Dynamic Sorptive Behavior of Tributyltin on Quartz Sand at Low Concentration Levels: Effect of pH, Flow Rate, and Monovalent Cations

MAÏTÉ BUENO,[†] ANNETTE ASTRUC,[†]
MICHEL ASTRUC,[†] AND
PHILIPPE BEHRA*,[‡]

Laboratoire de Chimie Analytique, Université de Pau et des Pays de l'Adour, LCBIE, EP CNRS 132, Helioparc, 2 Avenue du Président Angot, 64000 Pau, France, and Institut de Mécanique des Fluides, UMR 7507 Université Louis Pasteur-CNRS, 2 rue Boussingault, 67000 Strasbourg, France

The highly toxic organotin compounds which have been used as biocides in ship antifouling paints have been introduced into aquatic ecosystems. Among them, tributyltin (TBT) is the most important organotin compound which has been produced on the largest scale. Understanding its fate in the environment is therefore of primary importance to prevent its migration. TBT sorption from aqueous solutions was studied at much lower concentrations (10 nM to 2 μM) than those used in previous studies. Experiments were performed using column reactors filled with a quartz sand. The influence of physicochemical parameters on TBT partitioning, i.e. ionic strength, pH, and nature of electrolyte cation was investigated. Equilibrium times were short as TBT retention appeared to be independent of the mean pore velocity. TBT sorption was affected strongly by the pH and slightly by the ionic strength of the solution. Competitions with monovalent alkaline cations showed a small influence of Li^+, Na^+, K^+, Rb^+, with respect to Cs^+ on TBT retardation. Moreover, the injection of two different TBT concentrations accounted for the nonlinearity of TBT sorption. The theory of nonlinear chromatography was used for the calculation of convex adsorption isotherms. Retardation factors and distribution coefficients were estimated.

Introduction

Due to their extensive use in various areas of human activity, large amounts of organotin compounds have been and, despite some regulations, are still introduced in aquatic ecosystems. Most of them, and particularly trisubstituted ones, are highly toxic (*1*). Organotin cations consist of a central Sn atom linked to organic substituent groups, thus phenomena controlling their liquid−solid partitioning should depend on both the cationic and hydrophobic characteristics of these compounds.

The tri-*n*-butyltin cation (TBT^+ or TBT) is the most important organotin compound which has been producing on the largest scale. Its fate in the environment is therefore of primary importance. Degradation processes leading to the less toxic products are slow in the aqueous phase and very slow after transfer to the sedimentary phase (half-life times of some years) (*2*−*4*). A very large number of papers deal with pollution due to organotins in marine systems, a few with their sorptive behavior in coastal marine environments or freshwater systems (*5*−*15*) but none with their transfer from surface freshwaters to aquifers.

Champ and Bleil (*9*) concluded that, TBT sorption process being reversible, contaminated sediments could act as sources for the water column. Values of the distribution coefficient K_d were evaluated by a number of authors (*5*−*16*). They vary by several orders of magnitude (6−2.9×10^5 L kg^{-1}) depending probably on water salinity and sediment mineralogy. Positive or negative salinity effects have been reported (*9*−*12*) as well as pH influence (*11*, *12*). Sun et al. (*8*) proposed an ion exchange mechanism with little influence of lipophilic partitioning for eight organotins and estuarine sediments. The lack of precise definition of the solid phases in these studies prevents from establishing general conclusions.

Batch equilibrium sorption studies have been conducted with pure solid phases such as silica, clays, or alumina and much higher TBT concentration (0−150 μM and 0.05−2.5 M, respectively, for refs *17* and *18*). Weidenhaupt et al. (*17*) indicated a specific sorption of TBT^+ onto surface sites. No information on the kinetic aspects of the sorption−desorption process was given. Dowson et al. (*13*) simulated estuarine and freshwater conditions using iron oxide as particulate matter. They observed that TBT sorption was considerably higher with this model substrate compared with natural particulate matter. This remark points out that it is necessary to identify relevant mechanisms in order to understand this discrepancy and then to predict the TBT behavior in natural conditions.

At the difference of all previous investigations, this study was conducted using an open flow-through reactor (column) which more closely represented some relevant field conditions during water transfer to aquifers from surface waters (*19*, *20*). At the cost of the lengthy experiments the kinetic aspects may be examined and adsorption−desorption data obtained in a single run by using methods borrowed from nonlinear chromatography (*20*−*22*). Furthermore, it allows to access the reversibility of mechanisms without artifacts due to disturbance of the solid phase (*21*). This method has already been used sometimes to study the sorption of trace metal species (*22*−*27*).

The sorbent used was a quartz sand very similar to a natural aquifer material. Using a very sensitive analytical procedure, TBT sorption was studied at initial concentrations much lower than those of previous works (by a factor of ca. 200). Desorption was even studied down to extremely low aqueous concentrations (ca. 10 nM), i.e. in the upper range of TBT concentrations found in some lake or river waters. The effect of hydrodynamic, chemical, and physicochemical parameters such as mean pore velocity, TBT concentration, ionic strength, pH, and nature of electrolyte cations was investigated in order to better understand the retention of organotin compounds at laboratory scale. The next step will be to model their transport and fate in soil and subsoil compartments.

