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Evaluation of two cross-flow ultrafiltration membranes for isolating marine organic colloids

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Abstract

Laboratory and field studies were performed to evaluate two 1 kilo-Dalton (kD) cross-flow ultrafiltration (CFF) membranes (a Millipore Prep-scale CFF membrane constructed primarily from regenerated cellulose and an Amicon CFF polysulfone membrane) to isolate colloids (operationally defined as particles or macromolecules between 1 kD and 0.2–1 μm) from sea water. We focused on three crucial aspects when applying the CFF technique: retention characteristics, sorptive potential and ultrafilter breakthrough. Lab results showed that both CFF systems retained $\geq$ 91% of a 3000 nominal molecular weight (NMW) dextran standard, consistent with the manufacturer's rated cutoff. The Millipore membrane showed essentially no loss of a dextran standard, while 33% was lost for the same molecule onto the Amicon CFF membrane. Both membranes showed higher losses of a protein standard (Lactalbumin) added to sea water. For bulk organic carbon (OC), both membranes usually had reasonable recovery (100 $\pm$ 10%) as long as the membranes were preconditioned. This was true for both lab experiments and field investigations in open ocean water off Bermuda. However, data from ^{234}Th and ^{230}Th analysis of samples from a station off Bermuda showed very large losses and hence low recovery from CFF. Results of these fractionated OC and ^{234}Th distributions are also discussed in the context of prior studies. Ultrafilter breakthrough of both high molecular weight (HMW) and low molecular weight (LMW) compounds may occur throughout the CFF process, especially when processing coastal sea water where COC is relatively enriched. A permeation coefficient model provides an overall reasonable fit to the data characterizing the permeation behaviour of CFF; the retentate prediction based on the model indicates that breakthrough becomes more significant after the concentration factor (cf) is higher than 5, which implies that fractionation of organic components increases at higher cf. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: organic colloids; coastal sea water; cross-flow ultrafiltration; organic components; organic carbon

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1. Introduction

Over the last few years, colloids have received increasing recognition for their important role in the biogeochemical cycling of organic materials, trace elements, and radionuclides in marine environments (e.g., Honeyman and Santschi, 1989; Benner et al., 1992, 1997; Moran and Buesseler, 1992; Dai, 1995; Guo et al., 1996; Dai and Martin, 1995; Greenamoyer and Moran, 1996; Buesseler, 1996; Guo and Santschi, 1997; Gustafsson and Gschwend, 1997). This recognition is based upon three main lines of evidence. First, colloids were found to be highly abundant in sea water (Koike et al., 1990; Wells and Goldberg, 1991; Longhurst et al., 1992) and formed a significant fraction of the so-called dissolved organic carbon (DOC) pool (Carlson et al., 1985; Cauwet and Sidorov, 1996; Dai et al., 1997). Secondly, at least some fractions of the colloidal material are thought to be labile and rapidly cycled in the water column, and hence, colloids might hold a key to understanding the potentially dynamic nature of OC cycling (Moran and Buesseler, 1992, 1993; Benner et al., 1992, 1997; Amon and Benner, 1994; Santschi et al., 1995). Finally, organic-rich colloids may influence the transport and bioavailability of associated trace elements in aquatic systems.

Recent studies have improved our understanding of the role of colloids in marine biogeochemistry. This improvement is based largely upon the application of CFF to marine systems because of its potential for isolating colloids in a non-destructive manner with reduced concentration polarization effects at the membrane's surface. This makes it possible to process larger volume samples at lower molecular weight cutoffs with reduced membrane fouling. It should be noted, however, that commercially available CFF membranes are designed primarily for water purification, biomedical and food processing, and not for the fine characterization of natural organic assemblages which are both highly diluted and of widely varying size and chemical composition in sea waters.

Some CFF membranes appear to be less suitable for marine application due to their inaccurate retention coefficients and substantial losses of a wide range of chemicals to the membranes (e.g., Osmonics-112-PT1, Gustafsson et al., 1996), while other membranes are thought to exhibit better performance for application to marine studies (e.g., Amicon polysulfone S10N1, Guo and Santschi, 1996; Benner et al., 1997). Nevertheless, the results from CFF remain highly system specific, as documented in a CFF intercomparison experiment conducted on surface coastal waters organized at the Woods Hole Oceanographic Institution (WHOI), and on surface and mid waters off Hawaii (referred to as Colloid Cookout hereafter, see Buesseler, 1996). The Colloid Cookout demonstrated that colloidal concentrations vary widely as determined by different CFF systems and/or the same CFF system while varying the CFF processing protocol (e.g., %COC, colloidal OC, ranges from 4–50% of DOC in Woods Hole). Blanks of the CFF systems can also be very significant if improperly handled (COC blank ranged from 2 to >100 μM). Potential problems were also seen in two other areas, namely sorption of compounds to the membrane and the breakthrough of HMW and LMW molecules during ultrafiltration (i.e., an increase in permeate concentration with time). The effects of sorption are most easily seen at the beginning of the ultrafiltration processing, while breakthrough occurs throughout a CFF run. Therefore, it is becoming increasingly crucial to evaluate CFF system performance, integrity, and membrane characteristics prior to their use or the interpretation of the CFF results. In this paper, we report on a series of lab and field experiments designed to evaluate and compare a commonly used Amicon polysufone membrane and a Millipore regenerated cellulose membrane. Special attention is paid to their retention characteristics, sorptive potential and ultrafilter breakthrough.

2. Methods

2.1. CFF processing

We shall use the following terms in the text. 'Permeate' is the fraction passing through a CFF membrane while the 'retentate' is the fraction retained by the membrane. 'Integrated' refers to a single sample taken from the final permeate and retentate reservoirs. 'Preconditioning' refers to a sample solution which is processed by the CFF after

cleaning and just prior to sampling, and is typically discarded prior to a given sample run.

Our CFF system is composed of a Flojet polypropylene diaphragm pump, plumbing (mostly of Teflon) and one of two CFF membranes. Two different CFF membranes were used: an Amicon S10N1 10 ft^2 surface area spiral wound polysulfone membrane (this type of membrane is no longer commercially available because Amicon has merged with Millipore), and a Millipore Prep/Scale™-TFF PLAC regenerated cellulose membrane with a surface area of 6 ft^2. We used 3 Millipore filters in parallel (surface area 18 ft^2) to increase the ultrafiltration rate. Amicon membranes are also commonly joined into multiple membrane systems to increase flow rate, though in this study only a single Amicon CFF membrane was used. Each of these CFF filters has a manufacturer's reported cutoff of 1 kD. The prefiltered sea water (through either 0.4 μm Nuclepore or 0.2 μm cartridge filters, detailed later) is continuously passed into a 4 l fluorinated polyethylene bottle. During operation the membrane pressure is maintained at $\sim$14–16 psi.

Brand new membranes were first cleaned with a large volume of Nano-pure Q water (Q-water hereafter), followed by recirculation with a 2% Micro detergent solution and rinsed thoroughly with Q-water. Then, the system was recirculated with a 0.01 N NaOH solution followed by a 0.01 N HCl solution for 1 day with Q-water rinsing in between. Finally, the CFF system was washed with large volumes of Q-water. Usually, an OC blank was run at this point: 4 l Q-water was recirculated for 30 min and then both the permeate and the retentate were sampled. These samples were analyzed for OC and are reported as the system Q-water blanks. After this initial cleaning procedure, the CFF system, after a typical sample run, was cleaned by flushing with $>$ 20 l Q-water followed by 0.01 N NaOH and 0.01 N HCl solutions made from the same Q-water. The base or acid solution was recirculated for at least 1 h followed by rinsing with Q-water until pH $\sim$ 7. These cleaning steps were followed by preconditioning with prefiltered sea water (4–6 l). The cleaning was conducted just prior to each sample run.

Two modes of ultrafiltration processing were used in the study: recirculation and sampling. In recirculation mode, the sample volume remains constant as the permeate is recycled back into the sample reservoir and, hence, there is no net concentration of colloids within this reservoir. In sampling mode, the permeate is collected in a separate reservoir and fresh sample solution from a source outside the system loop is used to maintain a constant volume in the retentate reservoir. Concentration of the colloids in the retentate reservoir increases with time. For the field work presented in this paper, only sampling mode was employed except when specifically indicated as a recirculation mode.

In all test modes, samples were collected at various times or cf from the permeate and retentate lines for OC analysis. Samples were also collected from the sample reservoir before and after processing and in some cases at intervals during the processing. Samples for ^{234}Th and ^{230}Th analysis were collected from the integrated permeate and retentate fractions.

