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ULTRAFILTRATION BEHAVIOR OF MAJOR IONS (Na, Ca, Mg, F, Cl, AND SO₄) IN NATURAL WATERS

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Abstract—Aquatic colloids, including macromolecules and microparticles, with sizes ranging between 1 nm to 1 μm, play important roles in the mobility and bioavailability of heavy metals and other contaminants in natural waters. Cross-flow ultrafiltration has become one of the most commonly used techniques for isolating aquatic colloids. However, the ultrafiltration behavior of chemical species remains poorly understood. We report here the permeation behavior of major ions (Na, Ca, Mg, F, Cl, and SO₄) in natural waters during ultrafiltration using an Amicon 1 kDa ultrafiltration membrane (S10N1). Water samples across a salinity gradient of 0–20‰ were collected from the Trinity River and Galveston Bay. The permeation behavior of major ions was well predicted by a permeation model, resulting in a constant permeation coefficient for each ion. The value of the model-derived permeation coefficient (P_c) was 0.99 for Na, 0.97 for Cl, and 0.95 for F, respectively, in Trinity River waters. Values of P_c close to 1 indicate that retention of Na, Cl, and F by the 1 kDa membrane during ultrafiltration was indeed minimal (< 1–5%). In contrast, significant (14–36%) retention was observed for SO₄, Ca, and Mg in Trinity River waters, with a P_c value of 0.64, 0.82, and 0.86 for SO₄, Ca and Mg, respectively. However, these retained major ions can further permeate through the 1 kDa membrane during diafiltration with ultrapure water. The selective retention of major ions during ultrafiltration may have important implications for the measurement of chemical and physical speciation of trace elements when using cross-flow ultrafiltration membranes to separate colloidal species from natural waters. Our results also demonstrate that the percent retention of major ions during ultrafiltration decreases with increasing salinity or ionic strength. This retention is largely attributed to electrostatic repulsion by the negatively charged cartridge membrane.
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Key words—ultrafiltration, major ions, colloids, water, Trinity River, Galveston Bay

INTRODUCTION

Aquatic colloids, including macromolecules and microparticles, are abundant in natural waters (e.g. Buffle, 1990; Wells and Goldberg, 1991; Guo *et al.*, 1994; Buffle and Leppard, 1995; Gustafsson and Gschwend, 1997). The presence of a colloidal phase in natural waters plays a central role in regulating the speciation, bioavailability, and mobility of many trace metals, radionuclides and trace organic compounds in aquatic systems (Tipping, 1988; Sigleo and Means, 1990; Honeyman and Santschi, 1992; Honeyman, 1999; Kersting *et al.*, 1999; Santschi *et al.*, 1999). Due to the significance of colloidal phases in aquatic environments, the isolation and measurement of aquatic colloids has

received increasing attention in recent years (e.g. Buffle *et al.*, 1992; Buessler *et al.*, 1996; Guo and Santschi, 1997; Burba *et al.*, 1998; Cai, 1999; Dupre *et al.*, 1999; Guo *et al.*, 2000a). One of the most commonly used techniques for isolating colloids from natural waters is cross-flow ultrafiltration (e.g. Buessler *et al.*, 1996; Guo and Santschi, 1997). However, the ultrafiltration behavior of chemical species during ultrafiltration is still poorly understood, although this information is very important to understand the ultrafiltration process and to correctly interpret size fractionation data (Guo and Santschi, 1996; Guo *et al.*, 2000b).

A number of previous laboratory studies focused on the effects of natural organic matter, such as humic substances, on the overall ultrafiltration performance of membranes (Cheryan, 1998; Cai, 1999; Lin *et al.*, 2000). Recently, the ultrafiltration behavior of specific organic compound classes with different molecular weights has also received increasing attention. Using molecular probes, the permeation and retention behavior of both lower and higher molecular weight molecules (compared to the normal

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Table 1. Major cations and anions and dissolved organic carbon concentrations and other parameters in water samples ultrafiltered. TR = Trinity River and GB = Galveston Bay

Sample ID	Location	Salinity	DOC (ppm)	Na (ppm)	Ca (ppm)	Mg (ppm)	F (ppm)	Cl (ppm)	SO ₄ (ppm)
1	TR	<0.2	6.8	18	36.1	3.0	0.19	25	29.8
2	GB	5	6.4	1539	101	203	3.5	2760	429
3	GB	9.5	5.6	2932	157	370	8.0	5535	738
4	GB	19.5	4.3	6018	260	708	16	10,794	1403

MW cutoffs of ultrafiltration membranes) have been investigated through controlled laboratory experiments (e.g. Gustafsson *et al.*, 1996; Guo and Santschi, 1996; Guo *et al.*, 2000b). In addition, Mukai *et al.* (2000) examined the ultrafiltration behavior of extracellular and metabolic products and found different ratios of proteins to sugars in the retained fraction.

