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Association of Triorganotin Compounds with Dissolved Humic Acids

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Sorption to dissolved organic matter (DOM) may influence significantly the fate and the effects of organic pollutants in the aquatic environment. To date, most studies on DOM−water partitioning have focused on neutral hydrophobic compounds. Very little is known on the binding of hydrophobic organic cations to DOM. In this study, the association of triorganotin compounds (TOTs) with dissolved Aldrich and Suwannee River humic acids has been systematically investigated as a function of pH and sodium perchlorate concentration. The organotin compounds studied include the two widely used biocides tributyltin (TBT) and triphenyltin (TPT) as well as other trialkyltin compounds of various hydrophobicities. Between pH 3 and pH 9, for both TBT and TPT, the overall DOM−water distribution ratio (D_{DOM}) was strongly pH-dependent and exhibited a maximum close to the acidity constant (pK_a) of the compounds. The observed pH dependence of D_{DOM} could be described successfully with a semiempirical discrete log *K* spectrum model. It was found that, over the whole pH range investigated, sorption was governed by complexation of the corresponding TOT cation (TOT^+) by negatively charged ligands (i.e., carboxylate and phenolate groups) of the humic acids. The determining factors of the TOT^+ binding are postulated to be (i) complex formation between the tin atom and the deprotonated ligands and (ii) hydrophobic interactions. Significant differences in D_{DOM} of TBT were observed between Suwannee River and Aldrich humic acid. D_{DOM} values of TOTs determined for Aldrich humic acid were in the same range as particulate organic matter−water distribution ratios reported in the literature for soils and sediments.

Introduction

Association with dissolved organic matter (DOM), i.e., sorption to DOM, may have a significant effect on the transport and reactivity as well as on the bioavailability of trace organic and inorganic contaminants in the aquatic environment (*1*−*3*). To date, most studies on DOM−water partitioning of organic contaminants have focused on neutral compounds for which hydrophobic interactions play the dominant role. These studies have demonstrated that the organic matter−water partition constant of a given hydrophobic compound (K_{om} or K_{oc}), may vary by more than 1 order of magnitude between DOM originating from different sources (*4*−*7*). This variability in K_{om} was attributed primarily to differences in molecular weight distribution, aromaticity, and polarity of the DOM constituents (*4, 5*). Furthermore, it has been shown that, for neutral compounds, the influence of pH on K_{om} is rather marginal over the ambient pH range (*6, 8*) and that a significant effect of the major cations is only found at high ionic strength (*6, 8*). It should be noted that K_{om} values obtained by fluorescence quenching have purposely not been cited here because the suitability of this method for systematic studies is presently the subject of controversy (*9, 10*). However, the same trends have generally been observed (*11, 12*).

Compared to neutral organic compounds, much less data are available on the association of cationic organic species with particular and dissolved organic matter (POM and DOM) including organic cations such as tetraalkylammonium and alkylpyridinium species or ionizable organic compounds that are present as cations at lower pH values (e.g., quinolines, methylmercury or triorganotin compounds). From the few studies conducted, it can be concluded that interactions between organic cations and deprotonated functional groups (e.g., carboxyl and phenolic groups) of organic matter are important. Thus, for example, for ditallowdimethylammonium and cetyltrimethylammonium ions (*13*), due to the increasing number of negatively charged sites, an increasing sewage sludge−water distribution ratio was observed with increasing pH. For quinoline, an organic base with an acidity contant (pK_a) of 4.9, the dissolved organic matter−water distribution ratio (D_{DOM}), reached a maximum around pH 5, with a value approximately equal to three times that measured for the neutral quinoline species at pH values above 7 (*14*). In the case of methylmercury, Hintelmann et al. (*15, 16*) suggested that complexation of the cationic species $MeHg^+$ [pK_a 4.5 (*17*)] by functional groups of dissolved humic acid governed the sorption of methylmercury in the whole considered pH range (3−7), i.e., even at pH values at which MeHg−OH is the dominating species. Finally, for triorganotin compounds (TOTs) that exhibit pK_a values between 5 and 7 (see Table 1), the results of a variety of studies suggest that specific interactions between polar natural organic matter constituents (POM and DOM) and the TOT cations might play an important role in determining their overall organic matter−water distribution ratio D_{OM} (*18*−*25*). However, to date, no systematic investigations have been conducted to evaluate the effect of pH and major ion composition on the DOM−water partitioning behavior of cationic hydrophobic organic compounds, and no quantitative models have been derived to describe the D_{DOM} value of such compounds as a function of these important environmental variables.

In the study presented in this paper, we have systematically investigated the effect of pH and sodium ion concentration on the DOM−water partitioning of tributyltin (TBT) and triphenyltin (TPT). For evaluating the experimental data, a discrete log *K* spectrum model with four binding sites, as proposed by Westall et al. (*26, 27*) for the description of the binding of metallic cations to natural organic matter, has been adopted. Aldrich humic acid (AHA) and Suwannee River humic acid (SRHA) have been used as model DOM. TBT and TPT have been chosen as major model compounds for several reasons. First, both compounds may undergo

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TABLE 1. Acidity Constants (pK_a) of TOT_{aq}^+, Octanol−Water, and AHA−Water Partition Constants (K_{ow}, K_{DOM}) of TOT−OH, Overall AHA−Water Distribution ratio (D_{DOM}) at pH 5.8, Complexation Constants (K_i, $i = 1-4$) with AHA, and Dialysis Experiment Mass Balances of the Triorganotin Compounds Investigated

compound	pK_a	log K_{ow}[a]	log K_{DOM}[b]	log D_{DOM}[c]	log K_1[d]	log K_2[d]	log K_3[d]	log K_4[d]	mass balance[e]
Triethyltin (TET)	6.8[f]	0.6[g]	−0.2	3.4	nd[m]	nd	nd	nd	93 (85−97)
Tripropyltin (TPrT)	6.3[h]	2.1[h]	1.3	3.9	nd	nd	nd	nd	93 (89−98)
Tributyltin (TBT)	6.3[i]	4.1[i]	3.3	5.1	4.6	5.5	—[j]	7.3	78 (63−89)
Tripentyltin (TPeT)	6.3[k]	5.8[l]	5.0	6.0	nd	nd	nd	nd	31 (20−39)
Triphenyltin (TPT)	5.2[i]	3.5[i]	2.7	5.1	4.8	5.8	7.0	8.4	63 (45−84)

