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Adsorption and absorption of polycyclic aromatic hydrocarbons to rice roots

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A sequential extraction method was applied to divide the PAHs accumulated on rice roots into PAHs in root exudates, PAHs adsorbed on root surfaces, and PAHs absorbed in root tissue.

Abstract

Rice roots and surrounding air, soil and water samples were collected for polycyclic aromatic hydrocarbon (PAH) analysis. The rice roots were separated into lateral roots and nodal roots, and the PAH concentration in the former was found to be higher than that in the latter. In addition, root physiological characteristics including root biotic mass, root lipid content and specific surface area are also discussed. When normalizing the total, adsorption and absorption PAH fractions on a dry root weight basis to root biomass, root lipid, and surface area bases respectively, the differences between PAHs in the two types of roots diminished by 2 to 3 times on average. Results from sequential extraction indicated that PAHs were more easily absorbed by interior rice roots than adsorbed on the surface. In addition, more than 60% of total PAHs accumulated in root tissue for both lateral and nodal roots. However, the results were highly related to the solvent used, extraction time and methodology. Correlation analysis between bioconcentration factors (root over environment) and K_{OA}, K_{OW} showed water to be more significant for PAH adsorption in rice roots than other environmental media.

Keywords: Rice roots; Polycyclic aromatic hydrocarbons; Adsorption; Absorption

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are among the most widely spread pollutants in the environment. Their carcinogenic nature also makes them target pollutants (ATSDR, 1999). PAHs in soil pose a significant threat to environmental, ecological and human health, and are a main concern when seeking remedies for polluted sites (Jones et al., 1989). Because plant roots generate enzymes, amino acids and growth hormones that help maintain root activity, vegetated soils are highly effective in PAH degradation, removal, and mineralization (USEPA, 2000). Equally important are the intricate set of relationships between plant roots, microbes, soils and contaminants that make various phyto-remediation processes possible (USEPA, 2000).

A number of studies have been conducted to determine which factors are most influential in root-soil PAH behavior (Topp et al., 1986; Paterson et al., 1990; Weiss, 2000; Fismes et al., 2002). Soil-bound PAHs are strongly associated with soil organic matter and as such, are not readily available for root uptake. Furthermore, while most PAH compounds are adsorbed to the root surface, there is little transfer to the interior portions of the plant or transformed up to the shoots (Wang and Jones, 1994; Fismes et al., 2002). There is some evidence, however, that PAH accumulations in plant roots could be made available to the shoots via transpiration steam (Sicbaldi et al., 1997; Gao and Zhu, 2004). Efforts have been made to improve extraction methods to better clarify the distinction between

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adsorbed and absorbed PAHs on the root surface and in root tissues. Schwab et al. (1998) measured the affinity of plant roots for naphthalene by extracting root samples using $CaCl_2$ and methanol in sequence, while Binet et al. (2000) washed anthracene from ryegrass root surfaces with chloroform, and then ground the same root sample to extract PAHs in root tissue with chloroform. Further studies have explored new techniques to directly observe the uptake, storage and metabolism of organic contaminants within plant roots. In Wild's study, TPEM (two-photon excitation microscopy) was used to visualize and track the uptake and movement of anthracene and phenanthrene from a contaminated growth medium into living unmodified maize and wheat roots (Wild et al., 2005). By taking UV illuminated photographs at nine positions, Thoma et al. (2004) was able to visualize the effect a dynamic rhizosphere has on chemical degradation. Most previous studies have focused on PAH accumulations in roots from land-grown vegetables and crops, such as lettuce, potatoes, carrots, and maize, while corresponding studies on aquatic plants have rarely been undertaken. Paddy rice is the main food crop planted in China, and more than two thirds of the total population considers it the staple food (NBSC, 2000). As such, a better understanding of PAH distributions in rice roots may be important in assessing the risk such PAHs pose to human health.

Rice roots are aerial roots and can exchange with the outer air through a hollow stem. The roots can be divided into lateral roots and nodal roots (Pan, 1979). The current study is an attempt to develop an improved sequential extraction method to investigate the adsorption and absorption status of PAHs in rice roots, with an aim at better understanding the PAH accumulation process in plant roots.

2. Materials and methods

2.1. Reagents and standards

A mixed standard solution of 16 PAHs was obtained from Supelco Co., USA. All solvents (dichloromethane, acetonitrile, hexane) used for sample preparation and analysis were HPLC grade from Tedia Co., USA. The chromatography silica gel (100–200 mesh) used for sample purification was purchased from Huadong Medical Corp., China.

