HALOGENATED AND AROMATIC CONTAMINANTS IN SEDIMENTS: K_d MATTERS

Örjan Gustafsson, Thomas Bucheli, Hans Bärring, Gerard Cornelissen, and Johan Persson

Institute of Applied Environmental Research (ITM), Stockholm University,
10691 Stockholm, Sweden. (orjan.gustafsson@itm.su.se)

Introduction

Sorption of hydrophobic organic contaminants (HOCs) to soils and sediments is a key process controlling their environmental fate. For instance, sorption can limit both biological uptake and microbial degradation of HOCs. Hence, a quantitative understanding of HOC solid-water distribution (K_d) is a necessary prerequisite for estimation of the various hazards that organic pollutants may pose in the environment. Laboratory-based studies from the 1970s-1980s suggested sorption predictability based on apparent linear partitioning of HOCs into a bulk organic matter absorption domain[1,2]. However, results from studies over the past decade suggest that this model paradigm of organic-matter partitioning (OMP) is not sufficient to alone explain HOC sorption behavior and distribution in the environment. Sorption experiments conducted at aqueous concentration that were low relative to the compound-specific aqueous solubilities were shown to exhibit non-linear sorption isotherms inconsistent with OMP model[3-6]. Further, it has been observed that polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and other hydrophobic and aromatic compound classes exhibit K_d in real field situations that are much higher than predicted from the OMP model[7-10]. Based on such information, it was proposed that the sorption non-linearity and elevated K_d of such compounds reflect a dynamic distribution process between water and a strongly sorbing pyrogenic subfraction of the sediment termed interchangeably soot carbon, SC, and black carbon, BC[11-13]:

$$K_d = f_{oc}K_{oc} + f_{bc}K_{bc}C_w^{n-1} \tag{1}$$

where f_{oc} and f_{bc} is the sedimentary mass fraction of organic and soot carbon, respectively, K_{oc} is the organic-carbon normalized partition coefficient [L_w/kg_{oc}], K_{bc} is the BC-normalized Freundlich distribution constant [$(L_w/kg_{bc})^n$], C_w is the site-relevant dissolved concentration [µg/L] and n is the Freundlich non-linearity parameter. Importantly, a ubiquitous presence of BC in coastal marine sediments at 2-20% of total organic carbon has recently been observed[14-16]. In further support of this BC supersorbent hypothesis, it has now been demonstrated that PAHs exhibit high distribution coefficients and nonlinear adsorption isotherms on BC particles[12,13,17]. Hence, it appears that the environmental distribution of many planar aromatic compounds may be explainable by a combination of absorptive partitioning into the amorphous natural organic matter and concentration-dependent adsorption onto soot surfaces.

Here we synthesize published and new data on both the f_{sc} and K_{bc} parameters. Application of the soot-inclusive distribution (SID) model (Eqn 1) to explain solid-water distribution coefficients in the environment will be evaluated.

Material and Methods

Determination of BC in sediments: A chemothermal oxidation (CTO) method for sequential isolation and quantification of the operational BC residue is evaluated[11,16]. The CTO method and others are tested using positive and negative standards, molecular and isotopic marker techniques as well as evaluation of environmental geochemical consistency of CTO-BC sediment data.

BC sorption experiments: Quantification of the soot interactions was achieved with both batch and column experiments that were specifically designed for distribution experiments with highly hydrophobic and strongly sorbing matrices such as soot[12]. To supplement previously published PAH-BC results[12], experiments e were conducted to constrain the effect of molecular structure on the strength of HOC-BC interaction using series of ortho-substituted and co-planar polychlorinated biphenyls (PCBs), PCDDs, PCDFs, and polybrominated diphenyl ethers (PBDEs).

