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# An intercomparison of cross-flow filtration techniques used for sampling marine colloids: Overview and organic carbon results

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**Abstract**

An intercomparison was conducted between 14 different cross-flow filtration (CFF) systems. Each CFF membrane had a 1000 nominal molecular weight cut-off, and five different manufacturers' membranes were tested. The goal of this exercise was to examine whether the different CFF systems were behaving in a well-defined and operationally reproducible manner in marine applications. Surface seawater from Woods Hole and mid-depth waters from Hawaii were prefiltered ($< 0.2$ μm) and subsamples were processed according to individual protocols. The main criterion for this intercomparison was the agreement of bulk organic carbon (OC) content of the permeate and colloidal fractions. OC blanks ranged from $< 10$ to $> 100$ μ*M*. The variation in OC blanks between CFF systems, even of a single type, suggested that cleaning and handling protocols were critical. One of the primary features of this intercomparison was the large range in apparent retention characteristics of the different CFF systems when used on natural seawater samples. In both settings, the quantity of colloidal material retained by the CFF systems followed the order: Amicon > Filtron ≥ Osmonics > Membrex. For example, in the Hawaii sample, the Amicon CFF system retained on average 43% colloidal OC, while the Filtron, Osmonics and Membrex retained $< 4\%$. Variations within a factor of 2–5 were found within a single membrane type. Other results from

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this intercomparison suggested that these same relative retention characteristics hold for Fe and Al, organic nitrogen and organic phosphorus, optical properties, and colloid standards. Time-series samples of permeate showed a generally increasing OC concentration with time or concentration factor which must be taken into account when interpreting CFF data. We recommend that considerable care be taken in quantifying CFF blanks and in assessing the CFF cut-off for each system prior to use in marine applications. Time-series sampling and the use of standard molecules in controlled experiments are encouraged in order to further our understanding of the behavior of natural compound assemblages during CFF processing.

*Keywords:* colloidal materials; filtration; interlaboratory comparison

## 1. Introduction

The number of studies of marine colloids has dramatically increased over the past 5 years. These studies have shown that sub-μm sized colloids are abundant in seawater ($10^6$–$10^8$ per ml; Koike et al., 1990; Wells and Goldberg, 1991, 1994), and that the colloidal phase can comprise a significant fraction of dissolved organic matter (DOM) in seawater (Moran and Moore, 1989; Benner et al., 1992; Guo et al., 1994). Because the marine DOM reservoir is comparable in size to the atmospheric carbon pool and since at least some fractions may have high turnover rates, processes which influence marine DOM cycling may have significant ramifications to global carbon studies. In addition to bulk organic carbon, there is evidence that bioactive metals and specific organic compounds are associated with marine colloids (Brownawell and Farrington, 1986; Moran and Moore, 1989; Chin and Gschwend, 1992; Benoit et al., 1994; Dai et al., 1995; Stordal et al., 1996). Thus, identifying and characterizing the marine colloidal phase is important for understanding the biogeochemical cycling of both organic carbon and trace metals.

Part of the recent interest in colloidal organic matter (COM) stems from improvements in marine organic carbon analyses (e.g., Sharp, 1993). New studies show large horizontal and vertical gradients in dissolved organic carbon suggestive of rapid production and consumption (Peltzer and Hayward, 1996; C.A. Carlson et al., 1994). This is consistent with the rapid uptake and release of DOM from microbial and planktonic food webs (Johnson and Kepkay, 1992; Amon and Benner, 1994). The evidence for a reactive DOM pool is difficult to reconcile with the old apparent $^{14}C$ ages of bulk DOM (> 1 kyr; Williams and Druffel, 1987; Druffel and Williams, 1990; Bauer et al., 1992) unless some fraction of the DOM pool is labile. Attention has recently focused on the chemical characteristics and $^{14}C$ ages of the colloidal size classes. Benner et al. (1992) report that up to one-third of the DOM pool is colloidal, consisting primarily of reactive polysaccharides which may support much of the heterotrophic activity in the surface ocean. The $^{14}C$ age of colloids appears to be a function of molecular weight and location, with new reports of contemporary $^{14}C$ ages for at least a small fraction of the total COM pool (Santschi et al., 1995), and old $^{14}C$ ages for COM from benthic nepheloid layers (Guo et al., 1996).

Studies of the reactivity and turnover of colloids in seawater using the radionuclide $^{234}Th$ (half-life = 24 days) suggest that colloidal turnover rates are rapid, on the order of days to weeks (Baskaran et al., 1992; Moran and Buesseler, 1992, 1993). As with thorium, particle-reactive trace metals and organic compounds are likely to be sorbed to colloidal surfaces. Examples in marine systems include the association of PCBs with colloids in sediment pore waters (Brownawell and Farrington, 1986), and the association of trace metals with COM (Stordal et al., 1996; Dai et al., 1995; Moran et al., 1996). The extent of these colloid interactions depends upon the surface reactivity of the colloids and the geochemistry of the specific trace constituent. Indeed, "dissolved" trace-metal chemistry of some bioactive metals in seawater is controlled not by the free ion in solution, but rather by abundant natural organic metal-complexing ligands (Bruland et al., 1991; Rue and Bruland, 1995; van den Berg, 1995), some of which are likely to be in the colloidal size range. Colloids may therefore have a significant role in regulating the bioavailability of toxic and nutrient metals to the plankton.

The tools used to identify or isolate material in the sub-μm to nm size classes include particle coun-

ters (Koike et al., 1990; Longhurst et al., 1992), ultracentrifugation (Wells and Goldberg, 1991, 1994), dialysis (de Mora and Harrison, 1983), gel-permeation chromatography, field-flow fractionation (Giddings, 1988), selective adsorption to XAD resin, and cross-flow filtration (also called tangential-flow filtration, and more generically, ultrafiltration; D.J. Carlson et al., 1985; Whitehouse et al., 1986; Whitehouse et al., 1990; Moran, 1991). Of these methods, cross-flow filtration (CFF) is the only practical technique for processing the large volume samples (10–1000 l) required for the analysis of trace-level constituents associated with natural colloids. Because of this, CFF has become increasingly popular among the many groups undertaking studies of marine colloids.

With the application of an ever increasing variety of CFF system designs and reports of spatial and seasonal differences in the abundance and composition of marine colloids (e.g., Baskaran et al., 1992; Moran and Buesseler, 1993; Niven et al., 1995), it became clear that a careful evaluation of the performance of currently available CFF technologies was needed. To begin this assessment, thirteen different groups gathered first at the Woods Hole Oceanographic Institution and later at the National Energy Laboratory of Hawaii to process simultaneously common seawater samples with their CFF systems. The goal of this study was to assess quantitatively whether ultrafiltration systems from different manufacturers used under different operating conditions provided results which were consistent in both nearshore and offshore environments.

Since the bulk of the mass of colloidal material in seawater is thought to be organic in nature (Benner et al., 1992), the primary criterion for this intercomparison was agreement between analyses of the bulk organic properties of the dissolved and colloidal fractions, and these data are presented in this paper. Colloids are proposed to be important intermediaries in the cycling of many particle-reactive trace metals; therefore, the behavior of two trace metals, Al and Fe, was also examined as part of the intercomparison (Reitmeyer et al., 1996-this issue). Cd, Cu and Ni were also examined on a selected set of samples (Greenamoyer and Moran, 1996-this issue) and inductively coupled plasma mass spectrometric (ICP–MS) trace-metal analyses were conducted on a colloid fraction from a single CFF system (Bertine and VernonClark, 1996-this issue). Other analyses of the intercomparison samples included absorbance and fluorescence spectra (Mopper et al., 1996-this issue), nutrients, organic nitrogen and organic phosphorus (Bauer et al., 1996-this issue), as well as one tracer experiment conducted with a standard macromolecule of known size which was added to seawater and processed similarly to the samples (Gustafsson et al., 1996-this issue). Some of these results will be highlighted here, with reference to detailed discussions elsewhere in this volume on specific aspects of the intercalibration study and independent CFF integrity studies.

