Environ. Sci. Technol. **1998**, *32*, 232−237

Dialysis Investigations of Atrazine-Organic Matter Interactions and the Role of a Divalent Metal

ERIN C. DEVITT AND MARK R. WIESNER*

Department of Environmental Science and Engineering
MS-317, Rice University, P.O. Box 1892,
Houston, Texas 77251-1892

Contamination of surface and groundwaters by atrazine is a problem for water utilities in the United States and Europe. Though not removed by traditional liquid-solid separation, it is removed by nanofiltration. Retention of atrazine by a series of dialysis membranes was investigated over a range of solution chemistries with the goal of better understanding how the solution matrix may influence atrazine retention by membranes. Atrazine was significantly retained by membranes with molecular mass cut-offs less than 500 Da in the presence of natural organic matter (NOM), presumably by association with NOM. Atrazine retention was independent of the initial concentration. Solution chemistry was important in determining the extent of atrazine retention. Where NOM aggregation and hence NOM retention increased, atrazine retention decreased, and vice versa. Atrazine retention tended to decrease at higher ionic strengths. This effect was significantly stronger with divalent calcium than with monovalent sodium. Partitioning coefficients calculated here are much higher than values reported from experiments of atrazine retention by soil organic matter. It is speculated that the most likely mechanism of atrazine retention by NOM is through association of atrazine with interior adsorption sites on the NOM molecule by transitory hydrogen bonding and subsequent physical entrapment.

Introduction

Contamination of surface and groundwaters by herbicides such as atrazine is a problem for water utilities both in the United States (*1*) and in Europe (*2*). In the American Midwest, agricultural runoff seeping into groundwaters threatens to push concentrations of atrazine beyond the U.S. drinking water maximum contaminant level (MCL) of 3 μg/L. Surveys of the lower Kansas River basin and other drainage basins in the midwestern United States have detected atrazine in at least 95% of the samples collected from streams, reservoirs, and major rivers after spring application to cropland, frequently at concentrations above the MCL (*1*, *3*). The problem is also a great concern in the European Union where an MCL of 0.1 μg/L has been set.

Nanofiltration has been proposed as one means of removing atrazine from source waters. Removals of 80 to more than 95% have been reported using a variety of commercial membranes (*4*−*6*). Data from a recent pilot study in which a surface water was treated by nanofiltration suggest atrazine removal increased as the natural organic matter (NOM) concentration in the feed water rose (*4*). The work presented in this paper was motivated by a desire to understand how atrazine interactions with NOM may affect atrazine transport across semipermeable membranes. We present results from dialysis experiments designed to investigate atrazine retention by dialysis membranes as a function of a variable solution matrix which included NOM and electrolytes.

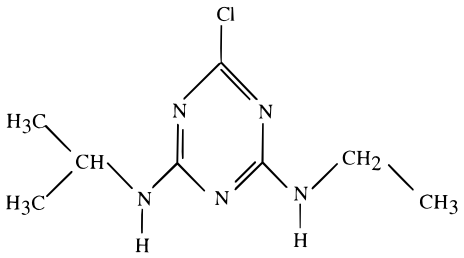

FIGURE 1. Chemical structure of atrazine.

Background. Atrazine is a triazine herbicide (Figure 1) which is both moderately soluble (38 mg/L at 22 °C) and moderately hydrophobic (log K_{ow} = 2.3−2.7). It is not significantly protonated at pH values two units or more above its pK_a of approximately 1.7. Thus, atrazine is significantly protonated (by addition of a hydrogen at the *p*-nitrogen position) only at very low pH (<∼3.7), but may be prone to a slightly polar character in aqueous solutions. Welhouse and Bleam observed four conformational isomers of atrazine due to delocalization of lone-pair electrons on the side-chain nitrogens into the triazine ring, allowing restricted rotation of the side chains (*7*). This charge separation "creates conditions favorable for hydrogen-bonding interactions involving either the acidic NH protons of the alkylamino side chains or the basic lone-pair electrons on the triazine ring, or both." This is more pronounced in polar solvents. Previous investigations have considered interactions between triazines and NOM, primarily in the context of a soil or soil extract matrix (*8*−*10*). The main degradation products of atrazine are hydroxyatrazine (HYA), deisopropylatrazine (DIA), and deethylatrazine (DEA). The primary mode of abiotic degradation is hydrolysis to HYA, shown to be catalyzed by the presence of organic matter (*8*).

Calculated heats of adsorption and formation constants (between atrazine and organic molecules) as well as NMR and IR spectrophotometry evidence strongly suggests that one, if not the primary, mode of interaction between the weakly polar atrazine molecule and NOM is hydrogen bonding (*9*−*12*). Such bonds are weak, typically implying reversibility of the atrazine-NOM association. Nonetheless, NOM (from soil and sediment) appears to have a substantial influence on the transport and fate of atrazine and other micropollutants in surface and groundwater (*13*−*17*).