The colloidal fraction of certain major ions in fresh waters has been measured using either ultrafiltration (e.g. Eyrolle *et al.*, 1996; Dupre *et al.*, 1999) or ultracentrifugation (e.g. Grout *et al.*, 1999). These studies found that colloidal fractions of Ca and Mg were probably insignificant in tropical surface and urban storm waters (Eyrolle *et al.*, 1996; Grout *et al.*, 1999) and that $\leq 5\%$ of Ca, Mg and Na were complexed with organic material in wetland waters (Dupre *et al.*, 1999). However, significant differences in SO₄ concentrations were observed in different filtrates of fresh waters, e.g. 0.2 μm filtrates processed by either frontal filtration or tangential filtration (Dupre *et al.*, 1999) and 0.2 and 0.025 μm filtrates (Viers *et al.*, 1997). These previous ultrafiltration studies and many others focused on either natural organic matter or trace metals in fresh waters (Viers *et al.*, 1997; Dupre *et al.*, 1999). The permeation and retention behavior of major ions in natural waters has not been systematically examined. In addition, whether the permeation characteristics of the major ions during ultrafiltration changes with water salinity (or ionic strength) is still unclear.

Our previous studies have shown that a significant fraction of LMW molecules (<1 kDa) can be retained by a 1 kDa ultrafiltration membrane (Guo and Santschi, 1996). In addition, metals complexed by low molecular weight (LMW) ligands can also be retained (Guo *et al.*, 2000b). It is possible that major ions in natural waters, which can be present as ion pairs, surrounded by hydration spheres or sorbed onto surfaces of microparticles and macromolecules, could also be retained by a 1 kDa membrane during ultrafiltration.

The objective of this study was to examine: (1) the permeation characteristics of major ions in natural waters during ultrafiltration using a 1 kDa ultrafiltration membrane, and (2) effects of salinity (ionic strength), concentration of dissolved organic carbon (DOC), and diafiltration on the retention behavior of major ions during ultrafiltration. Water samples examined included river water, estuarine water, and

seawater. Representative cations (Na, Ca, Mg) and anions (F, Cl, SO₄) were measured in time series ultrafiltration samples.

MATERIALS AND METHODS

Sampling

Water samples were collected at a freshwater station in the Trinity River and at three stations from Galveston Bay or the Gulf of Mexico coastline, with a salinity ranging from 0 to ~ 20 . Concentrations of major ions (Na, Ca, Mg, F, Cl, and SO₄) and dissolved organic carbon (DOC) in these natural water samples along with salinity values, are listed in Table 1. The samples were prefiltered through a 0.2 μm Nucleopore filter cartridge (Nucleopore[®]) and stored in acid-clean 201 polyethylene carboys. Sub-samples for DOC analysis were kept in pre-combusted (500°C for 6 h) glass vials with Teflon lined caps (Guo *et al.*, 1994). Prefiltered water was ultrafiltered immediately after sample collection, usually within 6–12 h.

Ultrafiltration

A spiral-wound 1 kDa Amicon S10N1 ultrafiltration cartridge (with polysulfone as membrane material) was used for the ultrafiltration of all water samples. A Teflon diaphragm pump head (from Cole-Parmer) was equipped with Teflon fittings and tubings to decrease sorptive losses and any possible contamination from the apparatus (Guo *et al.*, 2000b). Calibration of this 1 kDa ultrafiltration membrane using standard macromolecules with known MWs showed a retention of 83% for a 1.3 kDa vitamin B₁₂ (Sigma Chemical Co), 97% for a 3 kDa fluorescein-tagged dextran, and >99% for a 10 kDa dextran (Molecular Probe, Eugene Oregon), respectively. These calibration results are consistent with the specifications given by the manufacturer (Amicon, 1995). The ultrafiltration cartridge was thoroughly cleaned before each experiment with 1–2% Micro detergent, 0.05 M NaOH, and 0.02 M HCl, respectively (Guo and Santschi, 1996). Each chemical was recycled for 20–30 minutes and soaked for another 20–30 min. Between each solution, $\sim 40\text{ l}$ of ultrapure water (with a DOC concentration of $\leq 2\ \mu\text{M}$) was flushed through the ultrafiltration system, and after chemical cleaning, another 40–80 l of ultrapure water was flushed again under normal operating conditions. The clean membrane was then preconditioned before ultrafiltration by cycling $\sim 1\text{ l}$ of the prefiltered water for 10–20 min. About 21 l of prefiltered water was used for ultrafiltration.

During ultrafiltration, the ultrafiltration reservoir was under continuous stirring using a magnetic stirring bar. Discrete samples from the permeate line were collected at different concentration factors, ranging from 1 to >20. All samples were taken in duplicate for the analysis of major ions.