Experimental Section

Sorbent Material. Column experiments were carried out with a quartz sand provided by ≪Quartz d'Alsace≫ Company in Kaltenhouse (near Strasbourg, France). This sand was a natural product which was washed, sieved, and dried at 105

* Corresponding author phone: 33 (0) 388 416 563/565; fax: 33 (0) 388 614 300; e-mail: behra@imf.u-strasbg.fr.
† Laboratoire de Chimie Analytique.
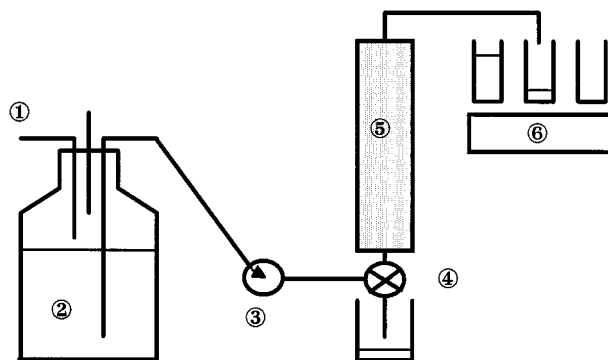‡ Institut de Mécanique des Fluides.

FIGURE 1. Experimental column setup: 1, nitrogen flow; 2, solution reservoir; 3, peristaltic pump; 4, three-way valve; 5, filled column; 6, fraction collector.

°C by the manufacturer and was not submitted to any chemical purification or treatment. A geochemical study indicated that the sand contains 99% SiO_2, 1% potassic feldspars, 1‰ mineral clays (among: kaolinite, illite), and traces of Al, Fe, and Mn (hydr)oxides (23). Grain size distribution showed a polydisperse distribution with a characteristic diameter $d_{10} = 430$ μm (23). BET (Kr, 77 K) measurements indicated a specific surface area $a = 0.16$ m² g⁻¹ (28). The pH of point of zero charge (pH_{pzc}) was determined by potentiometric titrations to be around 6 (29). This value appeared quite high for a quartz surface which exhibits usually much lower pH_{pzc} values (between 2 and 3). This was attributed to the presence of low surface concentrations of Fe and Al which were observed after surface characterization of the sand by X-ray Photoelectron Spectroscopy (XPS): 0.3% of the total Fe and 7−10% of the total Al present in surface. This sand was then used without any preliminary treatment.

Reagents. Solutions were buffered with 0.001 M imidazole (Merck, >99%), pH being adjusted at desired values with dilute nitric acid or sodium hydroxide (Merck) solutions. The interaction of imidazole with the sand surface was verified, showing the same behavior as a tracer. Lithium and potassium nitrates (Prolabo), sodium nitrate (Fluka), and rubidium or cesium nitrates (Aldrich) were used to adjust the ionic strength and pretreat the sand before TBT injection. For sorption experiments, tributyltin chloride (Merck, 96%) concentration was adjusted by successive dilutions with Milli-Q water (Millipore, 18.2 MΩ) of a 8.42 mM TBT solution in methanol stored at 4 °C in the dark. In these conditions this stock solution was stable for several months (30). A methanolic stock solution of TBT was used because of the very low TBT solubility in water. Working aqueous TBT solutions contains therefore 0.01 or 0.025% (v/v) methanol. Preliminary experiments (data not reported) showed that these low methanol concentrations have no detectable effect on TBT sorptive behavior.

Column Experiments. The experimental device shown in Figure 1 was made of Teflon and glass as these materials had demonstrated by preliminary experiments to be non-adsorptive toward TBT in the conditions used and not to leach butyltin compounds. Experiments were conducted at room temperature (20 ± 2 °C).

The sand was packed into a 20 cm length, 2.5 cm inner diameter glass chromatography column wrapped with an aluminum foil to protect TBT from photolytic degradation. The outflow was monitored for conservative tracer experiments (calcium nitrate, Merck, 99−103%) with a UV/vis flow-through detector at $\lambda = 215$ nm (Varian UV-50), to determine column characteristics such as pore volume (V_p) and porosity (ϵ). Typical column parameters were 39 mL pore volume and 0.36 porosity, for 170 g sand mass.

The column was first filled with Milli-Q water into which the sand was slowly added. It was then washed by Milli-Q water until a stable outlet pH value was obtained. A TBT free solution of adjusted pH and ionic strength was then added until equilibrium was reached (typically 30 V_p of effluent). A TBT solution in the same electrolyte was then introduced at constant flow rate till steady-state was reached. Elution of sorbed TBT was then performed with a TBT free aqueous phase. The column effluent was sampled during the two last steps by a fraction collector; pH was measured, flow-rate controlled, and TBT concentrations determined by Hydride Generation Quartz Furnace Atomic Absorption Spectrometry (HGQFAAS).

Analytical Procedure. HGQFAAS has been selected due to its high sensitivity (detection limits in the low pM range) and ability to detect eventual degradation or transformation of TBT to other species. The analytical apparatus has been previously described in detail elsewhere (31). Subsample volumes of 5−0.1 mL were analyzed as follows. Organotin hydrides were generated by the addition of 10 mL of a 10% sodium borohydride solution to an acetate buffer. They were then carried out by a flow of helium to a short glass chromatographic column (packed with Chromosorb W-HP, 10% OV101) cooled in liquid N_2, where they are trapped during 5 min. After removing the cooling bath, electrical heating of the column selectively volatilized the hydrides in a He flow carrying them into an electrically heated (950 °C) quartz furnace placed in the light beam of the atomic absorption spectrophotometer ($\lambda = 286.3$ nm).

Quantification was performed using tripropyltin (TPT) as an internal standard with a relative standard deviation evaluated to 7%. Overall quality control of the method was made by analyzing all available Certified Reference Materials (PACS-1 Harbor sediment, CRM 462 marine sediment, NIES CRM 11 «fish tissue») and participation to several European Certification exercises.

Experimental data are shown in the form of breakthrough curves, either C or $C/C_0 = f(V/V_p)$, where C is the total TBT concentration measured in each effluent fraction, V the volume eluted since the beginning of the injection of TBT, and C_0 the inlet TBT concentration.

