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EFFECTS OF NATURAL ORGANIC MATTER AND THE RAW WATER MATRIX ON THE REJECTION OF ATRAZINE BY PRESSURE-DRIVEN MEMBRANES

E. C. DEVITT[1]*, F. DUCELLIER[1], P. COTE[2] and M. R. WIESNER[1]

[1]Department of Environmental Science and Engineering, MS-317, Rice University, P.O. Box 1892, Houston, TX 77251-1892, U.S.A. and [2]Anjou Recherche, Chemin de la Digue, BP 76, 78603 Maisons-Laffitte Cedex, France

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Abstract—This work explores the role of the raw water matrix, particularly natural organic matter (NOM), in determining the removal of atrazine by nanofiltration membranes. The nature and relative concentration of NOM, the presence of calcium and ionic strength affected atrazine rejection. Dissolved organic matter (DOM) enhanced atrazine rejection in most cases and was dependent upon the relative concentrations of the DOM and the atrazine and the ionic strength. Atrazine rejection was greatly enhanced in the presence of the NOM surrogate, tannic acid. Less enhancement of atrazine rejection by NOM in comparison with tannic acid is attributed to relatively high concentrations of cations in the raw water and NOM concentrate and difference in molecular weight distribution. Higher ionic strengths decreased atrazine rejection. Trends in atrazine rejection as a function of recovery suggest that free atrazine rejection is mass transport-limited. Atrazine associated with DOM is removed by mechanical sieving. © 1998 Elsevier Science Ltd. All rights reserved

Key words—atrazine, natural organic matter, tannic acid, ionic strength, nanofiltration, ultrafiltration, semipermeable membrane, calcium, rejection, membrane filtration

INTRODUCTION

Loading of micropollutants to surface and ground waters is a growing problem for U.S. and European drinking water utilities. As regulatory MCLs (maximum contaminant levels) are being lowered, anthropogenic loading of micropollutants to drinking water sources is growing. Pesticides are a case in point. Their usage in agricultural regions contributes a heavy contaminant load to surface runoff. The U.S. MCL for atrazine is 3 μg/l. Europe's current standard is even lower, at 0.1 μg/l. During much of the year these standards are easily met. However, in the spring, post-application rainfall events can leach large dosages of atrazine into field runoff and can impact utilities at high concentrations (Thurman *et al.*, 1992; Stamer and Zelt, 1994; Stamer, 1996; Stamer and Wieczorek, 1996).

Compounding this problem is the fact that traditional liquid/solid separation does not significantly remove atrazine (Miltner *et al.*, 1989). Addition of such expensive processes as granular activated carbon or ozonation is required to meet the MCL. One emerging alternative advanced treatment technology is nanofiltration (NF). NF offers a high performance method for removing atrazine and other micropollutants left behind by liquid/solid separation as well as offering softening and excellent trihalomethane precursor removal at a comparatively low cost (Bourbigot *et al.*, 1993; Bergman, 1995).

Removal of atrazine by various commercially available nanofiltration membranes may be quite variable. In an NF pilot study of atrazine from a surface water, Agbekodo (1994) noted an increase in atrazine rejection with an increase in natural organic matter (NOM) in the influent Oise River water. Atrazine removals varied between approximately 50 and 90%. Preliminary investigations of atrazine retention in dialysis experiments using simulated Oise River waters showed a like trend (Devitt and Wiesner, 1995). Further investigation indicated that ionic strength may significantly influence this NOM "enhancement effect". As the ionic strength was raised by addition of calcium and sodium, the organic matter rejection was seen to rise while atrazine rejections decreased. This trend was observed using a concentration gradient-driven method. It does not necessarily follow that it will be true for pressure gradient-driven processes. Moreover, the trend of increasing atrazine rejection with increasing total organic carbon (TOC) observed by Agbekodo is difficult to interpret since the changes in TOC resulted from the removal of organics during coagulation, clarification, filtration,

*Author to whom all correspondence should be addressed. [Tel: +1-713-2854951; Fax: +1-713-2855203].

ozonation and carbon adsorption. Thus, the characteristics of the organic matter applied in the pilot experiments varied radically with concentration. This paper reports the results from a series of experiments investigating the retention of atrazine by a variety of UF and NF membranes under the driving force of transmembrane pressure in dead-end filtration (DEF). Of particular interest is the role of organic matter and ionic composition on atrazine removal.