[a] Log K_{ow} of TOT−OH. [b] Estimated using the relationship log K_{DOM} = 1.0 log K_{ow} − 0.8 derived by McCarthy and Jimenez (*45*) for the sorption of hydrophobic organic compounds to dissolved AHA, K_{DOM} in L/kg_{DOM}. [c] Determined at pH 5.8, 10 mM $NaClO_4$, and 1 mM MES; D_{DOM} in L/kg_{DOM}. [d] K_i values are defined by eq 4 and were determined from the experimental D_{DOM} values, see text. [e] Mean (min − max). [f] Ref *48*. [g] Ref *49*. [h] Ref *50*. [i] Ref *35*. [j] No significant contribution of these sites to the overall D_{DOM}. [k] Estimated in analogy to TBT and TPrT. [l] Estimated from the log K_{ow} values of TET, TPrT, and TBT by calculating a $-CH_2-$ fragment constant (see refs *51* and *52*). [m] nd, not determined.

innersphere complexes with anionic species including carboxylate and phenolate groups (*28*−*33*). Second, the two compounds differ significantly in their pK_a values as well as in their hydrophobicities (see pK_a and log K_{ow} (TOT−OH) values given in Table 1), thus allowing us to probe for both specific binding as well as for hydrophobic effects. For the evaluation of the effect of hydrophobicity on D_{DOM}, some additional experiments were conducted with triethyltin (TET), tripropyltin (TPrT), and tripentyltin (TPeT). Finally, the major model compounds TBT and TPT are widely used biocides, and because of their high toxicity to aquatic life (*3*, *34*), they are of great environmental concern. Thus, this study does not only give basic insight into the factors that control the binding of hydrophobic organometallic compounds to natural organic matter, it also provides important data for two prominent pollutants.

Theoretical Considerations

Model for the Description of the DOM−Water Partitioning of TOTs. As we have shown in earlier work (*35*), depending on pH and ion composition, in aqueous solution TOTs may be present as cations (TOT_{aq}^+), as hydroxide complexes ($TOT-OH_{aq}$), and/or as complexes with other negatively charged inorganic ligands. Under the conditions used in this study, which are representative for freshwater environments, only TOT_{aq}^+ and $TOT-OH_{aq}$ have to be considered:

$$TOT_{aq}^+ \rightleftarrows TOT-OH_{aq} + H^+ \quad (1a)$$

$$K_a = \frac{[TOT-OH_{aq}][H^+]}{[TOT_{aq}^+]} \quad (1b)$$

where K_a is the acidity constant of TOT_{aq}^+ (Table 1). The fractions α_{TOT^+} and α_{TOT-OH} of the two species present at a given pH can be calculated from eq 1:

$$\alpha_{TOT^+} = \frac{1}{1 + 10^{pH-pK_a}} \quad (2a)$$

$$\alpha_{TOT-OH} = \frac{10^{pH-pK_a}}{1 + 10^{pH-pK_a}} \quad (2b)$$

For each of the two species, one major sorption mechanism is considered. For the neutral TOT−OH species, only *hydrophobic partitioning* is taken into account:

$$TOT-OH_{aq} \rightleftarrows TOT-OH_{DOM} \quad (3a)$$

$$K_{DOM} = \frac{[TOT-OH_{DOM}]}{[TOT-OH_{aq}]} \quad (3b)$$

where K_{DOM} is the DOM−water partition constant. For the TOT^+ species, in analogy to the adsorption of TOTs at mineral surfaces (*36*), *complexation* with deprotonated DOM ligands (L_{DOM}^-), such as carboxylate or phenolate groups, can be postulated to be the major sorption mechanism:

$$L_{i,DOM}^- + TOT_{aq}^+ \rightleftarrows L_i-TOT_{DOM} \quad (4a)$$

$$K_i = \frac{[L_i-TOT_{DOM}]}{[L_{i,DOM}^-][TOT_{aq}^+]} \quad (4b)$$

The subscript i indicates that there is a continuous spectrum of different ligands $L_{i,DOM}$ exhibiting different K_i values. Each of these ligands has a specific acidity constant, K_{ai}:

$$L_iH_{DOM} \rightleftarrows L_{i,DOM}^- + H^+ \quad (5a)$$

$$K_{ai} = \frac{[L_{i,DOM}^-][H^+]}{[L_iH_{DOM}]} \quad (5b)$$

In addition, any other cation present (in this study only Na^+) may form complexes with the DOM ligands. Hence, for this study, the additional reaction

$$L_{i,DOM}^- + Na^+ \rightleftarrows (L_i^-Na^+)_{DOM} \quad (6a)$$

$$K_{Na,i} = \frac{[(L_i^-Na^+)_{DOM}]}{[L_{i,DOM}^-][Na^+]} \quad (6b)$$

has to be taken into account. Using eqs 4−6, the fraction of deprotonated ligands, $\alpha_{L_i^-,DOM}$ can be expressed by

$$\alpha_{L_{i,DOM}^-} = \frac{1}{1 + 10^{pK_{ai}-pH} + K_{Na,i}[Na^+] + K_i[TOT_{aq}^+]} \quad (7)$$

For low TOTs concentrations, as found in the environment, eq 7 can be simplified to

$$\alpha_{L_{i,DOM}^-} = \frac{1}{1 + 10^{pK_{ai}-pH} + K_{Na,i}[Na^+]} \quad (8)$$

Thus, using eqs 1−8, the overall DOM−water distribution ratio (D_{DOM}) can be expressed by

$$D_{DOM} = \frac{[TOT_{DOM}]_{tot}}{[TOT_{aq}]_{tot}} = \frac{[TOT-OH_{DOM}] + \sum_i [L_i-TOT_{DOM}]}{[TOT-OH_{aq}] + [TOT_{aq}^+]} \quad (9a)$$

or

$$D_{DOM} = \alpha_{TOT-OH}K_{DOM} + \alpha_{TOT^+}\sum_i \alpha_{L_{i,DOM}^-}K_i[L_iH_{DOM}]_{tot} \quad (9b)$$

