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Enhancement effect of water associated with natural organic matter (NOM) on organic compound–NOM interactions: A case study with carbamazepine

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ABSTRACT

Natural organic matter (NOM) in soils and sediments is recognized to strongly affect environmental distributions of organic compounds. Water associated with NOM may have a significant impact on NOM–organic compound interactions. The objectives of this research were (1) to determine the effect of hydration of a model NOM sorbent on interactions with a probe organic compound, carbamazepine (CBZ), and (2) based on the comparison with the literature data, to evaluate the effect of organic compound structure on the cooperative participation of water molecules in organic sorbate–NOM interactions. CBZ is one of the most widely reported water pollutants from the pharmaceutical and personal care products family. Therefore, CBZ sorption on Pahokee peat was compared from water and from *n*-hexadecane, using solubility-normalized solute concentrations. CBZ–NOM interactions were enhanced by one to two orders of magnitudes when NOM became fully hydrated. This enhancement is associated with the distinct ability of CBZ to undergo strong, specific interactions with NOM which was revealed by comparing the transfer of CBZ and another model sorbate, phenanthrene, from solution in *n*-hexadecane to the hydrated NOM sorbent. The enhancing effect of NOM hydration on CBZ–NOM interactions was also observed when CBZ sorption was examined on partially hydrated NOM. In comparison with a smaller-size organic sorbate such as phenol, CBZ needs more NOM-associated water in order to demonstrate the strengthening of interactions with NOM. Therefore, for penetration of the larger sorbate molecules into the NOM interior, a greater number of water molecules are needed to compensate for the local NOM disintegration thus suggesting the greater extent of the cooperativity in an involvement of water molecules in the CBZ–NOM interactions.

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1. Introduction

Natural organic matter (NOM) in soils and sediments is known to control the environmental distributions of various organic compounds between natural solids and water (Schwarzenbach et al., 1993). Water associated with NOM may suppress (Mills and Biggar, 1969; Rutherford and Chiou, 1992) or enhance (Ong and Lion, 1991; Graber and Borisover, 1998) organic sorbate–NOM interactions. NOM hydration-assisted sorption was expressed for compounds capable of strong specific interactions rather than for compounds lacking this ability (Graber and Borisover, 1998; Borisover and Graber, 2002a). When increasing the size of non-polar, aliphatic fragments of polar organic sorbates (e.g. in aliphatic alcohols), the NOM hydration-induced assistance in sorption may be replaced by sorption suppression (Niederer et al., 2006).

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There is a general understanding of the processes and mechanisms that could underlie the NOM hydration effect on sorption interactions of organic compounds. So, depending on the hydration status, molecules and macromolecules present in NOM may change their configurations thereby inverting sorption sites available in the NOM interior and at interfaces (Mingelgrin and Gerstl, 1993; Liu and Lee, 2006; Lattao et al., 2008). Polarity of the NOM phase was also expected to increase due to its hydration (Rutherford and Chiou, 1992). The involvement of water molecules in bridging different NOM moieties (Schaumann and Bertmer, 2008) and the plasticizing of suggested glassy-like NOM phases (LeBoeuf and Weber, 1997) may potentially have an effect on the ability of organic sorbates to penetrate into and interact with NOM. The interplay between wetting of NOM and organic compound sorption may be suggested (Belliveau et al., 2000).

The rearrangement of NOM components due to a change of the NOM hydration status was seen as a cooperative reorganization process (Todoruk et al., 2003). Indeed, sorbate–NOM interactions were demonstrated to increase in a cooperative manner at increasing solvent activity (Borisover and Graber, 2002b; Graber et al.,

2007). This effect was linked to a disruption of intra-NOM interactions and exposure of new sorption sites for organic sorbing molecules. The cooperativity was understood there to reflect a participation of several solvent molecules in organic compound–NOM interactions. The combined uptake of water and an organic compound capable of strong specific interactions on the humic and atmospheric humic-like substances was also found to increase cooperatively as a function of water activity, in contrast to the combined uptake of water and a non-specifically interacting organic probe molecule (Taraniuk et al., 2009). Yet, due to the strong lack of data, it is not clear whether (and how) the cooperativity extent associated with the water involvement in the exposure of new NOM sorption sites depends on the structure and properties of organic sorbates.

Hence, one aim of this research was to determine the effect of hydration of a model NOM sorbent, Pahokee peat, on interactions with a probe organic compound, carbamazepine (CBZ). CBZ is the aromatic polycyclic compound including N-heterocycle and amide group and capable of specific interactions. CBZ is a commonly used anticonvulsant and bipolar disorder drug that is one of the most widely reported water pollutants from the pharmaceutical and personal care products family (Chefetz et al., 2008; Zhang et al., 2008). Hence, multiple studies have shown that the presence of CBZ in ground or surface water indicates a high probability of anthropogenic contamination. Thus, CBZ sorption was measured from water on the fully hydrated peat and from *n*-hexadecane on differently hydrated peat.