Diafiltration

Our previous studies have found that the retained LMW macromolecules can further permeate through the

membrane during diafiltration using ultrapure water (Guo *et al.*, 2000b). However, it is still unclear whether the retained major ions can also be washed away during diafiltration.

After ultrafiltration, the retentate solution was further diafiltered using ~20l of ultrapure water. Diafiltration was carried out by maintaining the volume of the retentate solution at ~1l through a continuous replacement flow of ultrapure water. Time-series samples from the diafiltration permeate line were collected and quantified for the concentration of selected major ions.

Determination of DOC, cations (Na, Ca, Mg) and anions (F, Cl, SO₄)

Concentrations of DOC were measured on a high-temperature combustion TOC analyzer (MQ Scientific 101). Each duplicate sample was injected three times and the mean value was reported. Precision, in terms of coefficient of variation, was better than 2% (Guo *et al.*, 1994).

Sodium, Ca, and Mg were measured separately on a flame AAS with a laminar flow burner (PE-5000). An acetylene-air mixture gas was used to generate the flame for atomization. A calibration curve was run before sample measurements. In addition, a standard solution with intermediate concentration was run as a sample to ensure data quality. All samples were measured in duplicate. Precision was usually better than 2% for Na, Ca, and Mg.

Sulfate, F, and Cl were measured using a Dionex Ion Chromatography. The liquid mobile phase used was a mixed solution with 1.8 mM sodium carbonate and 1.7 mM sodium bicarbonate. The column was cleaned and flushed with 25 mM sulfuric acid regenerant between samples. Ultra high-purity helium gas, maintained at a flow rate of 5 psi, was used to degas the solutions. Flow rates were maintained at 3–5 ml/min for the regenerant and 2.0 ml/min for the buffer. All samples were measured in duplicate and the mean value is reported. Standard solutions were run frequently as a sample to check the performance of the instrument. Precision was <5% or better.

Ultrafiltration permeation model

At any given time of ultrafiltration, the relationship between the concentration of a given chemical species in the permeate (C_p) and the concentration factor (CF, defined here as the volume ratio of initial water to retentate solution) can be described by the following equation (e.g. Logan and Jiang, 1990; Kilduff and Weber, 1992; Logan, 1999):

$$\ln C_p = \ln(P_c \times C_f^0) + (1 - P_c) \times \ln(\text{CF}), \quad (1)$$

where P_c is the permeation coefficient, defined as the ratio of C_p to C_f (feed concentration) at any given time during the ultrafiltration, while C_f^0 is the initial concentration of permeable species in the upstream feed solution.

A linear relationship between $\log C_p$ and $\log \text{CF}$ indicates a constant permeation behavior. If the value of P_c for a chemical species is equal to 1, the concentration of that chemical species in the permeate should be equal to that in the feed solution at any given time during ultrafiltration. This means that there is no retention for that chemical species. On the other hand, if a chemical species has a P_c value < 1, this indicates a retention for that chemical species at each cycle of the ultrafiltration. The smaller the P_c value, the more retention the chemical species will be. As a result of retention, the concentrations of chemical species in the permeate will increase with increasing concentration factor. The P_c value of a given chemical species can be calculated from the slope ($1 - P_c$), derived from the linear relationship between $\log C_p$ and $\log \text{CF}$ described in Eq. (1).

RESULTS AND DISCUSSION

Permeation characteristics of major ions

Variations of major ion (F, Cl, SO₄, Na, Ca, and Mg) concentrations in the discrete permeate time-series samples during ultrafiltration are shown in Fig. 1. If major ions in natural waters are mainly in a free ionic or complexed form and can freely pass through a 1 kDa ultrafiltration membrane, their concentrations in the discrete permeate samples should be constant as the concentration factor (CF) increases during ultrafiltration. As shown in Fig. 1, concentrations of F, Cl, Na, and K (not shown) in the permeate time-series samples change little with increasing concentration factor. In contrast, concentrations of SO₄, Ca, and Mg in the permeate time-series samples increase, to a different extent, with increasing concentration factor (Fig. 1). Nearly constant concentrations of F, Cl, and Na in the permeate time-series samples indicate that there is little interaction between these ions and the ultrafiltration membrane. In other words, F, Cl, Na, and K can, indeed, pass through the membrane almost freely without significant retention during ultrafiltration. However, increasing permeate concentrations for SO₄, Ca, and Mg are a testimony of significant retention of these ions during ultrafiltration, suggesting that either there is interaction between these ions and the membrane surface (most likely), or significant fractions of these ions are associated with macromolecular colloidal materials (less likely).