NOM is composed of an extremely diverse group of materials, including carbohydrates, alcohols, amino acids, carboxylic acids, lignins, and pigments, whose origin greatly influences its character and behavior. Though various fractions of NOM can be defined by operational procedures for separating organic matter from water, a general structural characterization can never be determined as the exact NOM composition varies greatly as a function of NOM source, aqueous solution conditions, season, etc. It is therefore reasonable to assume that NOM−micropollutant interactions may vary as a function of properties of different NOM fractions and origins.

Due to the great variability in NOM, numerous experimental surrogates have been proposed including rigorously

* Author to whom correspondence should be addressed. Fax: (713) 285-5203; email: wiesner@rice.edu.

S0013-936X(97)00179-X CCC: $15.00 © 1998 American Chemical Society
Published on Web 01/15/1998

characterized fractions of reference NOM, tannic acid, salicylic acid, and others. In this work, the interaction between atrazine and NOM is examined using NOM concentrated from a surface water and tannic acid and salicylic acid serving as NOM surrogates.

Experimental Section

Materials. Radiolabeled atrazine (C^{14}, specific activity 7.8 Ci/mol) was purchased from Sigma Chemical Co. (St. Louis, MO). Radiolabeled naphthalene (1,4,5,8-C^{14}, specific activity 55.9 Ci/mol) was purchased from Isotopchim (France). High concentration stock solutions of atrazine and of naphthalene were prepared. In all cases, concentrations of atrazine and naphthalene were measured by scintillation counter and reported in units of micrograms per liter.

Three types of organic matter were used in our experiments: NOM from the Oise River, tannic acid, and salicylic acid. Tannic acid has been used as a NOM surrogate in several previous membrane-related research efforts due in part to its relatively low cost, which allows for continuous flow experiments at various scales. Tannic acid has many of the drawbacks of commercially available "humic acids", however it is a lower molecular mass fraction of material and may be a more representative surrogate for NOM. Consensus in the literature is that low molecular mass fulvic acids typically make up the majority of the humic substances in water. The choice was made within that context. Salicylic acid was chosen because it is a simple, unbranched molecule with a functional group (phenolic) in common with the tannic acid which could be used to test the possibility of a strong chemical interaction between the functional groups on the organic matter and the atrazine. If the atrazine chemically bonded through charge transfer, it would be retained with the salicylic acid. The experimental evidence reported here suggests that this is not the case.

A concentrated stock solution of NOM from the Oise River at Méry-sur-Oise, France, was prepared by Bernard Legube and co-workers at the Université de Poitiers Laboratoire Chimie de l'Eau et des Nuisances. It was filtered to remove suspended materials and concentrated by two-stage nanofiltration, distillation, and a cycle of evaporation and redilution (to remove salts) from approximately 3 mg/L total organic carbon (TOC) to a final concentration of 2500 mg/L TOC. This stock solution was later rediluted to the desired NOM concentrations. Some alteration of the organic matter in the water was inevitable, but dead-end filtration comparisons using grab samples compared rather favorably with respect to size distribution and adsorptive capacity, though there was a small shift in distribution (*18*). Dead-end, or "frontal" filtration occurs with flow orthogonal to the membrane surface. At 7.50 mg/L TOC, the rediluted Oise water had a calcium concentration of 210 mg/L, alkalinity was 575 mg/L as $CaCO_3$, and hardness was 625 mg/L as $CaCO_3$.

Powdered tannic acid (average composition $C_{76}H_{52}O_{46}$) from EM Science (Gibbstown, NJ) and salicylic acid ($C_7H_6O_3$) from Sigma Chemical Co. (St. Louis, MO) were used as "model" NOM surrogates. Tannic acid had a reported formula weight of 1701, which presumably corresponds to an average. Solutions of these compounds were prepared by adding water to the dry powder and stirring to dissolve the organic matter. In all cases, concentrations of organic matter were measured by a TOC Analyzer (Shimadzu, Japan) and UV absorbance at 254 nm calibrated to direct measurements of TOC and reported in units of milligrams per liter of TOC.

Experimental Solution Preparation. Three types of solutions were used in these experiments: free atrazine, atrazine in the presence of organic matter, and atrazine in the presence of organic matter with elevated salt concentration. The free atrazine solutions were prepared by dilution of a small measure of the atrazine stock solution in ultrapure water. To prepare the atrazine and NOM solutions, concentrated Oise water or one of the powdered NOM surrogate compounds was added to ultrapure water to achieve the desired TOC concentration. Atrazine stock solution was then added. In the cases where the salt concentrations were altered, this was accomplished by the addition of either calcium as calcium nitrate or sodium as sodium nitrate to the atrazine-organic matter solution. The initial TOC concentration was maintained at or around 7.50 mg/L (detection limit = 0.5 mg/L) and the initial atrazine concentration ranged from 1.3 to 2.2 μg/L (detection limit = 0.1 μg/L). Atrazine retention of less than 10% was at or below the detection limit at these initial concentrations and was not statistically significant.