As in the recent studies of the OH-containing aromatic compounds (Graber et al., 2007; Taraniuk et al., 2009), CBZ–NOM interactions were expected (i) to demonstrate the enhancement on hydrated NOM and (ii) to increase in a cooperative manner with water activity. Therefore, the second aim was to compare the obtained data for CBZ with the literature results for the OH-containing organic probe sorbate (phenol). This comparison provides a new insight into the effect of organic compound structure on the participation of water molecules in organic sorbate–NOM interactions.

CBZ appears in natural soil/water compartments with effluents from wastewater treatment facilities, thus being in an essentially hydrated environment. In addition, CBZ (as many other organic pollutants) can be introduced to the soil via sewage sludge (biosolids) application (Kinney et al., 2006) and eventually may be affected by soil drying/wetting cycles that influence the organic compound–soil interactions and the reactivity. Therefore, the overall motivation for investigating the effect of NOM hydration on sorption is toward developing a mechanistic understanding of organic sorbate–NOM interactions in differently hydrated environments.

2. Experimental section

2.1. Materials and chemicals

Pahokee peat (83% of organic matter) was supplied by International Humic Substance Society. It has been widely used as a model NOM sorbent in studies on organic compound sorption (Xing et al., 1996; Graber and Borisover, 1998; Wang et al., 2007). After freeze-drying, its moisture content was 4.9% w w⁻¹. Partial hydration of the peat sorbent was achieved by adding the required amount of water to a pre-weighed amount of Pahokee peat, followed by incubation of the sorbent at 23 ± 2 °C for 12 d (Graber et al., 2007). At the end of incubation period, the sorbent moisture content was verified by oven-drying (at 105 °C, until constant weight). Carbamazepine (5H-dibenz[*b,f*]azepine-5-carboxamide) was purchased from Sigma–Aldrich, Rehovot, Israel (>98%). *n*-Hexadecane

(>99%, Fluka) and water (Millipore-filtered) were used as solvents in the sorption experiments.

2.2. Sorption examination

Sorption of CBZ was studied at 23 ± 2 °C from water (on fully hydrated peat) and from *n*-hexadecane (on differently hydrated peat), according to a batch protocol similar to that described earlier (Borisover and Graber, 2003; Graber et al., 2007). The sorbent solution ratio (in g to mL) was 1:150 and 1:20 in typical sorption experiments in aqueous and *n*-hexadecane environments, respectively. It was selected to involve the CBZ removal from solutions due to sorption by 30–70% of the initial CBZ amount dissolved. Aqueous sorption experiments were carried out in the presence of CaCl₂ (0.01 M) and NaN₃ (200 mg L⁻¹) to minimize solute biodegradation. In order to obtain sorption isotherms, the triplicated initial CBZ concentrations were varied between 1 and 94 mg L⁻¹ in aqueous solutions, and between 4 and 22 mg L⁻¹ in *n*-hexadecane solutions.

For sorption experiments in the aqueous phase, solutions were equilibrated for 192 h (however, even after 24 h of equilibrating, no meaningful changes in sorbed concentrations were observed in separate kinetics tests carried out at two different CBZ concentrations, 0.5 and 10 mg L⁻¹). In the sorption experiments in *n*-hexadecane with a variable peat moisture content, the sorption kinetics were studied for up to 700 h, at an initial CBZ concentration of 10 mg L⁻¹. It was found that 336 h were sufficient to reach the sorption equilibrium in most of the systems (although at certain intermediate moisture contents even less time was needed to reach the sorption equilibrium). Hence, the CBZ sorption isotherms in the *n*-hexadecane environment were measured after equilibration for 336 h.

For supernatant solution analysis, the suspensions were centrifuged and filtered through a PTFE filter (0.45 μm; Millipore, USA). No sorption of CBZ was detected on the filters used. pH of aqueous supernatants was between 6.1 and 6.7; CBZ does not ionize in this pH range (Bui and Choi, 2010). Losses in the duplicated blank samples (with solute, without sorbent) did not exceed 2%.

The attainment of the CBZ sorption equilibrium was also supported by the lack of distinct desorption hysteresis (as compared with sorption isotherm) on the peat sorbent that was fully wet (in water) or minimally hydrated (in *n*-hexadecane). The one-step desorption tests were carried out by the remove-refill method at different sorbed CBZ concentrations. 240 and 72 h were given for desorption equilibration in aqueous and *n*-hexadecane samples, respectively. Separate desorption kinetics tests demonstrated that in both solvent environments the CBZ sorbed concentrations did not change after 24 h of the desorption equilibration.