EXPERIMENTAL METHOD

Materials

Radiolabeled atrazine from Sigma Chemical Co., St. Louis, (^{14}C, specific activity 7.8 mCi/mmol) was dissolved in ultrapure water to a concentration of 280 μg/l. In all cases atrazine was measured by a scintillation counter and reported in units of μm per liter.

The NOM used in these experiments was from the Oise River (France). Bernard Legube and co-workers at the Université de Poitiers Laboratoire Chimie de l'Eau et des Nuisances prepared a concentrated stock solution from a sample filtered and concentrated by 2-stage nanofiltration at a pilot facility operated by Compagnie Générale des Eaux at Méry-sur-Oise. Using distillation and a cycle of evaporation and redilution (to remove salts), they concentrated the water from approximately 3 mg/l total organic carbon (TOC) to a final concentration of 2,500 mg/l TOC. This concentrated Oise water was subsequently rediluted to desired concentrations in the feed solutions. At a concentration of 5 mg/l, the associated calcium concentration was approximately 140 mg/l and the alkalinity was 383 mg/l as $CaCO_3$. The bulk of the NOM was distributed below 10 kDa MWCO. A sample of unconcentrated Oise River water was also filtered to compare TOC rejection with and without preconcentration. At 3.4 mg/l TOC, its calcium concentration was 98 mg/l and its alkalinity was 220 mg/l as $CaCO_3$.

As the Oise River water had a high associated electrolyte concentration, tannic acid (FW 1701, average composition $C_{76}H_{52}O_{46}$) was used as a surrogate for natural organic matter to simulate conditions of controlled electrolyte strength and composition. In all cases, the organic matter concentration was characterized by TOC using a Shimadzu TOC Analyzer or by UV absorbance at 254 nm calibrated to TOC measurements on dilutions of a given feed water.

The nature of the membrane can have a major impact on its performance. In these experiments, four membranes with molecular weight cutoffs (MWCOs) in the NF range were used. Three were aromatic polyamide membranes with reported MWCOs of ~300 Da: NF 45, NF 200 and NF 70 (FILMTEC, Dow Chemical Co., Midland, MI). A cellulose ester membrane with a MWCO of 100 Da was also used (Spectrum, Los Angeles). Two UF membranes were also investigated: a YC 05 membrane (Amicon, Beverly, MA) and a 500 Da cellulose ester membrane (Spectrum). Membrane characteristics are summarized in Table 1.

Solution preparation

Three types of solutions were used: solutions of atrazine in ultrapure water ("free" atrazine solution), atrazine and organic matter (NOM or tannic acid) and atrazine and organic matter with elevated ionic strength. To prepare the atrazine and organic matter solutions, diluted Oise water concentrate, a volume of the unconcentrated Oise water, or powdered tannic acid in ultrapure water was combined with a small volume of concentrated atrazine stock solution. In the cases where the ionic strength was elevated, this was accomplished by the addition of calcium as calcium nitrate and/or sodium as sodium nitrate. For the feed concentrations used in the cellulose ester membrane and Oise water low-atrazine experiments (0.6–2.4 μg/l), atrazine rejections of less than 10% are at the detection limit and are therefore not statistically significant.

Once a solution with the desired concentrations of NOM, atrazine and salt was prepared, it was placed in a foil-covered container (to prevent atrazine degradation by exposure to light) and stirred for 24 h, after which it was assumed to be at equilibrium. 24 h was chosen based on protocol used by earlier researchers (Peck *et al.*, 1980) and our own equilibrium studies (data not presented here).

Dead-end filtration

DEF experiments were performed in triplicate using 47 mm diameter, 200 ml jacketed pressure filter holders with stir bars (Sartorius, Gottingen, Germany). A 47 mm diameter disc was cut from flat membrane material and placed on the filter support at the bottom of the cell. The cells were then filled with 100–200 ml of the sample solution, sealed, and placed on stir plates. Each cell was attached to a zero grade air cylinder and pressurized to 207 kPa (30 psi). Roughly 75% of the feed solution was filtered through the membranes in dead-end mode. The solution was stirred throughout the experiment to introduce mixing and minimize concentration-polarization. Samples of the concentrates and permeates were collected and analyzed for atrazine and TOC.