The prepared solutions were placed in foil-covered containers (to prevent atrazine degradation from exposure to light) and stirred for 24 h. The 24 h equilibration period was chosen based on protocol used by earlier researchers (*19*) and our own preliminary studies (data not presented here).

Experimental Dialysis Procedure. Dialysis was accomplished using a simple apparatus consisting of a solution-filled dialysis bag, suspension bath, and stir plate. Spectra/Por CE dialysis tubing (Spectrum, Los Angeles, CA) was rinsed and then soaked for 30 min in ultrapure water. This process removed the sodium azide preservative in which the membranes were stored. The 3 orders of magnitude spanned by the molecular mass cutoffs (MWCOs) of the membranes used in these experiments (100, 500, 1000, 5000, 10 000, and 50 000 Da) roughly correspond to molecular masses in the NF and ultrafiltration (UF) ranges.

Dialysis bags were made by clamping the ends of a segment of tubing with Spectra Por Closures (also from Spectrum). Before the second end was clamped shut, a volume of the prepared test solution (5−8 mL) was pipetted into the bag. The dialysis bags were suspended in foil-covered Spectra/Por Dialysis Reservoir baths filled with ultrapure water adjusted to an ionic strength equal to that of the test solutions pipetted into the dialysis bags. During 4 days of dialysis, the baths were continuously stirred and changed daily to maintain a maximal concentration gradient across the membrane. As with the solution equilibration procedure, the 4 day dialysis time period was chosen based on protocol used by earlier researchers (*13*) and our own preliminary studies (data not presented here). Equilibration was virtually complete at 1−2 days.

At the end of 4 days, the dialysis bags were emptied and the contents' volume and final TOC and atrazine concentrations were measured. Preliminary experiments indicated no significant loss to sorption on the membrane. Percent retention (% retention) is calculated as the percent of the initial mass retained by the membrane:

$$\%\ \text{retention} = 100\left(1 - \frac{m_p}{m_o}\right) = 100\left(\frac{m_c}{m_o}\right) = 100\left(\frac{C_c V_c}{C_o V_o}\right) \quad (1)$$

where m_p, m_o, and m_c are the mass which permeated the membrane, the original mass in the sample, and the mass measured in the dialysis bag after four days, respectively. C_o and C_c are the concentrations measured in the original sample solution and the liquid remaining in the dialysis bag at the end of each experiment, respectively. V_o and V_c are the volumes of solution initially placed in the dialysis bag and that remaining after 4 days. In most cases, these volumes were virtually identical.

Results and Discussion

Retention of Atrazine in Electrolyte Solution. Dialysis of 70 μg/L atrazine in ultrapure water showed no statistically

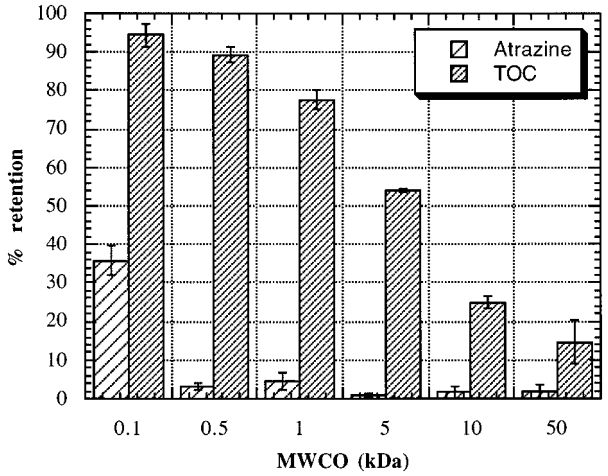

FIGURE 2. Atrazine and TOC retention in the presence of NOM as a function of MWCO.

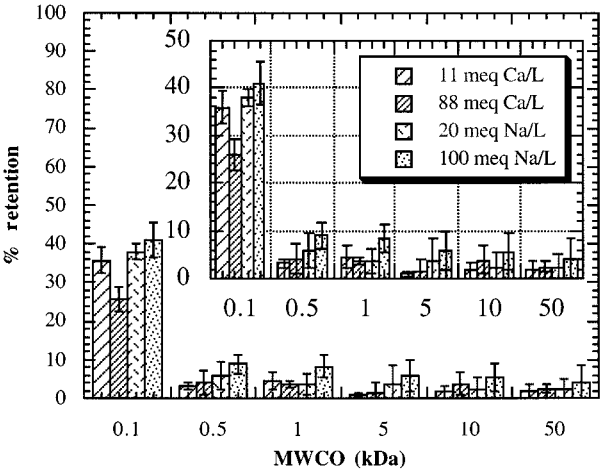

FIGURE 3. Retention of atrazine in the presence of NOM at two calcium and two sodium concentrations.

significant retention of atrazine over the range of MWCOs investigated. Similarly, atrazine was not retained with dialysis bags in solutions of 11 mequiv/L Ca as calcium nitrate or 20 mequiv/L Na as sodium nitrate. In all cases, over 95% of the atrazine was accounted for with mass balances on the retained and permeated fractions (in the bag and in the bath as well as on the membranes). No significant sorption of atrazine by the cellulose ester dialysis membranes or other surfaces was seen.