2.3. Analytical measurements

Concentrations of CBZ in aqueous solutions were measured using a Shimadzu HPLC (column RP-18, 5 μm, Lichrospher[®] 100; the Lichrocart[®] 250–4 cartridge; mobile phase acetonitrile: water 60:40; 1 mL min⁻¹) with detection at 233 nm by a UV diode array detector. In *n*-hexadecane solutions, the CBZ concentration was obtained spectrophotometrically in a 1 cm quartz cuvette using Genesys 10UV (Thermo Scientific), at the wavelength of 288 nm. No CBZ adsorption from *n*-hexadecane to the quartz cuvette was observed. The 288 nm wavelength provided minimal interference between the UV-absorbance of CBZ and *n*-hexadecane-soluble organic matter released from the peat sorbent. To quantitatively account for (small) non-zero absorbance of the *n*-hexadecane phase due to released organic matter, absorbance of the background solution was separately determined and subtracted. In both types of analytical determinations, i.e. in aqueous and

n-hexadecane phases, concentrations of CBZ were obtained from instrumental responses linearly calibrated against external standards.

2.4. Determination of CBZ solubility

CBZ solubility in aqueous and *n*-hexadecane solutions was obtained at 23 ± 2 °C by the shake-flask method, in the presence of excess CBZ. The solubility values of CBZ in water and *n*-hexadecane were 126.1 ± 3.0 and 25.7 ± 0.4 mg L⁻¹, respectively (these values did not change between 3 and 12 d of suspension shaking). The CBZ solubility values in either salt background solution (124.9 ± 5.9 mg L⁻¹) or aqueous peat extract (125.9 ± 4.2 mg L⁻¹) were statistically similar to the value obtained in pure water.

3. Results and discussion

3.1. Comparing CBZ sorption by NOM in water and *n*-hexadecane: the impact of sorbent hydration

The isotherms of CBZ sorption on peat sorbent from water and *n*-hexadecane demonstrate (Fig. 1A) that, depending on specific solute concentrations, CBZ sorption from water is 4–8 times stronger as compared with sorption from *n*-hexadecane. In order to use sorption isotherms for comparing the CBZ-sorbent interactions in two different media, the different contributions of CBZ-bulk solvent interactions should be eliminated. This elimination is possible when the solution concentrations in Fig. 1A are replaced with the sorbate activity referred to such a standard state which is not affected by a solvent. The solution concentration normalized by the solubility of a compound can be an approximation for such a compound activity. After re-plotting (Fig. 1B), the differences between sorbed concentrations obtained from water and *n*-hexadecane increased such that aqueous sorption can exceed sorption from *n*-hexadecane, at the same solubility-normalized CBZ concentration, by a factor of 20–40. No quantitative estimates of these differences were obtained from sorbed concentrations beyond the comparable range of solubility-normalized CBZ concentrations.

It is known that the saturated aqueous solution of CBZ is in equilibrium with the solid CBZ dihydrate that is the thermodynamically stable hydrated form (Murphy et al., 2002). For example, the CBZ aqueous solubility obtained in this work, i.e. 126.1 mg L⁻¹, is in agreement with reported aqueous solubility values of the CBZ

dihydrate at 25 °C (i.e. 125 and 126 mg L⁻¹, Murphy et al., 2002; Ono et al., 2002, respectively). CBZ is known also to form solvates with acetone, dioxane, dimethylsulfoxide (Hilfiker et al., 2003). To our knowledge, no formation of solid solvates of CBZ crystallized from saturated hydrocarbons has been reported. Hence, in order to properly use the normalized solution concentrations for comparing the CBZ sorption isotherms measured in *n*-hexadecane and water, the solubility of an anhydrous CBZ in water should be used instead of the solubility of dihydrate.

Since the CBZ dihydrate is thermodynamically stable, the solubility of any anhydrous form will be larger than the solubility of the CBZ dihydrate. The aqueous solubility of anhydrous monoclinic CBZ which is the most stable and least soluble of all anhydrous forms (Li et al., 2008) was estimated to be between 379 and 315 mg L⁻¹ (Murphy et al., 2002; Ono et al., 2002, respectively). Use of aqueous solubility of an anhydrous CBZ form (379 mg L⁻¹; Murphy et al., 2002) instead of aqueous solubility of the CBZ dihydrate results in even larger differences between aqueous sorption and sorption from *n*-hexadecane at the same solubility-normalized CBZ solution concentration (as shown in Fig. 1B). It should be noted that the large differences in Fig. 1B are hardly affected by the possible release of dissolved organic matter (DOM) from the peat sorbent during sorption experiments. So, the decrease of the sorbent to solution ratio by two and three times (in water and *n*-hexadecane, respectively) had no (or possibly, slightly reducing) effect on sorption isotherms (data not shown). Also, the solubility of CBZ in an aqueous peat extract containing 80 mg L⁻¹ of DOM did not differ from its solubility in water. Thus, the hydration of the peat sorbent markedly enhanced CBZ-NOM interactions as compared with the CBZ-NOM interactions in the *n*-hydrocarbon environment. The magnitude of this enhancement effect by NOM-bound water significantly exceeds earlier reported effects for organic sorbate-NOM interactions (Borisover and Graber, 2004; Graber et al., 2007).