Various models have been applied to describe the spectrum of binding sites $L_{i,DOM}$ (for a review, see refs *27* and *37*). A satisfactory approximation is provided by the semiempirical discrete log K_i spectrum model developed by Westall et al. (*27*) for the description of complexation of metal cations by humic substances. In this model, the spectrum of binding sites is reduced to four discrete sites (i.e., $i = 1-4$ in eqs 4−9) exhibiting fixed pK_{ai} values of 4, 6, 8, and 10 (see Results and Discussion). The total concentration of binding sites, $[L_iH_{DOM}]_{tot}$ (eq 9) as well as $K_{Na,i}$ (eq 6b) can be determined by potentiometric titration of the DOM solution at different ionic strength, i.e., different Na^+ concentrations (*27*). The binding constants K_i (eq 4b) can be obtained by fitting them to the pH dependence of D_{DOM} at a given ionic strength. The hydrophobic DOM−water partition constant, K_{DOM} (eq 3b), can either be obtained by fitting it to the experimental D_{DOM} values, or it can be estimated from the K_{ow} value of the TOT−OH. Details on the determination of the various constants are given in the Experimental Section.

Experimental Section

Chemicals. Tributyltin chloride, (97%, pract.), triphenyltin chloride (97%, pract.), morin (Fluka standard), Triton X-100 (Fluka BioChemika), citric acid monohydrate (>99.5%, puriss p.a.), oxalic acid dihydrate (>99.5%, puriss p.a.), lithium hydroxide (>99%, puriss p.a.), 2-(*N*-morpholino)ethanesulfonic acid (MES, $pK_a = 6.15$) and 3-(*N*-morpholino)-propanesulfonic acid (MOPS, $pK_a = 7.20$) were obtained from Fluka Chemie AG (Buchs, Switzerland). Triethyltin chloride (>98%, pract.), tripropyltin chloride (>98%, pract.), sodium perchlorate monohydrate (99%, p.a.), orthophosphoric acid (85%, p.a.), sodium dihydrogen phosphate monohydrate (>99%, p.a.), perchloric acid (60%, p.a.), acetic acid (100%, p.a.), sodium nitrate (>99.5, p.a.), and sodium hydroxide (Titrisol 1 M) were purchased from E. Merck (Darmstadt, Germany). Tripentyltin chloride (95%, pract.) was obtained from Aldrich Chemie GmbH (Steinheim, Germany). Methanol (99.8%, HPLC prep grade) and HPLC water (HPLC grade) were obtained from Scharlau (Sentmenat, Spain). The water used for the sorption experiments was doubly distilled in quartz.

Analytical Procedures. The concentrations of TET, TPrT, TBT, TPeT, and TPT were determined with cation-exchange HPLC with fluorescence detection after postcolumn derivatization with morin in a micellar solution (see also refs *38* and *39*). The HPLC equipment consisted of a Gynkotek M 480 HPLC pump, a GINA 50 autosampler, a Shimadzu RF-551 fluorescence detector, all from Gynkotek (Gynkotek AG, München, Germany), and a 125 × 4.6 mm Metrosep Cation 1-2 column (Metrohm AG, Herisau, Switzerland). The eluent was pumped at a flow rate of 1 mL/min. Isocratic elution was used for TPrT [25 mM citric acid and 20 mM oxalic acid in 10:90 (v:v) methanol:water]. The following gradient program was used for TBT, TPT, and TPeT: from 0 to 1 min, 45 mM citric acid in water; from 1.1 to 5 min, 25 mM citric acid and 20 mM oxalic acid in water; from 5.1 to 15 min, 25 mM citric acid and 20 mM oxalic acid in 50:50 (v:v) methanol:water. For TET, the following gradient program was used: from 0 to 5 min, 15 mM citric acid, 12 mM oxalic acid, and 40 mM LiOH in water; from 5.1 to 17 min, 20 mM citric acid, 16 mM oxalic acid, and 20 mM LiOH in 5:95 (v:v) methanol:water. The reagent solution [2% (w/v) Triton X-100, 160 μM morin, 360 mM citric acid, and 810 mM lithium hydroxide in water] was pumped by a Jasco pump 880-PU (Japan Spectroscopic Co. Ltd., Tokyo, Japan) at a flow rate of 1 mL/min. The mobile phase and the reagent solution were then combined using a T-piece (Valco, Houston, TX). A 2 m × 0.3 mm PTFE reaction coil (ict, Frankfurt, Germany) ensured good mixing prior to fluorescence detection. The excitation and detection wavelengths were 403 and 533 nm, respectively. Excitation and emission slits were set at a bandwidth of 18 nm. The sample volume was 100 μL for the TBT measurements, 200 μL for the TPrT and TPT, and 600 μL for TET and TPeT. Peak areas were determined using Gynkosoft software version 5.42 (Gynkotek AG, München, Germany). TOTs were quantified with external standards prepared in solutions with the same composition (with or without humic acid) as in the sorption experiments.

Humic Acids. Suwannee River Humic Acid Reference (1R101H) was received from the International Humic Substance Society (IHSS). Aldrich humic acid, sodium salt (lot no. 01816-104, Aldrich Chemie GmbH, Steinheim, Germany) was purified according to the following procedure: 20 g of commercial Aldrich humic acid was dissolved under nitrogen at pH 10 (NaOH) and stirred for 30 min. The insoluble humin fraction was removed by filtration though a 0.45-μm cellulose nitrate filter (Sartorius AG, Goettingen, Germany). The solution was then acidified to pH 2 with 0.1 M HCl. The precipitated humic acids were collected on a ceramic filter (Schott filter no. 4, Schott, Mainz, Germany), washed with 0.01 M HCl and freeze-dried. The dissolved fraction (mainly fulvic acids) was discarded. The ash and moisture content of nontreated Aldrich humate (AH), treated Aldrich humic acid (AHA), and Suwannee River humic acid (SRHA) were determined at 500 and 105 °C, respectively. The carbon, hydrogen, nitrogen, and sulfur content of AHA were determined in triplicate using a CHNS-analyzer (Carlo Erba Elemental Analyzer, EA 1108). A summary of the measured data is presented in Table 2.