Quantitative permeation of these major ions can be further evaluated using the simple ultrafiltration permeation model given in the previous section. As is evident from Fig. 2, the ultrafiltration behavior of these major ions can be well predicted using the simple permeation model (Logan and Jiang, 1990; Kilduff and Weber, 1992). All major ions show a linear relationship between $\log C_p$ and $\log \text{CF}$ (Fig. 2), indicating a constant permeation behavior during ultrafiltration. The permeation coefficient (P_c) of a given ion can then be calculated from the slope ($1 - P_c$), derived from the linear relationship between $\log C_p$ and $\log \text{CF}$. Using the slope values given in Fig. 2, calculated permeation coefficients for each ion are listed in Table 2 (note that Trinity River water is the one with a salinity of <0.2‰). Model-derived P_c values are 0.95, 0.97, and 0.94 for F, Cl, and Na, respectively. On average, 95% of F, 97% of Cl and 94% of Na in the Trinity River water permeate through the 1 kDa membrane during each cycle of ultrafiltration. These P_c values correspond to a retained fraction of 0.05, 0.03 and 0.06 for F, Cl, and Na, respectively, which is consistent with their relatively constant permeate concentrations shown in Fig. 1. For Ca and Mg, the model-derived permeation coefficient is ~0.86 and 0.87, respectively (Table 2). This indicates that, on average, about 14% of Ca and 13% of Mg can be retained during each cycle of ultrafiltration. The value of the model-

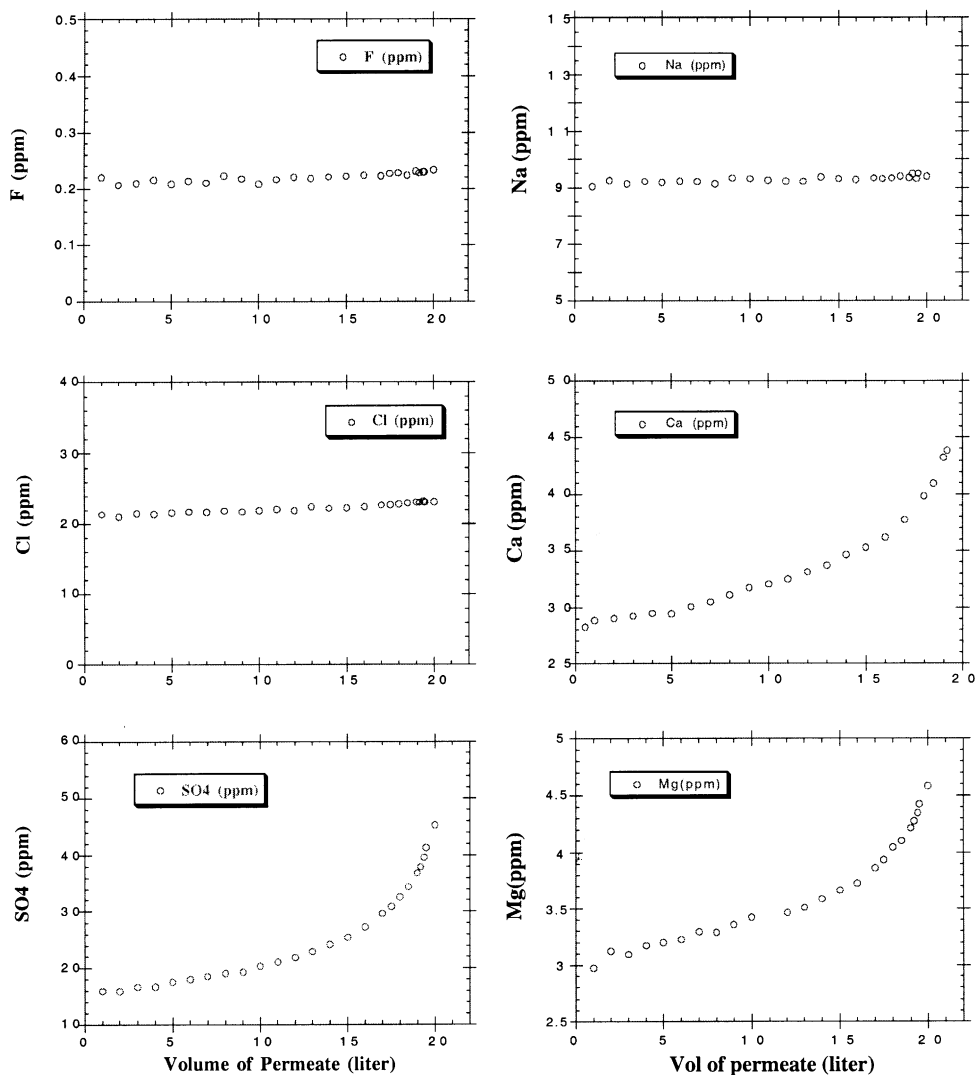


Fig. 1. Variations of concentrations of major ions (F, Cl, SO₄, Na, Ca, and Mg) in time series permeate samples collected during the ultrafiltration of a Trinity River water.

derived permeation coefficient for SO₄ is only 0.64, which is the lowest permeation coefficient observed for all major ions. A P_c value of 0.64 corresponds to a 36% retention for SO₄. This is a somewhat surprising observation in the ultrafiltration of natural water. Selective retention of major ions during ultrafiltration have significant implications for trace element size fractionation or phase speciation studies when using ultrafiltration techniques.