One explanation of this profound difference between solubility-normalized sorption isotherms obtained in water and *n*-hexadecane might be related to selective CBZ interactions with some “non-polar” NOM sites on the hydrated peat sorbent (in water). These “non-polar” sites could be occupied by competing *n*-hexadecane molecules in the *n*-hexadecane environment. Yet, this competitive effect of a saturated hydrocarbon is not a major factor due to the fact that the sorption isotherms of saturated hydrocarbons obtained on this peat sorbent both from the gas phase (Chiou and Kile, 1994) and from water (Zhu and Pignatello, 2005) were

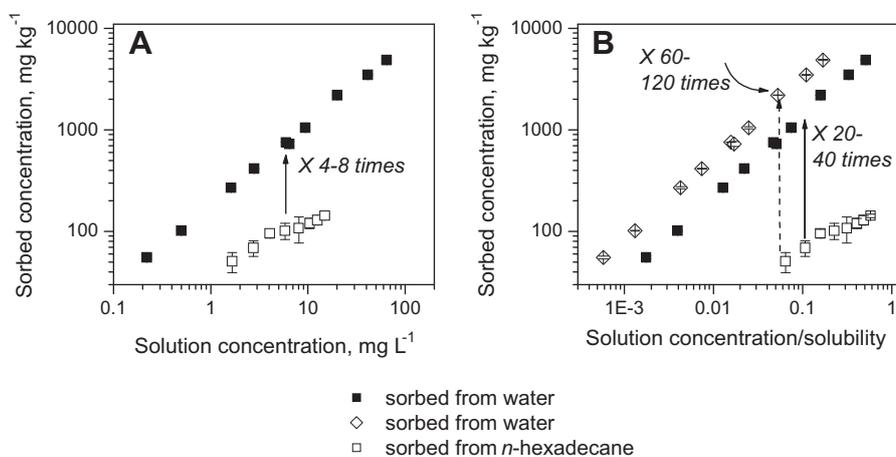


Fig. 1. Sorption of CBZ on Pahokee peat in water and *n*-hexadecane. A. Sorbed concentrations plotted against solution concentrations. B. Sorbed concentrations plotted against solution concentrations normalized by solubility. Two data series for sorption from water (presented by filled squares and diamonds in plot B) correspond to the normalization of a solution concentration by two different solubilities for dihydrate and anhydrous CBZ, respectively. Averaged data replicates are shown with standard deviations used as error bars; where no error bars are seen they are smaller than the size of data symbol.

essentially linear. In the next section, it is demonstrated that the strength of CBZ interactions with a hydrated NOM significantly exceeds that of the non-polar analog, thus implying that “non-polar” sites are unimportant in sorption of CBZ by the hydrated NOM.

3.2. Strong, specific interactions of CBZ with the NOM sorbent

In order to examine the strength of CBZ interactions with NOM, CBZ sorption by the hydrated Pahokee peat was compared with sorption of phenanthrene on the same hydrated sorbent. Phenanthrene and CBZ have comparable molar volumes (i.e. $151.2 \text{ cm}^3 \text{ mol}^{-1}$ for phenanthrene vs. $166.6 \text{ cm}^3 \text{ mol}^{-1}$ for CBZ; Windholz, 1983; Latere Dwan'lsa et al., 2007; respectively). Similarly, phenanthrene and CBZ are characterized by comparable molar refractivities which are 62.2 and $72.3 \text{ cm}^3 \text{ mol}^{-1}$, respectively (Borisover and Graber, 1997; Tasso et al., 2000). Similar molar refractivity is related, via molecular polarizability, to the similar ability of molecules to undergo dispersion interactions. The formation of π - π electron donor-acceptor complexes between polycyclic aromatic hydrocarbons and the hydrated Pahokee peat sorbent studied was suggested to be unimportant (Borisover and Graber, 2003). Thus, phenanthrene lacking polar functional groups and imitating the aromatic backbone of the CBZ molecule was considered to be a non-specific model compound for CBZ.

