



Combined effects of aqueous suspensions of fullerene and humic acid on the availability of polycyclic aromatic hydrocarbons: Evaluated with negligible depletion solid-phase microextraction



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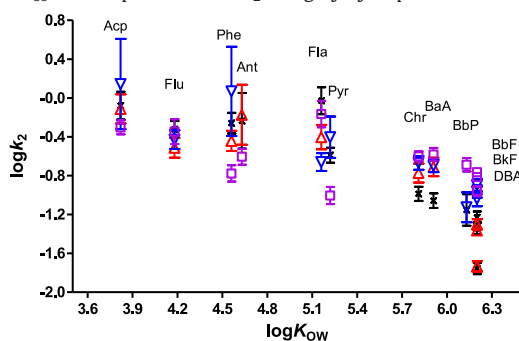
HIGHLIGHTS

- HA accelerated the rate constants (k_2) of PAH uptake to nd-SPME fibers.
- The mixture promoted or retarded the k_2 depending on PAH hydrophobicity.
- Coexistence with HA reduced PAH availability in nC_{60} solutions.
- Higher PAH sorption coefficients were obtained in aqu/nC_{60} than in son/nC_{60} .
- PAH hydrophobicity played an important role in determining availability.

GRAPHICAL ABSTRACT

Relationship between $\log k_2$ and $\log K_{OW}$ of 12 types of PAHs in different matrices. (×) aqueous solutions without any matrix; (Δ) $5 \text{ mg L}^{-1} nC_{60}$; (∇) $5 \text{ mg L}^{-1} \text{ HA}$; (\square) $5 \text{ mg L}^{-1} nC_{60} + 5 \text{ mg L}^{-1} \text{ HA}$. k_2 : rate constant of PAH uptake on the negligible depletion solid-phase microextraction (nd-SPME) fibers; nC_{60} : aqueous suspensions of fullerene; HA: humic acid.

HA accelerated the rate constants (k_2) of almost all PAH uptakes to the nd-SPME fibers; the combined matrices of nC_{60} and HA promoted the k_2 of highly hydrophobic PAHs whereas it retarded the k_2 of less hydrophobic PAHs.



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ABSTRACT

The wide application of engineered carbon nanomaterials, such as fullerene (C_{60}), will inevitably result in their introduction into the aqueous environment. Interactions of C_{60} with abundant natural organic matter (NOM) will likely alter the bioavailability of organic compounds to aquatic organisms. The availability of 12 types of polycyclic aromatic hydrocarbons (PAHs) in various aqueous suspensions of fullerene (nC_{60}) prepared by different methods, e.g., in humic acid (HA) and particularly in combined systems of nC_{60} and HA, was investigated by negligible depletion solid-phase microextraction (nd-SPME). The results showed that HA accelerated the rate constants (k_2) of almost all PAH uptakes to the nd-SPME fibers compared with the solutions without the matrix; the combined matrices of nC_{60} and HA significantly promoted the k_2 of highly hydrophobic PAHs ($\log K_{OW}$ 5.81–6.20), whereas they retarded that of less hydrophobic ones ($\log K_{OW}$ 3.82–4.63) ($p < 0.05$). Remarkable or minor reduction of free concentration of PAH was observed in the combined system of nC_{60} and HA depending on the properties of individual PAHs. Sorption coefficients (K_{HA} , $K_{C_{60}}$ and $K_{C_{60} + HA}$) of various PAHs in different matrices were provided, and matrix concentrations showed no significant effects. For highly hydrophobic PAHs ($\log K_{OW}$ 5.16–6.20), the $\log K_{C_{60} + HA} \geq \log K_{HA} > \log K_{C_{60}}$, whereas for less hydrophobic PAHs ($\log K_{OW}$ 3.8–4.63), the K_{matrix} values in various matrices showed no noticeable trend. In addition, higher $K_{C_{60}}$ values were obtained for aqu/nC_{60} than for son/nC_{60} for most highly hydrophobic PAHs. The above results suggest

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that hydrophobicity plays an important role in determining K_{matrix} in addition to the matrix effects. The interactions between $n\text{C}_{60}$ and HA have critical or minor impacts on availability, and thus bioavailability, of PAHs. This paper contributes to the understanding of the bioavailability mechanisms of organic pollutants in the aquatic environment with both $n\text{C}_{60}$ and NOM.

