Influences of binding to dissolved organic matter on hydrophobic organic compounds in a multi-contaminant system: Coefficients, mechanisms and ecological risks

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ABSTRACT

The complexation flocculation (CF) method was successfully employed to identify binding coefficients (K_{doc}) of specific organic contaminants to dissolved organic matter (DOM, often indicated by dissolved organic carbon, DOC) in a multi-contaminant hydrophobic organic contaminant (HOC) system. K_{doc} values were obtained for most of the evaluated 33 HOCs, indicating the feasibility and applicability of the CF method in a multi-contaminant system. Significant positive correlations were observed between binding coefficients and octanol–water partition coefficients (K_{ow}) for organic halogen compounds, such as polybrominated diphenyl ethers (PBDEs) ($R^2 = 0.95$, $p < 0.05$) and organic chlorine pesticides (OCPs) (methoxychlor excluded, $R^2 = 0.82$, $p < 0.05$). The positive correlations identified between the lgK_{doc} and lgBCF (bioconcentration factor) for PBDEs and OCPs, as well as the negative correlation observed for polycyclic aromatic hydrocarbons (PAHs), indicated that different binding or partition mechanisms between PAHs and organic halogen compounds exist. These differences further result in discriminative competition partitions of HOCs between DOM and organisms. Assuming that only freely dissolved HOCs are bioconcentrative, the results of DOM-influenced bioconcentration factor (BCF_{DOM}) and DOM-influenced lowest observed effect level ($LOEL_{DOM}$) indicate that the ecological risk of HOCs is decreased by DOM.

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1. Introduction

Hydrophobic organic contaminants (HOCs) are a group of chemicals that are toxic to humans and pose potential risks to the ecosystem. In an aquatic environment, the fate, transport and risk of HOCs are influenced by interactions with dissolved organic matter (DOM) (Cho et al., 2002; Laor and Rebhun, 1997; Moeckel et al., 2013). DOM has a major impact on the transport of HOCs in surface water and groundwater by enhancing solubility of contaminants (Yu et al., 2011). In most cases, the presence of DOM diminishes the bioavailability of HOCs. Studies demonstrate that DOM mitigates the bioconcentration factor (BCF) and biotoxicity of several HOCs for various organisms, including invertebrates, terrestrial plants, and vertebrates (Bejarano et al., 2005; Chen et al., 2008; Haitzer et al., 1998; Landrum et al., 1987; Yang et al., 2006). Furthermore, DOM can alter photolysis and transformation rates of organic pollutants (Aajoud et al., 2003; Burns et al., 1996). Binding of HOC to DOM is regarded as the most likely mechanism explaining these interactions (Burns et al., 1996; Krop et al., 2001) because only freely dissolved compounds are assumed to be taken up and accumulated by organisms (Gourlay et al., 2003; Haitzer et al., 1999).

Experimental determination of binding coefficients (K_{doc}) of HOCs began in the 1970s (Krop et al., 2001) and has become a subject of intense interest due to the need to monitor and control HOCs. Initially, studies investigated PAHs (e.g., pyrene and naphthalene), polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethanes (DDTs) and hexachlorocyclohexanes (HCHs) (Carter and Suffet, 1982; Chiou et al., 1986; Cho et al., 2002; Laor and Rebhun, 1997; McCarthy and Zachara, 1989). Additionally, di-(2-ethylhexyl) phthalate (DEHP) was the only compound studied in

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the phthalic acid ester (PAE) class (Carter and Suffet, 1983). As a result of increasing awareness regarding emerging contaminants, the binding coefficients of a variety of other contaminants are currently being investigated. These contaminants include polybrominated diphenyl ethers (PBDEs) (Kuivikko et al., 2010; Wang et al., 2011), other PAEs (Yamamoto et al., 2003), endocrine disrupters (Lee et al., 2011; Yamamoto et al., 2003), synthetic pyrethroids (Delgado-Moreno et al., 2010), pharmaceuticals and personal care products (Maoz and Chefetz, 2010), and other pollutants (e.g., naphthol (Ahmed et al., 2012)).

Various methods, including solubility enhancement (Chiou et al., 1986), membrane dialysis (Carter and Suffet, 1982), fluorescent quenching (Backhus and Gschwend, 1990), solid-phase microextraction (Wang et al., 2011), and complexation flocculation (Laor and Rebhun, 1997), have been developed to determine K_{doc} values. These methods each have advantages and limitations. Generally, a simple HOC-DOM interaction system includes only one pure HOC is utilized to determine the binding coefficient. Recently, multi-contaminant systems in which more than one HOC is present have been intensively investigated because a combination of pollutants more closely represents the real environment (Moeckel et al., 2013; Wang et al., 2011). Complexation flocculation was considered to be suitable for all classes of compounds in a multi-contaminant system (Krop et al., 2001).