Retention of Atrazine in the Presence of NOM. In contrast with the free passage of atrazine through dialysis membranes observed in solutions made from ultrapure water or ultrapure water with electrolytes, significant retention of atrazine was observed in solutions of Oise water NOM. In all cases mentioned herein, "NOM solutions" refer to solutions made of reconstituted Oise water NOM. These experiments were run in triplicate with an initial NOM concentration of 7.50 mg/L TOC and an initial atrazine concentration of 1.27 μg/L. Only the 100 Da membrane retained atrazine (36%) in the presence of Oise NOM (Figure 2). On the basis of the molecular mass distribution of NOM, estimated by observing retention of TOC in dialysis, the atrazine retained was associated solely with the smallest size fraction of NOM retained ($100 \leq x \leq 500$ Da). Retention of Oise NOM ranged from 94% at 100 Da to 15% at 50 000 Da. If the atrazine were influenced to a significant degree by the larger size fractions, significant atrazine retention would have been expected at the larger MWCOs.

Retention of atrazine in the presence of NOM suggested that increased retention of NOM might enhance the retention of atrazine associated with NOM. NOM retention can often be enhanced by increasing the ionic strength of the solution. At higher ionic strengths (i.e., electrolyte concentrations), NOM molecules tend to coil up (*20*). Repulsion between functional groups on the NOM may be reduced due to charge shielding and neutralization and result in shrinking of individual NOM molecules while increasing their hydrophobicity, making them more likely to form aggregates. Aggregation increases the apparent molecular mass of the NOM and reduces its permeability through membranes.

Experiments with atrazine and NOM at higher ionic strength did, in some cases, exhibit greater retention of NOM. However, atrazine retention decreased rather than increased where NOM retention increased. In these experiments, Oise NOM and atrazine concentrations were kept constant and the calcium concentration was elevated from its background concentration of 11−88 mequiv/L. Experiments were also performed in which the sodium concentration was elevated to either 20 or 100 mequiv/L. With elevation of the calcium concentration, atrazine retention by the 100 Da membrane dropped from 36 to 26% (Figure 3). Retention remained insignificant at all other size fractions. As anticipated, retention of NOM remained constant or was moderately increased at the higher ionic strength. Enhanced NOM retention was most evident in experiments using dialysis membranes with MWCOs of 5000 and 10 000 Da; retention increased from 54 and 24% to 82 and 43%, respectively.

The sodium adjusted systems showed no statistically significant change in retention of atrazine in the presence of NOM over the entire MWCO range when compared with the background case (Figure 3). NOM retention increased slightly at the 500−5 000 Da pore sizes, while the largest (10 000 and 50 000 Da) and smallest (100 Da) fractions remained constant.

These data suggest that a reduction in atrazine retention may be due to changes in the conformation and charge of the organic matter produced as calcium concentration increases. The higher the functional group content of an organic molecule, the greater its ability to sorb organic pollutant (*10*, *12*) and the more open its conformation. Addition of calcium may shield NOM's anionic charge. When associated with NOM macromolecules, calcium ions may reduce the number of potential interaction sites available to atrazine and promote coiling of NOM molecules which would have the effect of further restricting access to interior sorption sites. This is supported by atrazine-humic acid adsorption data reported by Li and Felbeck (*8*). They observed the adsorption capacity of atrazine on humic acid in an ethanol solution to be 29.41 μmol/200 mg of humic acid. Saturation of the humic acid with calcium reduced this value to 4.06 μmol/200 mg of humic acid.

While calcium appeared to moderately depress atrazine retention and enhance NOM retention, the effects of calcium in the NOM concentrate are difficult to discern due to the manner in which the NOM concentrate was obtained. The nanofiltration membranes used to obtain the NOM concentrate also rejected calcium, resulting in a considerable intrinsic calcium concentration associated with the Oise NOM, 11 mequiv Ca/L at 7.50 mg/L TOC. Thus, it was not possible to conduct experiments where the effects of NOM could be evaluated independently from the calcium.