2.2. Colloidal concentration

We define the colloidal fraction as the material which passes through a 0.2 or 0.4 μm filter and is retained by a 1 kD CFF membrane. When analysing data from the sampling mode, the concentration was calculated at each time point when samples were collected. At each sampling point:

$$[\text{colloidal}] = \frac{[\text{retentate}] - [\text{permeate}]}{\text{cf}} \quad (1)$$

$$\text{cf} = \frac{\text{retentate volume} + \text{permeate volume}}{\text{retentate volume}} \quad (2)$$

and,

$$\text{Sum concentration} = [\text{colloidal}] + [\text{permeate}]$$

The mass balance can then be calculated by comparing the sum with the initial source solution concentration.

2.3. Standard macromolecular tracer experiments

Two colloid standards were used in the lab tracer experiments: a 3 kD dextran carbohydrate and a 14.5 kD Lactalbumin protein, both of which were fluorescein tagged. The applicability of the standards for determining relative membrane retention and sorp-

tive losses in sea water has been described previously (Gustafsson et al., 1996 and the references therein). In these experiments, sea water that had been run through a 0.2 μm prefilter was spiked to a nanomolar level of individual macromolecules, which are equivalent to the natural OC concentration of similar molecules in sea water. The excitation and emission wavelengths of flourescein are distinct from natural fluorescence so it should be a good marker. The spiked solution was then run through CFF and samples were collected as described below.

2.4. Sampling

The coastal sea water used for the lab experiments was obtained via a PVC sea water line in the Coastal Research Lab at the Woods Hole Oceanographic Institution. The inlet for these source waters lies approximately 1 m off the bottom in 3 m of water in Vineyard Sound, MA. The sea water was run through a prefiltration rig that consisted of a 10 μm and a 1 μm polypropylene filter cartridge, followed by a 0.2 μm polycarbonate filter cartridge. The prefiltrate was collected in 20 l acid-cleaned Teflon bags supported within a high density polyethylene jug (NOWPACK, Bag-in-a-bottle, Berghof) prior to the CFF experiments. More than 50 l of sample water were filtered through the system prior to collection of the samples.

We also collected open ocean water near Bermuda during a cruise on the R/V Weatherbird (October 1995). Samples, collected from 30 l Niskin bottles, were pumped directly via Bev-a-line tubing through acid-cleaned 142 mm, 0.4 μm acid cleaned Nuclepore filters and subsequently through the CFF system. Ultrafiltration was also conducted using a homemade in situ CFF system (referred to as ISCFF). In this case, ultrafiltration was carried out in situ under our standard sampling mode at selected depths. Because pressure effect is the primary concern while running a CFF membrane in situ, we have tested this pressure effect by subjecting the membrane to 5000 psi at a WHOI pressure facility. The membrane was then re-tested with standard molecules and it was shown that there was no net change in the integrity of the CFF membrane. The consistence between the data from in situ experiments and deck experiments that will be shown later, confirms that no significant changes occurred in the performance of the CFF membranes under high pressures.

2.5. Analysis

2.5.1. Organic carbon

Subsamples for OC analysis were collected in either 125 ml precombusted glass bottles or 20 ml glass scintillation vials with precleaned Teflon lined caps. Samples were acidified with 50% H_3PO_4 to pH ~ 2 (500 μl for 100 ml sample) immediately upon collection and stored at 4°C for up to a few weeks or at -18°C for longer term storage. OC concentrations in the permeate, retentate or prefiltrate fractions were analyzed, in duplicate, with a high temperature catalytic oxidation (HTCO) analyzer (Peltzer and Brewer, 1993). Instrumental blanks (usually < 10 μM) were estimated daily using UV-irradiated Q-water with very close to zero C content. Calibration was also run daily using potassium hydrogen phthalate dissolved into aged sea water as standards. The precision for OC measurement was $< 2\%$.

2.5.2. Fluorescence

The sea water which was spiked with our fluorescein-tagged standards was collected in pre-cleaned amber glass bottles and the fluorescence was measured using a Kratos Spectorflow 980 fluorometer or a Hitachi F-1000 with the excitation wavelength set at 493 nm and a 520 nm cutoff emission filter. Source sea water without any spikes was used for background substitution.

2.5.3. ^{230}Th and ^{234}Th

Samples for ^{230}Th analysis were collected in acid-cleaned 2 l polyethylene bottles. ^{230}Th was analyzed by thermal ionization mass spectrometry (TIMS) after co-precipitation with $Fe(OH)_3$ carrier, and separation and/or purification by anion exchange chromatography in a clean room according to the method of Edwards (1988). ^{234}Th activity was determined by counting the stronger beta emissions of its daughter ^{234}Pa, as described in prior publications (Buesseler et al., 1992; Moran and Buesseler, 1993).

3. Results and discussions

3.1. Blank evaluation

Table 1 shows one example of the evolution of OC concentration during the cleaning and rinsing steps as the Amicon CFF system was treated progressively using Q-water, base, and acid solutions after a typical sample run. The source Q-water OC concentration ≈ 2 μM. Elevated OC concentrations (38 μM for the retentate and 4 μM for the permeate when cf = 1) in the first Q-water rinse (recirculation for 20–30 min prior to collection) may be related to the release of OC that was retained by the CFF membrane due to sorptive processes, and/or sample solution carryover due to incomplete draining of the system from the preceding CFF sample. The OC concentration increased in the retentate to 72 μM as CFF processing progressed (cf = 4), indicating the continued release of OC. A subsequent base rinse appeared efficient at lowering the OC blank of the system (OC = 17–19 μM). After the base rinse, the blank of the system was indistinguishable from the source Q-water (OC = 2–3 μM). It is interesting to note that a subsequent HCl rinse resulted in a slightly higher OC concentration both in the permeate and retentate (3–5 μM), which might be related to the chemical properties of membrane OC foulants which were not removed with either the base or Q-water solutions. The 3rd Q-water rinse had an OC concentration that was again equivalent to the source Q-water. For the Millipore CFF system, the equivalent OC blank after acid and base rinses was 1–4 μM, again indistinguishable from the source Q-water.

These results demonstrate that a low bulk OC blank is achievable for these two CFF membranes after careful cleaning. The high bulk OC blank shown by many of the CFF systems during the Colloid Cookout (Buesseler et al., 1996) is not apparent for these two systems, though the sequential results show the need for multiple cleaning steps. Due to differences in our sample sea water media and Q-water, these OC blanks cannot be directly applied as a correction to OC results for sea water processed by CFF, as noted by Buesseler et al. (1996). However, a Q-water OC blank test represents an essential first order check on the performance of the CFF membrane. A low Q-water blank suggests adequate desorption or degradation of the membrane OC foulants and furthermore attests to the lack of carryover of sample solution. Moreover, as shown by Gustafsson et al. (1996), the OC blank will increase if the system is left for even a few hours. Therefore, cleaning must be performed after each sample run and again immediately prior to new sample processing.

Table 1
Organic C concentrations in Q-water and in rinse solutions from the Amicon polysulfone CFF

OC (μM)			cf
Rinse solution	Permeate	Retentate	
1st Q-H_2O	4	38	1
	4	72	4
NaOH (0.01 N)	8	17	1
	5	19	4
2nd Q-H_2O[a]	3	2	1
	1	3	4
HCl (0.01 N)	4	3	1
	5	5	4
3rd Q-H_2O	1	2	1

[a]Rinse the system with Q-H_2O until pH ~ 7 after the base and acid rinses.
cf = concentration factor.
Source Q-H_2O organic C concentration, ~ 2 μM.
The volume of each rinse solution used, ~ 4 l.

3.2. Retention characterization

We evaluated the retention coefficient (RC % = (1 − [permeate]/[retentate]) × 100) of both CFF membranes using prefiltered (< 0.2 μm) sea water sample spiked with nM levels of either fluorescein tagged dextran (3 kD) or Lactalbumin (14.5 kD) standard molecules. Tests were run in recirculation mode, and the RC was calculated using the data when no further losses of standards to the membrane could be observed. Both membranes showed $> 91\%$ retention coefficients for both molecules with slightly higher retention for the Amicon CFF system (Table 2). As compared to many other CFF membranes used in the Colloid Cookout, these two membranes showed reasonably accurate retention characteristics under these conditions, similar to the manufacturer's specification. Membranes such as Osmonics, Filtron and Membrex that were evaluated by Gustafsson et

Table 2
Retention of flourescein tagged dextran carbohydrates and Lactalbumin proteins by CFF membranes and their losses to the membranes

Membrane	Standard	Retention coefficient (%)	Loss (%)
Millipore regenerated cellulose	3 kD Dextran	> 91	undetectable
	14.5 kD Lactalbumin	> 94	40–70
Amicon polysulfone	3 kD Dextran	> 99	35
	14.5 kD Lactalbumin	> 99	40

al. (1996) during the Colloid Cookout have shown much lower RCs than the manufacturer's specification. Using 3 kD fluorescing dextran standards, Gustafsson et al. (1996) also tested two Amicon 1 kD membranes identical to the Amicon membrane used in this study. These results showed that the two CFF membranes retained only 33% and 75% of the 3 kD standard. As pointed out by Buesseler et al. (1996), rating systems for CFF cut-offs are not uniform between manufacturers, and thus, some variations might be expected, even between different batches or across membranes of different designs within one company. Therefore, it is essential that the retention characteristics be known prior to making any determination of sample size distributions based upon CFF data. Moreover, membrane RCs could change with use, and therefore, the RC for a CFF membrane must be estimated frequently.