Possible explanations for the retention of major ions, such as SO₄, Ca, and Mg during ultrafiltration include the complexation of major ions with colloids or macromolecular materials in natural waters and the interaction of major ions with the membrane during ultrafiltration. It has been shown that most aquatic humic substances can contain significant amounts of Ca and Mg (Buffle, 1990). In addition, Ca can play an important role in the coagulation of macromolecular organic matter as a bridging agent

(e.g. Chin *et al.*, 1998). Therefore, fractions of major ions which are associated with colloidal macromolecules will be retained by a 1 kDa membrane during ultrafiltration. However, 36% of SO₄, 14% of Ca and 13% of Mg are too high and too close to electro-neutrality (0.24 meq/l of anions and 0.29 meq/l of cations) to be accounted for being associated with macromolecular organic matter (see Table 1 mass concentrations of each ion and total dissolved organic carbon). For example, with 100 μ M of DOC retained by ultrafiltration, 1 meq/g of negatively charged groups in colloidal macromolecular organic matter (Santschi *et al.*, 1995), there could only have been about 1 μ eq/l negatively charged groups in colloidal organic matter available for complexation with Ca²⁺.

The more likely reason for the retention of these major ions is the interaction between major ions and membrane surfaces, such as electrostatic and

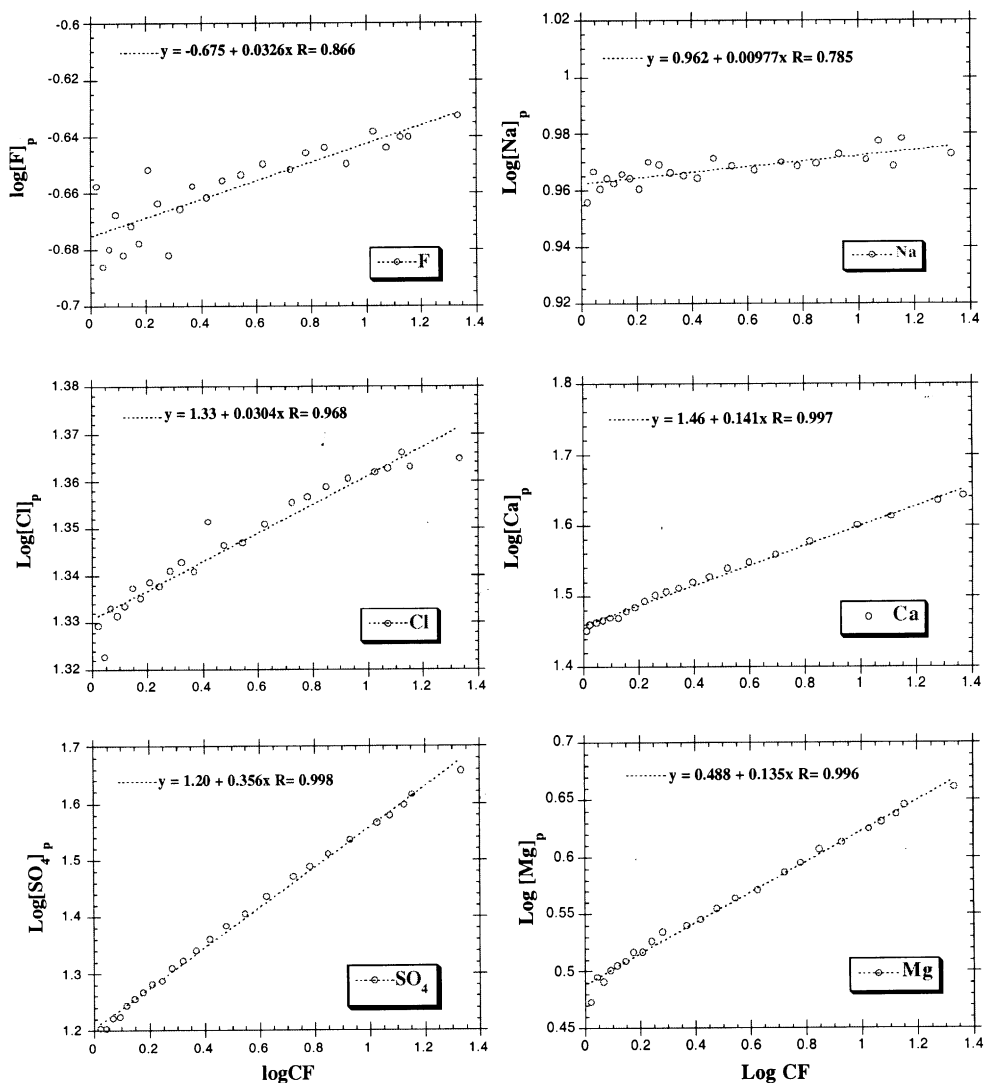


Fig. 2. Log–log relationship between permeate concentration (C_p) and concentration factor (CF) for F, Cl, SO_4 , Na, Ca, and Mg in the Trinity River water (see text for explanation of relationship of $\log C_p$ and $\log \text{CF}$).

Table 2. Permeation coefficients (P_c) of major ions during ultrafiltration

Species	Permeation coefficient (P_c)			
	Sal = <0.2 ^a	Sal = 5	Sal = 9.5	Sal = 19.5
F^-	0.95	0.97	0.96	— ^b
Cl^-	0.97	— ^b	— ^b	— ^b
SO_4^{2-}	0.644	0.775	0.839	0.844
Na^+	0.991	0.964	0.981	0.960
Ca^{2+}	0.859	0.894	0.929	0.949
Mg^{2+}	0.865	0.928	0.940	0.939

^aTrinity River water.

^bNot measured.

electrokinetic effects (Buffle, 1990), which can result in a selective retention for major ions during ultrafiltration. The membrane material of the 1 kDa Amicon S10N1 ultrafiltration cartridge is polysulfone

which carries a negative charge on the membrane surface. Therefore, electrostatic repulsion by a negatively charged surface is the most likely cause for the high retention of SO_4 , especially in the fresh water samples. This retention mechanism for SO_4 is also consistent with the fact that the P_c value of SO_4 increases with increasing salinity as discussed in the next section.

Effect of ionic strength on the retention of major ions

In order to examine the effect of ionic strength (expressed here as salinity, ‰) and concentration of dissolved organic carbon (DOC) on the ultrafiltration behavior of major ions, estuarine waters with different salinities and DOC concentrations were also ultrafiltered and time-series permeate samples collected for F, Cl, SO_4 , Na, Ca, and Mg measurements.