Results

The influence of mean pore velocity (u), inlet TBT concentration (C_0), ionic strength (I), pH, and the nature of the background electrolyte cation was successively studied (Figures 2−5). All through these experiments, TBT was the only species of tin detected. This point indicated that the sorption−desorption mechanism did not involve any degradation of TBT that could occur during the establishment of sorbent−sorbate bonds during the sorption step.

The adsorption front combines two fronts: a first part which is sharp and the second part which is more diffuse especially at low concentration (Figures 2 and 3). The desorption curve shows a full diffuse desorption front, which reaches a final outlet TBT concentration of about 1−3% C_0 (i.e. 10−30 nM). Mass balances were calculated as the difference between the breakthrough data of the conservative tracer and TBT for each experiment and for both adsorption and desorption fronts. The amounts of sorbed and released TBT showed that the TBT sorbed onto the sand was quantitatively eluted, that is sorption phenomena involved were fully reversible (see Tables 1 and 2). Furthermore, the reproducibility of an entire experiment was verified by performing twice three of them. The relative standard deviation obtained from material balances was always below 10%.

Effect of Mean Pore Velocity. Sorption experiments were performed for three different mean pore velocity values, 0.05, 0.5, and 5 cm min⁻¹, with a 0.84 μM TBT sorbate solution,
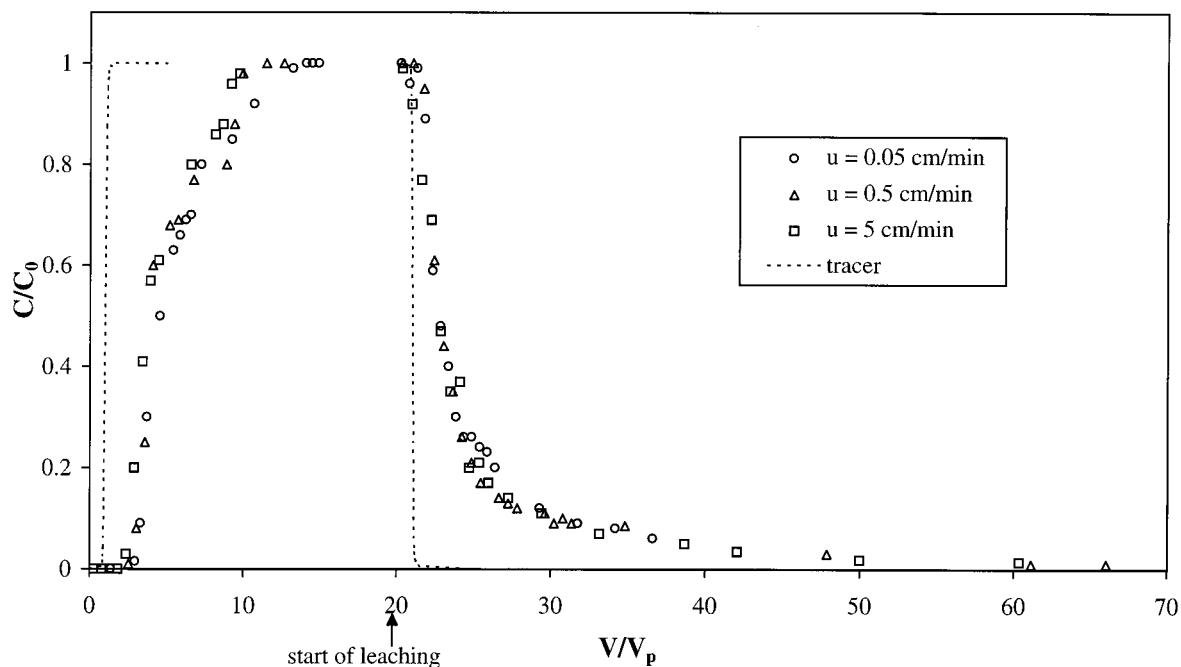
FIGURE 2. Effect of mean pore velocity on breakthrough of TBT (I = 0.1 M NaNO$_3$, pH = 8, TBT concentration = 0.84 μM); for comparison, tracer breakthrough is given (dashed line).
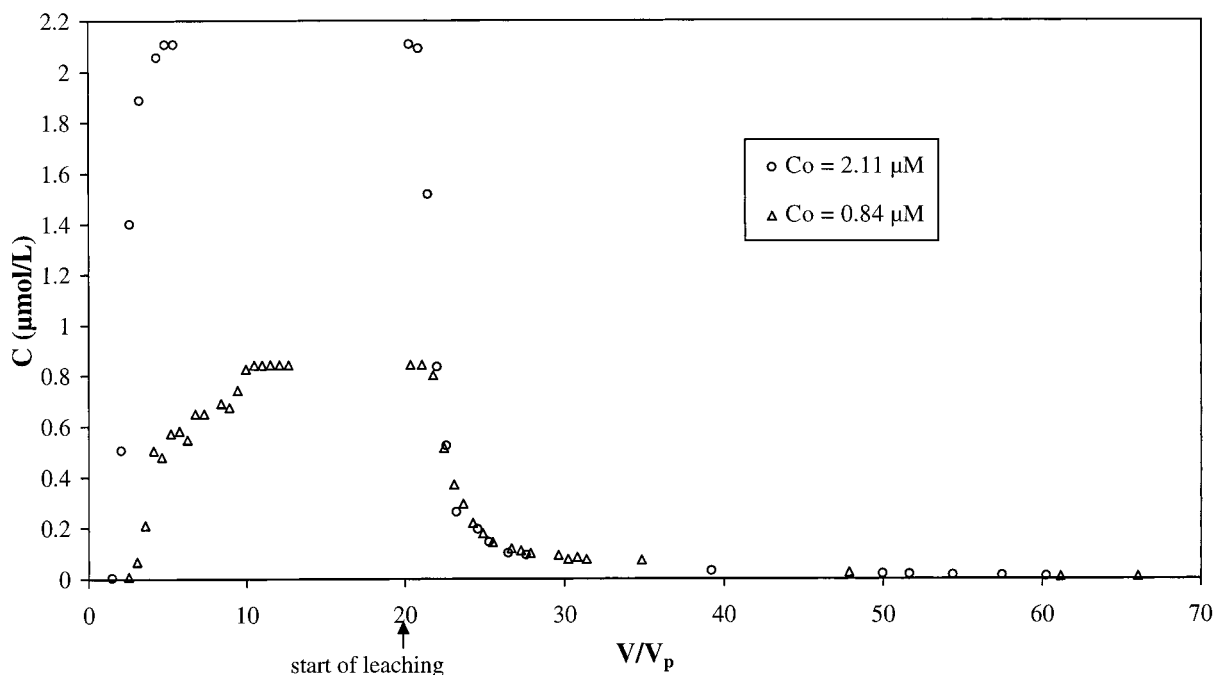

