The Emergence of Black Carbon as a Super-Sorbent in Environmental Chemistry: The End of Octanol?

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The distribution of aromatic contaminants between environmental solids and water solution reflects both absorption by the organic matrix (organic carbon, OC) and adsorption to black carbon (BC). In many instances, adsorption to BC dominates the interaction between aromatic contaminants and environmental solids. This holds especially true for the pyrogenically produced PAHs and PCDD/Fs, but also for the industrially produced PCBs and PCNs. In the future, research will need to surface-normalize the adsorption onto BC surfaces. One of the key questions to be addressed is the relative distribution and availability of contaminants associated with OC and BC fractions in environmental solids.

Keywords: organic matter, soot, adsorption, partitioning, organic contaminants, bioavailability

Introduction

A paradigm shift can be observed in our understanding of the environmental chemistry of many organic contaminants. The distribution of organic contaminants is less and less described as pure "absorption" in organic matter (the properties of which are often correlated to octanol). Instead, the importance of black carbon (BC)-based adsorption for many contaminants is recognized more and more (e.g., Büchel and Gustafsson, 2000, 2001; Allan-King et al., 2002; Jonker and Kooijmans, 2002; Accardi-Dey and Gschwend, 2002, 2003). There are many observations simultaneously exposing the limitations of the absorption hypothesis while suggesting that adsorption to the reduced carbon (i.e., BC) fraction plays a major role in sediments and soils (e.g., McGroddy et al., 1996; Gustafsson et al., 1997; Accardi-Dey and Gschwend, 2002, 2003; Persson et al., 2002). Soils and sediments contain the bulk of the organic contaminant mass (e.g., Mackay et al., 2000). The absorption ("dissolution") hypothesis suggests that aromatic organic contaminants are dissolved in the organic matter fraction of sediments and soils (e.g., Karickhoff et al., 1979). However, such a solution process implies the full and immediate availability of the organic contaminants. Numerous investigations, both laboratory-based and field studies, found evidence for very strong sorption processes (often referred to as "resistant" or even "irreversibly bound" fractions), coupled with different desorption kinetics (e.g., Di Toro and Horzempa, 1982; Cornelissen et al., 1997; Huang and Weber, 1997; Ten Hulscher et al., 1999; Xia and Pignatello, 2001; Allen-King et al., 2002).

Clearly, these observations contradict any purely "solution"-based partitioning of organic contaminants between interstitial water and soil or sediment particles. Laboratory observations found correlation of the contaminant concentrations (normalized per unit dry weight) with the sediment's or soil's organic carbon (OC) content (e.g., Karickhoff, 1979; Chiu et al., 1983). However, a wide range of dissolved contaminant OC-normalized solid-phase distribution coefficients, \(K_{OC}\), has been observed in subsequent field and laboratory studies (e.g., Goss and Schwarzenbach, 2001). In light of the complexity of naturally occurring organic matter, this is not surprising; little is known about its exact structures. Further investigation also revealed the disparity of predicted dissolved concentrations, based on the OC-fraction (\(f_{OC}\)) and the corresponding \(K_{OC}\), and those observed (e.g., McGroddy et al., 1996; Büchel and Gustafsson, 2001). Observed dissolved concentrations of polycyclic aromatic hydrocarbons (PAHs) were lower than predicted, suggesting that additional sorption occurred.

Black Carbon versus Organic Carbon

Definitions

There are many terminologies in use for materials containing carbon on their surface, such as elemental carbon, char,
soot, graphitic carbon, or high-surface-area carbonaceous material (e.g., Allen-King et al., 2002). In this article, they will be summarized as black carbon (BC), which according to Goldberg is “an impure form of the element produced by the incomplete combustion of fossil fuels or biomass” (Goldberg, 1985). However, as discussed by Allen-King et al. (2002), thermally altered materials, such as bituminous coals and anthracites, can be present in sediments and soils due to erosion processes, too. BC is hydrophobic and highly persistent in the environment (Goldberg, 1985).