In an evaluation of RCs, one should note that the RC depends on the effective molecular weight of the solute in a given media, the retention profile or the nominal pore size of the membrane, and the conditions under which the CFF device is being operated. Each CFF membrane being used must therefore be evaluated for its performance characteristics under the conditions expected by the user regardless of the manufacturer's rated cutoff (PDA, 1992). The conditions of the experiment are thus very critical to the determination of the RC for a given CFF membrane. Recirculation mode is the preferred processing technique in this respect, as it minimizes ultrafilter breakthrough because there is no net concentration factor in this mode (see later discussion). Moreover, as suggested by Gustafsson et al. (1996), recirculation mode allows one to deconvolute the true RC since there may be temporal changes in either permeate or retentate concentrations due to naturally occurring sorption or breakthrough processes.

Similar studies in standard sampling mode (continuous losses could occur in sampling mode and hence, lower permeate concentrations, which may result in an overestimation of RC, Gustafsson et al., 1996) or studies using artificial media might not be reliable for the prediction of the RC for marine applications. Matrix effects on the determination of the RC have been shown by Guo and Santschi (1996). The RC for raffinose (0.6 kD) was halved from 48% in Q-water to 26% in artificial sea water using the same model of Amicon CFF membrane as evaluated in this study. Note that two different Amicon membranes were used in their two experiments, hence the RCs' differences could be due to membrane to membrane variability, though this is quite unlikely. For a Vitamin B-12 (1.3 kD) solution, they found a similar RC of 80% in both Q-water and artificial sea water solutions in their experiments (Guo and Santschi, 1996). We note that the RC experiments performed by Guo and Santschi (1996) were run in sampling mode and at much higher standard concentrations than in our study. Gustafsson et al. (1996) reported that an Osmonics 1 kD membrane had an apparent cut-off close to 50 kD under similar conditions to those used here. The retention coefficient for a molecule larger than the membrane cutoff will never be exactly 100%, neither will the RC for a molecule smaller than the membrane cutoff be 0%. This is the fundamental reason why concentrations can change with cf: 'breakthrough' occurs. This will be addressed in a later section.

3.3. Sorption behaviour

3.3.1. Standard colloids experiments

In our RC experiments, we calculated the loss of the standard molecules to the membranes by attempting to mass balance our original fluorescein signal

with the final permeate and retentate results (using the data when no further losses were observable, Table 2). The Amicon polysulfone membrane showed a 33% loss for our carbohydrate standard (dextran) and a 40% loss of our protein standard (Lactalbumin). Hence, the Amicon CFF membrane appeared to sorb both carbohydrate and protein standards to a significant degree. The Millipore membrane showed no measurable loss for the dextran standard and a 40–70% loss (range for two experiments) for the protein standard.

Apparent sorptive losses of the protein standard were also observed during another experiment conducted using the sampling mode (Fig. 1). Here we see that the losses were highest for our protein standards during the early stages of preconditioning and reached a relatively constant value after cf ≈ 2. It is odd that the first two points at the start of sample processing (cf = 1) indicated very little loss to the membrane, but this may be due to macromolecule carryover from the preconditioning process. The final loss to the Amicon membrane was roughly 50%, and was consistent with the result from the recirculation mode (Table 2). This is an important result and caution should be taken when interpreting the CFF results for trace organic studies, particularly for the more hydrophobic or particle-reactive species. In fact, protein losses to various membranes have been observed previously by Philp et al. (1994) and Gustafsson et al. (1996). Such sorptive losses have the potential to bias COC compositional results or bulk isotopic signatures.

Differences in membrane composition between the Amicon polysufone membrane and the Millipore regenerated cellulose membrane probably account for the different sorption behaviours. The difference in sorption with respect to different molecules for the same CFF membrane most likely indicates that the losses to the membrane are chemical specific, but only after quasi-equilibrium between different molecules and the membrane is reached. The time it takes to reach equilibrium will be a function of the chemical of interest, the membrane surface area, the concentrations of various COC and DOC species, and the ionic strength and composition.

3.3.2. Bulk organic carbon mass balance

A demonstration of a proper mass balance represents an essential first order check of the performance of any CFF experiment. In most cases, we observed the largest losses of bulk OC during the preconditioning stage where equilibrium between solutes and membranes have not yet been reached. It is expected that some natural organic solutes will sorb to the membrane (see prior examples in RC experiments). As a consequence of sorption we can usually

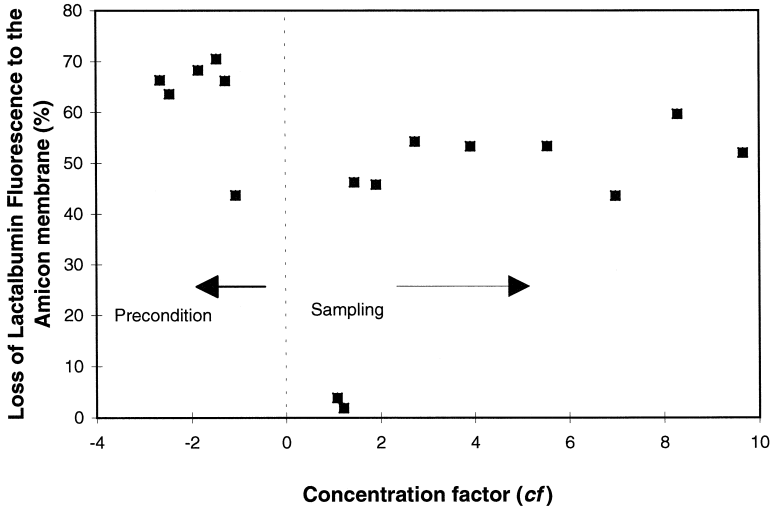

Fig. 1. Percentage of Lactalbumin standard losses to the Amicon polysulfone CFF membrane throughout CFF preconditioning and sampling processes.

observe mass balances below 100% for bulk OC during the preconditioning process. Table 3 shows two examples of the mass balance evolution during both the preconditioning and sampling stages. We can see that the mass balance was as low as 66% at the very beginning of the Amicon CFF preconditioning but increased to essentially 100% recovery. For the Millipore CFF system, the mass balance remains $<100\%$ throughout the CFF preconditioning steps. This may be related to the larger membrane surface area of this system (using three membranes in parallel), and hence the need for more preconditioning in order to reach equilibrium between bulk OC and the membranes. For the Millipore membrane, the last two points (cf = 3.8 and 4.1) shown in Table 3 have higher recoveries due to improper sample handling and a slight contamination.

It is therefore recommended to precondition any CFF system before running samples while thorough cleaning is essential to avoid carryover between samples as shown earlier. Preconditioning appears efficient at minimizing losses of bulk OC. Some chemical losses are governed by their specific interactions with the membranes, however, and cannot be excluded by preconditioning, as shown for the dextran standard losses to the Amicon CFF membrane and the Lactalbumin standard losses to both CFF membranes tested. Some particle-reactive elements, such as Th, have shown the same behaviour, which we will present in a later section.

Table 3
Mass balance of organic carbon at each sampling point throughout the CFF preconditioning and sampling processing for Amicon and Millipore membranes

	Amicon		Millipore	
	cf	*R* (%)	cf	*R* (%)
Preconditioning	1.0	65.7	1.0	88.7
	1.2	98.2	1.1	84.3
	1.4	96.6	1.3	80.6
	1.8	98.4	1.8	91.0
	2.4	79.8	2.6	80.1
	2.6	98.0	2.9	89.0
	2.7	102.7		
Sampling	1.0	104.6	1.0	111.2
	1.2	104.4	1.2	104.2
	1.4	104.2	1.5	96.8
	1.8	100.3	1.9	97.8
	2.5	99.8	3.0	94.4
	3.5	101.8	3.8	125.4[a]
	5.0	102.0	4.1	123.8[a]
	6.2	100.9		
	7.4	99.9		
	8.6	105.1		

R is the recovery at each sampling point, see text for detailed calculation.
cf is the concentration factor.
[a]These two samples are most likely elevated due to contamination during sample processing.