## 2. Cross-flow filtration: background

In CFF, a prefiltered sample solution flows parallel to the CFF membrane, and hydrostatic pressure drives solutes, with an effective molecular size less than the cut-off of the membrane, through the membrane (permeate). The remaining solution (retentate), containing both smaller solutes and larger colloids, is swept along the membrane surface and recycled through the retentate reservoir. Compounds which are rejected by the membrane are thus increasingly concentrated in the retentate over time. In any filtration procedure, compounds larger than the pore size are rejected at the membrane surface and a concentration gradient forms between the membrane surface and the bulk solution. In CFF, these "concentration polarization" effects decrease the flow of water and small molecules through the membrane. The degree of concentration polarization is determined by the concentration of retentate molecules, the transmembrane pressure drop (i.e. the pressure difference between the retentate and permeate), and the recirculation hydrodynamics. Total flow of permeate through the membrane is controlled by the transmembrane pressure and the hydraulic resistance of both the membrane and the concentration polarization layer.

CFF membranes are rated by their ability to retain standard molecules of a known nominal molecular weight (1000 nominal molecular weight = 1 kilodalton = 1 kD). The retention coefficient, RC, is defined by:

$$RC = 1 - ([X]_{perm}/[X]_{ret}) \quad (1)$$

Table 1
Colloid intercomparison CFF system descriptions

| CFF ID | Type | Membrane ID | Surface area ($ft^2$) | Pump type | Plumbing materials | Sample reservoir | Transmembrane pressure [a] (psi) |
|---|---|---|---|---|---|---|---|
| A1 | Amicon DC-10L | S10N1 | 20 | SS impeller | acrylic, PVC, ester-grade PVR tubing | fluorinated-HDPE | 5–10 |
| A2 | Amicon DC-10L | S10N1 | 10 | SS impeller | Tygon and PVC | LDPE | 50 |
| A3 | Amicon-modified | S10N1 | 10 | Diaphram | C-flex and Teflon | Teflon | 20 |
| A4 | Amicon DC-10L | S10N1 | 10 | SS impeller | Silicone and Tygon | fluorinated-HDPE | 31 |
| A5 | Amicon DC-10L | S10N1 | 20 | SS impeller | PVC and Silicone | glass | 20 |
| F1 | Filtron Centrasette | OS001C05 | 15 | Diaphram | Teflon | fluorinated-HDPE | 8–10 |
| F2 | Filtron Centrasette | OS001C05 | 10 | peristaltic | Teflon and Silicone | glass | n.d. |
| F3 | Filtron Centrasette | OS001C05 | 20 | peristaltic | Teflon and Silicone | fluorinated-HDPE | n.d. |
| F4 | Filtron Ultrasette | OS001C70 | 0.5 | peristaltic | Pharmed | glass | n.d. |
| O1 | Osmonics SEPA-PS (full fit with SS tube) | 112-PT1 (PS) | 11 | SS metering | SS | glass | 10 |
| O2 | Osmonics SEPA-PS | 112-PT1 (PS) | 11 | peristaltic | Bev-a-line and Teflon and Silicone | fluorinated-HDPE | < 5 |
| O3 | Osmonics SEPA-PS | 112-PT1 (PS) | 11 | Diaphram | Delrin and PVC and epoxy and ceramic seal | fluorinated-HDPE | < 5 |
| X1 | Membrex vortex flow filtration | ultrafilic | 200 $cm^2$ | peristaltic | C-flex and Tygon and SS and graphite/ceramic | fluorinated-HDPE | n.a. |
| Z1 | Desalination systems (Desal) | thin film membrane | 93 | impeller | polypropylene | polyethylene | 10 |

| CFF ID | Total pressure [b] (psi) | Recirculation flow rate [c] (l/min) | Sample volume (l) | Permeate flow (ml/min) | Preconditioning volume [d] (l) | Cleaning steps [c] (a = pre; b = between) |
|---|---|---|---|---|---|---|
| A1 | 40–50 | 20 | 20 | 300 | 30 | a: 0.1 *N* NaOH (20 l) and Q (20 l)<br>b: Q (30 l) |
| A2 | 40 | 10 | 20–200 | 230 | 5 | a: Micro and NaOH and HCl and Q — many liters<br>b: NaOH and HCl and Q — many liters |
| A3 | 20 | 0.8 | 10 | 85 | 2 | a: Micro and HCl and NaOH and HAc and Q — 20 l per solution and 40 lQ between<br>b: HCl and NaOH and HAc — 20 l solution and 40 l Q between |

| | | | | | | |
|---|---|---|---|---|---|---|
| A4 | 40 | 10 | 25 | 100 | 20 | a: 20 l Q and 20 l seawater<br>b: 20 l Q and 20 l seawater |
| A5 | 50 | 20 | 200 | 333 | 12 | a: Q and micro and 0.01 *M* HCl and pH = 11 Q — 10's of liters<br>b: Q (6 l) and seawater (12 l) |
| F1 | 18 | 4 | 18 | 130 | 4 | a: dilute acid and MeOH and Q<br>b: none |
| F2 | 15–25 | 4 | 20–80 | 100 | 1–3 | a: 0.5 *M* NaOH (2 l) and Q (60 l)<br>b: MeOH and HCl and Q and NaOH and Q — 10's of liters |
| F3 | 10 | 3 | 20 | 100 | 0.5–1 | a: 0.5 *M* HCl (20 l) and Q (40 l)<br>b: none |
| F4 | 33 | 0.7 | 4 | 5–10 | 0.1 | a: Q (4 l); 0.5 *M* NaOH (0.5 l); Q (4 l)<br>b: MeOH:water (0.5 l); MeOH:HCl (0.5 l); Q (4 l); 0.5 *M* NaOH (0.5 l); Q (12 l) |
| O1 | 15 | 1.2 | 60 | 250 | 20 | a: Q (20 l) and 0.01 *N* NaOH and 0.01 *N* HCl and MeOH (3 each recirculation w/10 l Q between solutions) and Q (60 l)<br>b: as in a |
| O2 | 15–20 | 1–2 | 25–30 | 140 | 5 | a: 80 l Q and soak with 0.1 *N* HCl<br>b: soak with seawater |
| O3 | 10 | 8 | 25 | 100 | 4 | a: Q and HCl and NaOH 10's of liters<br>b: Q and HCl — 10's of liters |
| X1 | 8 | n.a. | 18 | 140 | 4 | a: Q and MeOH in HCl<br>b: Q |
| Z1 | 12 | 41 | 160 | 680 | 5–20 | a: Q and NaOH and NaClO and Terg-a-zyme and $HNO_3$ — 100's of liters<br>b: Q and HCl — 10's of liters |

1 psi = 6.9 kPa; 1 $ft^2$ = 929 $cm^2$; n.a. = not applicable; n.d. = not determined; SS = stainless steel. All CFF membranes made from polysulfone, except Z1 which was made from regenerated cellulose.

[a] Transmembrane pressure = (average pressure of retentate stream) − (pressure of permeate stream).

[b] Total pressure = average pressure of retentate stream.

[c] Recirculation flow rate = flow rate across CFF membrane.

[d] Preconditioning volume = volume of sample solution passed through CFF immediately prior to processing sample.

[e] Cleaning steps = summary of cleaning solutions and volumes used "a" (pre) and "b" (between) samples.

where $[X]_{perm}$ and $[X]_{ret}$ are the concentrations of a given colloid standard in the permeate and retentate, respectively. The major applications of CFF have typically been industrial or biomedical, and thus the RC ratings are based primarily upon testing of standard molecules such as globular proteins and polysaccharides at high concentrations (mg/l–g/l) and at high pressures (50–100 psi or 345–690 kPa). The retention properties of natural compounds in dilute solutions have not been characterized by the manufacturers. Since CFF membranes act as depth filters with a range of operational pore sizes, some compounds smaller than the rated cut-off will be retained while some fraction of compounds larger than the cut-off will pass through the membrane. For example, a 1-kD membrane may be designed to retain 90% of a standard 1-kD molecule (i.e. RC = 0.9) under the specific manufacturer's test conditions, but these retention characteristics will almost certainly change under a different set of operating conditions. Moreover, tertiary shape, electrostatic attraction or repulsion and other physicochemical interactions of the compounds in solution with the membrane also will affect the cut-off characteristics of the membrane, so that molecule retention is not simply a function of molecular weight (for recent review, see Buffle et al., 1992).