Most naturally occurring organic matter (OM) stems from terrestrial and, to a lesser degree, aquatic biomass (proteins, lipids, carbohydrates, pigments, and lignins) (Brownlow, 1996). In general, the OC fraction is measured directly, and factors are applied to represent the total OM content. Other than biomass, additional OC is directly emitted into the atmosphere (primary OC) or condenses after atmospheric reactions (secondary OC aerosols; Seinfeld and Pandis, 1998). Biogenic sources dominate global OC emissions, but anthropogenic sources account for a third up to almost half the atmospheric OC (Seinfeld and Pandis, 1998). For the Mississippi River, 27% of BC was thought to originate from fossil fuel combustion (Mitra et al., 2002). Combustion of fossil fuels and, to a lesser degree, biomass burning are the main BC emission sources (Penner et al., 1993; Cooke and Wilson, 1996). The majority of BC emissions is thought to occur in the submicron particle size range, making it susceptible to long-range atmospheric transport (Cooke et al., 1999).

Atmospheric BC and OC display highest concentrations in urban/industrial locations, where BC makes up ca. 10% and OC ca. 30% of the total aerosol mass. In remote regions, the BC fraction drops to less than 0.1%, reflecting the pyrolytic origin of BC-aerosols (Seinfeld and Pandis, 1998). Natural emissions sustain higher atmospheric OC concentrations, so that even in remote regions OC makes up ca. 10% of total aerosol mass.

Due to atmospheric long-range transport (e.g., Eolian dust collected off the African coast; Eglinton et al., 2002), BC is present in deep-sea sediments. However, higher concentrations are found near the mostly anthropogenic emission areas. It was calculated that the Mississippi River alone accounted for 5% of the BC buried annually in the Atlantic Ocean (Mitra et al., 2002). Concentrations in the Pacific sediments were as low as <0.01% per g dry weight near the equator, and up to 0.10% at 60°N (Goldberg, 1985). Sediments influenced by urban environments typically contain 0.1 to 1.0% (dry mass) BC. In general, the BC content of sediments is 5 to 10 times lower than the OC content of sediments (e.g., Mitra et al., 1999; Tsapakis et al., 2003).

### Measurements

There are different techniques available for determining the OC and BC fractions in an environmental media. Atmospheric scientists rely on thermo-optical methods; environmental scientists often employ thermal oxidation methods; and chemists frequently use chemical oxidation methods. A more detailed description of the different methods and their respective reproducibilities has been reported as part of a round-robin study (Currie et al., 2002). The authors reported that optical carbon methods detect consistently higher BC concentrations than thermo-gravimetical methods (Currie et al., 2002). Highly aromatic, high-surface carbon phases, such as coals and chars, will be detected by the optical methods and yet be, at least partially, combusted by the thermal-gravimetical methods.

### The Role of BC Adsorption

Numerous studies have demonstrated the dominance of adsorption onto BC for the partitioning of organic contaminants in sedimentary systems (e.g., Bücheli and Gustafsson, 2000, 2001; Accardi-Dey and Gschwend, 2002, 2003). The additional effect of the dilute BC phase on the sorption of organic compounds was parameterized as

\[
K_d = f_{OC} K_{OC} + f_{BC} K_{BC} C_{\text{diss}}^{n-1}
\]

with \(K_{BC}\) the partitioning coefficients to BC [(mol kg\(_{-1}\) of BC)/(mol/L)]\(^{n}\), \(n\) the Freundlich exponent for adsorption onto BC, and \(C_{\text{diss}}\) the dissolved concentration (μg/L).

Accardi-Dey and Gschwend (2002) reported a log \(K_{BC}\) of 6.25 ± 0.14 with \(n\) of 0.62 for pyrene in experiments using a sediment from the Boston Harbor. Pyrene's \(K_{BC}\) was determined in a series of pyrene additions to the thermally pretreated sediment (hence the non-BC organic matter was removed). Log \(K_{BC}\) was deduced from the equilibrium isotherm, assuming a log \(K_{OC}\) of 4.7 for pyrene, which is close to the value derived by Karickhoff (1979). Using these values in Equation (1) for a typical sediment containing an \(f_{OC}\) of 10% dry weight (dw) and an \(f_{BC}\) of 1% dw, the dependency of the solid-water distribution coefficient of \(C_{\text{diss}}\) was calculated and is shown in Figure 1.