Aqueous humic acid solutions were freshly prepared for each experiment according to the following procedure: between 10 and 100 mg of humic acid was exactly weighted, dissolved under nitrogen at pH 10 (NaOH) in 250 mL water, and stirred for 30 min. The humic acid solution was then percolated through a 2.5 × 3 cm cation-exchange column [Amberlite Ir 120(plus), Aldrich Chemie GmbH, Steinheim, Germany] that had been previously washed with 1 L of doubly distilled water. The dissolved organic matter contents of the humic acid solutions were determined using a Shimadzu 500 TOC analyzer (Shimadzu Corporation, Kyoto, Japan) calibrated with phthalic acid solutions.

Titrations of AHA and SRHA were performed under argon atmosphere in a glovebox equipped with a CO_2 adsorber. Titrations were performed at 25 °C for both humic acids at 10 and 100 mM ionic strength ($NaClO_4$) with 0.01 M NaOH. A dosimat 665, a pH-meter 713, and a 12 × 125 mm pH electrode (Solitrode 6.0220.100) were used (all from Metrohm AG, Herisau, Switzerland). The water was boiled and degassed with argon. The operational definition of the titration equilibrium was drift of less than 10^{-3} pH unit per second for at least 5 s.

Determination of Sorption Isotherms: Description and Evaluation of the Dialysis Experiments. The sorption experiments were conducted in home-built dialysis cells that consisted of two glass chambers (1.2 mL each) separated by a dialysis membrane made of asymmetric cellulose ester (Spectrum, Houston, TX) with a molecular weight cutoff (MWCO) of 500 Da (a more detailed description of the cells is given in ref *40*). One of the chambers was filled with a TOT solution, and the other one was filled with a humic acid solution containing the same total TOT concentration, except for the kinetic experiments (see below) where the latter initial TOT concentration was zero. In general, no pH buffer was used except for experiments for which it was crucial to work

TABLE 2. Characteristics of Aldrich Humic Acid (AHA) and of Suwannee River Humic Acid (SRHA)

	AHA	SRHA
%ash	5.2[a,c]	4.9[a]–3.5[b]
$\%H_2O$	9.7[a]	4.2[a]–9.8[b]
Elemental Composition[d]		
%C	57.8[a]	52.9[b]
%H	3.7[a]	4.14[b]
%N	0.7[a]	1.17[b]
%S	4.2[a]	0.58[b]
%O	(33.6)[e]	43.4[b]
Molecular Weight		
wt av, M_w (Da)	4100[f,g]–14500[h]	2200[f]–4400[h]
no. av, M_n (Da)	1600[f]–3000[g,h]	1300[f]–1600[g]
Percent of Humic Acid Diffusing through the Dialysis Membrane (MWCO 500)		
	NUF[i] UF[i]	NUF[i] UF[i] PD[i]
pH ≈ 3	0.9 0.6	2.5 1.9 1.6
pH ≈ 7	0.6	1.1
Acidic Functional Groups (mol/kg_{DOM}) and Complexation Constants with Na^+ [j]		
L_1H_{DOM} $pK_a = 4$	2.16	3.45
L_2H_{DOM} $pK_a = 6$	1.59	1.66
total carboxylic groups	3.75 (3.3[k])	5.11 (4.9[l])
L_3H_{DOM} $pK_a = 8$	0.83	0.82
L_4H_{DOM} $pK_a = 10$	1.42	2.43
total phenolic groups	2.25 (2.3[k])	3.25 (2.9[l])
log K_{Na^+}[m]	1.48	1.34

[a] This work. [b] As reported by Huffman Laboratories, Wheat Ridge, Co. [c] For comparison, nontreated AH: 27%. [d] Ash-free and moisture-free basis. [e] Estimated by difference. [f] Ref *53*. [g] Ref *54*. [h] Ref *55*. [i] NUF, UF, and PD mean non ultrafiltrated, ultrafiltrated, and predialyzed, respectively. [j] Determined by titration according to eqs 5–6, see text. [k] Ref *56*. [l] Ref *57*. [m] Defined by eq 6, equal for all four $L_{i,DOM}^-$, see text.

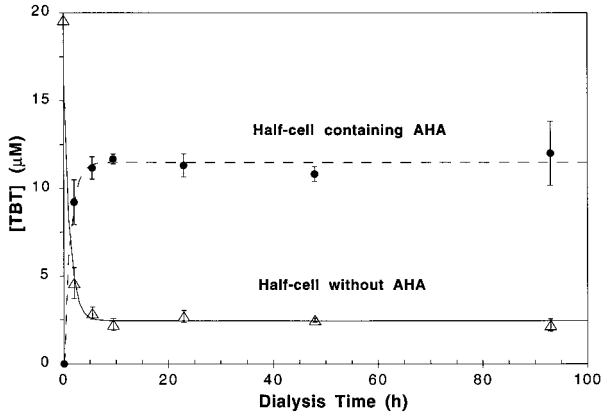

FIGURE 1. Diffusion kinetics of TBT through the dialysis membrane and subsequent association with AHA (87 mg/L, pH 7.5, 10 mM MOPS buffer). (△) TBT concentration in the half cell without humic acid (initial concentration was 19.6 μM), (●) TBT concentration in the half cell containing humic acid (initial concentration was zero). Error bars represent the standard deviation of three replicates.

at a constant pH. In these cases, MES and MOPS buffers that do not complex with TOTs (*35*) were used. Some preliminary experiments with and without these buffers showed that neither of them had a significant effect on the sorption isotherms.