Results and Discussion

Black carbon is recognized to play significant roles in the global carbon cycle, atmospheric chemistry, and in the fate of organic pollutants, yet ambiguity persists concerning the levels of BC in complex matrices such as marine sediments. Intercomparison studies reveal that different methods yield highly variable results[15,18]. Such variability may in part result from the range of properties exhibited by different forms of BC and reflected to different extents with disparate methods. The variability may also stem from limitations unique to each quantification method. Extensive evaluation of a chemothermal oxidation (CTO) method with potentially interfering non-BC matrices (e.g, large biomacromolecules, melanoidin, pollens, kerogen and coals of varying degree of maturity) suggests that the method is applicable to distinguish between non-pyrogenic organic matter and BC in marine sediments. The BC results obtained in natural matrices were tested for their geochemical consistency. The radiocarbon content of the BC isolate in a dust sample was shown to be similar to the radiocarbon signature of pyrogenic polycyclic aromatic hydrocarbons (PAHs), here serving as molecular markers of combustion (fraction modern f_M of BC was 0.065 ± 0.014 and of PAHs 0.056 ± 0.020), while being clearly distinct from the radiocarbon content of the bulk TOC ($f_M = 0.61 \pm 0.08$) (ref. 16). Further, a lacustrine sediment profile of BC over the paste century qualitatively follows the time trends of PAHs and society´s energy usage while a clear decoupling from the bulk TOC rules out any significant charring[11]. The ability of CTO method constrained BC measurements to explain the distribution of pyrogenic molecular markers such as PAHs both lend credence to the analytical method and implies a coupling in the fate of these two substances in the environment. Also the geographical distribution of both PAHs[19] and PCDD/Fs[20] in surface marine sediments are better explained by the sedimentary BC content than by bulk TOC. Hence, it appears that it is possible to constrain the BC content (i.e., the f_{bc} parameter in Eqn 1) at least in anthropogenically-perturbed sediments.

It has recently been demonstrated that PAHs exhibit extremely high distribution coefficients and nonlinear adsorption isotherms on BC particles[12,13,17]. The BC sorption of a suite of halogenated aromatic compounds has now also been investigated (Fig. 1).
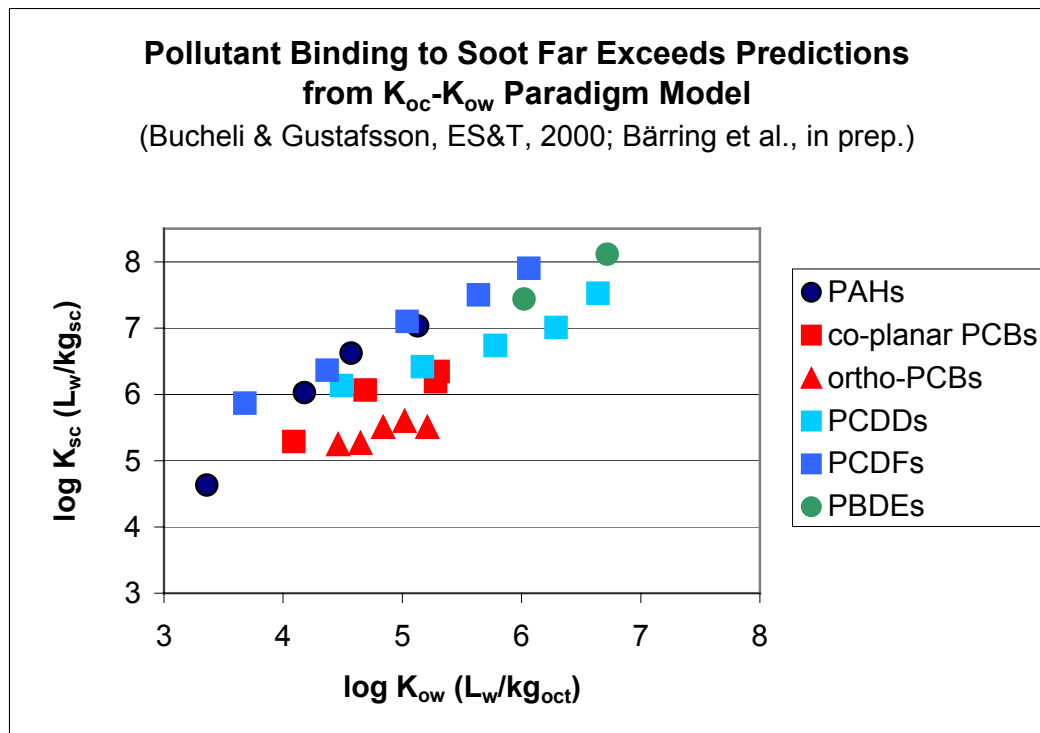
Figure 1.