There are two different partitioning domains evident in Figure 1—for very low dissolved concentrations (<1 μg/L) the overall partitioning of pyrene is dominated by adsorption onto BC (left-hand side of Figure 1). However, for very high \(C_{\text{diss}}\) (near the solubility of pyrene, ca. 100 μg/L; Mackay et al., 2000) the overall partitioning of pyrene falls back in-line with

![Figure 1](https://example.com/figure1.png)
the absorption model, as predicted by the straight $f_{oc}K_{oc}$ line. The nonlinearity in the adsorption can be understood as BC having a range of surface sites with varying affinities for pyrene. The most attractive sites will be occupied preferentially, thus dominating the overall distribution at low $c_{solv}$. As $c_{solv}$ increases, more and more of these attractive surface sites become occupied, and slowly absorption into organic matter becomes more important. At a given $c_{solv}$, most favorable BC sites have been occupied. At this stage, an increased pyrene concentration in the dissolved phase will be accommodated by adsorption into the sediment’s organic matter fraction. In the hypothetical sediment described in Figure 1, at $c_{solv}$ of 28 μg/L, 50% is of pyrene can be attributed to adsorption, while the other 50% is being absorbed. It can be expected that such a nonlinear description extends to all aromatic contaminants, although with varying Freundlich coefficients. As a direct consequence, at the low dissolved concentrations usually found in sediments and soils, BC can be expected to dominate the sorption of organic contaminants.

The dispersion of BC, through atmospheric, riverine, and oceanic transport, results in the widespread distribution of the organic contaminants bound to its surface. This has been established for PAHs and BC (e.g., Mitra et al., 2002). The use of radiocarbon dating further allows one to apportion the fraction of BC and associated contaminants originating from the burning of fossil fuels versus biomass burning (e.g., Eglington et al., 2002; Reddy, 2002).

Currently, the adsorptive term is described by the product of the weight fraction of the BC ($f_{BC}$) and the compound’s partitioning constant to BC ($K_{BC}$), even though $K_{BC}$ describes an adsorptive process. The applicability and reproducibility of the $K_{BC}$ suggests that for the urbanized sediments studied, there is a constant surface-to-weight ratio of BC present (Accardi-Dey and Gschwend, 2002; Lohmann et al., 2002; Bücheli and Gustafsson, 2001). The importance of adsorption to BC has been stipulated for PAHs for some time (e.g., McGroddy et al., 1996). Recently, however, evidence was presented encompassing further classes of organic contaminants, such as polychlorinated dibenzox-p-dioxins and -furans (PCDD/DFs), polybrominated diphenylethers (PBDEs) and polychlorinated biphenyls (PCBs) (Bärring et al., 2002).

Within the PCBs, a higher affinity was reported for those congeners that can take up a planar configuration and thus maximize their interaction with an aromatic BC surface (Bärring et al., 2002). In general, adsorption constants to BC exceed those of $K_{oc}$ by 1 to 2 orders of magnitude. In summary, a high affinity for BC can be stipulated for all organic, planar aromatic molecules.