The sorption isotherms of phenanthrene (Borisover and Graber, 2003) and CBZ from water on the Pahokee peat sorbent are presented in Fig. 2A. Solute-bulk water interactions differ substantially for two sorbing compounds. Hence, in order to elucidate the differences in sorbate-hydrated sorbent interactions, the aqueous sorption isotherms of both organic compounds were converted to isotherms describing a hypothetical sorption of each compound from its infinitely diluted solution in the inert solvent, *n*-hexadecane, on the fully hydrated NOM sorbent (Borisover and Graber, 2003). To do this, for a given sorbed concentration $C_{A,\text{sorbed}}^h$ of a compound A on a fully hydrated (*h*) sorbent, the solution concentrations in an aqueous phase ($C_{A,\text{sln}(aq)}$) are converted to the solution concentrations in the inert solvent (*n*-hexadecane; $C_{A,\text{sln}(i)}$) where the solute-solute interactions are considered unimportant (Eq. (1)):

$$C_{A,\text{sln}(i)} = C_{A,\text{sln}(aq)} \frac{H_{A(aq)}}{H_{A(i)}} = C_{A,\text{sln}(aq)} \frac{\text{Sol}_{A(i)}}{\text{Sol}_{A(aq)}} \quad (1)$$

where $H_{A(i)}$ and $H_{A(aq)}$ are Henry's coefficients for compound A air/inert solvent and air/water distributions, respectively; $\text{Sol}_{A(i)}$ and $\text{Sol}_{A(aq)}$ are the compound A solubilities in an inert solvent *i* and water, respectively.

For phenanthrene, this conversion was carried out using available air/solvent distribution coefficients in water and *n*-hexadecane (Abraham et al., 1994). For CBZ, due to the lack of Henry's coefficients, the computation was carried out using the determined solubility in *n*-hexadecane and the available data on the aqueous solubility of the anhydrous CBZ form (379 mg L^{-1} , Murphy et al., 2002). Then, the coefficients $K_{d,A}^*$ associated with a hypothetical distribution of a compound A between the hydrated peat sorbent and *n*-hexadecane were calculated for CBZ and phenanthrene by Eq. (2):

$$K_{d,A}^* = \frac{C_{A,\text{sorbed}}^h}{C_{A,\text{sln}(i)}} \quad (2)$$

The $K_{d,A}^*$ values of CBZ and phenanthrene were plotted against sorbed concentrations in Fig. 2B. For comparison, Fig. 2B also uses an additional data set of aqueous phenanthrene sorption by Pahokee peat which was simulated using a fitting model (Wang et al., 2007) and converted with Eqs. (1), (2). Although the plots of the $K_{d,A}^*$ values vs. sorbed concentrations obtained from two independently determined data sets on phenanthrene sorption are not identical, two conclusions can be made unambiguously. (1) It is clear from Fig. 2B that phenanthrene distribution between hydrated peat sorbent and *n*-hexadecane is beneficial for solutions in the hydrocarbon: the relevant distribution coefficients are generally less than one. (2) Fig. 2B also shows that at a given sorbed concentration, CBZ distribution coefficients exceed phenanthrene distribution coefficients by almost four orders of a magnitude.

CBZ and phenanthrene have similar polarizabilities and, therefore, a similar ability to dispersion interactions. Minor differences in polarizabilities are unimportant when comparing isotherms of sorption from a hydrocarbon medium on a hydrated NOM (Borisover and Graber, 2003). The large differences between the $K_{d,A}^*$ values of CBZ and phenanthrene may be considered as an estimate for interactions associated with the heterocyclic N and amide group of the CBZ molecule and, particularly, for hydrogen bonding formed between CBZ and the hydrated NOM phase. π - π Electron donor-acceptor interactions between CBZ and NOM would hardly