FIGURE 3. Effect of TBT concentration on breakthrough of TBT (I = 0.1 M NaNO$_3$, pH = 8, u = 0.5 cm min^{-1}).

and ionic strength (I) fixed at 0.1 M by NaNO$_3$ and pH = 8. The three breakthrough curves (Figure 2) were superimposed, which indicates that the sorption equilibrium was reached at the experimental time scale. In other words there was no kinetic effect in the range of the mean pore velocities studied. The following experiments were therefore conducted at a mean pore velocity of 0.5 cm min^{-1}.

Effect of Physicochemical Parameters. Experiments were run using two different initial concentrations of TBT (0.84 or 2.11 μM) buffered at pH = 8 and I = 0.1 M (NaNO$_3$). It appeared that the retardation of the sorption fronts (Figure 3) depended on the initial concentration, whereas the desorption fronts were diffuse and broad. In a (C, V/V_p) coordinate system, desorption curves superimpose inde-

pendently of the input concentration when C reaches 0.84 μM during the concentration decrease. This behavior typically indicates a nonlinear TBT sorption (21, 22).

Using a 0.84 μM TBT solution at pH = 8, ionic strength was adjusted with 0.1, 0.01, or 0.001 M NaNO$_3$. The breakthrough curves obtained indicate that the lower the ionic strength, the greater the retention of TBT (Figure 4). The mass balances were 0.77, 1.03, and 1.33 nmol g^{-1} for 0.1, 0.01, and 0.001 M ionic strength, respectively. The difference in the mass balances indicates an increase of 34% and 55% when mass balances obtained at 0.1 M ionic strength are compared to those obtained at 0.01 and 0.001 M, respectively.

The effect of pH on TBT (0.84 μM) was studied between pH 2 and 10, in the presence of 0.001 M imidazole, at I = 0.1
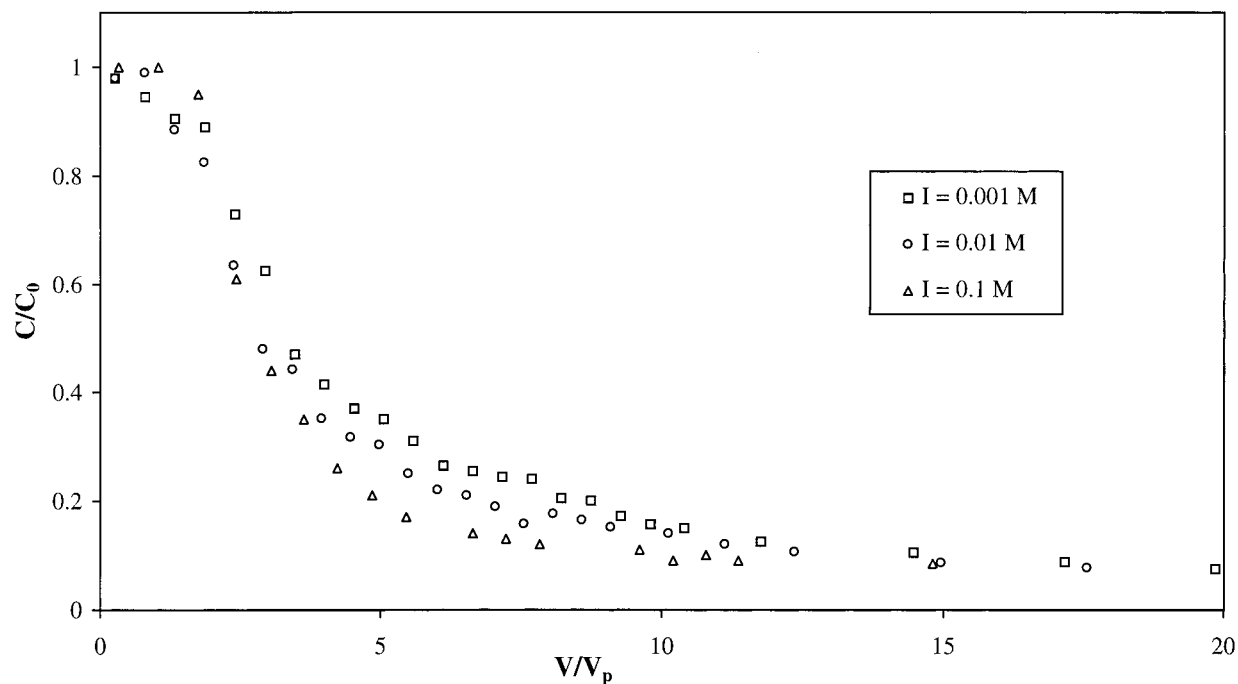
FIGURE 4. Effect of ionic strength on breakthrough of TBT (TBT concentration = 0.84 μM, pH = 8, u = 0.5 cm min^{-1}), only a part of the desorption curves are presented (desorption was run during 90 V/V_p).