The Challenges Ahead

Surface Normalization

As mentioned above, most of the currently available sorption constants, $K_{BCs}$, for the sorption of organic contaminants to BC are described on a BC weight basis, which inherently assumes a constant surface-to-weight ratio of environmental BC. To move ahead, means and methods are needed to quantify the sorption of a contaminant to BC as adsorption to the available BC’s surface area. In a literature review, Bücheli and Gustafsson (2000) reduced the different sorption strengths of phenanthrene and pyrene to activated carbons and soots from over 3 orders of magnitude to less than a factor of 2 when normalizing to the available surface. Clearly, surface normalization is a key step forward in an accurate description of the environmental partitioning. However, a routine determination of the available BC surface in complex environmental matrices, such as aerosols or sediments, is immensely difficult. A convenient and simple way forward is to probe the available surface with a well-known adsorbent, such as pyrene (Bücheli and Gustafsson, 2000). Pyrene is a ubiquitous and well-studied contaminant. As a consequence, pyrene’s $K_{BCs}$ to different sediments are well known. Moreover, pyrene is available at low cost and high purity and can be obtained as a deuterium-labeled compound.

Role of Organic Matter Association

Convincing evidence has been presented for the dominant role of BC in the sorption of organic compounds, of especially PAHs and PCDD/Fs, in the sinks of many environmental cycling processes, such as sediments and soils. Many organic contaminants, like PAHs and PCDD/Fs, but also certain PCB and polychlorinated naphthalenes (PCNs) congeners, are by-products of incomplete combustion processes themselves (e.g., Helm and Bidleman, 2003). A key question therefore is to what degree the association between BC and the contaminants happened straightaway at the emission source, and/or what fraction of the contaminants is actually available for environmental partitioning. The deduction of the organic contaminant fraction free to partition, for example into the food chain, is of increasing importance. As a first approximation, it can be stipulated that organic matter–based contaminants are available for biotakeout. The observed slow ("retarded") release times of many contaminants from environmental solids can be interpreted as their diffusion-limited desorption from BC. Future research will clarify how much of the OM- and BC-associated contaminants are available and what fraction of the initially bound form might be released while being transported across different environmental phases. For example, Dachs and Eisenreich (2000) deduced the association of PAHs with atmospheric BC for samples taken in Baltimore and Chesapeake Bay. Using their average ambient concentrations, particle-bound PAHs were associated with BC to over 85% in Baltimore and up to ca. 95% over Chesapeake Bay. In two sediments from the eastern U.S. coast, BC accounted for over 80% (New York Harbor) to over 90% (Boston Harbor) of PAHs sorption (Lohmann et al., 2002). Considering these cases, the data suggest that the majority of particle-bound PAHs was already adsorbed to BC in the atmosphere and that only a minor fraction was available for partitioning to other environmental phases.

Persson et al. (2002) measured the vertical water column gradients of PCDD/Fs in the Greenlandsfjords, Norway, and found an increasing importance of BC (reflected in increasing $K_{ds}$). In the water column, particulate organic carbon was reduced from
a high of 240 μg/L at 0–2 m to less than 50 μg/L at 2–16 m. Carbon mineralization is known to happen for settling biomass (e.g., Gobas and MacLean). Simultaneously, the measured dissolved concentrations of tetra- and penta-chlorinated PCDD/Fs increase five-fold, but not those of the higher chlorinated congeners. This study gives an indication that some PCDD/Fs were liberated from the organic carbon pool while settling in the water column, with subsequent adsorption to BC particles. However, the heavier PCDD/Fs appear to have been adsorbed to the more recalcitrant BC. These source-to-sink gradients have to be better understood and characterized to further our understanding of the cycling and availability of many organic contaminants.

In summary, the distribution of aromatic contaminants between environmental solids and water solution reflects both adsorption by the organic matrix and adsorption to BC. In many instances, adsorption to BC dominates the interaction between aromatic contaminants and environmental solids. This holds especially true for the pyrogenically produced PAHs and PCDD/Fs, but also for the industrially produced PCBs and PCNs. Nevertheless, the fraction associated with organic matter is at least as important because it constitutes the readily bioavailable fraction. Hence, OC and octanol-based partitioning will continue to play an important role for organic contaminants. Consequently, measurements of OC partitioning (or its approximation through octanol-water partitioning) remain important descriptors for understanding the distribution of aromatic contaminants in the biosphere. However, the environmental transport, distribution, and partitioning of many aromatic organic contaminants is greatly influenced by adsorption onto BC.

References