Calculation of rejection

In this work, the percent rejection is defined as the percent fraction of the initial mass of material retained by the membrane as concentrate in the cell:

$$\% \text{ Rejection} = 100 \times \frac{C_c V_c}{C_0 V_0} = 100 \times \left(1 - \frac{C_p V_p}{C_0 V_0}\right) \quad (1)$$

where C_c and C_p are the concentrations in the concentrate and permeate respectively and V_c and V_p are, respectively, the volumes of concentrate remaining and permeate fil-

Table 1. Characteristics of the membranes used in this study

Membrane	MWCO[a]	Composition	Specific flux[b] (l/m^2/h/bar)
NF 45	300	polyamide, thin film composite	2.3
NF 200	300	polyamide, thin film composite	2.9
NF 70	300	polyamide, thin film composite	2.6
YC 05	500	polymer	6.2
CE 100	100	cellulose ester	0.3
CE 500	500	cellulose ester	43.7

[a]As reported by manufacturer.
[b]Evaluated at 207 kPa (30 psi).

tered at the time of sampling. Similarly, C_0 and V_0 correspond to the initial concentration and volume introduced to the cell. Note that the ratio V_p/V_0 is analogous to the recovery of the system. Thus, this definition of rejection is a function of recovery. The permeate concentration implied in equation 1 is the concentration measured in the cumulative volume, V_p, collected. However, under certain conditions, the instantaneous permeate concentration may vary over time as the material retained in the filtration cell becomes more concentrated leading to an instantaneous rejection that varies over time.

Atrazine losses to adsorption to the cell were accounted for. The overall mass balances typically ranged from 90 to 95%. Significant loss of atrazine to the cellulose ester 100 Da membranes occurred in the presence of tannic acid and tannic acid with calcium cases. When this loss was accounted for, atrazine rejections calculated from concentrate mass and permeate mass were comparable.

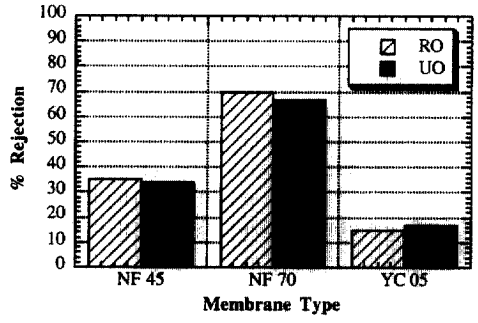

Fig. 2. Rejection of atrazine in reconstituted (RO) and unconcentrated (UO) Oise River water in the presence of NOM. (TOC/atrazine = 5.7 mg/μg).

RESULTS AND DISCUSSION

Rejection of atrazine in the presence of NOM reconstituted from Oise River water concentrate was monitored. Two NF membranes (NF 45 and NF 200) and a UF membrane (YC 05) were used. 200 ml feed solutions were used. Addition of 5 mg/l Oise NOM to 5 μg/l atrazine did not result in any significant increase in atrazine rejection for any of the membranes used (Fig. 1). Rejection of atrazine changed little, dropping from 31 to 28% for NF 45, rising from 38 to 42% for NF 200 and remaining at ~10% for YC 05. Differences in atrazine rejection between membranes and the degree of rejection in the absence of organic matter are particularly noteworthy. Removals of atrazine by the UF membrane (YC 05) were not statistically significant. Although the two NF membranes were reported to have similar MWCOs, there was in increase in atrazine removal of nearly 10% by the NF 200 membrane compared with the NF 45. The composition of these membranes is proprietary and it is therefore difficult to attribute the increase in atrazine rejection to any particular characteristic of the membrane. However, the NF 200 is formulated to allow for greater passage of calcium and has a slightly higher specific flux. Thus, this increase in rejection appears to reflect differences in membrane chemistry rather than in MWCO.

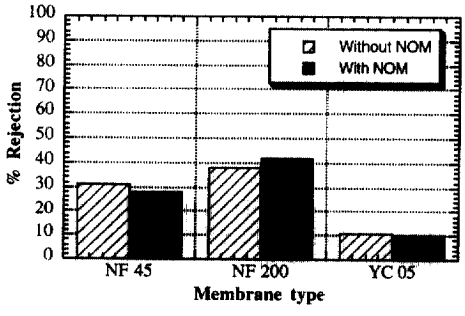

Fig. 1. Rejection of atrazine in the presence of NOM concentrated from the Oise River water for one UF (YC 05) and two NF membranes. (TOC/atrazine = 1 mg/μg).