To circumvent this problem, experiments were done using tannic acid and salicylic acid as surrogate NOM molecules. Although these two compounds differ considerably from one another, the functional groups and associated pK_as are similar to those reported for hydrophobic fractions of NOM. However, salicylic acid, unlike tannic acid and NOM, is not

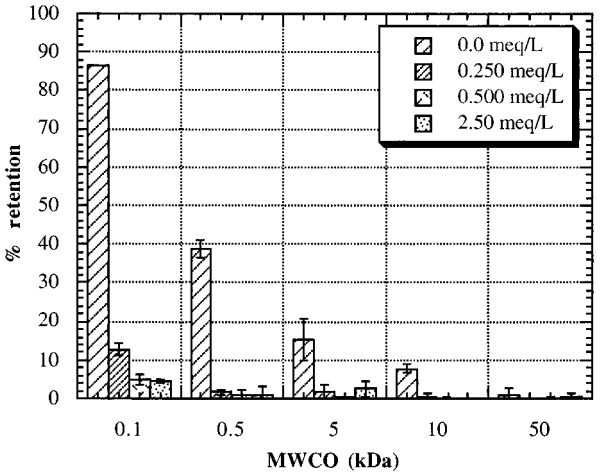

FIGURE 4. Retention of atrazine in tannic acid solution as a function of calcium concentration.

a branched molecule and does not undergo conformational changes with pH and ionic strength.

Retention of Atrazine in the Presence of NOM Surrogates. Trends in TOC and atrazine retention observed in experiments with NOM substitutes were mirrored or amplified in the experiments where NOM was replaced with tannic acid. Unlike the NOM and tannic acid, atrazine in salicylic acid solutions passed freely through all of the dialysis membranes.

The tannic acid experiments were run in duplicate with an initial NOM concentration of 7.49 mg/L TOC and an initial atrazine concentration of 2.21 μg/L. One thousand dalton MWCO membranes were not used in these experiments. As with the Oise NOM, retention of atrazine in the presence of tannic acid was negligible for membranes with high MWCOs. However, by comparison with results obtained in NOM solutions, the percent retentions of atrazine by the 100 Da membrane (86%) and the 500 Da membrane (38%) were significantly higher for the tannic acid solutions (Figure 4, 0.0 mequiv Ca/L case). Similar to the NOM, retention of atrazine was associated with the smallest size fraction ($100 \leq x \leq 500$ Da), but it was also associated with the second smallest size fraction ($500 \leq x \leq 5\,000$ Da). Retention of TOC ranged from 52% at 100 Da to 7% at 50 000 Da. It is particularly noteworthy that the atrazine was retained by the dialysis membranes in the presence of tannic acid (or NOM) over long periods of time (some dialysis experiments were allowed to run for more than twice as long and no significant increase in dialysis was observed), despite regular replacement of the dialysis bath with clean water (or electrolyte). Thus, atrazine appeared to partition irreversibly out of the free aqueous "phase" and into the tannic acid (or NOM) phase.

Comparing atrazine retention in the presence of tannic acid to its retention in the presence of the Oise water, it is clear that the tannic acid enhanced atrazine retention relative to the Oise NOM. This may be due in part to differences in the character of NOM and tannic acid macromolecules. It may also reflect the influence of salts, such as calcium, in the Oise NOM concentrate. Subsequent experiments involving the addition of calcium or sodium to tannic acid solutions resulted in similar, but more pronounced trends as those observed with Oise NOM solutions.

In the tannic acid experiments, run in duplicate, calcium nitrate was added to increase the calcium concentration by 0.25, 0.50, or 2.5 mequiv/L Ca. Background calcium in these solutions was negligible in all cases. As the calcium addition rose from 0.0 (in the first tannic acid experiment) to 0.25 mequiv/L, atrazine retention at 100 Da showed a sharp initial change, dropping from 86 to 13%. Larger increases in calcium produced marginally larger reductions in atrazine retention, decreasing to insignificance at 0.50 mequiv/L (Figure 4). In all cases, no statistically significant retention of atrazine was observed at 500 Da and higher MWCOs in the presence of calcium.

TOC retention increased substantially at all MWCOs, except the smallest, with the initial addition of 0.25 mequiv/L calcium, followed by a more gradual rise as the calcium concentration rose another order of magnitude to 2.5 mequiv/L, particularly at high molecular masses. TOC retention rose from 52 to 60% at 100 Da, but at 10 000 and 50 000 Da, it rose from 13 to 52% and from 7 to 47%, respectively. Increased retention of tannic acid by the higher MWCO membranes with calcium addition strongly suggests aggregation of these macromolecules.

Addition of sodium to the tannic acid solutions produced similar, though less pronounced, trends in atrazine and tannic acid retention. Sodium concentration was elevated to either 20 mequiv/L or 100 mequiv/L by addition of sodium nitrate. Initial NOM and atrazine concentrations in these experiments were 5.34 mg/L TOC and 1.06 μg/L, respectively. Dialysis was performed using 100 and 500 Da MWCO membranes. A 20 mequiv/L addition of sodium lowered atrazine retention from 86 to 28% with the 100 Da membrane and from 36 to 25% with the 500 Da membrane. Marginally greater reductions of 18% at 100 Da and 10% at 500 Da were obtained when the electrolyte concentration was increased to 100 mequiv/L Na. Just as atrazine retention was less depressed (than in the calcium case) by addition of sodium, TOC retention was not as greatly elevated. At 20 and 100 mequiv/L Na, respectively, TOC retention stayed relatively unchanged at 52 and 55% at 100 Da and 32 and 34% at 500 Da.