In most CFF applications, the prefiltered sample is concentrated from a single sample reservoir. In this case, the concentration factor, *cf* can be calculated from:

$$cf = (\text{initial sample volume}) / (\text{final retentate volume}) \quad (2)$$

In other systems (systems O1, O2, O3, A5 in Table 1), the retentate reservoir is considerably smaller than the sample volume and the retentate is continually, or periodically, supplied with fresh sample as the permeate flow progresses. In effect, this results in a shorter overall residence time of the sample within the recirculation loop of the CFF system and the elimination of a secondary sample container. In these cases:

$$cf = [(\text{permeate volume}) + (\text{retentate volume})] / (\text{retentate volume}) \quad (3)$$

In CFF, colloidal abundances are defined by their retention relative to a given CFF membrane. It is useful to define the colloidal concentration of a given compound, $[X]_{coll}$, as calculated from:

$$[X]_{coll} = ([X]_{ret} - [X]_{perm})/cf \quad (4)$$

The retentate and permeate concentrations are measured quantities, and Eq. (4) simply corrects for the presence of smaller solutes in the retentate sample and the degree of sample concentration. Generally, the retentate concentration of a given high-molecular-weight (HMW) compound will increase with increasing *cf*. If the low-molecular-weight (LMW) fraction passes through the CFF membrane without interaction (i.e. RC = 0) and the HMW fraction is completely retained (i.e. RC = 1) then the permeate concentration should be constant. Since RC is never exactly equal to zero or one for any single compound and CFF membrane, the permeate concentrations can also be expected to increase with increasing *cf* due to so-called breakthrough or permeation effects (Logan and Jiang, 1990; Kilduff and Weber, 1992). Some of our CFF data exhibit an increasing permeate concentration with increasing *cf*, and we discuss this issue later in this manuscript.

CFF systems are available in a variety of configurations using different engineering designs and components. These include flat-sheet configurations, where ultrafiltration membranes are stacked in a frame which is separated by fine screens; spiral-wound CFF membranes, where the feed enters one end of the ultrafilter module, and the permeate and retentate leave the other end of the unit; and hollow fiber units (the latter were not tested here). Several membrane compositions are available, ranging from regenerated cellulose to a variety of synthetic polymers. Polysulfone membranes were used for this intercomparison (with the exception of system Z1, Table 1), both to minimize inter-system variables and because polysulfone has been commonly used in marine studies. In this intercomparison, each CFF system was used according to the individual operating protocols of the participating labs. Because of time constraints, no attempt was made to determine the response of any given ultrafiltration system to variations in specific operating conditions; however, individual groups have made further progress in

characterizing their own CFF systems (Guo and Santschi, 1996-this issue; Gustafsson et al., 1996-this issue; Wen et al., 1996-this issue).

## 3. Details of colloid intercomparison

### 3.1. Cross-flow filtration system descriptions

Most recent studies of marine colloids use ultrafiltration membranes with cut-offs in the 1–10-kD size range, and we chose the smaller 1-kD cut-off as a starting point for this experiment. New 1-kD membrane cartridges were provided to each group for this experiment; and the same membrane was used throughout both the Woods Hole and Hawaii exercises. The membrane surface areas ranged from 0.5 to $> 90$ ft$^2$ (0.05 to $> 8.4$ m$^2$), and permeate flows ranged from a few ml/min to 680 ml/min (Table 1). CFF systems in this intercomparison had been designed to examine different aspects of the marine colloidal phase. Hence, there were differences in the plumbing materials, transmembrane pressures, sample volumes and the pre-sample and between-sample cleaning steps. CFF system designs ranged from a mostly stainless-steel configuration, optimized for hydrophobic organic compounds (O1), to Teflon and plastic designs (A3, F1, F3 and Z1) used in trace-metal studies. Four of the CFF systems (A3, F1, F3, X1) were operated within a high-efficiency particulate air (HEPA) filtered "clean" room, to minimize particulate contamination, while the rest were operated without cover in the laboratory. Only the Amicon DC-10L systems (A1, A2, A4, A5) were purchased as a single package that included the membrane, pump, and sample reservoir, although A5 used a modified glass reservoir.

Prior to using each membrane and between samples, the CFF membranes were leached or cleaned using a variety of solutions. Some of these cleaning protocols changed as our intercomparison progressed and these are summarized in Table 1. The solution contact time, temperature, and whether or not the leach solutions were recirculated or ultrafiltered may also have influenced membrane performance. In addition to cleaning, most of the participants "preconditioned" their CFF system. During preconditioning, the prefiltered sample was allowed to run through the permeate line (volumes listed in Table 1), and then both the permeate and retentate solutions were discarded, just prior to processing and collecting the real sample. Such procedures are thought by some to minimize contamination and reduce sorptive losses.

### 3.2. Site and sampling details

#### 3.2.1. Prefiltration

One prefiltration system provided $< 0.2$-μm filtered seawater to all participants during both the Woods Hole and Hawaii intercomparison exercises. The filtration rig consisted of three pairs of 10- and 1-μm filter cartridges, followed by two 0.2-μm filter cartridges, all connected via polyvinylchloride (PVC) tubing and fittings. The 10- and 1-μm cartridges were 100% polypropylene depth filters [HYTREX II, 10-in (25.4 cm) length; Osmonics Inc.] in a polycarbonate housing. The final 0.2-μm filters were either polycarbonate (MEMTREX-PC at Woods Hole) or polysulfone (MEMTREX-PS at Hawaii) pleated membrane filter cartridges [10-in (25.4 cm) cartridges with double Viton O-ring seal; Osmonics Inc.] in a polypropylene housing. All filters were presoaked in dilute HCl and rinsed with fresh water. More than 20 l of sample water were filtered through the system prior to collection. Filter sets were replaced between each seawater sample at Woods Hole. A single set was used at Hawaii. Sample water was filtered directly from the local seawater source lines and no appreciable change in flow was noted during filtration ($\sim$ 1 l/min at Woods Hole and $\sim$ 2 l/min at Hawaii).

#### 3.2.2. Source waters

The source waters for the Woods Hole intercomparison experiment in August 1994 were obtained via a PVC seawater line in the Coastal Research Laboratory at the Woods Hole Oceanographic Institution (WHOI). The inlet for these source waters lies $\sim$ 1 m off the bottom in 3 m of water in Vineyard Sound, Massachusetts. Some alteration of the seawater characteristics can be expected both as a result of the seawater handling system and tidal fluctuations. However, the organic carbon and particulate concentrations are generally representative of the local coastal waters. To eliminate the effects of any short-term variations in the source waters, 1300 l of seawa-

ter were prefiltered into a polyethylene bag that was supported in a large tank. The bag was precleaned with 0.5 *M* HCl and rinsed with Q-water and some of the prefiltered sample. Within 12 h of filling, sub-samples for the intercomparison exercise were distributed within an 8-h period from the bag via a Teflon feed line, a polyethylene diaphragm pump, and a polypropylene valve and manifold system.

The source waters for the Hawaii experiment in January 1995 were obtained from the deep-water pipeline at the Natural Energy Laboratory of Hawaii (NELH). The intake for the 1-m-diameter high-density polyethylene pipe is situated 1700 m offshore of Keahole Point, ~25 m above the sea floor at a depth of ~600 m. The pipe and large volume pumping system (0.5 $m^3/s$) were designed for an ocean thermal energy conversion research project. Regular analyses have shown that the composition of these waters is representative of the regional mean water composition at these depths (Sansone et al., 1988). Given the stability in composition of this source water, the prefiltered water was provided directly to each participant within a 4-h period, without using any intermediate storage container.