As is illustrated in Figure 1 for the sorption of TBT to AHA, equilibrium was reached after less than 10 h. In a blank experiment (i.e., without humic acid), a similar equilibration time was measured indicating that the rate-limiting step of the equilibrium dialysis experiments was the diffusion through the dialysis membrane and not the association with the dissolved humic acid. Hence, to ensure equilibrium conditions, the dialysis cells were always shaken for 24 h in the dark at 25 °C. Subsequently, the total TOT concentration was measured in each chamber by HPLC (see above). For each solution condition, experiments were conducted in triplicates for three to seven different initial TOT concentrations.

As also indicated by Figure 1 and summarized in Table 1, generally for all TOT investigated, mass balances were incomplete and they varied as a function of solution conditions. The major reason for incomplete mass balance was found to be sorption of the TOTs to the dialysis membrane and to the glass surface of the dialysis cells. However, since TOT concentrations were always determined in both dialysis cells, the results of the sorption experiments were not affected by these sorption losses.

Finally, the fraction of humic acid diffusing through the dialysis membrane was determined at pH 3.5 and pH 7 and at ionic strength of 1 mM (sodium nitrate and phosphate buffer, respectively). Solutions containing between 125 and 300 mg/L humic acid were dialyzed for 24 h, and the organic carbon contents were subsequently determined in each dialysis chamber. Ultrafiltration technique was also used to separate the small MW fractions of the humic acids. An Amicon 8050 filtration apparatus (Millipore Corporation, Bedford, MA) was used with an ultrafiltration membrane exhibiting a MWCO of 1000 Da (Molecular/Por Type C, Spectrum, Houston, TX). A total of 50 mL of a humic acid solution (250–500 mg/L) was ultrafiltrated to a final volume of 25 mL. Then, 25 mL of water was added to the retentate and again subjected to ultrafiltration. This procedure was repeated five times. In addition, a 300 mg/L SRHA solution was predialyzed for 1 week in a dialysis bag exhibiting a MWCO of 1000 Da (Spectrum, Houston, TX). The aqueous solution outside the bag (1 mM $NaClO_4$) was renewed twice a day. The fraction of ultrafiltrated and predialyzed humic acid diffusing through the dialysis membrane was then determined. As is indicated in Table 2, only a very small fraction of humic acid constituents diffused through the membrane. Furthermore, in parallel experiments conducted with ultrafiltrated and non-ultrafiltrated AHA (250 mg/L, pH 6.3, 10mM $NaClO_4$), no significant differences in the sorption isotherms of TBT were observed (data not shown). Thus, it can be concluded that the fraction of humic acid diffusing

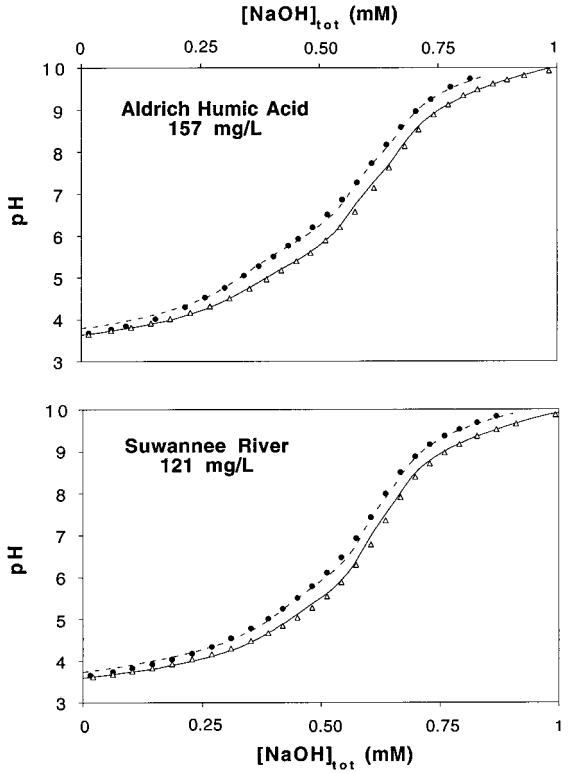

FIGURE 2. Acid−base titration of AHA and SRHA acid at 10 (●) and 100 (△) mM ionic strength ($NaClO_4$). The lines were modeled according to eqs 5 and 6 using a single K_{Na} value for the four acidic sites (see text).

through the dialysis membrane did not affect the results of the sorption experiments. Finally, mass balances of AHA and SRHA prior and after the dialysis experiments varied between 93 and 104%, indicating that no significant loss due to precipitation or sorption of the humic acids occurred.

Modeling of the Experimental Data. The titration data as well as the pH dependence of D_{DOM} were fitted according to eqs 1−9 using the computer code FITEQL (*41*). The procedure was very similar to that adopted by Westall et al. (*27*) to describe the complexation of Co(II) by Leonardite humic acid as function of pH and $NaClO_4$ concentration. Technical details on the modeling procedure, such as FITEQL matrixes, can be found in the above-mentioned reference. Briefly, the pK_{ai} values of the L_iH_{DOM} were fixed to 4, 6, 8, and 10. The total concentration of the L_iH_{DOM} species and the complexation constant $K_{Na,i}$ were fitted according to eqs 5 and 6 from the titration data at 10 and 100 mM $NaClO_4$ concentrations. These parameters were then used as constants for the modeling of the pH dependence of D_{DOM}. Subsequently, the binding constants K_i were adjusted according to eqs 1−9 to fit the 143 points of the 22 sorptions isotherms measured at 10 mM $NaClO_4$ concentration and various pH values. Using the determined K_i and $K_{Na,i}$, D_{DOM} values for higher ionic strength were predicted and compared with the experimental values.

Activity coefficients of the ionic species were calculated with the Davies equation (*42*). The activity coefficient of the neutral species were set equal to unity with one major exception. For predicting D_{DOM} for seawater solution conditions (i.e. high ionic strength), activity coefficients of TBT−OH and TPT−OH were calculated using eq 5 of ref *35* to be 2 and 1.5, respectively.

