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# Evaluating dissolved organic carbon–water partitioning using polyparameter linear free energy relationships: Implications for the fate of disinfection by-products

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ABSTRACT

The partitioning of micropollutants to dissolved organic carbon (DOC) can influence their toxicity, degradation, and transport in aquatic systems. In this study carbon-normalized DOC–water partition coefficients ($K_{DOC-w}$) were measured for a range of non-polar and polar compounds with Suwannee River fulvic acid (FA) using headspace and solid-phase microextraction (SPME) methods. The studied chemicals were selected to represent a range of properties including van der Waal forces, cavity formation and hydrogen bonding interactions. The $K_{DOC-w}$ values were used to calibrate a polyparameter linear free energy relationship (pp-LFER). The difference between experimental and pp-LFER calculated $K_{DOC-w}$ values was generally less than 0.3 log units, indicating that the calibrated pp-LFER could provide a good indication of micropollutant interaction with FA, though statistical analysis suggested that more data would improve the predictive capacity of the model. A pp-LFER was also calibrated for Aldrich humic acid (HA) using $K_{DOC-w}$ values collected from the literature. Both experimental and pp-LFER calculated $K_{DOC-w}$ values for Aldrich HA were around one order of magnitude greater than Suwannee River FA. This difference can be explained by the higher cavity formation energy in Suwannee River FA. Experimental and pp-LFER calculated $K_{DOC-w}$ values were compared for halogenated alkanes and alkenes, including trihalomethane disinfection by-products, with good agreement between the two approaches. Experimental and calculated values show that DOC–water partitioning is generally low; indicating that sorption to DOC is not an important fate process for these chemicals in the environment.

## 1. Introduction

The presence of dissolved and colloidal organic carbon can influence the fate of micropollutant in the aquatic environment. This interaction can have implications for micropollutant toxicity, degradation and transport (Burgess et al., 2005; Lam and Mabury, 2005). The interaction of micropollutants with dissolved organic carbon (DOC) can be quantified by their carbon-normalised DOC–water partition coefficient ($K_{DOC-w}$, L/kg). While DOC is ubiquitous in aquatic

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systems, the properties can vary significantly with origin, season and location (Chin et al., 1994), and this can have implications for micropollutant sorption. For example, previous partitioning studies have shown that terrestrial humic substances have a greater sorption capacity for organic micropollutants compared to aquatic humic substances (Chin et al., 1997; Niederer et al., 2007).

An additional factor that will influence DOC properties is the presence of effluent or wastewater derived DOC. Many streams and rivers in urban areas and/or arid climates can contain discharges from treated wastewater effluent, with some water bodies containing up to 90% effluent in low flow conditions (Fono et al., 2006). As wastewater derived DOC is rich in soluble microbial products, effluent impacted water tends to contain less aromatic carbon, have a smaller molecular weight and contain a high fraction of proteinaceous matter compared to natural DOC (Rosario-Ortiz et al., 2007). While there is no standard or reference material for wastewater derived DOC, aquatic Suwannee River fulvic acid (FA) was found to have a comparable sorption capacity for nonylphenol as wastewater derived DOC (Neale et al., 2011), as well as a similar protective effect against copper toxicity (Pernet-Coudrier et al., 2008). While FA is more aromatic and does not contain protein fractions, it is more polar than other organic components of natural waters, such as humic acid (HA), due to the high content of carboxyl groups and this may explain the similarities with wastewater derived DOC.

A considerable number of contaminants can be detected in urban water bodies. Wastewater effluent is a major source of micropollutants in the aquatic environment as many chemicals are poorly removed during wastewater treatment processes (Ying et al., 2009). In addition, disinfection byproducts (DBPs) can form during water treatment through the reaction of chlorine and/or chloramine with organic matter. Epidemiology studies have linked exposure to DBPs, such as halogenated alkanes, with health effects including bladder cancer and reproductive problems (Villanueva et al., 2007; Waller et al., 1998). Despite being volatile, such chemicals have been detected in purified recycled water (Hawker et al., 2011) and in an effluent impacted river (Chen et al., 2009) at μg/L concentrations. If sorption to DOC present in treated and/or natural waters is a significant fate process, this could contribute to retaining such compounds in the water phase.