### 3.2.3. Sampling and analyses

All participants were asked to collect samples at selected times during their ultrafiltration procedures. In general, the permeate line was sampled at a concentration factor of 2 ($cf = 2$) and just prior to completion of a given ultrafiltration experiment ($cf$ = final). On one sample at Hawaii, a sub-set of the participants collected the entire permeate stream or sub-sampled the permeate line in order to collect a sample that better represented the mean permeate concentration ($cf$ = integrated). The retentate solution was collected and subsampled at the end of each experiment only. Unless otherwise specified, $[X]_{coll}$ was calculated from Eq. (4) using the average of the two permeate concentrations. At both sites, the intercalibration began with the ultrafiltration of a common sample of ultra-pure water (Q1 at Woods Hole, Q2 at Hawaii). This sample was tap water that had been processed via reverse osmosis, followed by in-line UV irradiation and a standard Milli-Q type polishing unit. The polishing unit was equipped with an activated charcoal bed and mix-bed resin cartridges which can produce 18-MΩ water with 2–5 μ*M* OC (known as Type 1 water and termed Q-water throughout this paper). This Q-water was used by all participants for cleaning and other operations. At the Hawaii site, there was some degradation in the quality of this water with time, and after the Q2 sample, a Q-water system belonging to NELH that had similar characteristics was used. Following the Q-water sample, the intercalibration was conducted on two replicate seawater samples (SW1 and SW2 at Woods Hole; SW3 and SW4 at Hawaii).

A single laboratory took responsibility for cleaning all of the sample bottles of a given type according to accepted methods. The bottles, pre-labeled with a single ID number, were distributed to each participant. At both intercalibration sites, sample bottles for organic carbon and fluorescence analyses were stored at low temperature, either in a refrigerator or on ice, and analyzed as soon as possible after collection, typically within 12–24 h. We will use the term OC to describe organic carbon results from any size fractionated sample or the source waters. Our prefiltration operationally determines the source water cut-off (< 0.2 μm), and the 1-kD CFF membranes are used to delineate the permeate (< 1 kD) and the retentate (1 kD < $x$ < 0.2 μm) fractions.

Additional analyses on the common samples included Al, Fe, nutrients, absorbance and fluorescence. Selected samples were also analyzed for organic P and specific organic compounds. In this paper we present the OC and bulk fluorescence data only. Other manuscripts in this special issue focus on Al and Fe (Reitmeyer et al., 1996), organic nitrogen and organic phosphorus (Bauer et al., 1996), and absorbance and fluorescence spectra (Mopper et al., 1996) from these same samples.

Organic carbon was measured using high-temperature catalytic (HTC) techniques summarized in Williams et al. (1993). A single analyst measured all HTC-OC samples, except those collected during a time-series sampling of SW4 permeate (measured using an automated HTC-OC technique described in Qian and Mopper, 1996). For HTC-OC analyses, discrete amounts (50–100 μl) of acid-sparged sample were injected onto a 3% Pt on alumina catalyst (Rosemount-Dohrmann Instruments) at 680°C. The $CO_2$ produced from the oxidation of organic matter was detected using a Li-Cor detector (model 7120)

and signal peak area was integrated using MacIntegrator Software. Daily calibration curves were run using glucose standard solutions in Q-water. System blanks were determined daily from the peak area produced by injections of UV-oxidized Q-water, where it was assumed that the UV-oxidized Q-water was carbon-free. All HTC-OC data have been corrected for an instrument blank of 22 $\mu M$, and each determination represents the mean of up to 3 sample injections.

Fluorescence measurements were made with a SLM AB-2 spectrofluorometer with a 1-$cm^2$ fused silica cell. Full emission spectra (350–650 nm) were recorded for excitation = 337 nm. Data from WHOI are reported as integrated values (350–650 nm) minus Q-water blank levels normalized to quinine sulfate. One $\mu g/l$ quinine sulfate is equivalent to 10 fluorescence units. The Hawaii fluorescence results are reported only at 337-nm excitation, 420-nm emission, rather than as integrated values. More detailed fluorescence spectra results can be found in Mopper et al. (1996-this issue).

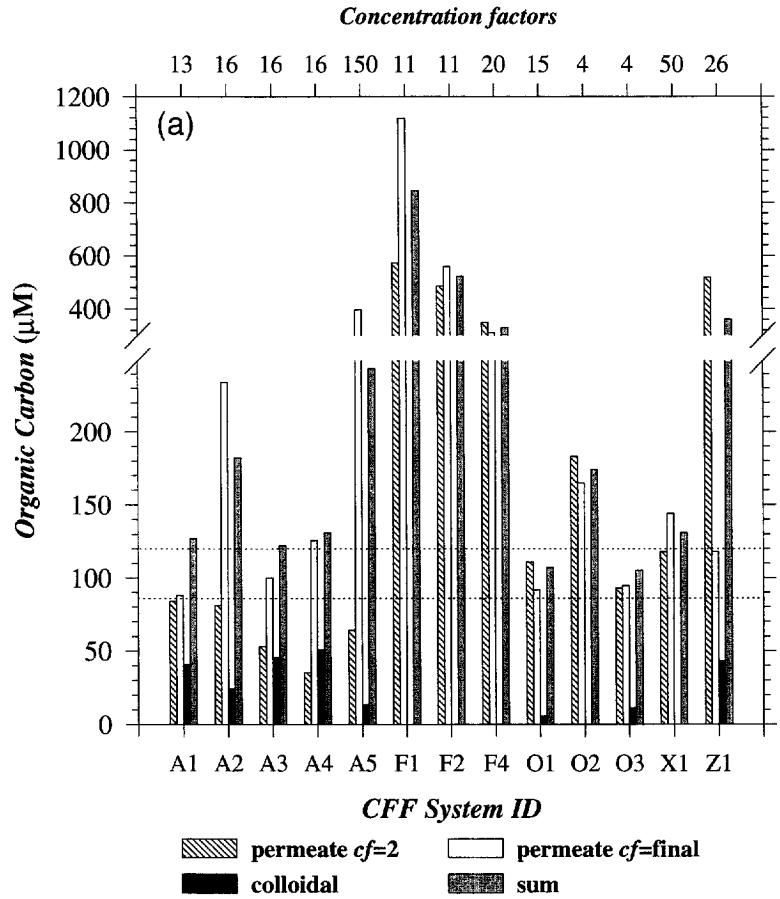


Fig. 1. Intercomparison of seawater organic carbon results for different cross-flow filter systems grouped by CFF ID (see Table 1) according to manufacturer: (a) Woods Hole sample SW1; (b) Woods Hole sample SW2; (c) Hawaii sample SW3; and (d) Hawaii sample SW4. CFF ID's are shown on lower $x$-axis and final concentration factors along upper $x$-axis. Data are shown for each system for the permeate concentration at $cf = 2$ (*diagonal fill*), permeate at $cf$ = final (*open fill*), the colloidal concentration (*solid fill*) calculated from the average of the two permeate values and Eq. 4, and for the sum of the average permeate and colloidal concentrations (*gray fill*). The < 0.2-μm prefiltered source water concentration range is shown by the two *horizontal lines*

## 4. Results

### 4.1. Seawater organic carbon results

Concentrations of OC for the ultrafiltered seawater samples collected in Woods Hole (SW1 and SW2) and Hawaii (SW3 and SW4) are shown in Fig. 1a–d and data are provided in Tables 2 and 3. The CFF systems are grouped according to the membrane manufacturer (see Table 1 for details). Data are shown for the concentration of OC in the permeate collected at $cf = 2$ and $cf =$ final. In addition, for each system the colloidal OC concentration (calculated from Eq. (4)) and the sum of the average permeate and colloidal OC concentrations are shown. Neither the individual permeate concentrations nor the calculated sum should exceed the source OC concentration. Organic carbon concentrations in the prefiltered source water were analyzed four to six times during each experiment and the range in values is shown by the horizontal dashed lines in each figure. Concentration factors ranging from 4 to 200 were used by the different groups, and these are shown for each experiment along the top horizontal axis in Fig. 1a–d. The wide range in *cf* reflects the wide range in sample volumes that the participants typically process (Table 1).