Results and Discussion

Characteristics of AHA and SRHA: Concentration of Acidic Sites and Complex Formation Constants with Na^+. Figure 2 shows the titration curves of AHA and SRHA in the presence of 10 and 100 mM $NaClO_4$, respectively. Note that, in both cases, $K_{Na,i}$ values were found to be very similar for all four sites, and as is evident from Figure 2, the titration curves could be described very well using a single K_{Na} value for each humic acid. This finding reflects the electrostatic nature of the $L_{i,DOM}$−Na complexes and agrees with the results of Westall et al. (*27*). The concentration of the four sites (L_iH_{DOM}, $i = 1-4$) as well as the K_{Na} values are summarized in Table 2. A comparison between AHA and SRHA shows that in the pK_a range corresponding to carboxylic acids (L_1H_{DOM} and L_2H_{DOM}) as well as in the range corresponding primarily to phenolic groups (L_3H_{DOM} and L_4H_{DOM}), acidic sites were approximately one-third more abundant in SRHA than in AHA. These results are in agreement with data reported in the literature for the two humic acids (see values in parentheses in Table 2). Note that the sites summarized under L_3H_{DOM} do not only represent phenolic groups but also include a small fraction of amino acid functional groups (*27*, *43*).

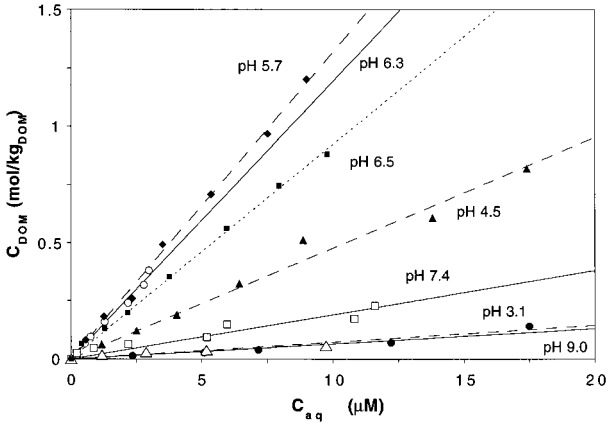

FIGURE 3. Sorption isotherms of TBT to AHA at various pH values and 10 mM $NaClO_4$.

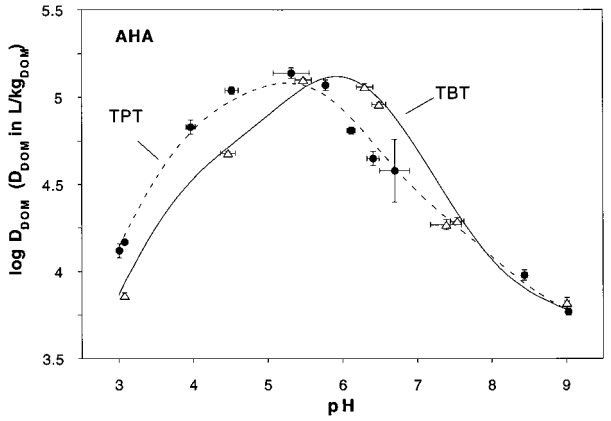

FIGURE 4. AHA−water distribution ratio (D_{DOM}) of TBT (△) and TPT (●) as a function of pH. Each point was determined from a sorption isotherm. Error bars are the standard deviation of the slope of the linear isotherm and of pH. The lines were calculated using the model described by eqs 1−9 (see text).

Sorption of TOTs to Dissolved AHA. As is illustrated for TBT in Figure 3, in all experiments with AHA, sorption isotherms were linear and strongly pH-dependent. In addition, it was found that the concentration of AHA did not have any effect on the slope of the isotherms (data not shown). In Figure 4, the logarithms of the D_{DOM} values (eq 9), calculated from the slopes of the isotherms, are plotted for TBT and TPT against pH. From these data, two important qualitative conclusions can already be drawn. First, both TBT and TPT

TABLE 3. Calculated and Experimental D_{DOM} Values Determined for AHA and D_{POM} Values Reported in the Literature

compound	solution conditions	log D_{DOM}[a] calcd	log D_{DOM}[a] exp	log D_{POM}[b]
TBT	pH 5.7, 10 mM Na^+	5.1	5.1	nd
	pH 5.8, 100 mM Na^+	4.9	4.8	nd
	pH 9.0, 10 mM Na^+	3.9	3.8	nd
	pH 9.3, 100 mM Na^+	3.5	3.6	nd
	Comparison with Literature D_{POM}			
TBT	pH 7.5, $Na^+ \leq 10$ mM	4.4	4.3	4.5[c]
	pH 8.0, 0.5 M Na^+ (seawater)	4.1	nd[f]	4.3[d]
TPT	pH $\approx$ 3.5, $Na^+ \leq 10$ mM	3.5	nd	3.2[e]

[a] Calculated according to eqs 1−9 and Tables 1 and 2. [b] D_{POM} values are calculated from the reported sorption coefficients K_d and fraction of organic matter (f_{POM}), i.e., $D_{POM} = K_d/f_{POM}$. [c] Ref *18*. [d] Median value of Figure 22.3 of ref *24*. [e] Ref *22*. [f] nd, not determined.

exhibited maximum D_{DOM} values in the pH region of their corresponding pK_a, which is consistent with the assumption that complexation of the cationic species by deprotonated acidic sites of AHA are primarily responsible for the sorption of the two TOTs. Second, at high pH values, i.e., above pH 8, a decrease in D_{DOM} was observed with increasing pH, suggesting that, despite of the low TOT^+ fraction, sorption of the cation was still dominating the overall partitioning of the TOTs. This hypothesis is supported by the fact that the observed D_{DOM} values at pH 9 (log $D_{DOM} \approx 3.8$ for both TBT and TPT) were significantly larger than the K_{DOM} values estimated for the respective TOT−OH species from their K_{ow} value (3.3 and 2.7, respectively, see Table 1). Note that K_{DOM} could, in principle, be determined at higher pH values, but such pH values are outside the domain of the stability of the dialysis membranes.