Rejection of atrazine in the presence of NOM originating from the reconstituted Oise water and in the presence of unconcentrated organic matter obtained from a grab sample of Oise River water was compared to determine the possible effect of concentrating Oise river water organics and divalent ions on atrazine rejection (Fig. 2). These comparisons were made using the NF 45 and YC 05 membranes. In addition, a third NF membrane (NF 70) was tested. With 3.4 mg/l Oise NOM and 0.6 μg/l atrazine in the feed solution, atrazine rejections by all three of the membranes tested were comparable for the two types of organic matter, implying the reconstituted Oise concentrate was a good simulation of the natural Oise water. Again, the most striking differences are those obtained for the two NF membranes.

In comparison with the experiments summarized in Fig. 1, the TOC/atrazine ratio used in experiments reported in Fig. 2 was significantly higher, 5.7 vs 1 mg/μg for the previous case. Along with this increase in TOC per atrazine in the feed, there is a slight increase in rejection of atrazine. With an increase in organic matter per atrazine, rejection by the NF 45 membrane rose from 28 to 36% and rejection by the YC 05 rose from ~10% (negligible) to 15–17%. Although the use of NOM and commercially available membranes is useful in examining a specific application of a given membrane for atrazine removal, the characteristics of the NOM and membrane are not well defined. Moreover, it is not clear that the influence of dissolved organic matter on the rejection of atrazine in these experiments can be isolated let alone generalized. For equal concentrations of atrazine, the addition of small amounts of NOM appears to have no impact on atrazine rejection, while rejection is slightly improved at higher TOC to atrazine ratios. In all of these cases, moderate to high concentrations of calcium were present with the organic matter.

The use of tannic acid as a NOM surrogate partially addresses some of these issues and, in particular, decouples the effects of calcium and other electrolytes in the water from the effects of dissolved organic matter. Experiments with tannic acid were also conducted using membranes of known composition (cellulose ester) to distinguish the effects of membrane composition from those of MWCO.

Rejection of atrazine by cellulose ester membranes. Similar to the commercial NF membranes used in experiments with NOM, the cellulose ester NF membranes rejected a significant fraction of free atrazine introduced at a concentration of 2.4 μg/l (Fig. 3). Approximately 48% of the atrazine introduced was retained by the 100 Da membrane. In contrast, atrazine rejection by the 500 Da membrane hovered near the detection limit, at 13%. Given that the MW of atrazine is 215.7, it is not surprising that atrazine readily passed through the 500 Da membrane.

When tannic acid was added at a concentration of 10.0 mg/l (yielding a TOC/atrazine ratio of ~4.2), atrazine rejection by both the 100 and 500 Da MWCO membranes was observed to increase considerably. As would be expected, both TOC and atrazine removals by the larger MWCO membrane were lower than those obtained with the 100 Da membrane. Tannic acid rejection was 83% at 100 Da and 35% at 500 Da. Atrazine rejection rose to 73% at 100 Da and 34% at 500 Da (Fig. 3). In this case, higher rejections of TOC were associated with higher rejections of atrazine. However, subsequent experiments demonstrated that enhanced TOC removal did not necessarily coincide with enhanced atrazine removal.

In particular, the addition of calcium or sodium salts tended to increase the retention of tannic acid while decreasing atrazine rejection. Increasing ionic strength results in charge shielding and neutralization of the organic matter's charged functional groups and can shrink the NOM matrix. Observations of this nature have been reported by numerous investigators (see for example, Rajalakshmi *et al.*, 1959; Ghosh and Schnitzer, 1980). It may also result in a substantial increase in the hydrophobicity of the molecules, making them more likely to form aggregates in order to sequester themselves out of solution. These aggregates have larger apparent molecular weights and should be retained to a greater extent.

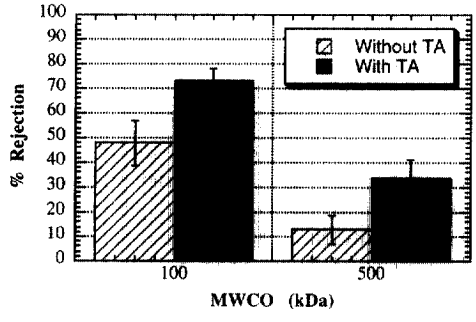

Fig. 3. Rejection of atrazine by cellulose ester membranes without and with addition of tannic acid (TA). (TOC/atrazine = 4.2 mg/μg).

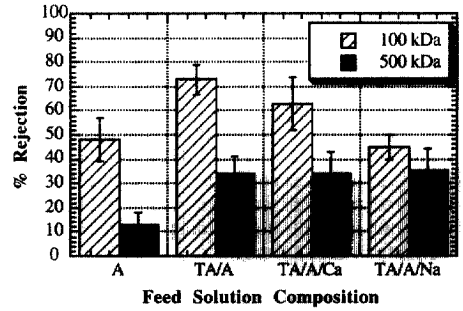

Fig. 4. Rejection of atrazine (A) by cellulose ester membranes as a function of feed solution composition. (TOC/atrazine = 3.1 mg/μg).