Within the literature, the number of studies that have experimentally determined micropollutant partitioning to FA is limited compared to HA (Kim and Kwon, 2010; Schlautman and Morgan, 1993), and none have considered the interaction of DBPs with FA. Given the ever increasing number of DBPs detected in drinking water (Krasner et al., 2006), it is not possible to measure $K_{DOC-w}$ for FA for all of them. In the past, some studies have attempted to predict $K_{DOC-w}$ using single parameters such as octanol–water partition coefficients ($K_{ow}$) or water solubility (Burkhard, 2000). While this may work for one class of chemical, such approaches are unsuitable for wider classes of chemicals, particularly polar compounds, as they cannot take into account the different molecular interactions between the chemical and DOC. Further, parameters such as $K_{ow}$ can vary considerably in the literature as a result of different calculation methods and this can increase $K_{DOC-w}$ calculation error. To overcome these limitations, polyparameter linear free energy relationships (pp-LFERs) can be applied to predict $K_{DOC-w}$ as they take into account both specific (hydrogen bond donor/acceptor and dipolarity/polarizability) and non-specific (van der Waals and cavity formation) intermolecular interactions (Goss and Schwarzenbach, 2001). To date, most studies have developed pp-LFERs for organic carbon in soil and sediment rather than DOC (Bronner and Goss, 2011a; Endo et al., 2009b). As partitioning can differ between DOC and soil organic carbon (Seol and Lee, 2000), pp-LFERs to accurately predict chemical sorption to DOC are necessary. Recently, Kipka and Di Toro (2011) made an attempt to calibrate a pp-LFER for FA by using data collected by Burkhard (2000). However, only 11 chemicals were used to calibrate the pp-LFER and none of these chemicals were hydrogen bond donors. Further, the model was calibrated only using estimated descriptors to represent intermolecular interactions and this reduces the reliability of the calibrated pp-LFER model. Consequently, a pp-LFER for FA should be calibrated with a larger number of chemicals that encompass a wide range of experimentally determined molecular descriptors.

Another approach to predicting chemical partitioning to DOC is to convert existing DOC–air partition coefficients ($K_{DOC-air}$, L/kg) to $K_{DOC-w}$ using air–water partition coefficients ($K_{air-w}$, L/L) via the thermodynamic cycle (Equation (1)).

$$K_{DOC-w} = K_{DOC-air} K_{air-w} \tag{1}$$

Niederer et al. (2007) measured a large selection of $K_{DOC-air}$ values for a range of DOC types, including Suwannee River FA, using glass beads coated with humic substances. This study measured the sorption from air at 98% relative humidity, where highly polar functionalized FA is expected to be well hydrated, but the sorbing properties of FA as a coating phase could still differ from those of FA dissolved in an aqueous solution. Bronner and Goss (2011b) found thermodynamic cycle conversions were applicable for the non-soluble organic carbon in Pahokee Peat. Currently, there is no experimental evidence to indicate whether or not the thermodynamic cycle conversion is appropriate for Suwannee River FA; however, if it is applicable it could greatly increase current knowledge of FA–water partitioning.

Consequently, the aims of this study were: 1) to determine if the thermodynamic cycle conversion is applicable for Suwannee River FA; 2) to calibrate a pp-LFER for aquatic Suwannee River FA and compare with a pp-LFER for a reference terrestrial DOC; and 3) to compare pp-LFER estimated $K_{DOC-w}$ values to experimental $K_{DOC-w}$ values for a range of halogenated alkanes and alkenes, including regulated DBPs.

## 2. Materials and methods

### 2.1. Materials

The test chemicals were purchased from different providers, while methanol and ethyl acetate were purchased from Merck. All experiments were conducted in 100 mM phosphate buffer ($NaH_2PO_4$ and $Na_2HPO_4$) made with water purified by