The K_i values determined for TBT and TPT from modeling of the sorption isotherms according to eqs 1−9 are reported in Table 1. Using the fitted K_i values, the concentration of the binding sites and K_{Na} values determined by titration, and K_{DOM} values estimated from K_{ow}, the D_{DOM} value of TBT or TPT can be calculated for any pH and Na^+ concentration. As is obvious from Figure 4, at 10 mM $NaClO_4$, the model provides a very good fit to the experimental data. In addition, as shown in Table 3 for TBT, the model could successfully predict D_{DOM} values determined at higher ionic strength (using a K_{Na} value determined by titration, i.e., independently of D_{DOM}).

Inspection of the K_i values obtained for TBT^+ and TPT^+ (Table 1) shows that these complexation constants are several orders of magnitude larger than K_{Na} and that, in contrast to what was observed for Na^+, the constants increase with increasing pK_{ai} of the acidic sites, L_iH_{DOM}. These results are a consistent with those of Mikami and Taki (*28*), who found that the complexation constant of TPrT with low molecular weight carboxylic acids in aqueous solution was linearly dependent on their pK_a value. These findings suggest that TOTs in contrast to Na^+ might form innersphere complexes with the carboxylate and phenolate moieties of AHA.

Useful information on the effect of hydrophobicity on the AHA−water partitioning of the TOT^+ species can be gained from the data presented in Figure 5. The logarithms of the apparent AHA−water distribution ratios of the TOT^+ species (i.e., D_{DOM}/α_{TOT^+}) determined at pH 5.8 are plotted against the log K_{ow} values of the corresponding neutral TOT−OH species [which are, in turn, linearly correlated with the log K_{ow} of the cations (*44*)]. For the trialkytin compounds, a good linear correlation between the logarithm of the respective parameters is found:

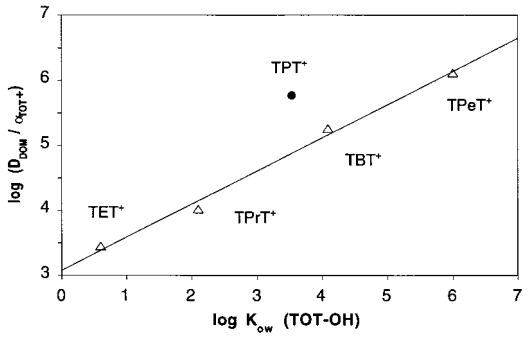

FIGURE 5. Effect of hydrophobicity on the AHA−water distribution of TOTs. Plot of log(D_{DOM}/α_{TOT^+}) determined at pH 5.8 and 10 mM $NaClO_4$ versus log K_{ow} of the corresponding TOT−OH species. The result of the regression analysis is given by eq 10.

$$\log\left(\frac{D_{DOM}}{\alpha_{TOT^+}}\right) = 0.51 \log K_{ow}(TOT-OH) + 3.1 \quad (R^2 = 0.993) \quad (10)$$

Comparison of the slope of the linear free energy relationship eq 10 with the slopes of similar equations derived for the sorption of organic compounds to natural organic matter or mineral phases suggests that the L_i-TOT_{DOM} complexes are only partly removed from the aqueous phase. This conclusion is based on the fact that, for the hydrophobic partitioning of neutral pollutants into POM or DOM, slopes close to 1.0 have been observed, whereas for the nonspecific adsorption to mineral surfaces much smaller slopes have been found (*1*). Nevertheless, hydrophobic interactions play still an important role in determining the overall D_{DOM} of a given TOT.

The second striking feature in Figure 5 is that, as compared to the trialkyltin cations, TPT^+ exhibits a significantly higher affinity to AHA than expected from its hydrophobicity. This finding can be rationalized by the fact that, as indicated by its lower pK_a value (see Table 1), TPT^+ is expected to form stronger complexes with oxygen ligands than trialkyltin ions. Hence, the enhanced sorption of TPT^+ supports the hypothesis that TOT^+ species might form innersphere complexes with the oxygen ligands present in AHA. Note, however, that due to their macroscopic nature, partitioning experiments only provide hints but no final proof on the type of binding mechanism(s).

Generalization of the Results Obtained with AHA: Sorption of TBT to SRHA and Comparison with Literature Data. Figure 6 summarizes the results of the experiments conducted to investigate the sorption of TBT to SRHA. The shape of the pH dependence was very similar to that observed for AHA, demonstrating that, as for the sorption to AHA, complexation of TBT^+ dominated the association with SRHA. Compared to AHA, two significant differences were observed: (i) D_{DOM} values increased with increasing TBT concentration (see insert in Figure 6), and (ii) they were approximately 5−10 times lower than for AHA. Since sorption isotherms determined with ultrafiltrated and predialyzed SRHA were similar to those obtained with untreated SRHA, artifacts due to incomplete retention of low molecular weight SRHA constituents in the dialysis chamber can be excluded. Both differences might be explained by hydrophobic effects. Because of the small size and polarity of its constituents (see Table 2), SRHA is to a lesser degree than AHA able to adopt a molecular conformation that permits removal of neutral compounds (e.g., uncharged pollutants or L_i-TBT_{DOM} complexes) from the aqueous phase (*46*). Thus K_{DOM} values of neutral pollutants with SRHA have been shown to be 10−20