The Woods Hole data indicate that the prefiltered source water had a mean OC concentration of 106 and 104 $\mu M$ for SW1 and SW2, respectively (excluding a single outlier of 174 $\mu M$ OC for SW2, Table 2). Variations between injections were much smaller than the sample to sample variability and no

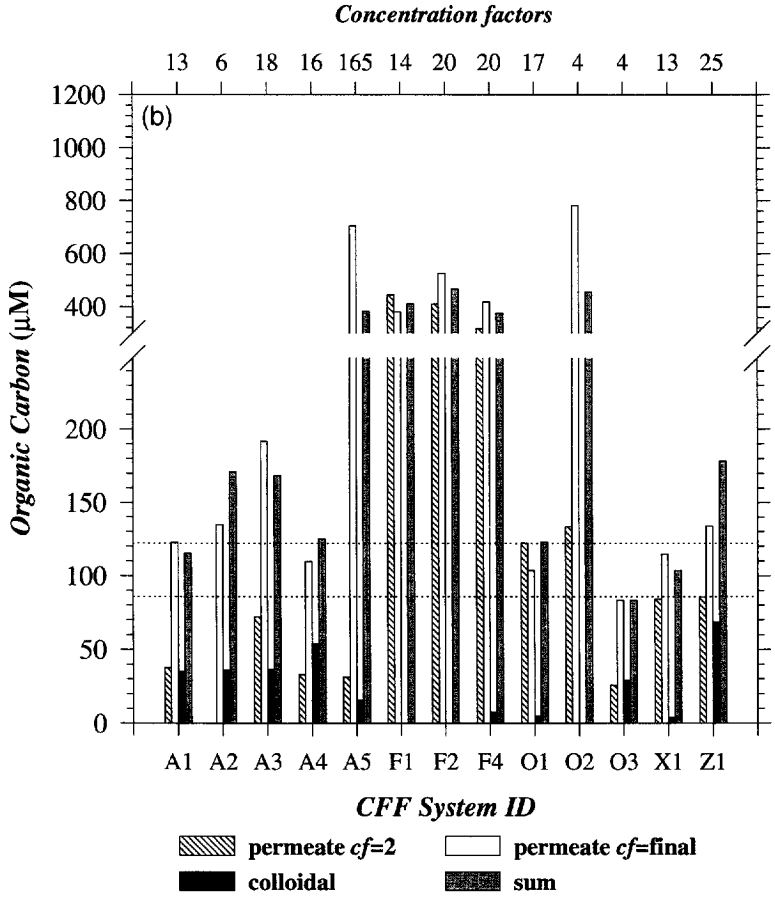


Fig. 1 (continued).

temporal trend in the OC source water data was found. The reason for any source water OC variability may be attributed in part to sampling or storage artifacts not uncommon in HTC-OC analyses (Hedges et al., 1993; Sharp, 1993); but even with this variability, the major features in the data set are clear.

In Woods Hole, many of the CFF systems had OC concentrations in the permeate and retentate that were 50–1000 $\mu M$ higher than the prefiltered source waters, indicative of severe contamination. Furthermore, contamination was evident in at least one CFF system of each membrane type. Between SW1 and SW2, there was generally a decrease in apparent OC contamination; however, this does not hold in all cases. A second feature of the Woods Hole OC data was that some of the CFF systems exhibited an increase in permeate OC concentration between $cf =$ 2 and $cf =$ final (compare 1st and 2nd bars in Fig. 1a and b). This change in permeate OC concentration with $cf$ led us to attempt time-series permeate sampling of SW4 (results to follow).

A major feature of the Woods Hole results is that the Amicon systems and system Z1 recovered higher apparent colloidal OC than any of the other CFF systems. For the Amicon CFF systems, calculated colloidal OC concentrations ranged from 14 to 54 $\mu M$, with a mean %COC of 33% [%COC = (colloidal OC)/(source OC); calculated here for those Amicon CFFs with a sum OC within 25 $\mu M$ of the source OC concentration — Table 4]. The Amicon system with the highest $cf$ (A5) had the lowest colloidal OC concentrations in general; how-

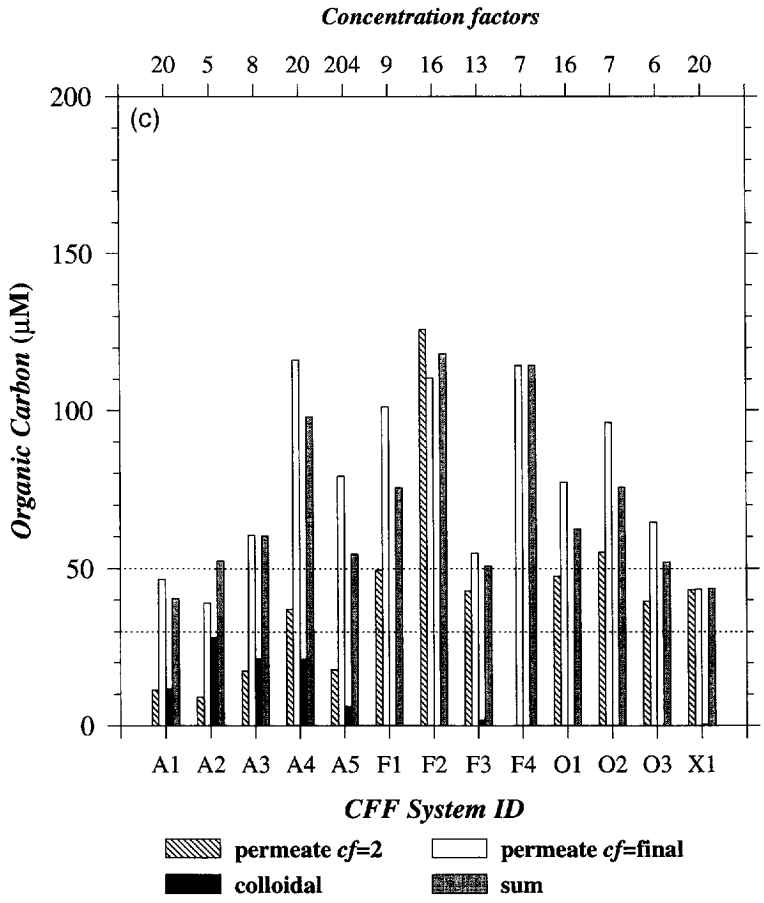


Fig. 1 (continued).

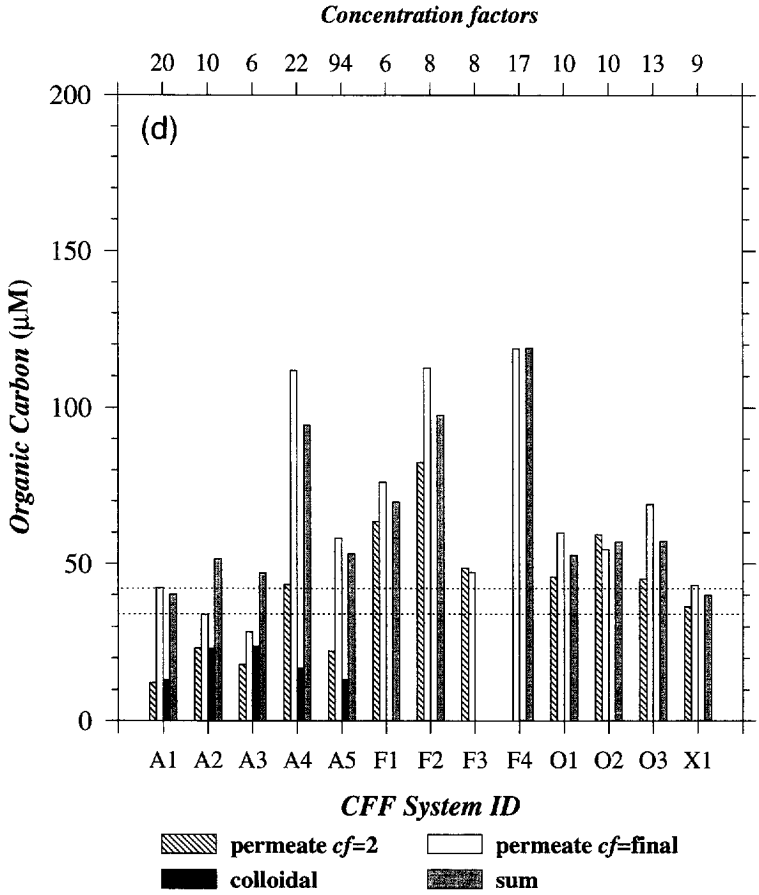


Fig. 1 (continued).