In separate experiments, ionic strength was elevated to 0.38 mM by addition of 0.13 mM calcium (approximately 5 mg Ca/l) as calcium nitrate and addition of 0.38 mM sodium as sodium nitrate. The atrazine concentration was maintained close to 2.4 μg/l and tannic acid concentration was approximately 7.50 mg TOC/l yielding a TOC/atrazine ratio of ~3.1. In these experiments, calcium and sodium slightly increased or had a negligible effect on TOC rejection. At 100 Da, TOC rejection rose from 73 to 93 and 91% with addition of calcium and sodium, respectively. At 500 Da, TOC rejection did not significantly change, rising from 35 to 39% with addition of calcium and remaining constant at 35% with addition of sodium. In contrast, higher ionic strengths tended to produce a slight decrease in atrazine retention in the presence of tannic acid at the lower MWCO (100 Da). Whereas TOC rejection at 100 Da rose approximately 20%, atrazine rejection dropped from 73 to 63% and to 45% with addition of calcium and sodium salts respectively (Fig. 4). As with the trend in TOC rejection, changes in atrazine rejection at 500 Da were statistically insignificant.

The commercial NF membranes evaluated with Oise River NOM are reported by their manufacturer to have MWCOs near 300 Da. Thus, it is particularly significant that tannic acid improved atrazine rejection across both the 100 and 500 MWCO membranes while changes in ionic strength appeared to affect primarily the lower MWCO membrane. In addition, it is important to recall that these are very low concentrations by comparison with the ionic strengths and associated calcium concentrations present in the Oise River water and solutions made up from the Oise NOM concentrate.

In summary, the effect of increasing ionic strength, even at relatively low levels, is to push atrazine rejections towards the "free" atrazine limit of rejection obtained in the absence of dissolved organic matter. This lower limit is likely to vary by membrane type (particularly by composition) and to increase when higher amounts of dissolved organic matter are present.

Comparison of membranes and the influence of recovery. The effects of dissolved organic matter and membranes of differing compositions (tannic acid vs NOM and commercial polyamide vs laboratory-grade cellulose ester, respectively) on atrazine rejection trends were assessed in a series of experiments in which atrazine and tannic acid were introduced to a NF 45 membrane. Experiments varied dissolved organic matter content and electrolyte strength. Also, these experiments entailed more detailed measurements of the permeate concentration over time to observe the instantaneous rejection of the membrane.

During batch dead-end filtration of a solute which is partially rejected by the membrane, the concentration progressively increases within the filtration cell. The decrease in volume remaining and the increase in concentration is analogous to a membrane operating in a continuous flow mode at progressively higher recoveries. Thus, when 50% of the solution originally present in the cell is filtered the concentration presented to the membrane approximates that of a continuous flow unit operating at 50% recovery. The concentration of solute measured instantaneously in the permeate for a given volume filtered may reveal the mechanism by which rejection occurs which in turn may be linked to the species rejected.

The evolution of atrazine concentrations in the permeate of NF 45 membranes during batch filtration of an atrazine solution (initial concentration = 5 μg/l) in otherwise organic-free water is shown in Fig. 5. In the absence of organic matter,

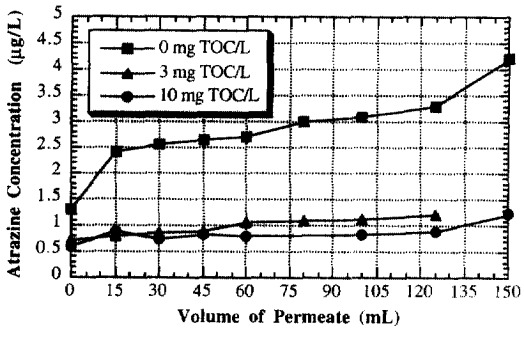

Fig. 5. Concentration of atrazine in the presence of varying concentrations of tannic acid in NF 45 permeates during the filtration of the first 150 ml of a 200 ml sample. Ionic strength was fixed at 1.5×10^{-2} M.