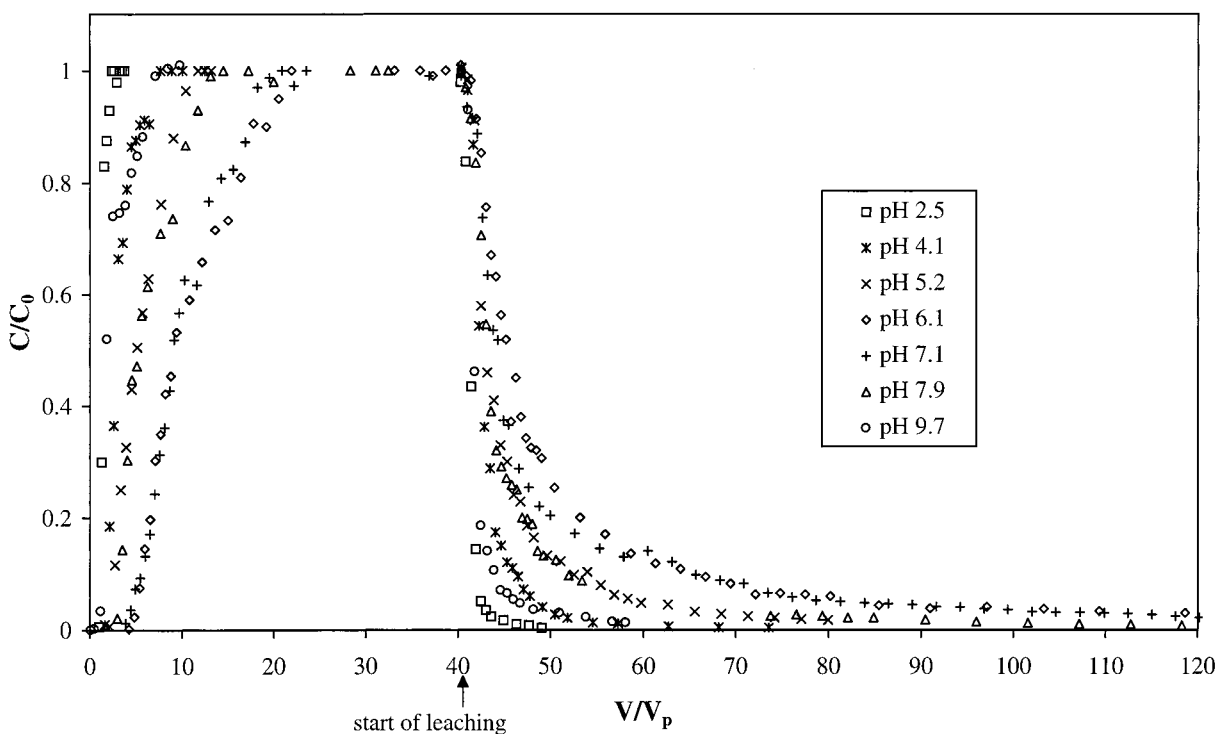FIGURE 5. Effect of pH on breakthrough of TBT (I = 0.1 M NaNO$_3$, TBT concentration = 0.84 μM, u = 0.5 cm min^{-1}).

M (NaNO$_3$) (Figure 5). The TBT retention is maximum between pH 6 and 7, that is close to the pK_a of TBT which is 6.25 (*32*). It steeply decreases for both higher and lower pH values (see Table 1) which is different from that of inorganic cations which display an abrupt sorption increase in a narrow field of 1−2 pH units (*33*).

Sorption competition between TBT and monovalent cations was studied with the series of alkaline cations: Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$. Experiments were performed at pH = 6, which allowed maximum adsorption of TBT as seen above, with 0.84 μM TBT solutions and a 0.1 M concentration

of alkaline cation. As shown in Table 2, concentrations of sorbed TBT are not significantly different using Li$^+$, Na$^+$, K$^+$, or Rb$^+$, the mean value for TBT retention being 2 ± 0.2 nmol g^{-1} corresponding to a relative standard deviation of 9% below the reproducibility value. On the other hand, TBT retention decreases when the electrolyte competing cation is Cs$^+$ with a 20% mass balance reduction.

Adsorption Isotherms. Because local sorption equilibria may be assumed at the time scale of the experiments, the theory of nonlinear chromatography can be used to interpret the results (*20−22*). The diffuse desorption front contains

TABLE 1. Mass Balances and Langmuir-Type Parameters Calculated from the Set of pH Column Experiments[a]

| | TBT sorbed[b] (nmol g^{-1}) | | | | Langmuir parameters | | |
pH	adsorption front	desorption front	R^c	r^d	S_{max} (nmol g^{-1})	K_L (L μmol^{-1})	K'_d (L m^{-2})
2.5	0.08	0.08	1.4	0.987	0.09	17.1	9.6 10^3
4.1	0.42	0.44	3.3	0.987	0.37	13.2	30.5 10^3
5.2	0.86	0.88	5.6	0.998	0.90	11.2	63.0 10^3
6.1	1.80	1.88	10.9	0.999	1.91	11.6	13.8 10^4
7.1	1.80	1.72	10.4	0.999	1.88	13.2	15.5 10^4
7.9	0.93	0.94	6.1	0.997	0.91	19.3	10.9 10^4
9.7	0.32	0.28	2.7	0.984	0.33	17.2	35.5 10^3

[a] See Figure 5; injected TBT concentration = 0.84 μM and I = 0.1 M NaNO$_3$. [b] These values are enclosed by a margin error corresponding to the reproducibility, i.e. 10%. [c] R: retardation factor. [d] r is correlation coefficient of isotherm equation.