If the atrazine were being retained by sorption to NOM molecules, some of this observed irreversible retention would likely be due to sorption of HYA. HYA should be not only the dominant byproduct, but the byproduct most likely to be bound (*21*). HYA's much higher pK_a (4.8) makes it prone to forming significant charge transfer complexes either by mixed-mode mechanisms like those proposed by Lerch and co-workers (*22*), or other, similar processes.

While a portion of the atrazine will likely degrade to HYA, it cannot account for the majority of the apparent atrazine retention. Li and Felbeck measured the degradation of atrazine (60 μmol/L) to HYA by acid-catalyzed hydrolysis in the presence of 2000 mg/L muck soil humic acid (*23*). We calculate a first-order rate constant for atrazine degradation to HYA ($\log K_{observed} = 12.3 - 3.84(1/T \times 10^3)$, $r^2 = 0.955$, where T is absolute temperature) from data taken at 12, 25, and 40 °C, pH 4. At 28 h (the incubation time plus the time in which the bulk of the atrazine and NOM dialyzing occurred in the course of the experiment) and 22 °C, the estimated degradation to HYA would be 22%. Degradation would be even less at the neutral pHs used in these experiments.

Even if the tannic acid in this system were more reactive than the humic acid in Li's and Felbeck's experiments and if it is assumed 44% would be hydrolyzed to hydroxyatrazine and that all of this were to form charge transfer complexes and irreversibly sorb to the tannic acid molecules, there would still be another 40% unaccounted for in the atrazine with tannic acid case.

Salicylic acid data indicates that the interaction between organic matter and atrazine is not simple chemical bonding between functional groups on the organic matter and atrazine or atrazine byproducts. In contrast with the trends observed using NOM and tannic acid, atrazine was not retained by any of the dialysis membranes when present in solutions of salicylic acid. Salicylic acid concentrations ranged from 3 to 10 mg/L TOC and initial atrazine concentrations were 0.90 μg/L. Approximately 65% of the salicylic acid was retained

by the 100 Da membrane. None of the remaining membranes retained salicylic acid. Addition of 11 mequiv/L Ca had no statistically significant effect on either atrazine retention or TOC retention.

Tannic acid and salicylic acid have qualitatively similar functional groups. However, salicylic acid is very small and geometrically simple, while over 40% of the geometrically complex tannic acid was seen to have an apparent molecular mass of 500 Da or larger. No salicylic acid was retained at this pore size or larger. The lack of significant retention of atrazine in the presence of salicylic acid suggests that chemical interactions, such as hydrogen, covalent, or ionic bonding, or hydrophobic interactions alone cannot account for the observed "irreversible" sorption of the atrazine to organic molecules.

One explanation for the free passage of atrazine through dialysis membranes in the presence of salicylic acid is that the more branched structures of tannic acid and NOM mechanically trap atrazine within these macromolecules. However, subsequent experiments, in which atrazine was replaced with a nonpolar microcontaminant, suggested that physical entrapment alone was equally unsatisfactory in describing atrazine−NOM interactions. Molecular conformations and weak interactions between functional groups may combine to produce physical entrapment of atrazine through a low multiplicative probability of escape resulting from a large number of encounters with low-energy sites on the tannic acid molecule (e.g., hydrogen bonding).

Retention of Naphthalene in the Presence of a NOM Surrogate. If physical trapping alone was the controlling mechanism, weakly polar and neutral micropollutants should be sorbed to similar degrees. To test this, the neutral molecule naphthalene was substituted for the weakly polar atrazine molecule and the previous experiments with tannic acid were repeated. In these experiments, the tannic acid concentration was elevated to 57.7 mg/L TOC and the naphthalene concentration was set at 3.1 μg/L. Calcium concentration was varied as before and sodium concentration was varied from 0.22 to 2.2 mequiv/L. The experimental conditions included naphthalene in water, naphthalene in the presence of tannic acid alone, and naphthalene in the presence of tannic acid with calcium or with sodium. In no case was naphthalene retained by any of the membranes.

These data suggest that the difference in ionic character between atrazine and naphthalene, weak polarity versus nonpolarity, may be a significant factor in their interaction with organic matter. As naphthalene is a neutral species, its interactions with the organic macromolecules should be largely limited to hydrophobic sorption. Physical trapping alone does not seem to be responsible for the atrazine-organic matter interactions. The fact that atrazine is retained, while naphthalene is not, suggests that polar interactions are needed to attract atrazine to interaction sites within the macromolecule where it can become physically constrained.