ever, colloidal OC varied from 24 to 51 $\mu M$ in three Amicon systems, each with a *cf* of 16 (A2, A3, A4 for SW1). The sum OC concentrations (average permeate plus colloidal OC concentrations) were $> 10$ to 25 $\mu M$ higher than the source waters for SW1 and SW2 in half of the Amicon samples, and $> 25$ $\mu M$ higher in the rest, suggesting that at least some of these were highly contaminated with organic compounds.

The Filtron CFF systems had such high OC contamination levels that the permeate was even larger than the retentate samples and hence the calculated colloidal concentrations were negative (Table 4). For the two Osmonics systems with a reasonable mass balance for organic carbon (sum within 20 $\mu M$ of source for O1 and O3), colloidal OC represented 5–28% of the source OC (mean = 8% for SW1; Table 4). System X1 (Membrex) retained 4% COC

Notes to Table 2:
n.a. = not analyzed.
[a] CFF ID = CFF ID as listed in Table 1 (CFF 0 = prefiltered source waters).
[b] *cf* = concentration factor (or time of collection for CFF ID 0).
[c] OC = organic carbon ($\mu M$).
[d] FLU = fluorescence (arbitrary units — see text for details).

Table 2
Woods Hole organic carbon and fluorescence data

| CFF ID [a] | Type | Q1 | | | SW1 | | | SW2 | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | *cf* [b] | OC [c] | FLU [d] | *cf* [b] | OC [c] | FLU [d] | *cf* [b] | OC [c] | FLU [d] |
| 0 | < 0.2 μm | (0 h) | 6 | 1.1 | (0 h) | 118 | 53.9 | (0 h) | 86 | 53.3 |
| | < 0.2 μm | (1 h) | 5 | 0.7 | (1 h) | 98 | 54.6 | (1 h) | 105 | 53.7 |
| | < 0.2 μm | (2 h) | 6 | 0.0 | (2 h) | 120 | 54.7 | (2 h) | 174 | 53.9 |
| | < 0.2 μm | (4 h) | 8 | 0.3 | (4 h) | 86 | 54.5 | (4 h) | 122 | 54.2 |
| A1 | permeate | 2 | 9 | 3.3 | 2 | 84 | 29.1 | 2 | 38 | 29.7 |
| | permeate | final | 32 | 6.3 | 13 | 88 | 51.9 | 13 | 123 | 69.1 |
| | retentate | | 98 | 12.4 | 13 | 618 | 199.9 | 13 | 535 | 191.9 |
| A2 | permeate | 2 | 15 | 4.1 | 2 | 81 | 51.1 | 2 | n.a. | 47.1 |
| | permeate | final | 39 | 2.8 | 16 | 234 | 105.9 | 5.5 | 135 | 63.2 |
| | retentate | | 19 | 2.4 | 16 | 540 | 188.4 | 5.5 | 333 | 104.1 |
| A3 | permeate | 2 | 23 | 0.7 | 2 | 53 | 37.6 | 2 | 72 | 38.0 |
| | permeate | final | 22 | 0.2 | 16 | 100 | 60.7 | 18 | 192 | 68.8 |
| | retentate | | 25 | 2.3 | 16 | 807 | 227.1 | 18 | 786 | 215.9 |
| A4 | permeate | 2 | 12 | 4.1 | 2 | 35 | 35.1 | 2 | 33 | 40.7 |
| | permeate | final | 26 | 6.0 | 16 | 126 | 70.6 | 16 | 110 | 75.1 |
| | retentate | | 38 | 9.9 | 16 | 876 | 261.3 | 16 | 913 | 253.0 |
| A5 | permeate | 2 | 79 | 5.9 | 2 | 64 | 34.4 | 2 | 31 | 32.0 |
| | permeate | final | 135 | 5.1 | 150 | 397 | 118.1 | 165 | 705 | 71.9 |
| | retentate | | 373 | 11.3 | 150 | 2272 | 839.8 | 165 | 2951 | 937.8 |
| F1 | permeate | 2 | 778 | 14.0 | 2 | 573 | 56.2 | 2 | 446 | 57.5 |
| | permeate | final | 793 | 23.1 | 11.1 | 1118 | 73.5 | 14 | 381 | 63.2 |
| | retentate | | 412 | 4.2 | 11.1 | 404 | 64.1 | 14 | 287 | 65.1 |
| F2 | permeate | 2 | 1161 | 19.5 | 2 | 486 | 50.9 | 2 | 412 | 48.0 |
| | permeate | final | 786 | 28.6 | 11 | 559 | 54.4 | 20 | 527 | 55.3 |
| | retentate | | 1028 | 19.4 | 11 | 288 | 58.1 | 20 | 131 | 61.2 |
| F4 | permeate | 2 | n.a. | n.a. | 2 | 349 | 51.1 | 2 | 318 | 52.7 |
| | permeate | final | 776 | 6.1 | 20 | 311 | 54.9 | 12 | 420 | 53.7 |
| | retentate | | 374 | 7.7 | 20 | 276 | 65.2 | 12 | 457 | 59.5 |
| O1 | permeate | 2 | 186 | 1.9 | 2 | 111 | 50.1 | 2 | 122 | 50.1 |
| | permeate | final | 41 | 0.4 | 15 | 92 | 51.1 | 17 | 104 | 50.1 |
| | retentate | | 41 | 1.5 | 15 | 189 | 53.9 | 17 | 192 | 52.0 |
| O2 | permeate | 2 | 378 | 1.8 | 2 | 183 | 52.0 | 2 | 134 | 53.7 |
| | permeate | final | 283 | 7.2 | 3.5 | 165 | 51.0 | 4.3 | 781 | 51.9 |
| | retentate | | 210 | 6.0 | 3.5 | 163 | 55.1 | 4.3 | 185 | 56.7 |
| O3 | permeate | 2 | 115 | 0.3 | 2 | 93 | 51.6 | 2 | 26 | 50.6 |
| | permeate | final | 116 | 0.8 | 3.8 | 95 | 52.2 | 3.9 | 83 | 51.0 |
| | retentate | | 63 | 0.7 | 3.8 | 136 | 54.4 | 3.9 | 169 | 52.2 |
| X1 | permeate | 2 | 6 | 1.1 | 2 | 118 | 49.3 | 2 | 84 | 51.2 |
| | permeate | final | 30 | 1.0 | 50 | 144 | 44.7 | 13 | 115 | 49.7 |
| | retentate | | 38 | 3.2 | 50 | 120 | 47.6 | 13 | 154 | 46.6 |
| Z1 | permeate | 2 | 9 | 1.2 | 1.2 | 518 | 26.2 | 2 | 86 | 31.1 |
| | permeate | final | 6 | 1.5 | 26 | 118 | 84.7 | 25 | 134 | 104.6 |
| | retentate | | 39 | 6.6 | 26 | 1435 | 471.3 | 25 | 1820 | 453.6 |