3.4. Permeation behaviour and ultrafilter breakthrough

3.4.1. Background on CFF breakthrough

An increase in the permeate concentration during CFF processing, termed 'breakthrough' was briefly mentioned by Benner (1991) in marine applications but wide discussion of this issue has not occurred in the marine science literature until the Colloid Cookout (Buesseler, 1996). The CFF membrane science literature and freshwater CFF studies have long addressed this issue more rigorously (Logan and Jiang, 1990; Kilduff and Weber, 1992; Douglas et al., 1993). For example, Douglas et al. (1993) have shown that there are changes in major cation concentrations during CFF processing, while Logan and Jiang (1990) and Kilduff and Weber (1992) established a permeation model to predict permeate concentration variations based upon the mass balance of a single molecule and the assumption of a constant RC and zero losses. Comprehensive discussions on the theoretical reasons for the permeate concentration changes can be found in these references and will not be repeated here. In an operational sense, as mentioned earlier, because the RCs for many LMW molecules are rarely zero, some fraction of LMW material will be retained by the CFF membrane and will be eventually concentrated during the CFF processing. Likewise, the RCs for HMW molecules are usually <1 (e.g., the RC for the 3 kD dextran standard is 91% for the Millipore 1 kD membrane as shown above), hence some fractions of HMW material, especially those with a molecular weight close to the membrane cutoff, will pass through the membrane. Thus, the breakthrough is not an artifact, per se, but a consequence of the limitations of CFF membranes and physical chemical interactions of

specific components with the membrane. As a consequence of breakthrough we may expect to see increases in the permeation concentration as concentration gradients increase in the retentate reservoir.

An increase in permeation concentration with increasing cf has been shown in the Colloid Cookout volume in terms of OC (Buesseler et al., 1996; Gustafsson et al., 1996; Guo and Santschi, 1996) and trace metals (Reitmeyer et al., 1996; Wen et al., 1996). The impact of CFF breakthrough can be important in terms of calculating colloid concentrations if concentrations change significantly between discrete sampling points during the CFF run. An example of the effect of changing permeate OC concentration on the estimate of COC abundance for Vineyard Sound water which was processed by the Amicon CFF is illustrated in Fig. 2. In this case, COC is calculated both by difference (i.e., source OC-permeate OC), and by calculation from the concentration factor and measured retentate and permeate OC concentrations at a specific point in time (according to Eq. (1)). As the permeate OC concentration increases, the apparent COC decreases. Therefore, calculation of colloidal concentrations by difference at a single sampling point may be problematic if breakthrough is significant. These changes

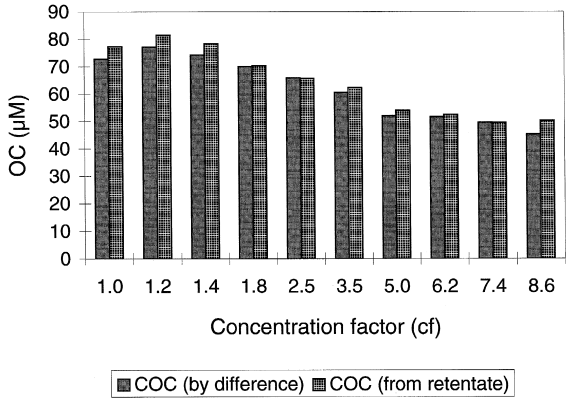

Fig. 2. Effect of changing permeate OC concentrations on the estimate of COC abundance. The example shown here is for Vineyard Sound water which was processed by the Amicon CFF. In this case, COC is calculated both by difference (i.e., [COC] = [source OC] − [permeate OC]), and by calculation from the concentration factor and measured retentate and permeate OC concentrations at a specific point in time ([COC] = ([retentate] − permeate])/cf). As the permeate OC concentration increases, the apparent COC decreases.

in permeate concentration must be taken into consideration in the design and interpretation of any CFF experiment. Recent studies have suggested that it is better to analyze integrated samples, i.e., the final bulk properties of the permeate and retentate to calculate the colloid concentration (Wen et al., 1996). While integrated samples provide a more accurate estimate of the mean colloidal concentration, even here the calculated colloidal concentration will vary with cf depending upon the extent of breakthrough and hence the final bulk properties.

3.4.2. Breakthrough: field data

In Figs. 3 and 4, we present time-series data for OC determined in both the permeate and retentate lines using the Amicon and Millipore 1 kD CFF membranes. Coastal waters (Vineyard Sound surface water for both systems, Fig. 3) and open ocean waters (Bermuda at 10 m-Millipore and 3000 m-Amicon, Fig. 4) were processed. For the Amicon CFF, the permeate concentrations increase with increasing cf in the Vineyard Sound sample, though there appears to be a break in permeate OC near cf = 5. At the same time, a significant decrease of permeate OC concentration is observed (from 26 to 20 μM) at the very beginning of CFF processing. This characteristic drop has been noticed by Guo and Santschi (1996), and is more likely to be the result of carryover from the precondition processing than a reflection of continued sorptive losses. For the Millipore CFF system (Fig. 3B), permeate OC concentrations remained relatively constant, apparently up to cf = 6 for the Vineyard Sound sample. It should be noted, however, that we missed a few sampling points between cf = 1 and 3, where there may have been a drop in permeate OC concentration, as observed for the Amicon CFF system. Actually, the 1st point from both the Amicon and Millipore experiment showed mass balances > 100% (105% for the Amicon CFF experiment, and 135% and 111% for the two Millipore CFF experiments, respectively). This higher recovery at the 1st sampling point is clear evidence of carryover of OC from preconditioning as also observed in our sorption experiment (Fig. 1). This concentration drop is clearly seen in another Millipore CFF experiment shown in Fig. 3C, where we have more early sampling points to better illustrate the decrease of permeate OC concentration.

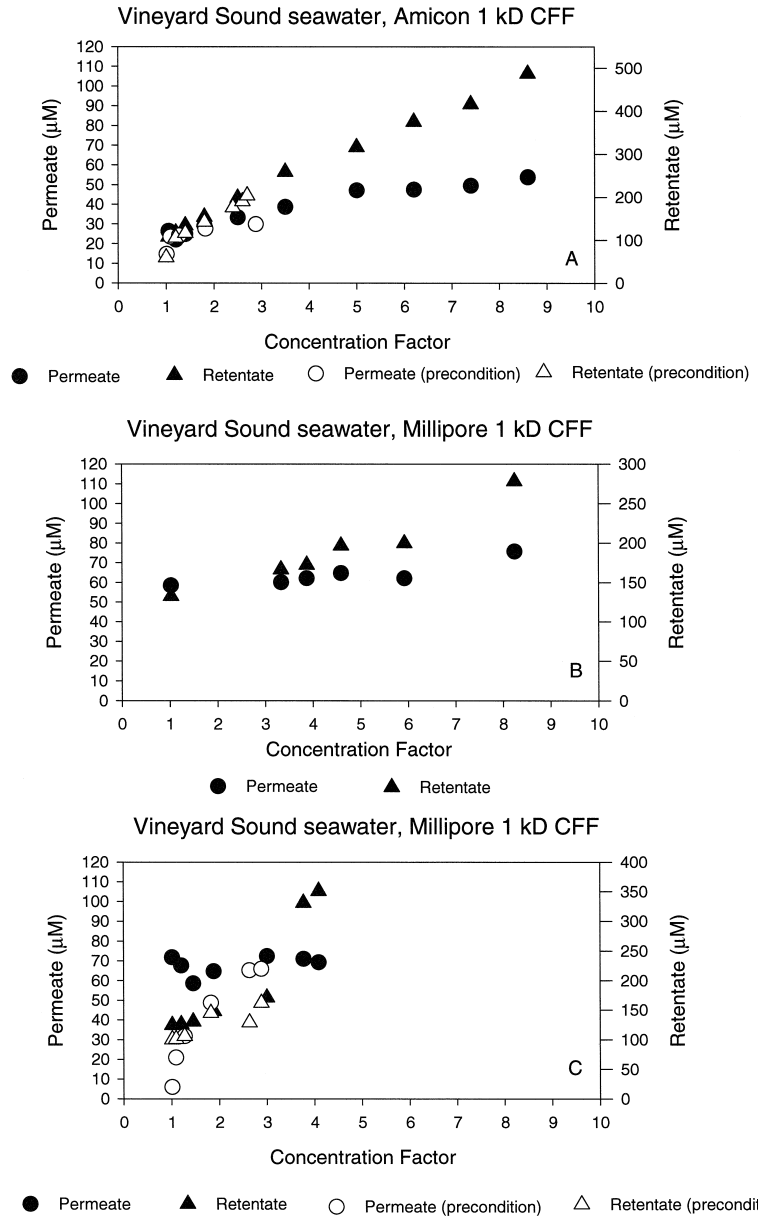

Fig. 3. Time-series results for OC determined in both the permeate and retentate lines from an Amicon and Millipore 1 kD CFF for surface coastal sea water sampled from the Vineyard Sound. 'Preconditioning' refers to sample solution which was passed through the CFF immediately after cleaning.

