Parrales et al., 2011; Liu et al., 2014). PAHs have relatively high quantum yields; therefore, among the mentioned methods, only fluorescence microscopy (FM) techniques can realize *in situ* visualization of the PAHs adsorbed onto the micro-zones of mangrove sediment, although this method cannot quantify the PAHs (Roper et al., 2006).

In recent years, the solid surface fluorescence (SSF) spectrum method, including the laser-induced fluorescence spectrum method (LIF) and the laser-induced nanosecond time-resolved fluorescence spectrum method, was confirmed as an effective *in situ* method with low detection limits of PAHs (~1 ng/spot) adsorbed onto solid samples (leaf or root) (Sun et al., 2013; Li et al., 2015a, 2015b). However, in contrast to mangrove leaves or roots, the autofluorescence of soil/sediment is complex and cannot be overcome by traditional SSF, LIF, and LITRF methods, as described by Lee et al. (Lee et al., 2004). Many reports have shown that derivative synchronous fluorescence spectroscopy (DSFS) has an excellent ability to narrow the band and suppress the background fluorescence signal compared with the conventional emission fluorescence method or the nanosecond time-resolved fluorescence

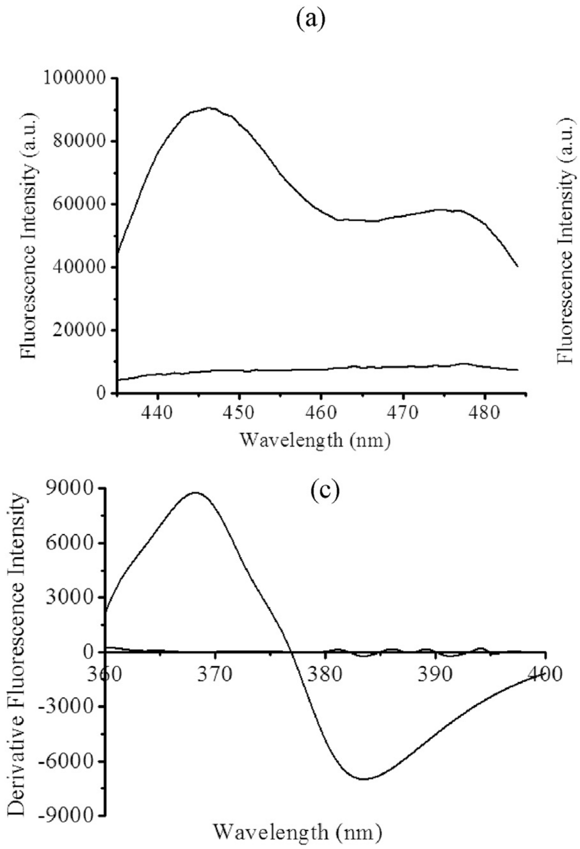

Fig. 1. Fluorescence spectra of mangrove sediment (Y) with and without Ant contaminated (1200 μg kg^{-1}) (a) emission fluorescence spectra, (b) synchronous fluorescence spectra, (c) DSFS.