TABLE 2. TBT Concentration Sorbed as a Function of Background Electrolyte Cation[a]

| | TBT sorbed[b] (nmol g^{-1}) | | |
background cation	adsorption front	desorption front	retardation factor R
Li$^+$	2.19	2.11	13.2
Na$^+$	1.80	1.88	10.9
K$^+$	1.91	1.98	11.2
Rb$^+$	2.09	2.02	12.6
Cs$^+$	1.60	1.49	10.0

[a] Injected TBT concentration = 0.84 μM, pH $\approx$ 6, and I = 0.1 M. [b] These values are enclosed by a margin error corresponding to the reproducibility, i.e. 10%.

the information necessary to calculate the adsorption isotherm which represents the concentration of solute adsorbed vs equilibrium aqueous concentration of solute. The desorption curves ended in an asymptotic decline such that zero TBT concentration would never be reached for the duration of experiments and for the given conditions. To establish a worthwhile comparison in a set of experiments, the sorption isotherm was calculated from desorption curves corresponding to the same number of eluted pore volumes (i.e. 90 V/V_p). The integration of the desorption front, as described by Schweich and Sardin (21) and Bürgisser et al. (22), provides a convex isotherm, $C_{ads} = f(C)$ (Figure 6). In a log(C_{ads}) vs log(C) plot (data not shown), the isotherm consists of two parts: at low concentrations the slope is one, and it decreases at higher TBT concentration, indicating saturation of some reactive sites. For all experiments good correlation coefficients are obtained when data are plotted in Langmuir-type coordinates, i.e. $1/C_{ads}$ vs $1/C$ (see Table 1). The relationship between the adsorbed and the aqueous TBT concentrations may therefore be calculated at equilibrium by

$$C_{ads} = S_{max} \frac{K_L C}{1 + K_L C} \quad (1)$$

where K_L is the Langmuir-type constant, C the total aqueous concentration of TBT, C_{ads} the total sorbed concentration of TBT, and S_{max} the equivalent of maximum surface site concentration for experimental conditions.

For low concentrations, $C \ll 1/K_L$, C_{ads} approximates $S_{max}K_L C = K_d C$ where K_d is the distribution coefficient as defined from a linear adsorption isotherm. For a better comparison with other sorbent materials, this coefficient has to be expressed as $K'_d = K_d/a$, in L m^{-2} (17). Values of the parameters K_L, K'_d, and S_{max} are given in Table 1 for the set of pH experiments. Moreover, retardation factors, R, which

were calculated from mass balances (Tables 1 and 2), express the delay of TBT elution relative to the tracer one, caused by sorption. For a column experiment, R is defined when steady-state is reached as

$$R = 1 + \frac{C_{tot,ads}}{C_0} \frac{m_S}{V_P} \quad (2)$$

where m_S is the sand mass packed in the column, C_0 the initial concentration of TBT in the injected solution, and $C_{tot,ads}$ the total sorbed concentration of TBT.

Discussion

The sorbent used is a natural aquifer material submitted to little pretreatment. Studied TBT concentrations (10 nM−2 μM) range down to values close to those found in some freshwater systems. Studying very low adsorbate concentrations is necessary especially when natural solids are used instead of high purity chemicals. Indeed several sorption mechanisms may be involved simultaneously, and each of them may take more or less importance at low concentrations.

As reported by studies making use of natural sediments (9−10, 34) or well-defined materials (17), TBT sorption decreases with increasing ionic strength which is often interpreted as a competition between TBT$^+$ and the electrolyte cation. However Langston and Pope (11) observed first a decrease at low to intermediate salinities and the reverse effect at high salinities in estuarine conditions. As a matter of fact, in high salinity solutions, the formation of the neutral TBTCl species (35) may lead to a different sorption mechanism consistent with the behavior of hydrophobic compounds. In this study, ionic strength was quite low (0.001−0.1 M) and fixed by nitrate salts. Since nitrates do not form a stable complex with TBT, log K = 0.62 (32), the change in ionic strength do not affect the speciation of TBT in our conditions (at pH 8). The proportion of TBT$^+$ form is thus the same for the set of experiments. The observed effect is then consistent with the behavior of a metal cation which compete with the electrolyte cation, Na$^+$, for the available adsorption sites.

No significant differences were observed in this work when Li$^+$, Na$^+$, K$^+$, or Rb$^+$ was used as a competing cation, whereas the presence of Cs$^+$ had a non-negligible negative effect on TBT sorption (minus 20%). This is somewhat different of results recently obtained by Weidenhaupt et al. (pH = 4, I = 0.001 M of chloride salt and a homoionic kaolinite) (17), who reported a TBT sorption decrease in the sequence Na$^+$ > K$^+$ ~ Rb$^+$ > Cs$^+$ corresponding to the Hofmeister series which accounts for the affinity of ions to most clays and oxide surfaces (33). This affinity sequence depends on the hydrated cation size increasing in the series Cs$^+$, Rb$^+$, K$^+$, Na$^+$, and Li$^+$. In this work, TBT initial concentration was 5 orders of magnitude lower than that of the competing alkaline cation. This concentration variation could explain that no significant effect was observed with Li$^+$, Na$^+$, K$^+$, and Rb$^+$ on TBT retention. On the other hand, the competition is more pronounced in the presence of Cs$^+$, whose hydrated radius is the smallest, indeed calculated binding coefficients to montmorillonite have showed a selectivity for Cs$^+$ 2 orders of magnitude greater than for Li$^+$, Na$^+$, and K$^+$ (36).