It is apparent that efficient sorption to soot/BC is not limited to PAHs but extends as a significant process to a wider range of compound classes such as co-planar PCBs[17,21], PCDD/Fs[22] and PBDEs[22]. The BC-enhanced sorption is strongest for PAHs and PCDFs (Figure 1). Co-planar PCBs, PCDDs, an PBDEs exhibit intermediate enhancement, whereas a smaller effect is noted for ortho-substituted PCBs. Reasons for these differences will be discussed. The revealed strong sorption of aromatic HOCs with environmentally ubiquitous BC suggests that it is necessary to consider BC sorption in predictions of the environmental fate and behavior of these compounds. The constrained K_{sc} values will be considered together with field measurements of f_{sc} to test the applicability of the SID model (Eqn. 1) to provide improved predictions of the solid-water distribution of such compounds in sediment-porewater systems.

References

(1) Chiou, C.T., L. J. Peters; V. H. Freed. *Science* **1979,** *206*, 831.
(2) Karickhoff, S. W., *Chemosphere* **1981**, 10, 833.

(3) Weber, Jr.,W.B.; P. M. McGinley; L. E. Katz, *Environ. Sci. Technol.* **1992,** *26*, 1955.

(4) Luthy, R.; G. R. Aiken, M. L. Brusseau, S. D. Cunningham, P. M. Gschwend, J. J. Pignatello, M. Reinhard, S. Traina, W. J. Weber and J. C. Westall. *Environmental Science and Technology* **1997,** *31*, 3341.

(5) Kleineidam, S.; H. Ruegner, B. Ligouis and P. Grathwohl, *Environ. Sci. Technol.* **1999**, *33*, 1637.

(6) Chiou, C. T.; Kile, D. E.; Rutherford, D. W.; Sheng, G. Y.; Boyd, S. A. *Environ. Sci. Technol.* **2000,** *34*, 1254.

(7) Prahl, F.G. and R. Carpenter *Geochim. Cosmochim. Acta* **1983,** *47*, 1013.
(8) Broman, D.; C. Naef, C. Rolff and Y. Zebuehr. *Environ. Sci. Technol.* **1991**, 25, 1850.
(9) McGroody, S. E.; Farrington, J. W. *Environ. Sci. Technol.* **1995,** *29*, 1542.
(10) Zhou, J. L.; Fileman, T. W.; Evans, S.; Donkin, P.; Readman, J. W.; Mantoura, R. F. C.; Rowland, S. *Sci. Total Environ.* **1999**, *243/244*, 305.
(11) Gustafsson, Ö.; Haghseta, F.; Chan, C.; MacFarlane, J.; Gschwend, P. M. *Environ. Sci. Technol.* **1997,** *31*, 203.

(12) Bucheli, T. D.; Gustafsson, Ö. *Environ. Sci. Technol.* **2000,** *34*, 5144.

(13) Accardi-Dey, A.; Gschwend, P.M. *Environ. Sci. Technol.* **2002,** *36*, 21.

(14) Gustafsson, Ö.; Gschwend, P. M. *Geochim. Cosmochim. Acta* **1998,** *62*, 465
(15) Middelburg, J. J.; Nieuwenhuize, J.; Van Breugel, P. *Marine Chem.* **1999**, *65*, 245.

(16) Gustafsson, Ö.; Bucheli, T. D.; Kukulska, Z.; Andersson, M.; Largeau, C.; Rouzaud, J.-N.; Reddy, C. M.; Eglinton, T. I. *Global Biogeochem. Cycles* **2001**, *15*, 881.

(17) Jonker, M. T. O.; Koelmans, A. A. *Environ. Sci. Technol.* **2001,** *35*, 3742.
(18) Currie L., *NIST J. Res.* **2002**, *107*, 279.
(19) Gustafsson, Ö.; Gschwend, P. M. In *Molecular Markers in Environmental Geochemistry, ACS Symposium Series 671*; Eganhouse, R. P., Ed.; American Chemical Society: Washington, DC, 1997; pp 365-381.

(20) Persson, J., Gustafsson, Ö., Bucheli, T.D., Ishaq, R., Naes, K., Broman, D. *Environ. Sci. Technol.* **2002,** *36*, 4968.

(21) Bucheli, T:D., Gustafsson, Ö. *Chemosphere,* Soot sorption of ortho- and non-ortho substituted PCBs, in review.

(22) Bärring, H., Bucheli, T.D., Broman, D., Gustafsson, Ö. *Chemosphere*, **2002**, 515.