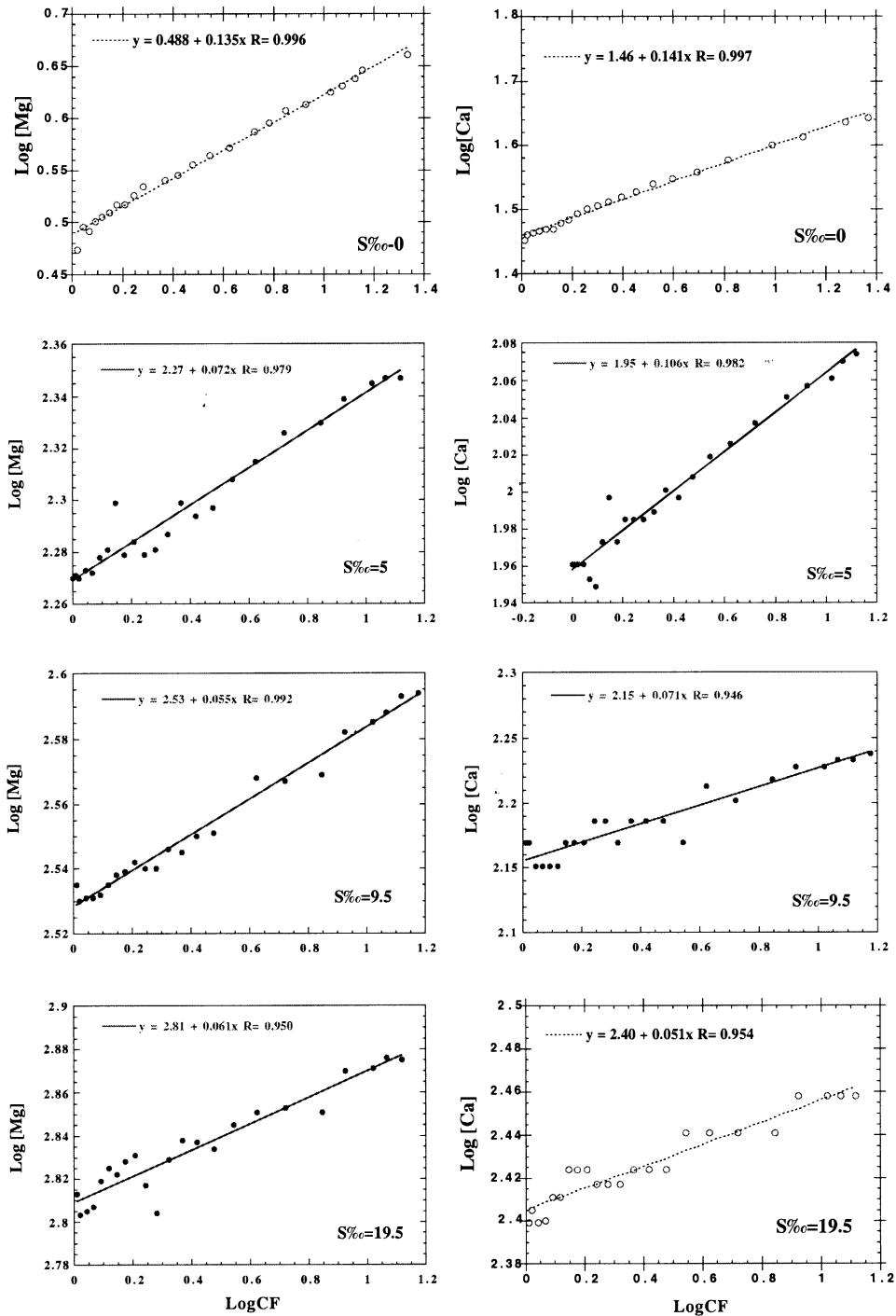


Fig. 3. Variation of cation retention during ultrafiltration with water salinity: example of Mg and Ca.

As in the case of fresh waters, the ultrafiltration behavior of major ions in sea waters can also be predicted by the permeation model, resulting in a linear relationship between $\log C_p$ and $\log CF$. Examples of relationship between $\log C_p$ and $\log CF$ for Ca, and Mg are shown in Fig. 3, while model-derived permeation coefficients are listed in Table 2.

As shown in Table 1, all major ion concentrations increase as salinity increases, while DOC concentrations decrease with increasing salinity of estuarine waters (Guo and Santschi, 1997b). On the other hand, model-derived permeation coefficients for major ions, in general, increase with increasing salinity (Table 2).

All major cations show consistent increases in their permeation coefficients with increasing salinity. For example, P_c values for Ca increase from 0.86 at salinity of $\sim 0\%$ to 0.93 at salinity $> 9.5\%$ whereas P_c values for Mg vary from 0.87 at salinity of $\sim 0\%$ to 0.94 at salinity $> 9.5\%$. Values of permeation coefficients for Na also show a slight increase as salinity increases, from 0.94 at salinity of $\sim 0\%$ to 0.98 at salinity of $> 9.5\%$ (Table 2). Values of permeation coefficients for SO_4 also increase consistently as salinity increases, varying from 0.64 at salinity of $\sim 0\%$ to 0.78 at salinity of 5‰ to 0.84 at salinity $> 9.5\%$. However, P_c values for F seem to vary little (Table 2).