This drop is a common feature whenever preconditioning is performed before a real sample run. Since it is never possible to completely drain the CFF system, some concentrated sample is carried over into the next sample. When we apply a permeation coefficient model (see Sections 3.4.3 and 3.4.4) to calculate the initial LMW material concentrations, these early sampling points must be excluded in the

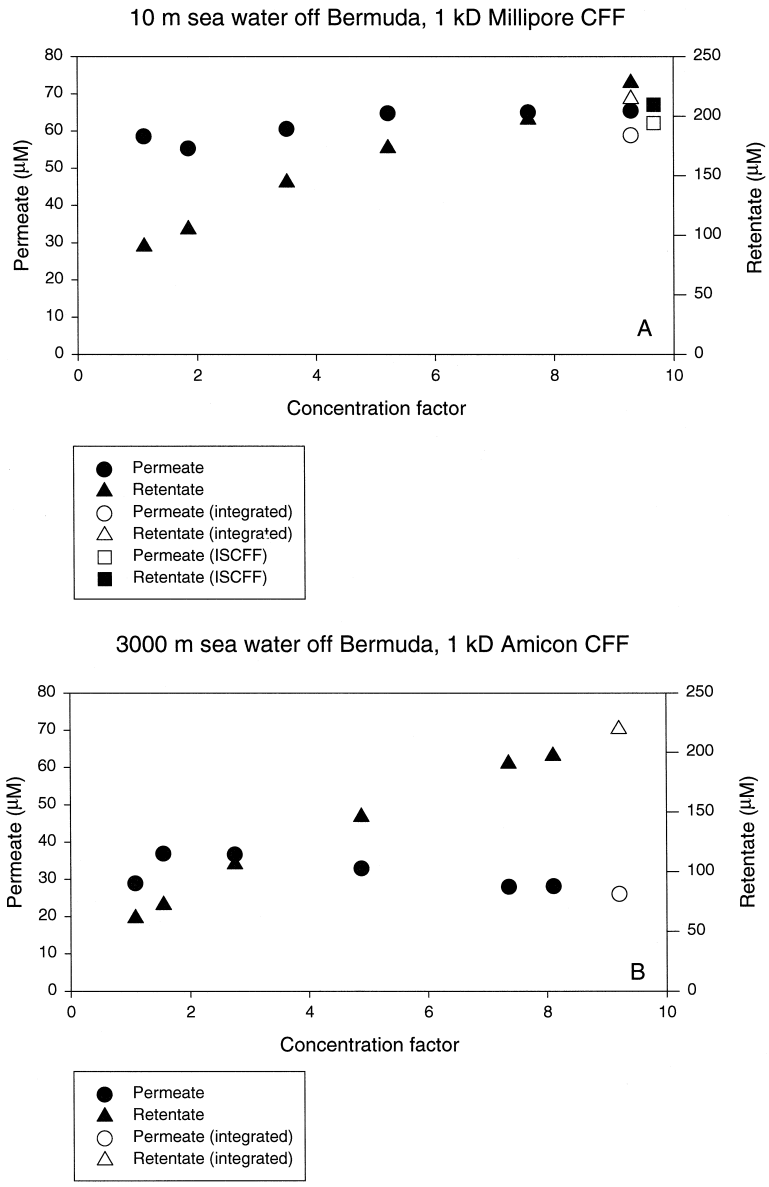

Fig. 4. Time-series results for OC determined in both the permeate and retentate lines from an Amicon and Millipore 1 kD CFF open ocean waters (Bermuda at 10 m Millipore and 3000 m Amicon). 'Integrated' refers to a single sample taken from the final permeate and retentate reservoirs; ISCFF results (Bermuda 10 m) refer to an in situ CFF system.

model fitting exercise otherwise the model derived results could be misleading.

In terms of permeate concentration variations, the increase for the Amicon CFF system is 4 μM per unit change in cf for the Vineyard Sound waters. By comparison, the increase is 3 μM/cf for the Millipore CFF system. Although this OC concentration increase per cf unit is not an absolute index of breakthrough, because permeate concentration does not increase linearly, it does suggest a relatively

greater breakthrough for the Amicon CFF system when processing coastal sea water.

For all of the CFF systems, retentate OC concentrations also increased as expected with cf, as material is retained and concentrated by the CFF membrane. Also shown in Fig. 3 are OC concentrations measured during preconditioning. As noted earlier, sorption of OC to the membranes is significant at the preconditioning stage. By comparison, the Millipore sees a larger net increase in the permeate OC concentration during preconditioning. This sharper increase may be attributed to the larger surface area of Millipore membrane, and hence greater initial OC sorptive losses.

In the open oceanic water off Bermuda, the permeate OC variation pattern (Fig. 4A) is nearly identical to Fig. 3B (Vineyard Sound sea water, 1 kD Millipore CFF system). But the increase in permeate OC concentration is only 1.3–1.5 μM/cf for the Millipore CFF at 10, 900 and 2000 m (Fig. 4A shows only the data for the 10 m Millipore CFF). This indicates that less breakthrough takes place when processing open sea water relative to coastal sea water. For the Amicon CFF system, however, permeate OC concentrations show a slight decrease instead of an increase (Fig. 4B). We cannot explain this slight decrease but given the much lower overall OC concentrations it may be related to analytical and/or handling errors. Clearly though, the breakthrough for the Amicon CFF system for open sea water sample is not as significant as for coastal sea water.

The differing patterns of these curves between CFF systems at any one site are obviously due to the CFF membrane differences. As shown, breakthrough is somewhat larger for the Amicon CFF system especially shown for the coastal sea water CFFs. The different extent of breakthrough between different sites (open ocean water vs. coastal sea water) is most likely due to the different molecular composition and abundance of COC. The coastal sea water exhibits a larger breakthrough effect than off Bermuda, which may indicate that the open ocean water contains simpler organic compounds with an average lower HMW concentration. Hence, less HMW materials may break through the ultrafilter at higher concentration factor. The implication is then that the breakthrough is likely more dependent on the concentration of HMW compounds rather than LMW compounds, which we will discuss further in Section 3.4.3.

3.4.3. Breakthrough: laboratory study

Evidence of breakthrough was clearly seen in a laboratory recirculation experiment. In this experiment, sea water from Vineyard Sound with a DOC concentration ~ 100 μM was initially ultrafiltered using the Amicon CFF system and then the permeate solution (OC = 38 μM) was immediately used as the source solution in a second CFF experiment using the same Amicon CFF system in recirculation mode. Samples were collected from both the permeate and retentate lines for OC analysis. The results (Fig. 5) indicate that the second CFF run retained an additional 15–20 μM OC, representing 15–20% of the initial Vineyard Sound DOC. We can rule out the formation of fresh colloids during recirculation because no significant COC increases could be observed throughout the second CFF experiment for up to 10 h. Thus, this fraction of retained OC from this second CFF experiment reflects OC that had originally 'broken through' into the < 1 kD permeate fraction and now had been retained by the same 1 kD membrane.

These data suggest that a significant fraction of the natural sample was not accurately separated with CFF and is thus prone to breakthrough effects. As

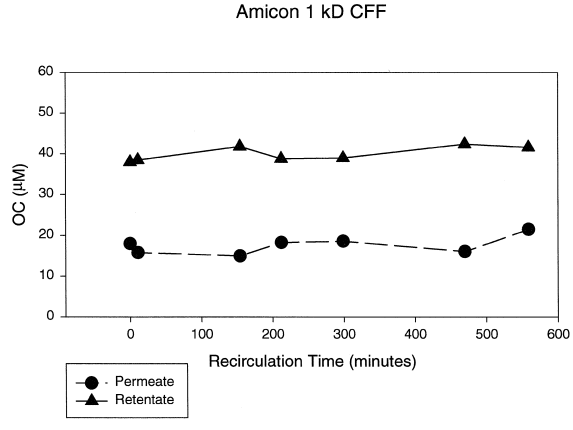

Fig. 5. Variation of OC concentration in the permeate and retentate in recirculation mode using pre-ultrafiltered sea water as the source water.

such, the distribution of this material between the retentate and permeate will vary with cf. We have pointed out earlier that few natural compounds that have been tested have a RC that is exactly $=1$ or $=0$, so CFF can never be considered an accurate/absolute separation device. The specific chemical characteristics one ascribes to the permeate and retentate fractions will therefore vary with cf. In theory, if breakthrough of HMW OC dominates, low cfs would be recommended while high cf will minimize LMW retainment by the CFF (assuming the retention characteristics do not change with increasing cf, which is not likely).