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1. Introduction

As a type of widely manufactured and applied carbon nanomaterial (CNM), fullerene (C_{60}) triggers concerns about its ecotoxicology and potential human health risk. Although raw C_{60} is generally considered hydrophobic due to its high $\log K_{\text{OW}}$ value (Jafvert and Kulkarni, 2008), stable aqueous suspensions of fullerene ($n\text{C}_{60}$) can be achieved by solvent exchange, extended hydraulic stirring or other environmentally relevant methods (Duncan et al., 2008; Kim et al., 2010), indicating more potential risk to aquatic organisms. It was found that stable $n\text{C}_{60}$ with concentrations as high as 35 mg L^{-1} can be formed by extended mixing of C_{60} with water (Oberdorster et al., 2006). There are already abundant reports about $n\text{C}_{60}$ intrinsic toxicity such as lipid peroxidation and embryo toxicity (Oberdorster, 2004; Kim et al., 2010).

Current research on nanotoxicity focuses on the intrinsic toxicity of nanomaterials. However, new insights in nanotoxicology suggest that the risk of CNMs are not only due to their own toxicity but also due to the toxic substances sorbed by them (Baun et al., 2008), therefore, the effects of CNMs on the bioavailability and toxicity of more toxic organic pollutants have raised growing concerns (Baun et al., 2008; Petersen et al., 2009; Hu et al., 2010; Park et al., 2010; De La Torre-Roche et al., 2012). Generally, in the soil or sediment system, CNMs can reduce extractability and bioaccessibility of hydrophobic organic compounds (HOCs) (Towell et al., 2011) and reduce HOC bioavailability to deposit-feeding organisms (Petersen et al., 2009) but enhance HOC bioavailability to crops (De La Torre-Roche et al., 2012) due to the different bio-uptake mechanisms. In the aquatic system, $n\text{C}_{60}$ decreases the freely dissolved concentrations (C_{free}) or availability of HOCs (Hu et al., 2008, 2010) but can either decrease or enhance the bioavailability and toxicity of other organic pollutants depending on the properties of the pollutants (Baun et al., 2008; Hu et al., 2010; Park et al., 2010). The effects of $n\text{C}_{60}$ on the bioavailability and toxicity of other toxic organic pollutants are complicated, and the mechanisms remain ambiguous. Compared with the complicated bioavailability and toxicity, the availability (chemical activity) of organic pollutants is easier to study by applying equilibrium passive sampling devices to determine the freely dissolved concentration (C_{free}) of organic pollutants (Reichenberg and Mayer, 2006). C_{free} is believed to be the driving force for the transportation, distribution, and bioaccumulation of a contaminant and thus a key parameter controlling the bioavailability and toxic effect of the pollutants. Negligible depletion solid-phase microextraction (nd-SPME), a biomimetic tool, extracts only a negligible portion of the freely dissolved fraction of analyte and leaves the equilibrium between freely dissolved fraction and bound fraction undisturbed, facilitating C_{free} determination of the organic pollutants (Heringa and Hermens, 2003). By using nd-SPME, the C_{free} of HOCs in $n\text{C}_{60}$ aqueous suspensions was successfully measured in our previous study (Hu et al., 2008, 2010), and it was indicated that nd-SPME can evaluate the bioavailability of HOCs in the $n\text{C}_{60}$ aqueous suspensions (Hu et al., 2010). Therefore, the nd-SPME technique can investigate the availability of organic pollutants and thus facilitate the bioavailability study in the $n\text{C}_{60}$ aqueous suspensions.