2.2. Sampling

Rice root, water, air and soil samples were collected between August 5 and 8, 2004 in southwestern Tianjin, China. In order to keep the roots intact for sampling, a block 20 cm deep and 5 cm distant around the root was cut with a stainless steel shovel. The samples were chose randomly in the field and were then transported to the laboratory in sealed plastic bags with the aerial parts discarded. Water samples were collected in brown wide-mouth bottles (2 L capacity). One parallel of three samples was taken from the nearby irrigation river and another from top clear water in the field. Air samples were collected at the same site using a portable air sampler (TMP-1500, China) for 8 h, with flow rate at 1.25 L/min. The samplers were equipped with Whatman glass fiber filters (GFFs; 25 mm, Whatman, UK) to collect particle-bound PAHs and XAD-2 (2.5 g) retaining gas-phase PAHs. Soils near the rice roots were taken as rhizosphere soil, while those on the ridges around the field were collected as bulk soil. The samples were put in sealed bags and transported to laboratory immediately.

After transport to the laboratory, the roots were washed until the attached soils were cleared away and rinsed with distilled water. Clean roots were mixed and separated into lateral roots and nodal roots and stored at 4 °C prior to extraction. All soils were freeze-dried and ground to pass through a 70-mesh sieve and kept at −18 °C for analysis.

2.3. Extraction and cleanup

Root samples were extracted in a 3-step procedure with the first two steps referenced from Schwab et al. (1998). Five grams of intact fresh roots were placed in 15 ml of 0.01 M $CaCl_2$ and shaken briefly at room temperature before being passed through a 0.45-μm micropore filter to a 50 ml separating funnel. The filtering solution was a liquid-liquid base extracted three times with 15 ml n-hexane. The extraction solution was reduced to 1 ml for PAH analysis by GC/MS (Agilent Technology). The result was taken to represent the PAHs dissolved in aqueous solution within the apparent free space of the roots (but not adsorbed). The roots were then translocated to a 100 ml triangular flask and immersed in 20 ml of methanol solvent for 3 min. The extracts were diluted with water to obtain a 10:90 (v/v) methanol/water mixture from which 25 ml was taken for liquid–liquid extraction with n-hexane. The recovered PAHs were multiplied by 8 to arrive at a total fraction, which was intended to represent root adsorbed PAHs. Steps one and two collectively were considered as PAHs on the root surface. After the first two extractions, the roots were freeze dried and extracted by accelerated solvent extractor (ASE) using 1:1 (v/v) mixed DCM and n-hexane as an extraction solvent according to Tao et al., 2004. The resulting fraction was intended to represent PAHs absorbed in root tissue. The procedure and conditions had been described elsewhere. For each extraction step, there were three duplicates with each sample undergoing the same procedure. It should be pointed that the sequentially extracted fractions were operationally defined.

The air samples were extracted by Soxhlet at 90 °C for 4 h with a 100 ml mixture of n-hexane and cyclohexane (1:1, v/v). The water samples were extracted using solid phase extraction with C18 Sep-Pak cartridges (Superclean ENVI, Supelco, USA). The soil samples were extracted using accelerated solvent extraction with a mixture of n-hexane and DCM (1:1, v/v). The extraction conditions and subsequent cleanup procedures are described in Tao et al., 2004. All the extracted PAHs were analyzed by GC/MS.

2.4. PAH analysis and quality control

PAH analysis was conducted using an Agilent 6890 GC coupled with an Agilent 5973 mass spectrometer detector and a 7683 auto-sampler (Agilent Technology). A 30 m × 0.25 mm i.d. × 0.25 μm film thickness HP-5MS capillary column (Agilent Technology) was used. GC temperature was programmed from an initial 60 °C with runs at 5 °C/min up to a maximum temperature of 280 °C and a final holding time of 20 min. Helium was used as the carrier gas. A 1.0-μl aliquot of the extract was injected while the injector port was held at 280 °C and operated in splitless mode at a flow rate of 1.0 ml/min. The head column pressure was 30 kPa. The mass spectrometer was operated in ion monitoring (SIM) mode with an electron impact ionization of 70 eV, an electron multiplier voltage of 1288 V, and an ion source at 230 °C.

The following 16 PAHs were determined: naphthalene (Nap), acenaphthene (Ane), acenaphthylene (Any), fluorene (Fle), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo[*a*]anthracene (Baa), chrysene (Chr), benzo[*b*]fluoranthene (Bbf), benzo[*k*]fluoranthene (Bkf), benzo[*a*]pyrene (Bap), indeno[123*cd*]pyrene (I1p), dibenzo[*ah*]anthracene (Daa), and benzo[*ghi*]perylene (Bgp). The total concentration of the 16 PAH compounds was expressed as PAH16.

Routine quality assessment procedures were followed. Reagent blank controls and procedural blanks were determined simultaneously for each series of samples. The measured procedure blanks were generally more than one order of magnitude lower than the sample measurements for most congeners. All of the results were blank corrected using the averages of all procedure blanks. All samples were analyzed in duplicate and the average coefficient of variation was 20%. Recoveries of the 16 PAHs were tested by spiking samples with mixed PAH standard solution and they ranged from 64.0% to 124.0% for rice roots, from 57.0% to 115.0% for soil, from 60.0% to 120.0% for air, and from 74.2% to 131.0% for water. The method detection limits were