Although we cannot conclude from the above experiment whether HMW or LMW breakthrough is more significant, elevated breakthrough in general in our coastal ocean samples with the highest %COC implies that HMW molecule breakthrough might dominate LMW breakthrough processes. We will also show in Section 3.4.4 that a better prediction of permeation behaviour can be achieved using a permeation model at lower cfs.

An important implication that can be drawn here is that if one sampled the permeate line using recirculation mode, one would minimize HMW material breakthrough. This minimized HMW breakthrough in recirculation mode can be seen in another lab CFF (Millipore) experiment using a 3 kD dextran standard. Here the fluorescence signal in both the permeate and retentate lines are relatively constant except during the early stage of the experiment when sorption of the dextran standards onto the membrane occurred (Fig. 6). This suggests that the RC under recirculation mode is relatively constant and partitioning between HMW and LMW molecules is stable at the membrane surface and hence breakthrough is minor. As a result, the permeate concentration would remain stable, and colloidal concentrations could be calculated by difference between the total feed source concentration and the permeate concentration. The method is practical if only the bulk OC or trace element concentrations are desired. It should be noted that mass balance should still be monitored and sampling should not be conducted until there are no observable losses to the CFF system. However, LMW breakthrough would still affect the permeate OC in recirculation mode because LMW breakthrough occurs whenever the RC for a LWM

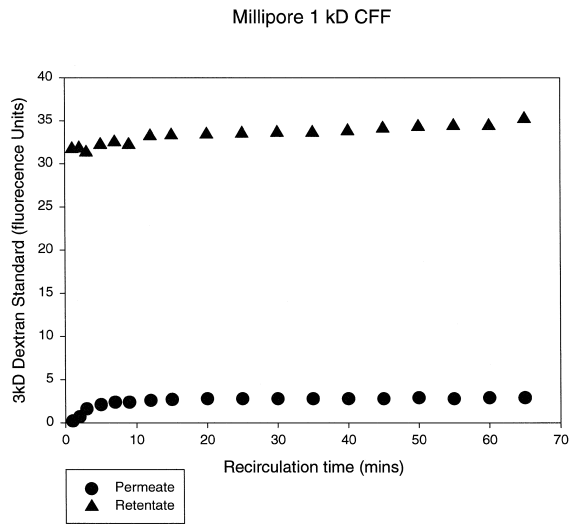

Fig. 6. Recirculation mode test using a 3 kD Fluorescein tagged dextran standard. This figure shows relatively constant permeate concentration and hence, less HMW breakthrough in recirculation mode.

molecule is >0. For example, Guo and Santschi (1996) reported that the RC for Raffinose (0.59 kD) relative to the Amicon 1 kD membrane was 26% in artificial sea water. As a consequence of LMW breakthrough, the membrane will retain some LMW material which should have passed through the membrane, resulting in lower permeate concentrations at lower cf. Frequent calibration of the membrane with standard molecules is greatly encouraged to demonstrate the performance of the membrane. The narrower the profile of molecular weight cutoff, the better the performance in terms of breakthrough.

In conclusion, both HMW and LMW molecule breakthrough can be expected for any CFF systems, though we suspect that HMW molecule breakthrough is more significant in our study. For the two CFF membranes tested using coastal sea water, the extent of breakthrough is greater for the Amicon CFF system. Breakthrough behaviour can also be shown to vary at different sites, depending presumably on the organic matter composition of the sample being processed and the final cf. Thus, compositional changes, i.e., fractionation, can be expected with changing cf and this may lead to uncertainties in the final interpretation of any natural CFF experiment.

3.4.4. Permeation coefficient model

We used the macromolecular solute permeation coefficient model of Logan and Jiang (1990) and Kilduff and Weber (1992) to model our time-series experimental data. The permeation model is designed for single molecules, and hence it is not strictly proper to apply this model to sea water OC permeation behaviour, since sea water colloidal organic carbon is likely a complex mix of individual compounds with different RCs. Moreover, the model assumes that sorption to the membrane is negligible, which, as we have shown, is not the case for some compounds. Certain trace elements and bulk OC in sea water do, however, show concentration patterns that are consistent with this simple permeation model (Wen et al., 1996, Guo and Santschi, 1996). It is, therefore, worthwhile to apply the model to see if we can improve our understanding of CFF behaviour and optimize sampling strategies.

Assuming negligible sorption and constant retention characteristics of the membrane, the permeation coefficient (P_c) can be written as:

$$P_c = 1 - \mathrm{RC} = \frac{C_p}{C_f} \quad (3)$$

where C_f is the upstream feed solution concentration, and C_p is the concentration in the permeate solution. According to Logan and Jiang (1990),

$$C_p = P_c \times C_f^0 (\mathrm{cf})^{\mathrm{RC}} \quad (4)$$

where C_f^0 is the initial concentration of species with any given P_c and RC in the upstream feed solution, and cf is the concentration factor. A plot of $\log(C_p)$ vs. log(cf) thus yields a slope of $\mathrm{RC} = 1 - P_c$, and an intercept of $\log(P_c \times C_f^0)$.

The application of the permeation model to our Bermuda OC data is shown in Fig. 7 and for Vineyard Sound sea water, in Fig. 8. The permeation model results shown are overall consistent with the measured OC data but deviate at the beginning of the ultrafiltration and during preconditioning. As expected, sorption of OC to the membrane exists during preconditioning as discussed above, and the deviation from the model fit is significant for the precondition sample points (Fig. 8). The first post-preconditioning sampling point has systematically higher permeate OC concentration than the model fit line. This

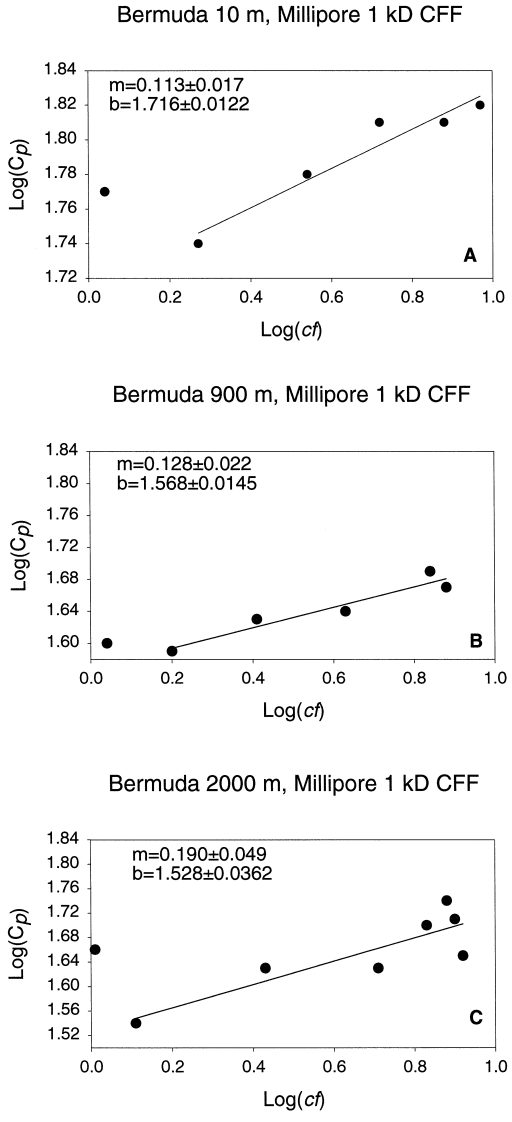

Fig. 7. Model fits of permeation concentration data from the CFF experiments conducted with sea water off Bermuda, where *m* represents the slope of the linear regression and *b* is the constant of regression equation.

is likely due to carryover of OC from the preconditioning as mentioned earlier. The modeled truly dissolved concentration, C_f^0, is mostly in agreement with the integrated permeate concentration (both the deck CFF and ISCFF results, Table 4). It is noteworthy that the two Millipore experiments conducted in different seasons did not show significantly different COC % for the coastal water. The Amicon mem-

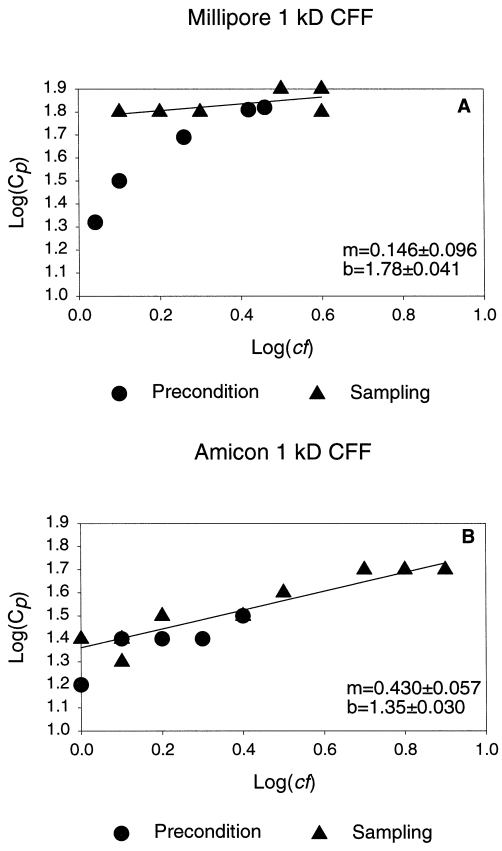

Fig. 8. Model fits of permeation concentration data from the CFF experiments conducted with coastal sea water, where *m* represents the slope of the linear regression and *b* is the constant of regression equation. Note the figures have included the feature at the preconditioning stage.

brane thus apparently retained more macromolecular materials than the Millipore membrane (COC% = 58% vs. 34–38%, respectively).