Retention of major electrolyte ions by negatively charged membranes has been described before, and was related to ion hydration energy (Staub *et al.*, 1984) and Donnan exclusion theory (Schaep *et al.*, 1998a, b). Because of the solution electroneutrality condition, not only anions but also cations have to be retained. Most importantly, the retention of major electrolyte anions can also affect the retention of minor ions (Staub *et al.*, 1984; Buffle, 1990). The observations of retention coefficients ($R = 1 - P_c$) of both anions and cations decreasing with increasing ionic strength (or salinity, see Fig. 4), and retention coefficients decreasing in the order of $\text{SO}_4 > \text{Ca} > \text{Mg} > \text{Na} > \text{F} > \text{Cl}$ during ultrafiltration through negatively charged membranes are broadly similar to those reported by Schaep *et al.* (1998a, b) and Ricq and Pagetti (1999), who were able to explain their

nanofiltration results of ion selectivity by charge effects between solutes and membrane pores. While streaming potential measurements would have been useful to model the selective permeation of solutes through membranes (e.g. Ricq *et al.*, 1999a, b; Ricq and Pagetti, 1999), our diafiltration results, described below, clearly demonstrate that retention of electrolyte ions can be reversed.

Permeation characteristics of major ions during diafiltration

If the major ions retained during ultrafiltration would be mainly associated with organic macromo-

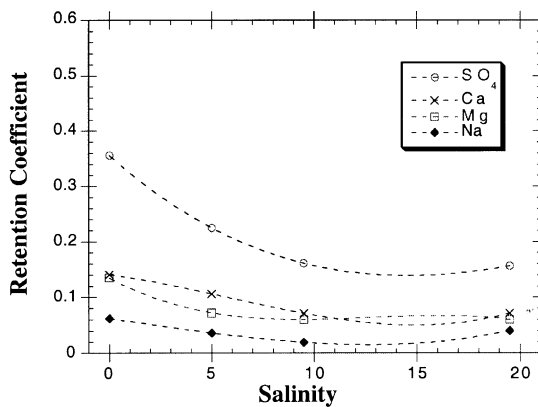


Fig. 4. Changes of retention coefficient ($R = 1 - P_c$) with water salinity, examples of SO_4 , Ca, Mg, and Na.