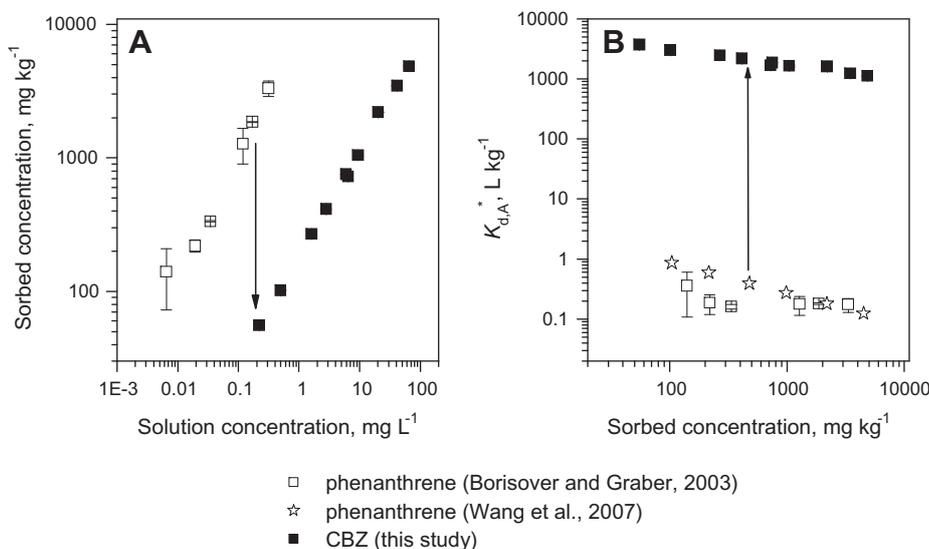


Fig. 2. Interactions with fully hydrated Pahokee peat NOM: a comparison between CBZ and phenanthrene. Phenanthrene sorption data on Pahokee peat are from Refs. (Borisover and Graber, 2003; Wang et al., 2007). A. Aqueous sorption isotherms of both compounds. B. The coefficients ($K_{d,A}^*$) representing the distribution of sorbate between fully hydrated peat and *n*-hexadecane are plotted against sorbed concentrations.

add to the differences between the K_{dA}^* values of CBZ and phenanthrene, due to CBZ non-planarity. Any potential specific interactions of phenanthrene with hydrated NOM (Zhu et al., 2004) would lead to an underestimation of CBZ–NOM specific interactions. Any CBZ–*n*-hexadecane interaction not accounted for with the phenanthrene model would lead to underestimating the strength of CBZ interactions with NOM as compared with phenanthrene–NOM interactions. Thus, the striking difference between the K_{dA}^* values of CBZ and phenanthrene shown in Fig. 2B indicates that increased CBZ interactions with the hydrated NOM (as compared with the dehydrated NOM immersed in *n*-hexadecane, Fig. 1B) can hardly be related to the blocking of “non-polar” NOM sites by competing non-polar hydrocarbon molecules in the *n*-hexadecane environment and their hypothetical exposure in water.

3.3. A sorbent hydration effect on CBZ–NOM interactions: interpretation and expectation of cooperative behavior

The Link Solvation Model (LSM; Borisover et al., 2001; Borisover and Graber, 2003; Graber et al., 2007) was developed to explain the sorbent hydration-induced enhancement of interactions of organic compounds with NOM. In terms of LSM (Graber et al., 2007), the sorbent (NOM) hydration effect on sorbate–NOM interactions (not associated with a change of the shape of sorption isotherms) may be described with Eq. (3):

$$\text{Hydration Effect} = \frac{C_{A,\text{sorb}(i)}^h}{C_{A,\text{sorb}(i)}^d} = \left[\frac{1 + \frac{K_{AW_{m-1}} a_W^{m-1}}{K_A}}{1 + K_W a_W + K_{W_m} a_W^m} \right]^n \quad (3)$$

where $C_{A,\text{sorb}(i)}^h$ and $C_{A,\text{sorb}(i)}^d$ are sorbed concentrations of a probe organic compound A which are obtained on hydrated (*h*) and dehydrated (*d*, e.g. placed in an inert medium *i*) sorbents, respectively, at a given sorbate A activity. a_W is the pure liquid state-referred activity of water; *n* characterizes the shape of organic compound sorption isotherms fitted by the Freundlich model (i.e. the model exponent).

This Eq. (3) describes interactions of a sorbate A and water molecules (or any other active solvent) with a NOM moiety internally linked via various non-covalent interactions which, if disrupted, can potentially provide *m* sorption sites. Hence, K_W , K_A , K_{W_m} and $K_{AW_{m-1}}$ are “equilibrium constants” that characterize the penetration of one water molecule, one sorbate A molecule, *m* water molecules and a successful penetration of a sorbate A molecule together with (*m* – 1) water molecules into the NOM moiety interior, respectively. The LSM concept states that several internal non-covalent NOM links may have to be cooperatively disrupted to allow an organic sorbate molecule to effectively interact with a NOM moiety. Depending on a sorbate/solvent pair, the *m* parameter of solvent cooperativity was estimated for Pahokee peat to vary between 6 (Borisover and Graber, 2002b) and 10 (Graber et al., 2007).

Based on this theoretical vision, the increased effect of sorption enhancement due to the NOM hydration could be expected for large compounds capable of strong specific interactions (e.g. such as CBZ as compared with earlier studied phenols, Borisover and Graber, 2004; Graber et al., 2007). This is because the penetration of large specifically interacting molecules into the NOM interior may need a concurrent rupture of even a greater number of links mediated by multiple functional groups and organic fragments in the NOM phase (thus involving the greater *m* value in Eq. (3)). The driving force for this disintegration of NOM moieties is the hydration of broken links which is accounted for by the larger $\frac{K_{AW_{m-1}}}{K_A}$ values. If this disintegration is indeed cooperative as suggested by the LSM (and Eq. (3)), then, the increased effect of

sorption enhancement due to NOM hydration should appear, for large molecules, at higher extent of the sorbent hydration (or higher water activities), as compared with smaller-size molecules. To test this assumption, in the next section, the effect of a variable sorbent hydration on CBZ–NOM interactions will be examined.