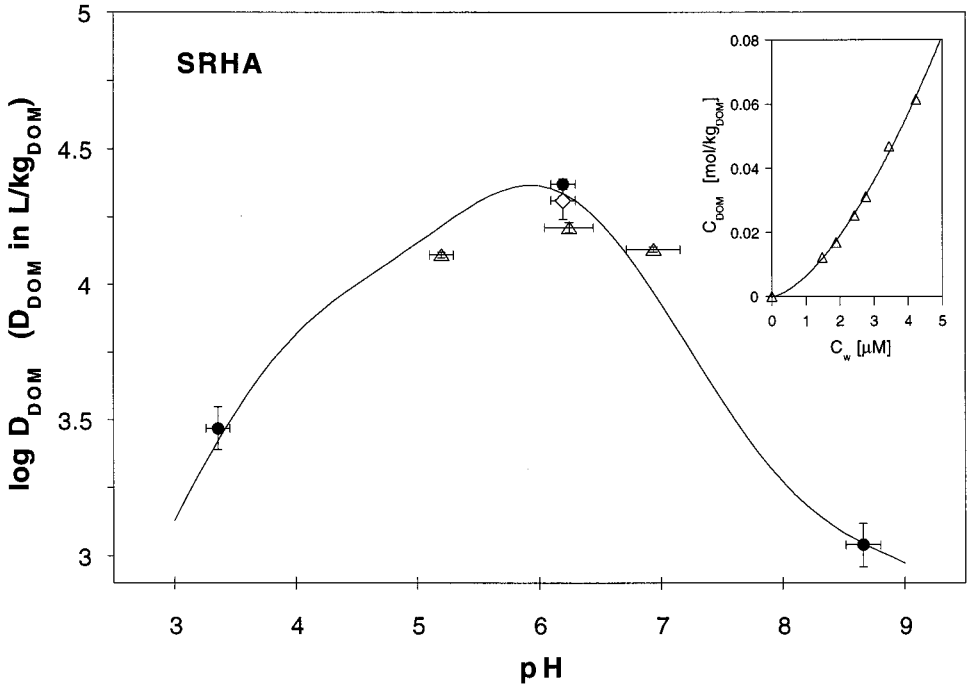

FIGURE 6. SRHA−water distribution ratio (D_{DOM}) of TBT at various pH, 10 mM $NaClO_4$, and 5 μM TBT_{aq} concentration. D_{DOM} were determined with untreated (●), ultrafiltrated (△), and predialyzed (◇) SRHA. The lines were calculated using the model described by eqs 1−9, using log K_i values of 3.63, 4.59, and 6.29 for the formation of L_1−TBT_{DOM}, L_2−TBT_{DOM}, and L_4−TBT_{DOM}, respectively (note that sites described by K_3 do not contribute significantly to the overall D_{DOM}); log K_{DOM} = 2.1, see text. The insert shows a typical sorption isotherm (ultrafiltrated SRHA, pH 6.2).

times smaller than those with AHA [i.e., log K_{DOM}(SRHA) ≈ log K_{DOM}(AHA) − 1.2, see refs *4* and *47*]. This decrease in hydrophobic interactions as compared to AHA is reflected in the 7−10 times smaller complexation constants of K_i obtained for SRHA (see caption of Figure 6) than for AHA (see Table 1). Therefore, despite of the larger abundance of binding sites in SRHA, smaller D_{DOM} values are observed. The nonlinearity of the sorption isotherms might be related to a significant modification of the SRHA constituents by bound TBT molecules, e.g., by aggregation of SRHA molecules, i.e., formation of SRHA molecules of larger apparent molecular weight. This hypothesis is supported by the observed precipitation of SRHA in a TBT-saturated aqueous solution. However, the effect of the association of hydrophobic organometallic compounds such as TOTs on the properties of humic acids is largely unknown and requires further research.

Comparison with Literature Data. As addressed in the Introduction, to date, very little data are available on DOM−water partitioning of TOTs. Similarly, studies on the POM−water partitioning of TOTs are very scarce. In addition, because key parameters such as pH, ionic strength, or presence of DOM were often neglected, the number of meaningful comparisons is very restricted. Nevertheless, as shown in Table 3, POM−water partition coefficients reported for various environmental conditions are consistent with D_{DOM} values calculated for AHA under the same solution conditions. Finally, sediment−water distribution ratios determined for TBT for organic-rich sediments from freshwater (*21*) and estuarine (*24*) environments show qualitatively a very similar pH dependence to that observed in Figures 4 and 6, suggesting that complexation of TBT^+ species by deprotonated organic matter ligands is responsible for the sorption.

In summary, it has been shown that the sorption of TOTs to DOM (and possibly POM) is dominated by the complexation of TOT^+ species by carboxylate and phenolate groups of the natural organic matter. Even though under environmental conditions the effect of other cations such as Ca^{2+} and Mg^{2+} has to be considered, the speciation of TOTs can be roughly estimated as a function of pH and DOM concentration using eqs 1−9 and the constants reported in Tables 1 and 2. As an example, in Figure 7, the aqueous

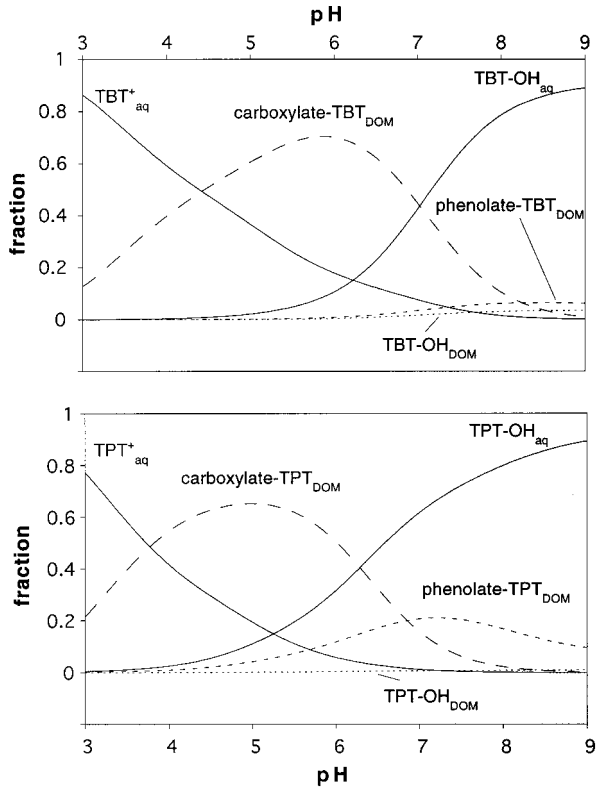

FIGURE 7. Calculated TBT and TPT speciation as a function of pH in an aqueous solution containing 20 mg/L dissolved AHA and 10 mM $NaClO_4$.

speciation of TBT and TPT is calculated as a function of pH for a DOM concentration typical for interstitial water of soils and sediments (20 mg/L). As is obvious, depending on the pH value, between 10 and 70% of the TOTs in the aqueous phase are bound to DOM. The results of such calculations provide a basis for assessing the transport, reactivity, and bioavailability of TOTs in the environment.

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