To explain the observed interactions between atrazine and dissolved organic material, the role of divalent ions in reducing atrazine retention by dialysis membranes as well as the apparent "irreversibility" of the atrazine "sorption" on NOM must be accounted for. These results suggest a model in which atrazine−NOM interactions are governed by a sequence of chemical associations between atrazine and NOM followed by a physical entrapment of atrazine within NOM molecules. As previously cited (*9*−*12*), hydrogen bonding appears to be the most likely mechanism of chemical interaction between atrazine and NOM. Paradoxically, the heat of formation of an atrazine−organic matter complex is reported to be small −8−13 kcal/mol (*8*). These small values are consistent with hydrogen bonding and so do not explain the apparent irreversibility of atrazine-NOM partitioning observed in our experiments.

TABLE 1. Retention of Atrazine as a Function of Concentration in the Presence of 7.38 mg/L Tannic Acid as TOC and 0.33 mM Ca

atrazine retention	C_o (μg/L)	C_e (μg/L)	q_e (μg/kg om)
14%	3.8	3.2	7.1×10^4
17%	7.1	5.9	1.6×10^5
15%	10.6	9.0	2.2×10^5
15%	13.5	11.5	2.7×10^5

Senesi and Testini have reported some evidence for electron donor-acceptor processes producing charge transfer complexes between humic acids and other *s*-triazines as significant binding mechanisms (*10*, *12*). While this may be true for some *s*-triazines, it is not likely true for the case of atrazine. One important difference in these studies as compared with atrazine is that their relative solubilities and pK_as were much higher. For example, both of these previous studies used Prometone and Methoprotryne, whose solubilities are 750 and 320 mg/L and whose and pK_as are 4.3 and 3.03, respectively. These solubility and pK_a values are all an order of magnitude higher than those of atrazine. This makes them much more likely to form ionic and covalent bonds than the atrazine molecule, which is much less polar in character and does not protonate significantly in the neutral pH range; this lack of ionic character is supported by the salicylic acid data. Rather, it is hypothesized that association of atrazine with interior functional groups on the complex organic molecule via hydrogen bonds may increase its likelihood of becoming physically constrained, trapped within the organic matrix.

Weak interactions through transitory hydrogen bonds may increase the time these molecules (atrazine and organic matter) associate and the intimacy of the interaction with charged sites within the matrix. This more prolonged, intimate interaction with the narrow interiors of the smaller branched organic molecules may significantly decrease its ability to back-diffuse out of the interior, physically constraining it within the matrix. When the much larger organic matter molecules are retained by the membrane, so too is the atrazine trapped within.

The addition of calcium may restrict association of atrazine and NOM by occupying interaction sites and/or reducing access to sites by changing molecular conformation, closing the organic molecules so atrazine is not as prone to close association with the interior either by a lack of bonding opportunity or by its inability to permeate the matrix.

Partitioning Behavior of Atrazine. As previously mentioned, one striking aspect of these observations is the apparent "irreversibility" of the atrazine−NOM partitioning. It appears that this partitioning as well as its reversibility is strongly influenced by the operational procedure used to separate "free" atrazine from the macromolecule-bound fraction. By varying the atrazine-to-TOC ratio under conditions of constant pH and electrolyte strength, partition coefficients can be calculated from the slope of a plot of bound atrazine versus free atrazine. A partition coefficient, K_{om}, of approximately 2.4×10^4 L/kg om for atrazine with tannic acid was obtained from experiments in which 0.33 mM Ca calcium was added (Table 1). This range of calcium concentrations, atrazine partitioning to tannic acid, was similar to that observed with Oise NOM at ambient calcium concentrations. The partition coefficient is approximately 2−3 orders of magnitude greater than values reported for partitioning of atrazine to organic carbon in suspensions of soil and soil-extracted humic acids (Table 2). This much larger value for the partition coefficient may indicate that

TABLE 2. Comparison of Empirical Values of K_{om} and K_{oc} for Atrazine Sorption to Organic Matter

K_{om} (L/kg om)	f_{oc} (%)	K_{oc} (L/kg oc)	method	suspension	ref
2.4×10^4	53.8	4.5×10^4	dialysis	tannic acid with Ca	this work
4.6×10^5	53.8	8.5×10^5	dead-end filtration	tannic acid	Ducellier *(18)*
7.8×10^5	53.8	1.4×10^6	dead-end filtration	tannic acid with Ca	Ducellier
48, 101	N/A	N/A	centrifuged batch solutions	soil-solution suspensions	DiToro and Horzempa *(24)*
N/A	1.93	41, 109	centrifuged batch solutions	soil-solution suspensions	Grover and Hance *(25)*
36	N/A	N/A	centrifuged batch solutions	soil-solution suspensions	Scott and Phillips (*26*)
N/A	N/A	216	centrifuged batch solutions	sediment-solution suspensions	Brown and Flagg *(27)*

atrazine associates with organic matter to a much higher degree in solutions of dissolved organic matter than in solutions of suspended soils.

