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Comparison of two reference black carbons using a planar PCB as a model sorbate

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Abstract

In studies assessing sorption of hydrophobic organic compounds (HOCs) in natural systems, the choice of an appropriate reference black carbon, which can represent environmental black carbon (BC), is essential. This study compared isotherms of two commonly available and distinct reference BCs (*n*-hexane soot (BCRM) and diesel particulate matter (SRM 2975)) and a natural sediment from a source with little black carbon (Lake Hartwell, SC) using 3,3′,4-trichlorobiphenyl (IUPAC #35) as a model sorbate. There was greater sorptivity for PCB-35 by BCRM than by SRM 2975. The observed differences in sorption between the two reference black carbons for PCB-35 may be ascribed to the different chemical characteristics of the black carbons. Differences in pore volume distribution at <16 Å pore width are less likely to be responsible for the observed differences in sorption. The elemental analysis confirmed that BCRM was a pure *n*-hexane soot because only C, H and O were measured. In contrast, SRM 2975 also contained N and S and a higher O% than BCRM. Compared to the low BC sediment, the two reference BCs had greater pore volume distributions, surface areas, total pore volumes and sorption. The observed n_F (i.e., Freundlich exponent) values for PCB indicated greater linearity of the isotherms for the natural sediment than for the reference black carbons. For designing studies of sorption of HOCs in natural systems, in particular, when PCBs are contaminants of concern, results of this study can aid selection of the appropriate reference BCs.

Keywords: *n*-hexane soot; Diesel particulate matter; Lake Hartwell sediment; Chemical composition; PCBs

1. Introduction

Despite the growing understanding of the role of black carbon (BC) in sediment (and soil) systems (Cornelissen et al., 2005; Koelmans et al., 2006), assessing environmental sorption of HOCs in complex field systems is still difficult. The challenges can be attributed to several factors such as the complexity of sediments, heterogeneity of black carbon, diverse origins of black carbon, and lack of standardization in definition, identification, and analytical techniques for black carbon (Luthy et al., 1997; Gelinas et al., 2001; Song et al., 2002). These issues make isolating and quantifying BC in natural settings problematic.

Cornelissen et al. (2005) in a thorough review of sorption by BC emphasized that, with the gradual change in the prevailing sorption paradigm to the BC-inclusive dual-mode paradigm, there are several issues with the isolation and quantification of BC in natural sediments that need to be resolved. For example, Song et al. (2002) developed experimental procedures for the fractionation and quantification of soil/sediment organic matter (SOM) fractions. In spite of their rigorous and thorough approach, this method is likely to change the properties of black carbon and may introduce more laboratory errors due to the labor-intensive approach. Cornelissen and Gustafsson (2004) suggested that their combustion procedure at 375 °C brought about an increase in the BC sorption strength. Therefore, an approach that uses available and representative reference BCs as models in laboratory

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studies can complement the approach that isolates and quantifies BC in natural sediments and soils.

There are several laboratory studies reporting sorption of HOCs to black carbon, but they lack standardization of the studied black carbons. For example, Cornelissen et al. (2004) studied BC in combusted sediment, which they collected from a freshwater lake in The Netherlands. Jonker and Koelmans (2002) investigated sorption of polyaromatic hydrocarbons (PAHs) and PCBs by various black carbons such as traffic soot, oil soot, wood soot, coal soot, fly ash, etc. However, except for one reference BC (SRM 1650), the studied BCs are not available to other researchers. It is important to have black carbon that is available to researchers and is representative of the range of environmental BCs.

Some studies have used at least one reference BC as model sorbents in laboratory settings (e.g., Jonker and Koelmans, 2002; Bucheli and Gustafsson, 2003; Nguyen et al., 2004; Nguyen and Ball, 2006). Most studies have used the diesel particulate matter that is available as a standard reference material (SRM) from the National Institute of Standards and Technology (NIST). For example, the study by Bucheli and Gustafsson (2003) reported column experimental results for sorption of non-ortho and ortho substituted PCBs, in which they used one of the SRMs (SRM 1650). One of the few studies that compares more than one reference BC is by Nguyen and Ball (2006) who investigated sorption of HOCs employing four black carbons with various properties (i.e., hexane soot, ozonated hexane soot, diesel soot SRM 2975, and diesel soot SRM 1650b).