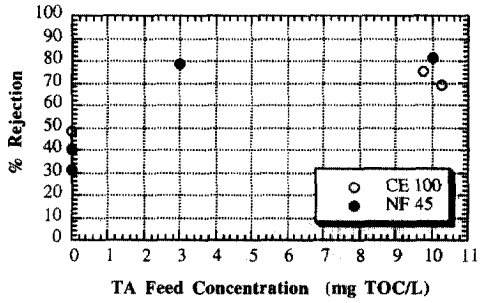

Fig. 6. Comparison of volume-average (150 ml) atrazine rejection for cellulose ester (CE 100) and NF 45 membranes at various concentrations of tannic acid.

the atrazine concentration in the permeate follows that in the concentrate, continually rising as filtration proceeds. This suggests that atrazine is rejected in this case due to mass transport limitations across the membrane which depend on trans-membrane concentration. Atrazine is able to enter the membrane, but is transported to a lesser extent than the water. In contrast, the presence of tannic acid results in a profile of permeate concentration as function of volume filtered which is relatively flat. Thus, permeate concentration is virtually independent in this case of the concentration within the cell. This suggests that rejection of atrazine in the presence of tannic acid occurs due to a size exclusion mechanism which strongly suggests the formation of an atrazine-organic matter association. We have shown in previous work (Devitt and Wiesner, 1998) that such associations are evident in dialysis separations and may greatly exceed separations predicted from simple hydrophobic or reversible partitioning of the atrazine into the organic macromolecule. The atrazine appears to associate directly with organic macromolecules such as NOM or tannic acid through hydrogen bonding, but depends on mechanical trapping as for example might occur through a low multiplicative probability of escape produced by a large number of encounters with the low-energy binding sites within a macromolecule or aggregate. One practical implication of the switch-over in rejection mechanisms in the presence of dissolved organic macromolecules is a greater insensitivity to degradation of atrazine concentrations in membrane permeates with staging. We attribute the relatively large effect of tannic acid on the removal of atrazine in comparison with that observed using Oise NOM to the higher concentrations of cations (principally calcium) present in the Oise River water and Oise NOM concentrates.

Instantaneous rejections of atrazine by the NF 45 polyamide membrane in the presence of tannic acid can be compared with the cumulative rejections measured using the cellulose ester membranes by

calculating the permeate volume-weighted concentration in the NF 45 permeates. The 100 Da cellulose ester and NF 45 polyamide membranes showed similar trends in rejections (Fig. 6). Atrazine rejection rose from approximately 40 to 80% as TOC was increased from zero to 10 mg/l. When the removals summarized in Fig. 6 are compared with those for atrazine removal by the NF 45 membrane in the presence of 5 mg TOC/l of NOM (Fig. 1) or atrazine removal by the cellulose ester membrane at higher ionic strengths (Fig. 4), it is apparent that while dissolved macromolecules tend to increase the retention of atrazine, higher ionic strengths tend to reverse this effect.

CONCLUSIONS

The rejection of atrazine by pressure-driven membranes with molecular weight cutoffs in the nanofiltration range (100 to 500 Da) is enhanced by the presence of dissolved organic macromolecules. However, there appears to be a fraction of organic matter which enhances atrazine rejection and is retained only by membranes with smaller MWCOs, which can be inactivated with respect to atrazine rejection at even moderate ionic strengths. We speculate that enhanced removals result from the formation of atrazine-macromolecule associations which are rejected primarily by size exclusion. As ionic strength increases, macromolecular conformation may change, altering the presentation of sites for atrazine interaction and making atrazine-macromolecular association more reversible. Previous investigators have shown that atrazine associated directly with molecules such as NOM or tannic acid through hydrogen bonding. We hypothesize that such weak interactions in concert with mechanical trapping of atrazine within the macromolecule may explain both enhanced rejections of atrazine in the presence of DOC and increased reversibility with changes in macromolecular conformation. The proposed mechanism is a low multiplicative probability of escape from the macromolecules produced by a large number of encounters with the low-energy binding sites within a macromolecular "cage". The smaller molecular weight fractions appear to be most effected. This in turn pushes atrazine rejections towards the "free" atrazine limit of rejection obtained in the absence of the lower molecular weight fraction of dissolved organic matter. In contrast with the rejection of macromolecule-bound atrazine by size exclusion, the rejection of "free" atrazine by these membranes appears to be a concentration-dependent process such as that described by solution-diffusion models for solute transport across membranes. One practical implication of the switch-over to a size exclusion mechanism for atrazine rejection in the presence of dissolved organic macromolecules is a decreased tendency for atrazine to find its way into the permeate with increased staging.

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