3.4. Effect of a variable sorbent hydration on CBZ–NOM interactions

The CBZ sorption isotherms measured in *n*-hexadecane on the differently hydrated peat sorbent are shown in Fig. 3 where the sorbed CBZ concentrations are plotted against solution concentrations in *n*-hexadecane. Clearly, the CBZ–NOM interactions are enhanced when the sorbent water content is increased. The hydration-induced enhancement of CBZ interactions at higher CBZ concentrations needs less NOM hydration. To illustrate this, the regular CBZ distribution coefficients (i.e. sorbed concentration/solution concentration) at two different equilibrium concentrations of CBZ in *n*-hexadecane solution (2 and 10 mg L⁻¹) were obtained from sorption data in Fig. 3 and normalized to the values obtained at the minimal peat hydration (i.e. 4.9% w w⁻¹). When necessary, the CBZ sorbed concentrations were found by interpolating values determined at the closest neighboring solution concentrations. These normalized CBZ distribution coefficients were plotted in Fig. 4 against the initial water content of peat and pure liquid-referred water activity. The sorbent water content was not affected by the presence of *n*-hexadecane (and by the small air volume in the vial) due to the sufficiently large amounts of water in differently hydrated peat samples (Graber et al., 2007). Water activities were computed for a specific peat water content by approximating the water sorption isotherm on Pahokee peat (Graber et al., 2007) with the Langmuir–Freundlich equation (Eq. (10); Sips, 1948; the root mean square error of approximation is 0.008).

For comparison, Fig. 4 also presents similar normalized data for phenol sorption on the same sorbent experiencing different hydrations (Graber et al., 2007), at the equilibrium concentration 10 mg L⁻¹ of phenol in *n*-hexadecane solution. At this phenol solution concentration, the range of sorbed phenol concentrations on differently hydrated peat samples was comparable with the range of CBZ sorbed concentrations (i.e. 180–1110 mg kg⁻¹ for phenol vs. 118–525 mg kg⁻¹ for 10 mg L⁻¹ of CBZ and 56–281 mg kg⁻¹ for 2 mg L⁻¹ of CBZ). Clearly, a strong rise in phenol sorption occurred

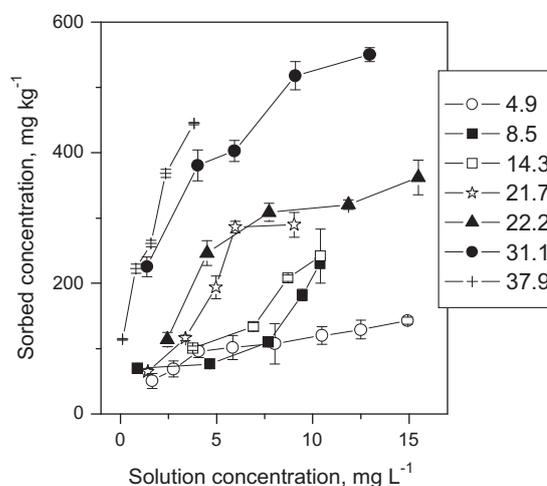


Fig. 3. CBZ sorption from *n*-hexadecane on differently hydrated Pahokee peat: sorbed CBZ concentrations plotted against equilibrium solution concentrations. The amount of water associated with Pahokee peat (g of water per g of a dry sorbent, %) is indicated in the legend.

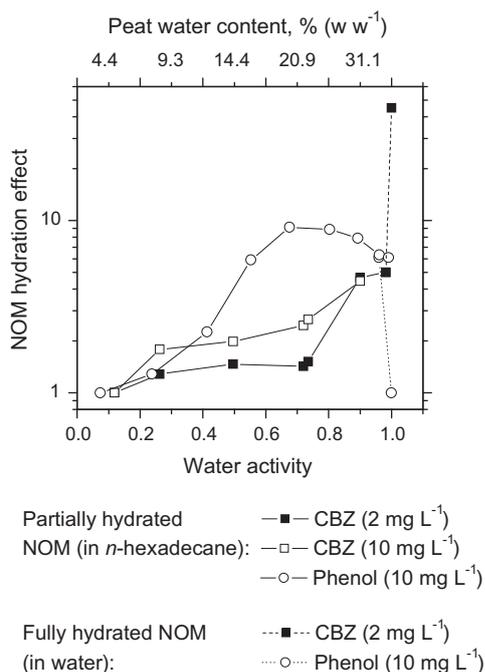


Fig. 4. Effect of partial and full Pahokee peat NOM hydration on sorption of phenol (data from Graber and Borisover, 1998; Graber et al., 2007) and CBZ: the coefficients of compound distribution between a differently hydrated sorbent and *n*-hexadecane were normalized to the value obtained at the minimal peat hydration and plotted against water activity and initial peat water content. Solution concentrations (in *n*-hexadecane) at which distribution coefficients were obtained are indicated in the legend. The Pahokee peat water content axis is not linear relative to the water activity axis.