TBT sorption onto the natural quartz sand used appears to be strongly pH dependent. This behavior has also been observed in batch studies for natural estuarine sediments (11) and for silica and homoionic clay minerals (17). TBT retention steeply decreases at pH values above and below pH ~ 6. In this pH domain two distinct phenomena occur: the protonation−deprotonation of surface hydroxyl-groups (pH$_{pzc}$ = 6) and the hydroxylation of TBT (pK_a = 6.25). The experimentally observed behavior of TBT is similar to what
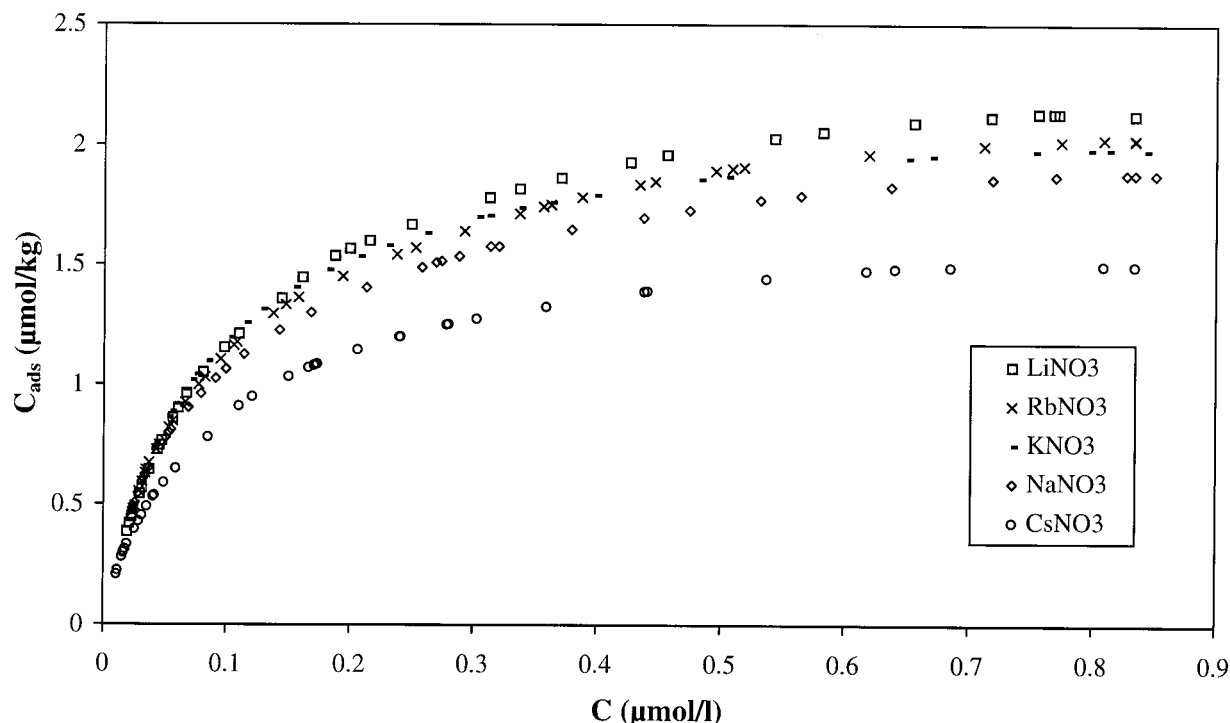
FIGURE 6. Effect of background electrolyte cation on TBT sorption (pH = 6, TBT concentration = 0.84 μM, u = 0.5 cm min^{-1}, background electrolyte concentration = 0.1 M). Sorption isotherms were derived from desorption front of column experiments.

has already been observed for the sorption of weak acid or organic bases such as aminonaphthalene and quinoline onto silica or subsurface materials ([37], [38]) suggesting a cationic adsorption mechanism as the major step of the binding process. TBT reactivity toward silica, studied by FTIR spectroscopy, showed a specific interaction between TBT and OH surface groups ([18]). Weidenhaupt et al. modeled TBT sorption at much higher concentrations (0−150 μM) by assuming formation of surface complexes between TBT$^+$ and deprotonated surface hydroxyl groups or neutral surface sites and neglecting the possible role of neutral TBT species ([17]).

The TBT species that may be present in the electrolyte solution consist of TBT$^+$, TBTOH, TBTCl, TBTNO$_3$, and a complex with imidazole used as buffer compound. The affinity of TBT$^+$ cation for OH$^-$ is 6 orders of magnitude greater than that for Cl$^-$ (log K_{Cl} = 0.60 ([35])), so that as total chloride concentration is very low in our experiments (0.84 μM), the TBTCl moiety can be neglected. The stability constant of the TBT−imidazole complex is very low (log K = 3.91 ([39])). Thus, TBT sorption could be mainly modeled by surface complexation of the TBT$^+$ cation with surface hydroxyl groups. The hypothesis of a cationic mechanism of TBT sorption onto surface sites is also consistent with the negative effect produced by the increase of ionic strength from 0.001 to 0.1 M at pH 8 and the competition for cation exchange sites with the electrolyte cation.

TBT partitioning is well described by the Langmuir-type isotherm indicating a saturation of sorptive sites for the given experimental conditions. Such behavior has also been observed for Na-kaolinite ([17]) and various suspended solids (bentonite, humic acids, ferric hydroxide) ([34]). Leguille et al. evaluated the maximal TBT adsorption capacity of these solids to quite low values, much lower than those found for metal cations ([34]). The natural quartz sand used for this study mainly consists of SiO$_2$ (99%) but also contains some impurities such as clays and Fe, Al, Mn (hydr)oxides. Moreover, from the point of view of transfer through a natural material, the retardation factor, R, which is around 10 for natural pH domain (pH 6−8), is relatively high for a material which does not contain too much highly sorptive compounds.