Two reference BC materials, SRM 1650b and SRM 2975, are currently available from NIST. Both of these are diesel particulate matter produced for verification of PAH analyses. SRM 1650b, which was produced by heavy duty diesel engines, was originally issued in 1985 as SRM 1650, which was reissued in 2000 as SRM 1650a and in 2006 as SRM 1650b. SRM 2975 consists of soot from a forklift diesel engine and was issued for the first time in 2000 (NIST, 2000). Both reference BCs have been used in laboratory studies (e.g., Nguyen and Ball, 2006). In 1999, the Black Carbon Steering Committee of the American Geophysical Union (AGU) was formed to make representative BC reference materials (BCRM) available to the environmental sciences research community. The Committee recommended that *n*-hexane soot be the standard for atmospheric BC and provided protocols and a limited supply produced under controlled conditions (Holzhauser, 2003).

The main objective of this work was to evaluate the use of two commonly available black carbon reference materials. A planar PCB congener (3,3′,4-trichlorobiphenyl) was selected as a model sorbate because there are no previous reports of a comparison using the two reference black carbons (SRM 2975 and BCRM) with PCBs. In addition, a natural sorbent from Lake Hartwell, SC, that was low in BC, was included because subsequent studies used it combined with the reference BCs for work with model sorbent systems (Im, 2006). Characterization of material made available by the AGU Committee as well as comparisons to the material available from NIST will allow researchers to make informed choices when developing model sediments. Just as a body of work has developed using the standard reference materials that were developed for natural organic matter by the International Humic Substances Society, it is important to provide data about black carbon reference materials to the research community.

2. Materials and methods

2.1. Chemicals/Sorbates

Two polychlorinated biphenyl congeners, 3,3′,4-trichlorobiphenyl (IUPAC #35) and 2,2′,6,6′-tetrachlorobiphenyl (IUPAC #54) with a purity of 100 ($\pm$ 0.5)%, were obtained from AccuStandard. The water solubility (mg l^{-1} at 25 °C), log K_{ow}, and Henry's law constant (atm m^3 mol^{-1} at 25 °C) are 0.0155–0.301, 5.70, and 3.745, respectively, for PCB-35 and 0.0027–0.616, 5.50, and 3.242, respectively, for PCB-54 (Mackay et al., 1992; Hansen, 1999).

Aldrin, used as the internal standard, was purchased from Supelco and had a purity of $\geq$99%. Sodium chloride (99.0% min), alumina (chromatographic grade, 80–200 mesh), and sodium sulfate (anhydrous, 99.0% min) were purchased from EM Science. Isooctane (2,2,4-trimethylpentane, nanograde) and acetone (pesticide grade) were obtained from Mallinckrodt Baker, Inc., and Fisher Scientific, respectively.

2.2. Sorbents

The black carbon reference material (BCRM) was provided by the BC Steering Committee of the AGU. It is *n*-hexane soot generated by the least turbulence method (Holzhauser, 2003; Schmidt et al., 2003). The standard reference material (SRM 2975), diesel particulate matter, was purchased from NIST.

Sediments used in this investigation were collected in 2003 from the Tugaloo arm of Lake Hartwell, which is a reservoir on the border of South Carolina and Georgia, using a gravity corer (Wildco) fitted with a polycarbonate tube (76 cm long, 5 cm diameter) and an egg shell core catcher (5 cm long). The collected cores were sectioned in 5 cm increments, transferred to glass jars, and frozen until use. The Tugaloo arm of Lake Hartwell, located far from any point source (Pakdeesusuk et al., 2003), was a sampling site that was relatively free of PCBs. The incremental sections of the sediment core from the Tugaloo arm of Lake Hartwell were extracted in duplicate followed by extensive PCBs analysis (Im, 2006). Calibration standards consisting of a 1:1 mixture of Aroclor 1016 and 1254 were employed. The reproducibility of duplicate sediment extracts was acceptable (Im, 2006). The observed values of total PCBs in the sediment sections confirm that the sediment was rel-