Natural organic matter (NOM) is ubiquitous in the aquatic environment and, when combining with the released $n\text{C}_{60}$, might change the bioavailability (or availability) and toxicity of the coexisting organic pollutants. The aggregation state of $n\text{C}_{60}$ has close connection with its environmental behaviors and toxicity and is affected by association of $n\text{C}_{60}$ with NOM (Li et al., 2009). Previous studies (Xie et al., 2008; Kim et al., 2012) demonstrated that 5 to 20 mg L^{-1} of Suwannee River humic acid (SRHA) and fulvic acid (SRFA) could cover the surface of

$n\text{C}_{60}$ and decrease the size of $n\text{C}_{60}$ aggregates due to the steric hindrance effects of NOM, thus reducing surface hydrophobicity and consequent toxicity of $n\text{C}_{60}$. Recent research proved that some NOM did stabilize $n\text{C}_{60}$ at a wide range of Ca^{2+} concentrations and more hydrophobic NOM was easier to adsorb to the surface of $n\text{C}_{60}$ (Mashayekhi et al., 2012). In the absence of NOM, $n\text{C}_{60}$ stability was attributed to static repulsion, while the mechanism could shift to steric hindrance in the presence of NOM (Mashayekhi et al., 2012). Alteration of $n\text{C}_{60}$ dispersions and stability might change correspondingly the sorption of organic pollutants to $n\text{C}_{60}$ and thus the availability of the organic pollutants (Hu et al., 2008). Gai et al. (2011) demonstrated that introduction of HA significantly reduced the size of the $n\text{C}_{60}$ particles and thus resulted in the increase of atrazine adsorption to $n\text{C}_{60}$. Therefore, comprehensive and proper evaluation of the $n\text{C}_{60}$ effects on the bioavailability and toxicity of other organic pollutants in the aquatic environment cannot disregard NOM because of the close relation between NOM and $n\text{C}_{60}$. To our knowledge, studies have been fixed on either the influences of NOM on the toxicity of $n\text{C}_{60}$ (Kim et al., 2012) or the influences of $n\text{C}_{60}$ on the bioavailability of other pollutants (Hu et al., 2010). However, few studies have focused on the combined effects of $n\text{C}_{60}$ and NOM on the bioavailability (availability) or toxicity of other pollutants. Thus, the combined effects of $n\text{C}_{60}$ and NOM on the availability of organic pollutants must be studied.

In the present study, which uses Aldrich HA as model NOM, the combined effects of $n\text{C}_{60}$ and NOM on the availability of 12 types of polycyclic aromatic hydrocarbons (PAHs) are investigated by the nd-SPME biomimetic method. The aims of our work are i) to compare the availability of 12 PAHs in a $n\text{C}_{60}$ and HA combined system with that in $n\text{C}_{60}$ or HA individual systems and ii) to investigate the effects of different $n\text{C}_{60}$ preparation methods on the availability of PAHs. The main aspects consisted of the kinetics of PAH sorption to nd-SPME fiber and measurements of C_{free} or free fractions of PAHs and sorption coefficients of PAHs in different matrix solutions. The relevant mechanisms of PAH sorption in the combined system are also discussed.

2. Materials and methods

2.1. Materials and chemicals

An EPA 610 standard polycyclic aromatic hydrocarbon (PAH) mixture in methanol and methylene chloride (1:1, v/v) with individual PAH concentrations in the range from 100 to 2000 mg L^{-1} was obtained from Supelco (Bellefonte, PA, USA). The standard PAH mixture was diluted 10 times with methanol and stored at $-20 \text{ }^{\circ}\text{C}$ as stock solution. Working solutions of PAHs with individual PAH concentrations in the range of 0.5 to $10 \text{ } \mu\text{g L}^{-1}$ were prepared daily by diluting the stock solution with distilled water (concentrations of individual PAHs are shown in Table S1 in the Supplementary material), and the volume content of the spiking organic solvent in the working solution was approximately 0.005% and negligible. Negligible depletion solid phase microextraction (nd-SPME) fibers, namely disposable glass fibers with a core diameter of $110 \text{ } \mu\text{m}$ and a $30 \text{ } \mu\text{m}$ polydimethylsiloxane (PDMS) coating (equivalently to $0.132 \text{ } \mu\text{L}$ PDMS per centimeter fiber), were obtained from Poly Micro Industries (Phoenix, AZ, USA). Fullerene (C_{60}) with 99.9% purity was purchased from Yongxin Technology (Puyang, China), and the composition of the C_{60} was verified in our previous paper (Chen et al., 2014). Humic acid (HA) sodium salt was obtained from Sigma-Aldrich (technical, lot: S15539-384, Steinheim, Germany), and the total organic carbon (TOC) content was 35.1% (determined by

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