As a conclusion of this discussion it appears that the surface complex model which involves cation exchange between TBT$^+$, H$^+$, and the monovalent background electrolyte cation, and takes into account the aqueous speciation of TBT, could be used to model its sorption. The necessary determination of the nature and reactivity of adsorbing sites involved could be attempted using various pretreatments of the porous matrix, extracting different trace minerals from the sand as described by Behra ([23]).

Literature Cited

(1) Fent, K. *Crit. Rev. Toxicol.* **1996**, *26*, 1.
(2) Sarradin, P. M.; Lapaquellerie, Y.; Astruc, A.; Latouche, C.; Astruc, M. *Sci. Tot. Environ.* **1995**, *170*, 59.
(3) Stewart, C.; de Mora, S. J. *Environ. Technol.* **1990**, *11*, 565.
(4) Dowson, P. H.; Bubb, J. M.; Lester, J. N. *Environ. Monit. Ass.* **1993**, *28*, 145.
(5) Champ, M. A.; Bleil, D. F. *Research Needs Concerning Organotin Compounds Used in Antifouling Paints in Coastal Environments*; U.S. Department of Commerce, Rockville, 1988.
(6) Valkirs, A. O.; Seligman, P. F.; Lee, R. F. *Oceans* **1986**, *4*, 1165.
(7) Kram, M. L.; Stang, P. M.; Seligman, P. F. *Appl. Organomet. Chem.* **1989**, *3*, 523.
(8) Sun, H.; Huang, G.; Dai, S. *Chemosphere* **1996**, *33*, 831.
(9) Unger, M. A.; MacIntyre, W. G.; Hugget, R. J. *Oceans* **1987**, *4*, 1381.
(10) Unger, M. A.; MacIntyre, W. G.; Hugget, R. J. *Environ. Toxicol. Chem.* **1988**, *7*, 907.
(11) Langston, W. J.; Pope, N. D. *Mar. Pollut. Bull.* **1995**, *31*, 32.
(12) Harris, J. R. W.; Cleary, J. J. *Oceans* **1987**, *4*, 1370.
(13) Dowson, P. H.; Bubb, J. M.; Lester, J. N. *App. Organomet. Chem.* **1993**, *7*, 623.
(14) Stang, P. M.; Seligman, P. F. *Oceans* **1987**, *4*, 1386.

(15) Watanabe, N.; Takatsuki, H.; Sakai, S. *App. Organomet. Chem.* **1997**, *11*, 273.

(16) Tolosa, I.; Merlini, L.; de Bertrand, N.; Bayona, J. M.; Albaigés, J. *Environ. Toxicol. Chem.* **1992**, *11*, 145.

(17) Weidenhaupt, A.; Arnold C.; Müller, S.; Haderlein, S. B.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1997**, *31*, 2603.

(18) Ballivet-Tkatchenko, D.; Dos Santos, J. H. Z.; Malisova, M. *Langmuir* **1993**, *9*, 3513.

(19) Schweich, D.; Sardin, M.; Gaudet, J.-P. *Soil Sci. Soc. Am. J.* **1983**, *47*, 32.

(20) Griffioen, J.; Appelo, C. A. J.; VanVeldhuizen, M. *Soil Sci. Soc. Am. J.* **1992**, *56*, 1429.

(21) Schweich, D.; Sardin, M. *J. Hydrol.* **1981**, *50*, 1.

(22) Bürgisser, C. S.; Cernik, M.; Borkovec, M.; Sticher, H. *Environ. Sci. Technol.* **1993**, *27*, 943.

(23) Behra, Ph. Ph.D. Thesis, Louis Pasteur University, Strasbourg, 1987.

(24) Saiers, J. E.; Hornberger, G. M. *J. Contaminant Hydrol.* **1996**, *22*, 255.

(25) Grolimund, D.; Borkovec, M.; Federer, P.; Sticher, H. *Environ. Sci. Technol.* **1995**, *29*, 2317.

(26) Meeussen, J. C. L.; Scheidegger, A.; Hiemstra, T.; van Riemsdijk, W. H.; Borkovec, M. *Environ. Sci. Technol.* **1996**, *30*, 481.

(27) Allen, H. E.; Chen, Y. T.; Li, Y.; Huang, C. P.; Sanders, P. F. *Environ. Sci. Technol.* **1995**, *29*, 1887.

(28) Alnot, M. CNRS−Université Henri Poincaré, Nancy, personal communication, 1995.

(29) Douch, J. Université Louis Pasteur-CNRS, Strasbourg and Agadir University, personal communication, 1997.

(30) Desauziers, V. Ph.D. Thesis, University of Pau, 1991.

(31) Pannier, F. Ph.D. Thesis, University of Pau, 1994.

(32) Arnold, C. G.; Weidenhaupt, A.; David, M. M.; Müller, S. R.; Haderlein, S. B.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1997**, *31*, 2596.

(33) Stumm, W.; Morgan, J. J. *Aquatic Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1996.

(34) Leguille, F.; Castetbon, A.; Astruc, M.; Pinel, R. *Environ. Technol.* **1993**, *14*, 949.

(35) Laughlin, R. B.; Guard, H. E.; Coleman, W. M. *Environ. Sci. Technol.* **1986**, *20*, 201.

(36) Nir, S.; Hirsch, D.; Navrot, J.; Banin, A. *Soil Sci. Soc. Am. J.* **1986**, *50*, 40.

(37) Zachara, J. M.; Ainsworth, C. C.; Felice, L. J.; Resch, C. T. *Environ. Sci. Technol.* **1986**, *20*, 620.

(38) Zachara, J. M.; Ainsworth, C. C.; Cowan, C. E.; Schmidt, R. L. *Environ. Sci. Technol.* **1990**, *24*, 118.

(39) Shoukry, M. M. *Bull. Soc. Chim. Fr.* **1993**, *130*, 117.