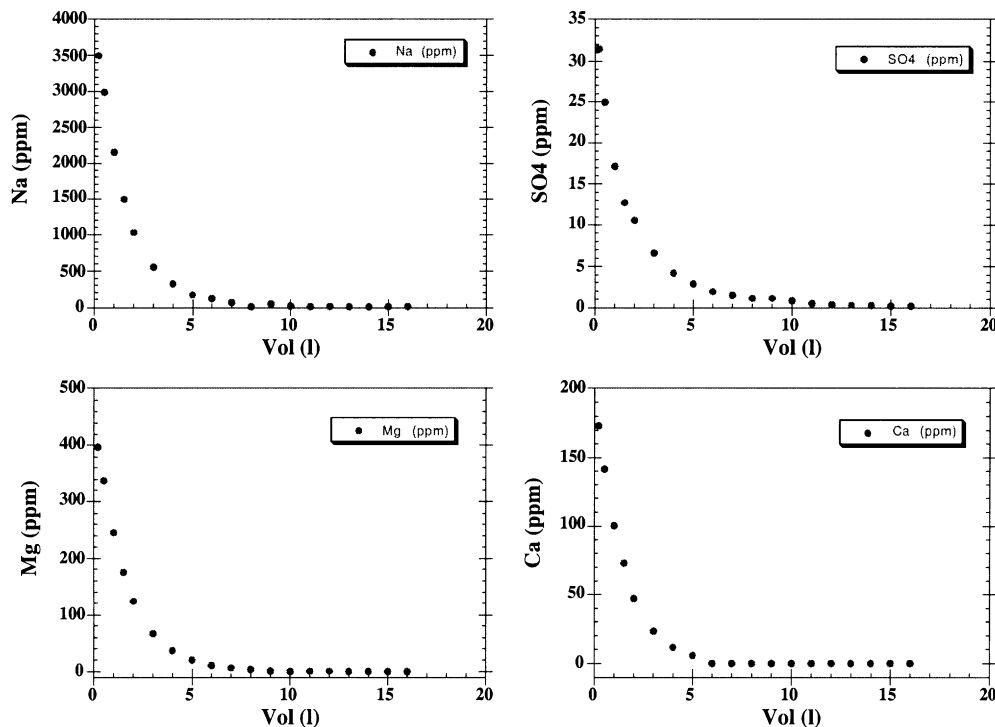


Fig. 5. Permeation behavior of major ions during diafiltration: examples from a water sample with a salinity of 9.5‰.

lecules, they should remain in the retentate fraction during diafiltration since previous studies have shown that losses of macromolecular organic matter during ultrafiltration are minimal (Guo *et al.*, 2000b). Following ultrafiltration of natural waters using the concentration mode, the retentate solution was further diafiltered using 20 l of ultrapure water. Time-series permeate samples were collected to monitor the dynamic changes in the concentrations of major ions during diafiltration. As is evident in Fig. 5, concentrations of major ions in the diafiltration permeate decrease rapidly as diafiltration proceeds, and are usually close to their detection limits, when the permeate volume reaches 10 l. Indeed, all major ions retained during ultrafiltration can be washed away during diafiltration. Therefore, the initial retention of major ions during ultrafiltration is likely controlled through a mechanism of electrostatic repulsion by the membrane, which can be reversed by diafiltration.

CONCLUSIONS

The permeation behavior of major ions (F, Cl, SO₄, Na, Ca, Mg) in natural waters can be well predicted by an ultrafiltration permeation model, resulting in a linear log-log relationship between concentration in the permeate (C_p) and concentration factor (CF). Experimental permeation coefficients are significantly less than 1 for SO₄, Ca and Mg, even though permeation coefficients for F, Cl, K, and Na are close to 1, indicating that fractions of some major ions can be retained by a 1 kDa membrane during ultrafiltration.

Unlike during the macrofiltration or microfiltration of natural waters, a significant fraction of selected major ions can be retained during ultrafiltration. On average, about 36% of SO₄, 14% of Ca and 13% of Mg in Trinity River water can be retained by a 1 kDa ultrafiltration membrane. However, these retained fractions were found to decrease with increasing salinity (or ionic strength), and also with decreasing DOC concentration in natural waters. Electrostatic repulsion by the negatively charged ultrafiltration membrane is likely the dominant retention mechanism for SO₄, with concomitant cation retention required to maintain charge balance.

Selective retention of major ions during ultrafiltration may significantly affect the results of trace element size fractionation or phase speciation studies when using ultrafiltration techniques, and will need to be taken into account.

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