Another very important and practical issue concerns how one should process a natural sample in order to obtain the most accurate estimate of colloidal concentrations. One way is to collect the integrated permeate sample and subsequently calculate the colloidal concentration by difference or using the cf and measured retentate concentration. Alternatively, one could calculate the colloidal concentration using time-series measurements of the permeate concentration and the permeation model (C_f^0). In fact, as stated above, if we only desire to quantify bulk colloidal partitioning, calculation of colloidal concentration by difference between the total and permeate concentrations using recirculation mode is the easiest and most reliable method if the system is properly cleaned and preconditioned. The volume of sample needed for preconditioning will vary with membrane type, surface area and chemical composition of the samples.

When using the permeation coefficient model to determine the initial LMW material concentration, Guo and Santschi (1996) speculated that LMW molecular breakthrough is the major process responsible for the variation in the permeation concentration. Hence they suggested that a high cf is preferred in order to minimize the retention of LMW molecules. We have shown here that there is also evidence of HMW breakthrough, hence high cf does not ensure reliable sampling. Furthermore, modelling of both the permeate and retentate concentrations using this mass balance approach leads us to suggest that the final cf should be kept as low as possible. Fig. 9 shows the predicted concentrations of OC in both the permeate and retentate. From the retentate data it appears that keeping the cf < 5 is in order since at higher cf, the model fit does a poor job fitting the retentate concentrations. For example, at cf = 8.7, 62 μM OC is missing from the measured retentate concentration if we assume zero losses and constant RC. This may be due to changes in RC with cf, as discussed by Kilduff and Weber (1992). If the same trend continues, we would expect 126 μM and 285 μM OC at cf = 20 and cf = 50, respectively (mostly HMW materials), to be missing. Similar results can be seen from the Millipore CFF retentate modelling, which show larger deviations at higher cf. In fact, when comparing the COC concentration calculated by difference with the value calculated according to Eq. (1), one can systematically observe lower COC concentration derived from the method of Eq. (1) (Table 4). This also suggests that the missing COC does originate from the measured retentate loop. In terms of our COC calculation, this missing OC corresponds only to a 5% error for the case in Fig. 10A, which is not extremely important. However, for characterizing the chemical composition of COC, if this 'missing' fraction of HMW OC is related to specific losses to our CFF systems, it is likely that significant chemical fractionation may occur.

Table 4
Comparison of measured OC concentration (in μM) with values predicted from the permeation coefficient model

Sample	DOC	Integrated			COC/DOC		Model fitted		COC/DOC
		cf	Permeate	Retentate	(*a*)	(*b*)	P_c	C_f^0	(*c*)
Millipore Bermuda 10 m	80	9.3	59	215	26%	21%	0.88 ± 0.02	60 ± 3	$26 \pm 3\%$
Bermuda ISCFF 10 m	80	9.7	62	210	22%	19%			
Millipore Bermuda 900 m	49	7.6	40	95	18%	15%	0.89 ± 0.02	41 ± 3	$14 \pm 5\%$
Millipore Bermuda 2000 m	48	8.3	41	96	15%	14%	0.81 ± 0.05	41 ± 6	$14 \pm 12\%$
Amicon Bermuda 3000 m	46	9.2	26	220	43%	46%	*	*	*
Millipore (Vineyard Sound, July 1995)	97	8.2	64	286	34%	28%	0.78 ± 0.08	55 ± 13	$40 \pm 13\%$
Millipore (Vineyard Sound, March 1996)	112	4.1	68		39%		0.83 ± 0.10	69 ± 15	$37 \pm 13\%$
Amicon (Vineyard Sound, March 1996)	99	8.7	42	473	58%	50%	0.57 ± 0.06	38 ± 7	61 ± 7

Integrated refers to a single sample taken from the final permeate or retentate reservoir. ISCFF refers to in situ CFF integrated. [DOC] = prefiltered source water OC concentration. $(a) = ([\text{DOC}] - [\text{permeate}])/(\text{cf} * [\text{DOC}])$. $(b) = ([\text{retentate}] - [\text{permate}])/(\text{cf} * [\text{DOC}])$. P_c is the permeation coefficient. C_f^0 is the initial concentration of species with any given P_c and RC in the upstream feed solution. $(c) = ([\text{DOC}] - C_f^0)/[\text{DOC}]$. * $P_c > 0$, does not fit the model.

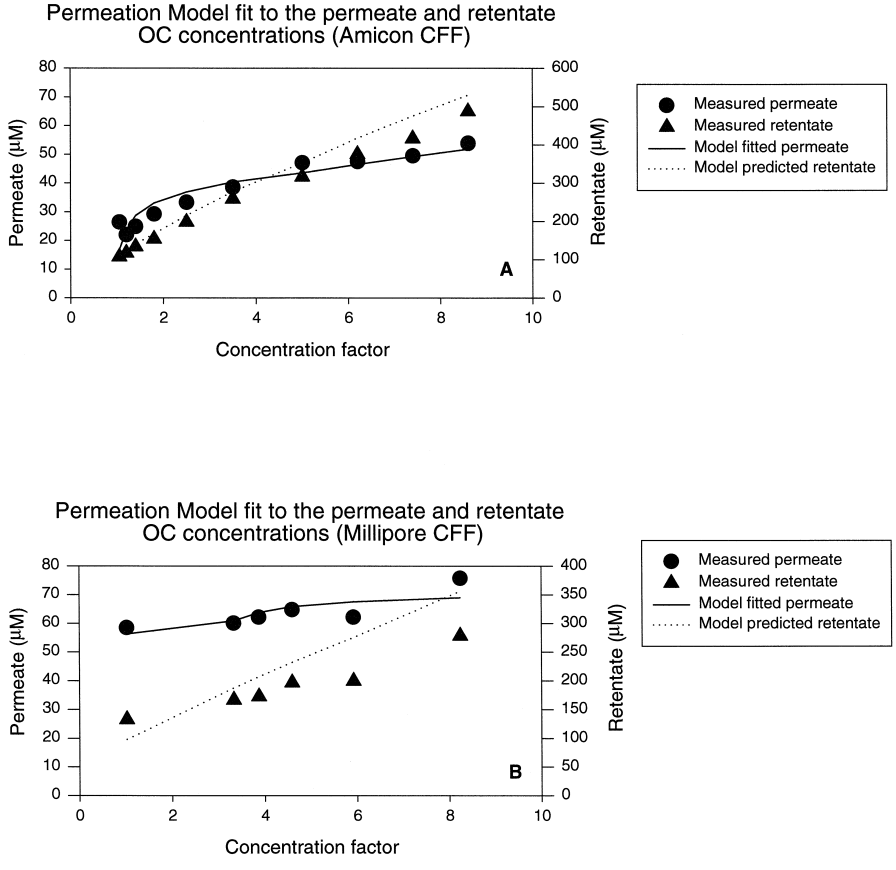

Fig. 9. Comparison of predicted retentate OC concentration based on the permeation coefficient model predicted permeate concentration.

3.5. Distribution of size fractionated organic carbon and ^{234}Th off Bermuda

Fig. 10 shows the vertical profiles of OC and ^{234}Th at our open ocean site off Bermuda. The source water OC concentrations vary from close to 80 μM in the surface waters to 45–50 μM in the deep waters, which agrees quite well with previous observations (e.g., Calson et al., 1994; Benner et al., 1997). The sum of the organic carbon fractions match this pattern quite well, which again indicates the reasonable recoveries of OC using both the CFF membranes. The COC concentration is highest at the upper 100 m (34% of DOC), corresponding to the fluorescence maximum layer. COC reaches its minimum at the depth of 2000 m then increases again in deep waters. This increase might represent another OC source, such as from resuspended particles in the bottom layer. Similar signals are also shown by particulate and colloidal ^{234}Th, which will be addressed later. The overall size distribution of OC is quite consistent with that observed by Benner et al. (1997) at the same site.