Table 3
Hawaii organic carbon and fluorescence data

| CFF ID | Type | Q2 | | | SW3 | | | SW4 | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | *cf* | OC | FLU | *cf* | OC | FLU | *cf* | OC | FLU |
| 0 | < 0.2 | (0 h) | 6 | 4.8 | (0 h) | 30 | 95.5 | (0 h) | 44 | 99.6 |
| | < 0.2 | (1 h) | 4 | 4.6 | (1 h) | 37 | 96.1 | (1 h) | 41 | 99.7 |
| | < 0.2 | (1 h) | 21 | 4.9 | (1 h) | 38 | 95.7 | (1 h) | 42 | 99.1 |
| | < 0.2 | (2 h) | 2 | 4.8 | (2 h) | 60 | 94.8 | (2 h) | 37 | 99.4 |
| | < 0.2 | (2 h) | 3 | 4.7 | (2 h) | 35 | 95.1 | (2 h) | 42 | 99.6 |
| | < 0.2 | (4 h) | 4 | 4.1 | (3.5 h) | 51 | 94.2 | (3.2 h) | 34 | 99.6 |
| A1 | permeate | 2 | 8 | 13.0 | 2 | 11 | 39.1 | 2 | 12 | 47.8 |
| | permeate | final | 18 | 14.4 | 20 | 47 | 70.2 | 20 | 42 | 109.2 |
| | permeate | | | | | | | integrated | 28 | 50.6 |
| | retentate | | 100 | 38.6 | 20 | 262 | 398.1 | 20 | 287 | 427.8 |
| A2 | permeate | 2 | 12 | 7.0 | 2 | 9 | 68.3 | 2 | 23 | 60.3 |
| | permeate | final | 15 | 6.3 | 5.2 | 39 | 130.3 | 10 | 34 | 85.5 |
| | permeate | | | | | | | integrated | 37 | 62.1 |
| | retentate | | 11 | 9.3 | 5.2 | 170 | 387.8 | 10 | 262 | 429.8 |
| A3 | permeate | 2 | 4 | 5.5 | 2 | 17 | 57.9 | 2 | 18 | 67.4 |
| | permeate | final | 18 | 4.1 | 8.3 | 61 | 85.8 | 6.1 | 28 | 88.0 |
| | permeate | | | | | | | integrated | 39 | 70.1 |
| | retentate | | 12 | 6.0 | 8.3 | 216 | 338.8 | 6.1 | 168 | 295.3 |
| A4 | permeate | 2 | 25 | 27.5 | 2 | 37 | 68.0 | 2 | 43 | 74.7 |
| | permeate | final | 61 | 42.6 | 20 | 116 | 146.8 | 22 | 112 | 164.0 |
| | permeate | | | | | | | integrated | 36 | 78.1 |
| | retentate | | 116 | 161.0 | 20 | 505 | 748.0 | 22 | 438 | 730.2 |
| A5 | permeate | 2 | 17 | 14.2 | 2 | 18 | 55.2 | 2 | 22 | 47.8 |
| | permeate | final | 22 | 19.5 | 204 | 79 | 123.6 | 94 | 58 | 125.8 |
| | permeate | | | | | | | integrated | 40 | 84.0 |
| | retentate | | 58 | 26.3 | 204 | 1310 | 1635.0 | 94 | 1264 | 1383.0 |
| F1 | permeate | 2 | 2 | 5.8 | 2 | 50 | 94.4 | 2 | 63 | 98.1 |
| | permeate | final | 8 | 6.6 | 9.2 | 101 | 103.8 | 9.2 | 76 | 108.4 |
| | permeate | | | | | | | integrated | 62 | 100.5 |
| | retentate | | 14 | 12.5 | 9.2 | 69 | 113.5 | 9.2 | 66 | 119.3 |
| F2 | permeate | 2 | 166 | 15.9 | 2 | 126 | 92.6 | 2 | 82 | 98.6 |
| | permeate | final | 515 | 18.5 | 16 | 111 | 95.8 | 6.0 | 113 | 103.9 |
| | permeate | | | | | | | integrated | 81 | 97.7 |
| | retentate | | 171 | 34.1 | 16 | 62 | 97.9 | 6.0 | 73 | 113.2 |
| F3 | permeate | 2 | 31 | 24.4 | 2 | 43 | 105.4 | 2 | 49 | 103.0 |
| | permeate | final | 32 | 28.9 | 13 | 55 | 117.8 | 7.8 | 47 | 110.8 |
| | permeate | | | | | | | integrated | n.a. | n.a. |
| | retentate | | 21 | 24.7 | 13 | 72 | 136.5 | 7.8 | n.a. | 132.6 |
| F4 | permeate | 2 | 63 | 7.5 | 2 | n.a. | n.a. | 2 | n.a. | n.a. |
| | permeate | final | | | 4.0 | 114 | 103.1 | 8.0 | 119 | 108.8 |
| | permeate | | | | | | | integrated | 127 | 104.7 |
| | retentate | | 31 | 10.8 | 4.0 | 89 | 111.6 | 8.0 | 120 | 117.7 |
| O1 | permeate | 2 | 20 | 3.8 | 2 | 48 | 89.6 | 2 | 46 | 91.8 |
| | permeate | final | 25 | 2.9 | 16 | 77 | 89.9 | 17 | 60 | 93.2 |
| | permeate | | | | | | | integrated | n.a. | n.a. |
| | retentate | | 22 | 5.6 | 16 | 56 | 90.2 | 17 | 38 | 96.2 |

Table 3 (continued)

| CFF ID | Type | Q2 | | | SW3 | | | SW4 | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | *cf* | OC | FLU | *cf* | OC | FLU | *cf* | OC | FLU |
| O2 | permeate | 2 | 35 | 4.4 | 2 | 55 | 97.7 | 2 | 59 | 98.0 |
| | permeate | final | 29 | 3.9 | 6.8 | 96 | 93.4 | 10 | 55 | 98.4 |
| | permeate | | | | | | | integrated | n.a. | n.a. |
| | retentate | | 152 | 30.5 | 6.8 | 53 | 95.1 | 10 | 56 | 100.3 |
| O3 | permeate | 2 | 15 | 5.3 | 2 | 40 | 95.8 | 2 | 45 | 98.8 |
| | permeate | final | 13 | 4.1 | 6.3 | 65 | 92.9 | 10 | 69 | 98.2 |
| | permeate | | | | | | | integrated | 43 | 99.2 |
| | retentate | | 15 | 7.0 | 6.3 | 32 | 96.0 | 10 | 58 | 101.6 |
| X1 | permeate | 2 | 62 | 9.2 | 2 | 43 | 77.1 | 2 | 36 | 82.6 |
| | permeate | final | 57 | 9.2 | 20 | 43 | 72.8 | 13 | 43 | 77.4 |
| | permeate | | | | | | | 13 | 61 | 86.6 |
| | retentate | | 35 | 9.9 | 20 | 51 | 72.2 | integrated | 42 | 77.0 |

See notes to Table 2.

for SW2, where the sum OC and source data agreed (Table 4). System Z1 (Desal) had high colloidal OC retention, but the sum OC data suggests significant contamination for both SW1 and SW2.

In contrast to the surface waters near Woods Hole, the Hawaii prefiltered OC source water concentrations averaged only 41 $\mu M$, which is characteristic of deep waters from this region (Druffel et al., 1992; Peltzer and Hayward, 1996). Overall, there was less apparent OC contamination in Hawaii than at Woods Hole (Fig. 1c and d, note change in *y*-axis), and at least one of the Filtron systems achieved a reasonable mass balance for OC (F3). An increase in the permeate OC concentration between $cf = 2$ and $cf =$ final was evident in many of these systems. In addition, it is even clearer in these Hawaii results that the Amicon CFF systems produced a higher colloidal OC concentration. Colloidal OC concentrations ranged from 6 to 28 $\mu M$ for the Amicon systems for SW3 and SW4 (Table 4). The sum OC concentrations were within 18 $\mu M$ of the source for all Amicons, except A4. Excluding A4, %COC ranged by more than a factor of 4, from 15% to 67% for SW3 and closer to a factor of 2, or 32% to 58% COC for SW4 (Table 4). Given the observed variations in permeate OC concentration with *cf*, many of the groups also sampled the permeate as a volume-integrated sample for SW4 as well. These integrated-permeate samples for the Amicon CFF had calculated colloidal OC concentrations of 13 to 22 $\mu M$, which were identical within 1–3 $\mu M$ in any individual case to the colloidal OC concentrations determined using the average of the two permeate samples at $cf = 2$ and $cf =$ final. Using the integrated permeate data, the sum OC concentrations ranged from 41 to 60 $\mu M$, relative to the 41 $\mu M$ source waters (Table 4).