While the proposed model is somewhat hypothetical at this time, it has raised some interesting questions in the field of pesticide−organic matter interactions, which has not been studied to a large degree in the aquatic environment as it has in the soil. These observations have obvious implications for pesticide bioavailability, transport and, potentially, treatment by membrane processes.

Acknowledgments

This work supported in part with funding from Compagnie Générale des Eaux, France, and the Hazardous Substances Research Center/South and Southwest. The authors gratefully acknowledge the contributions of Pierre Côté with Anjou Recherche, Compagnie Générale des Eaux; Bernard Legube and co-workers at the Université de Poitiers Laboratoire Chimie de l'Eau et des Nuisances; Jean-Yves Bottero, formerly at Laboratoire Environment et Minéralurgie, Ecole National Supérieure de Géologie de Nancy; and Mason Tomson, Department of Environmental Science and Engineering, Rice University.

Literature Cited

(1) Stamer, J. K.; Zelt, R. B. *J. Am. Water Works Assoc.* **1994**, *86*, 93−104.
(2) Montiel, A.; Welté, B. *Water Sci. Technol.* **1992**, *25*, 103−110.
(3) Thurman, E. M.; Goolsby, D. A.; Meyer, M. T.; Mills, M. S.; Pomes, M. L.; Kolpin, D. W. *Environ. Sci. Technol.* **1992**, *26*, 2440−2447.
(4) Agbekodo, M. K. A. Ph.D. Dissertation, L'Université de Poitiers, 1994.
(5) Hofman, J. A. M. H.; Noij, Th.H. M.; Kruithof, J. C.; Schippers, J. C. *Proc. Am. Wat. Works Assoc. Membr. Conf.*; Am. Wat. Works Assoc.: Baltimore, MD, 1993; pp 569−575.
(6) Hofman, J. A. M. H.; Noij, T. H. M.; Schippers, J. C. *Water Supply* **1993**, *11*, 101−111.
(7) Welhouse, G. J.; Bleam, W. F. *Environ. Sci. Technol.* **1992**, *26*, 959−964.
(8) Li, G.-C.; Felbeck, G. T., Jr. *Soil Sci.* **1972**, *113*, 140−148.
(9) Sullivan, J. D., Jr.; Felbeck, G. T., Jr. *Soil Sci.* **1968**, *106*, 42−51.
(10) Senesi, N.; Testini, C. *Soil Sci.* **1980**, *130*, 314−320.
(11) Welhouse, G. J.; Bleam, W. F. *Environ. Sci. Technol.* **1993**, *27*, 494−500.
(12) Senesi, N.; Testini, C. *Chemosphere* **1984**, *13*, 461−468.
(13) McCarthy, J. F.; Jimenez, B. D. *Environ. Sci. Technol.* **1985**, *19*, 1072−1076.
(14) Caron, G.; Suffet, I. H., Belton, T. *Chemosphere* **1985**, *14*, 993−1000.
(15) Perdue, E. M. In *Aquatic and Terrestrial Humic Materials*; Chistman, R. F.; Gjessing, E. T., Eds.; Ann Arbor Science: Ann Arbor, MI, 1983; pp 441−460.
(16) Gauthier, T. D.; Seltz, W. R.; Grant, C. L. *Environ. Sci. Technol.* **1987**, *21*, 243−248.
(17) Means, J. C.; Wood, S. G.; Hassett, J. J.; Banwart, W. L. *Environ. Sci. Technol.* **1982**, *16*, 93−98.
(18) Ducellier, F. M. S. Thesis, Rice University, 1995.
(19) Peck, D. E.; Corwin, D. L.; Farmer, W. J. *J. Environ. Qual.* **1980**, *9*, 101−106.
(20) Ghosh, K.; Schnitzer, M. *Soil Sci.* **1980**, *129*, 266−276.
(21) Raju, G. S.; Millette, J. A.; Khan, S. U. *Chemosphere* **1993**, *26*, 1429−1442.
(22) Lerch, R. N.; Thurman, E. M.; Kruger, E. L. *Environ. Sci. Technol.* **1997**, *31*, 1539−1546.
(23) Li, G.-C.; Felbeck, G. T., Jr. *Soil Sci.* **1972**, *114*, 201−209.
(24) Di Toro, D. M.; Horzempa, L. M. *Environ. Sci. Technol.* **1982**, *16*, 594−602.
(25) Grover, R.; Hance, R. J. *Soil Sci.* **1970**, *109*, 136−138.
(26) Scott, H. D.; Phillips, R. E. *Soil Sci. Soc. Am. Proc.* **1972**, *36*, 714−719.
(27) Brown, D. S.; Flagg, E. W. *J. Environ. Qual.* **1981**, *10*, 382−386.

Received for review February 28, 1997. Revised manuscript received October 21, 1997. Accepted October 22, 1997.[⊗]

ES970179M

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1997.