at a lower level of peat hydration as compared with CBZ. So, the maximal value of the normalized phenol distribution coefficient was reached at a water activity of 0.65 when the CBZ sorption is still on the rise. The water activity (and the extent of the peat hydration) associated with maximal enhancement of phenol sorption was the same for phenol solution concentrations varied between 10 and 1000 mg L⁻¹ (Graber et al., 2007).

Thus, to demonstrate an increase of sorption at increasing NOM hydration, CBZ needs more peat-bound water as compared with phenol. This can be explained when considering the larger size of CBZ molecules as compared with phenol (i.e. 166.6 cm³ mol⁻¹ vs. 87.9 cm³ mol⁻¹, respectively; Latere Dwan'Isa et al., 2007; Windholz, 1983). As was predicted by Eq. (3), the larger size of a specifically interacting sorbate may involve a greater disturbance of the NOM moiety, larger number of "broken" links and a greater number of water molecules are needed to compensate for this local NOM disintegration. Hence, for larger *m* values in Eq. (3), a larger water activity is needed in order to significantly increase the contribution from the a_W^{m-1} term. Fig. 4 also includes data on a hypothetical sorption of CBZ and phenol from *n*-hexadecane on fully hydrated peat sorbent (at the unit water activity). These data were obtained by (1) the above conversion of aqueous sorption data into the transfer from *n*-hexadecane to a fully hydrated sorbent, with Eq. (1), (2) calculating the distribution coefficient K_{dA}^* (Eq. (2)), and (3) normalizing the distribution coefficients K_{dA}^* to the values obtained experimentally in *n*-hexadecane, at the minimal peat hydration. Aqueous phenol sorption data is from Graber and Borisover (1998). Henry's coefficients (Abraham et al., 1994) and solubilities were used in Eq. (1) for phenol and CBZ, respectively. At 10 mg L⁻¹ of phenol in *n*-hexadecane solution, strong hydration-assisted interactions with NOM observed at the intermediate hydration (Graber et al., 2007) disappeared when peat was com-

pletely hydrated. In contrast, CBZ–NOM interactions suggest a further sharp rise when peat NOM is completely hydrated.

Thus, the shape of the curve illustrating the dependence of sorption enhancement on NOM hydration (or water activity), as well as the specific range of water activities at which this sorption enhancement becomes significant, are important. When the maximum point is reached (as for phenol in Fig. 4), a further decrease in sorption enhancement suggests water-sorbate competition at certain, "persistent" surfaces or varieties of sorption sites. Any additional NOM hydration, at higher water activities, will not "create" new sorption sites (for a given sorbate and in a given range of sorbed concentrations). If a maximum is not reached at an intermediate water activity (as for CBZ in Fig. 4), then, there is a good reason to conclude that the enhancement of CBZ interactions with the fully hydrated NOM is not a result of the interaction with persistent sorption sites formed due to the sorbent hydration. In such a case, successful sorbate interactions with a hydrated NOM are associated with the co-participation of organic sorbate and water molecules in further changing NOM structure (e.g. disrupting of relevant intra-NOM interactions) rather than with the hydration-induced NOM swelling *per se*.

4. Conclusions

Larger-size organic sorbates capable of strong, specific interactions may exhibit (i) substantial enhancement of interactions with NOM due to its hydration, and (ii) greater extent of the cooperativity in an involvement of water molecules in organic compound–NOM interactions as was demonstrated by the CBZ sorption.

This expectation will hardly be correct for organic molecules with a flexible structure that could be accommodated by NOM without the need for a considerable disruption of the sorbent interior. The differentiation between flexible and rigid structures of organic molecules could explain, in part, why a certain (small) hydration-induced enhancement observed for interactions of some polar molecules with Leonardite humic acid (Niederer et al., 2006) did not increase with enlarging alkyl chains in sorbate molecular structures. Considering that the molecular structures of many environmentally important organic pollutants include rigid organic fragments (e.g. aromatic rings) and are rich in functional groups capable of specific interactions (e.g. in pesticides or compounds from the pharmaceutical and personal care products family), the substantial dependence of the equilibrium sorption of organic compounds on the hydration of NOM (which is, often, the major environmental sorbent) is significant.

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