For the particle-reactive radionuclide ^{234}Th, the results are less encouraging. The sum ^{234}Th activity is much less than the total activity especially for the subsurface samples. The fundamental reasons causing these losses of ^{234}Th appear to be related to the interaction between ^{234}Th and the membrane. Earlier ^{234}Th CFF studies commonly used 10 kD CFF membranes and have shown varying results in terms of ^{234}Th mass balance during ultrafiltration. Some studies showed better mass balance (Moran and Buesseler, 1992, 1993; Niven et al., 1995, Huh and Prahl, 1995), while others have shown up to 50% losses to the 10 kD CFF systems (Baskaran et al., 1992; Baskaran and Santschi, 1993). Overall, regardless of the composition of the membrane (polysulfone, polypropylene, etc.), none of these 10 kD CFF membranes had as large a loss as we have seen in this study at the Bermuda site. This might suggest that 10 kD CFF membranes have physically less affinity for ^{234}Th because losses are both related to chemical sorption and physical interactions within the membrane (i.e., a function of pore size and membrane design). This trend has been found as well in recent

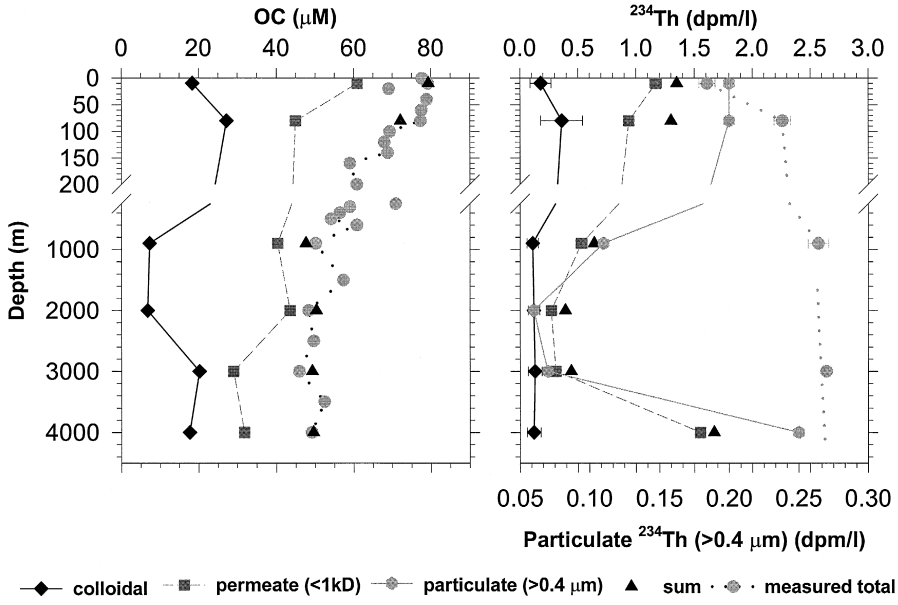

Fig. 10. OC and ^{234}Th distribution in the sea water off Bermuda, October 1995. In each profile, the concentrations of colloidal (black diamond), permeate (dark gray squares) and their sum (black triangle) can be compared to the source waters (gray circles). Also shown is particulate ^{234}Th data (gray hexagon). In all cases, a 1 kD Millipore CFF membrane was employed, except for 3000 m, where an Amicon 1 kD CFF membrane was used.

studies by Guo et al. (1997). They found ^{234}Th losses to a Amicon CFF membrane of 1–6% for the 10 kD membrane and 15–29% for a 1 kD membrane.

When we look at the loss pattern of ^{234}Th activity between depths, there seems to be a depth dependence in the dominant forms of 'free' and colloidally bound ^{234}Th. The highest losses (up to 80%) appear in the mid waters (2000–3000 m) while the smallest losses were found in the upper 100 m where COC concentrations are highest. For the 4000 m sample, the ^{234}Th losses appear to be minimized again. Coincidentally, the COC concentration is also relatively elevated at this depth. For a different Th isotope, results also showed that a large amount (70%) of ^{230}Th was lost to the Millipore membrane at 2000 m, the depth corresponding to the minimum COC concentration (unpublished data in collaboration with R.L. Edwards). These qualitative trends suggest to us that the largest losses were taking place when processing sea water with the lowest COC concentrations. In other words, it appears that a better ^{234}Th mass balance can be expected where colloidal concentrations are higher.

If this is universally true, we would expect smaller losses when processing coastal sea water samples. Indeed, in a recent CFF experiment using sea water collected from the Gulf of Maine (July 1996) and the same Millipore 1 kD CFF system, the ^{234}Th recovery was 74% (total dissolved = 1.29, permeate = 0.77, retentate = 2.8 dpm/l with a concentration factor of 10.7, Dai and Buesseler, unpublished data). More recently, we conducted a series experiments in the Gulf of Maine using the same Millipore CFF system, and the results also showed much better recoveries of ^{234}Th, ranging from 59–106% (Dai et al., in preparation). More noticeably, analyses of the rinse solutions (the post-sampling procedure is basically the same as the procedure used for blank evaluation described earlier but we combined all the rinse solutions together for ^{234}Th measurements) showed that 12% to 17% of the 'lost' ^{234}Th can be recovered (4–7% in the rinse retentate solution and 5–11% in the rinse permeate solution, Dai et al., in preparation). Assuming the colloidal materials sorbed to the membrane are not dissolved during the acid and base leaching, this result suggests the fraction of ^{234}Th lost to the membrane through sorption may occur both as LMW and HMW material. We should point out, however, that this assumption needs further experiments for confirmation, and most likely we would underestimate the colloidal fraction by correction based on the rinsing data, if some fraction of the lost colloids were dissolved or decomposed during the rinsing operation.

Based on a dextran ^{229}Th tracer CFF experiment, Liang et al. (1997) suggested the 'lost' fraction of ^{234}Th was predominately in the ultrafiltered fraction and cannot be added to the colloidal fraction. On the contrary, Baskaran et al. (1992) concluded that 'lost' fractions should be added to the colloidal fraction. Based on the conclusion of Baskaran et al. (1992), Guo et al. (1997) also added the washing/rinse fractions to the colloidal pool. Even when they did this, the CFF mass balance of ^{234}Th varied from 72% to 115% for the 1 kD Amicon CFF. From the results of this study, we believe that better practical corrections for the 'lost' Th should be based on individual samples of washing/rinse solutions with a separation between permeate and retentate solutions. It is noteworthy that if the mass balance of ^{234}Th remains $< 100\%$ even after this correction, some of the lost Th seems unrecoverable.

Beyond this mass balance issue for ^{234}Th, our overall ^{234}Th distribution is in agreement with previous observations, showing a maximum colloidal ^{234}Th at the depth of maximum fluorescence as observed by Huh and Prahl (1995) using a 10 kD CFF system. The particulate ^{234}Th pattern is quite similar to the colloidal fraction, with highest concentrations at the surface and decreasing with depth. An elevated concentration was again observed at 4000 m, as for the colloidal ^{234}Th and COC. The distribution of both fractions appeared well correlated with COC.

4. Conclusion

This study compared some major properties of the Amicon and Millipore spiral wound 1 kD CFF membranes. We have shown that a low OC blank can be achieved for both membranes after careful cleaning using serial rinsing with Q-H_2O, acid and base solutions. This cleaning procedure should be performed prior to each CFF run in order to avoid cross

contamination. In the lab, we observed significant losses of a carbohydrate (Amicon only) and a protein standard (both Amicon and Millipore) to the membrane. Though these results were obtained from lab experiments using standard molecules, it suggests some specific natural organic compounds with similar structural characteristics might have the same interactions with the membranes during CFF processing. While preconditioning may help to minimize losses, especially for bulk OC, losses may occur throughout the sampling processing for some organic compounds (e.g., protein shown by this study) and particle-reactive elements such as ^{234}Th. The loss of ^{234}Th to the CFF membrane appears to be associated with the abundance and composition of COC, and the 'lost' fraction can be partly recovered both in the permeate and in the retentate using our rinsing procedures. So far, no clear quantitative trends suggesting this lost ^{234}Th is LMW or HMW. Hence any corrections made to sample ^{234}Th partitioning should be done with caution.

When these CFFs were used in near shore and open ocean settings, there were some large differences in the time-series patterns of permeate and retentate OC, and in the relative retention of COC (Amicon > Millipore). Differences between membrane types, interactions between the membranes and natural compounds, and the cf used in the CFF processing will determine the extent of breakthrough. Based upon the permeation patterns with cf in coastal vs. open ocean and the poor fit of the retained OC at higher cf to the permeation model, we believe that breakthrough of HMW compounds may be greater than LMW breakthrough, and therefore a low cf is preferred in order to minimize these effects. In a profile of CFF samples collected off Bermuda, OC mass balances and the depth patterns appear reasonable, with higher COC abundance associated with surface waters and near bottom layers.

Acknowledgements

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