In previous multi-contaminant systems, the researchers have primarily investigated only a specific group of chemical species, such as PAHs (Moeckel et al., 2013), and little attention was devoted to other existing chemicals. Therefore, the values obtained could provide only limited information concerning multi-contaminant circumstances. No studies are currently available for K_{doc} determination in a multi-contaminant system with different groups of chemical species. A set of updated K_{doc}s would better reflect the real environment and would provide a more accurate means of monitoring and forecasting the fate of HOCs. Moreover, due to the binding behavior of HOCs with DOM, their BCFs and ecotoxicity may be altered (Bejarano et al., 2005; Haitzer et al., 1998; Landrum et al., 1987; Yang et al., 2006; Zhang et al., 2011). In addition, the BCF is influenced by DOM (BCF_{DOM}) and ecotoxicity. For instance, the lowest observed effect level (LOEL) is affected by DOM ($LOEL_{DOM}$). These influences have seldom been evaluated and warrant further study. Overall, the objectives of this paper are to 1) calculate binding coefficients in a multi-contaminant system using the CF method, 2) investigate correlations between K_{doc} and properties of HOCs (e.g., K_{ow}, BFC, and LEOL), and 3) evaluate the real BCF_{DOM} and $LOEL_{DOM}$ under the influence of DOM.

2. Materials and methods

2.1. Reagents and chemicals

In total, five PAHs (fluoranthene (FLU), pyrene (PYR), benz[a]anthracene (BAA), chrysene (CHR), and benzo[k]fluoranthene (BKF)), four PAEs (dihexyl phthalate (DnHP), hexyl 2-ethylhexyl phthalate (HEHP), dicyclohexyl phthalate (DCHP), and di-n-propyl Phthalate (DPP)), eleven PBDEs (BDE-17, 28, 47, 66, 71, 85, 99, 100, 138, 153, and 154) and thirteen organochlorine pesticides (OCPs) (α-HCH, γ-HCH, δ-HCH, aldrin, γ-chlordane, o, p'-DDE, α-endosulfan, α-chlordane, p, p'-DDE, o, p'-DDD, p, p'-DDD, p, p'-DDT, and methoxychlor) were selected. All selected HOCs were in solution and purchased from AccuStandard Inc. (New Haven, CT, USA). Lake humic acid (HA) reference (1R105H) was selected as the experimental DOM and obtained from the International Humic Substances Society (http://www.humicsubstances.org/). All other solvents and chemicals were of gas chromatography grade or analytical grade.

The stock solution (20 mg-C/L) was prepared by fully dissolving the HA in ultrapure water and subsequently diluted to 5 different proportions (1/5, 2/5, 3/5, 4/5, and 5/5 of the original concentration). The pH of each solution was adjusted to 6.00 ± 0.05 by 0.1 mol L^{-1} NaOH and 0.05 mol L^{-1} H$_2$SO$_4$, and the ionic strength was adjusted to 0.5 mequiv/L by 0.5 mmol L^{-1} NaHCO$_3$. A coagulant solution of aluminum sulfate (40 g L^{-1} Al$_2$(SO$_4$)$_3$) was prepared for the flocculation experiments (Laor and Rebhun, 1997; Moeckel et al., 2013).

2.2. Binding experiments

The flocculation experiment was performed according to procedures in Laor and Rebhun (1997) and was slightly modified for the multi-contaminant system. Each binding experiment was performed in 20-mL glass bottles sealed with Teflon® caps. After preparing working solutions of HOCs, the multi-contaminant system was prepared by adding selected HOCs (40 ng of each PAH, 50 ng of each PAE, 10 ng of each PBDE, and 20 ng of each OCP) into the bottles. After evaporating the HOC solvent (n-hexane) to near dryness, the bottles were filled with the respective HA solutions and the reference solution. The bottles were later shaken (180 rpm) in a dark box at room temperature (25 °C) for 48 h, and 20 μL of the coagulant solution was added to each bottle. To achieve a sufficient flocculation reaction, the samples were shaken on a vortex mixer (1 min) and a shaker (60 rpm for 2 h). The samples were subsequently allowed to stand for 2 h. Next, the bottles were centrifuged (4500 rpm) for 20 min to separate the free and bound HOCs. More than 95% of organic carbon was removed in this way. Free HOC in the supernatant was extracted using dichloromethane (20 mL, 3 times). After removing the water, samples were reduced to 1 mL on a rotary evaporator, and 10 mL n-hexane was added to change the matrix. Finally, the n-hexane solutions were reduced to 1 mL, blown down to 0.5 mL under a gentle stream of nitrogen, and transferred to small amber vials before GC–MS analysis.

2.3. Instrument analysis

The total organic carbon concentration of each HA solution was measured by a total organic carbon analyzer (TOC-VWP, Shimadzu, Japan). PAHs and PAEs were analyzed by Agilent 6890GC-5973 inert mass detector (MSD) with an electron impact source. OCPs and PBDE were analyzed by Agilent 7890GC-5975C MSD with a negative chemical ionization source. The instrument conditions, the ions selected for identification/quantification, and the instrument limit(s) of detection are referred to in previous studies (He et al., 2013, 2014). All of the glassware was cleaned in an ultrasonic cleaner and baked at 450 °C for 6 h. The samples and blanks in each binding experiment were performed in triplicate. The samples were corrected by blanks accordingly.

2.4. Binding coefficient calculations

The binding coefficients (K_{doc}, L/kg-C) are calculated using the following equation (Laor and Rebhun, 1997):

$$\left(C_{\text{free+bound}} \right) \Big/ C_{\text{free}} = 1 + K_{doc}[\text{DOC}] \qquad (1)$$

where C_{free} is the free concentration of HOCs as determined by the results for HA solutions, $C_{\text{free+bound}}$ is the total concentration represented by the results for reference solutions, and [DOC] is DOC concentration in mg-C/L.