An even sharper contrast exists in Hawaii relative to Woods Hole in the retention characteristics between the Amicon and the non-Amicon CFF systems. Many of the non-Amicon systems had either negative colloidal concentrations (indicative of contamination), or values of only 0–2 $\mu M$. Filtron system F3 was used for the first time in Hawaii and had 4% COC for SW3, but no significant colloidal OC for SW4. A single Osmonics system, O3, also had 4% COC for SW4, using the integrated permeate data. The rest of the Osmonics, Filtrons and Membrex systems did not show any elevation of OC in the retentate above the permeate concentrations.

### 4.2. Fluorescence results for seawater

Bulk fluorescence was determined on all of the CFF systems similar to the OC results outlined above Fig. 2. As presented, the absolute magnitude of these fluorescence units cannot be compared between the Woods Hole or Hawaii site, but are relative within each setting. Unlike the OC data, the prefiltered source waters exhibited much smaller variability in

their fluorescent properties, indicating that contamination by fluorescence material was low and that analytical reproducibility was quite good. The bulk fluorescence results contrasted with the OC measurements, in that many systems with elevated OC achieved a much closer mass balance. This is particularly striking for the Filtron systems, where total OC levels were quite high, but the fluorescence mass balance looked reasonable. The Amicon systems in general had a small excess fluorescence signal relative to the source. A few systems showed an apparent loss of fluorescence (system A1 for SW3; system O1 for SW3 and SW4; system X1 for SW1, SW3 and SW4). As with the OC results, the Amicon systems plus system Z1 had the highest colloidal signal. In all of the Amicon systems there was also a strong increase in fluorescence in the permeate between $cf = 2$ and $cf =$ final, in contrast to the other systems. Also similar to the OC data, system Z1 exhibited a higher sum fluorescence signal than the source waters.

### 4.3. Q-water organic carbon and fluorescence results

In an attempt to establish contamination levels for the CFF systems, Q-water was processed as a sample, although many of the participants processed smaller volumes or concluded the experiment at a lower concentration factor than was typical of their seawater samples. The Hawaii Q-water results are shown in Fig. 3a and b. The permeate data are plotted as before, with separate results at $cf = 2$ and $cf =$ final; however, the colloidal concentrations were not expressly calculated, but rather the total retentate concentration is shown. In this manner it is easy to demonstrate the absolute magnitude of the net blank, and whether or not the contaminant is retained by the membrane. The Woods Hole Q-water results (Table 2) had similar features; however, some of the absolute values were significantly higher.

The Hawaii Q-water OC results should be compared to a source water OC blank of 3–5 $\mu M$ (Fig. 3a). Almost every fraction for every system was elevated by at least a few $\mu M$, and approximately half of the CFF systems had at least one sample $> 20$ $\mu M$ above the blank. Some systems displayed elevated OC blanks in the retentate loop (A1, A4, A5, and O2), indicative of HMW contaminants and/or this could be partially due to some concentration of colloidal OC from the Q-water (2–5 $\mu M$ OC). In contrast, other systems had elevated OC levels in the permeate (F2, F3, F4 and X1). The Q-water blank was not directly reflected in the Hawaii seawater OC results (compare Fig. 3a with Fig. 1c and d). For example, system A1 had an elevated OC blank in Q-water but showed no apparent bulk contamination in the two Hawaii seawater samples. Conversely, system F1 had no appreciable OC blank in Q-water but apparently contaminated the seawater samples.

The Hawaii Q-water fluorescence blanks were relatively small and tightly constrained for many of the CFF systems (within 5 fluorescence units, FU, of source waters for A2, A3, O1, O3, X1). The fluorescence blank was highest in system A4, which also had one of the higher OC Q-water blanks. The Q-water fluorescence blank was $> 10$ FU (compared to the Hawaii seawater total fluorescence signal of 100 FU) in at least one sample for 6 of the CFF systems (A1, A4, A5, F2, F3, O2). With the exception of system F3, the blanks were elevated in the retentate relative to the permeate, indicating that the blank compounds were not able to freely pass through the membrane.

### 4.4. Time-series organic carbon measurements in the permeate

In almost all cases at Woods Hole and Hawaii when significant colloidal OC was observed, OC concentrations in the permeate increased between $cf = 2$ and $cf =$ final. Assuming the retention characteristics of the CFF membrane are constant and there are no sorptive losses or contamination, one can predict for single compounds the variation in the permeate concentration with increasing concentration factor (Logan and Jiang, 1990; Kilduff and Weber, 1992). We measured the temporal pattern of OC concentration in the permeate during one standard seawater ultrafiltration experiment in Hawaii (SW4, Fig. 4a–m).

At least two of the systems (A4 and F1) showed a sharp initial drop-off in OC concentration just after the first time collection point. This trend is likely indicative of OC contamination which decreases

Table 4
Colloidal and sum organic carbon results

| CFF ID | OC (μM) | | %COC [c] | OC (μM) | | %COC [c] | | | |
|---|---|---|---|---|---|---|---|---|---|
| | colloidal [a] | sum [b] | | colloidal [a] | sum [b] | | | | |
| | SW1 | | SW2 | | | | | | |
| Source | 106 [d] | | 104 [d] | | | | | | |
| A1 | 41 | 127 | 39 | 35 | 115 | 34 | | | |
| A2 | 24 | 182 | 23 | 36 | 171 | 35 | | | |
| A3 | 46 | 122 | 43 | 36 | 168 | 35 | | | |
| A4 | 51 | 131 | 48 | 54 | 125 | 51 | | | |
| A5 | 14 | 244 | 13 | 16 | 384 | 15 | | | |
| F1 | −40 | | | −9 | | | | | |
| F2 | −21 | | | −14 | | | | | |
| F3 | n.c. | | | n.c. | | | | | |
| F4 | −3 | | | 7 | 376 | 7 | | | |
| O1 | 6 | 107 | 5 | 5 | 118 | 4 | | | |
| O2 | −3 | | | −63 | | | | | |
| O3 | 11 | 105 | 10 | 29 | 84 | 28 | | | |
| X1 | 0 | 131 | 0 | 4 | 104 | 4 | | | |
| Z1 | 43 | 361 | 41 | 68 | 178 | 66 | | | |

| CFF ID | OC (μM) | | %COC [c] | OC (μM) | | %COC [c] | OC (μM) | | %COC [g] |
|---|---|---|---|---|---|---|---|---|---|
| | colloidal [a] | sum [b] | | colloidal [a] | sum [b] | | colloidakům [f] | | |
| | SW3 | | SW4 | | | SW4 | | | |
| Source | 42 [d] | | 41 [d] | | | 41 [d] | | | |
| A1 | 12 | 41 | 28 | 13 | 40 | 32 | 13 | 41 | 31 |
| A2 | 28 | 52 | 67 | 23 | 52 | 56 | 22 | 59 | 54 |
| A3 | 21 | 60 | 51 | 24 | 47 | 58 | 21 | 60 | 51 |
| A4 | 21 | 98 | 51 | 17 | 94 | 41 | 19 | 55 | 45 |
| A5 | 6 | 55 | 15 | 13 | 53 | 32 | 13 | 53 | 32 |
| F1 | −1 | | | 0 | 70 | 0 | 0 | 62 | 0 |
| F2 | −4 | | | −4 | | | −1 | | |
| F3 | 2 | 51 | 4 | −6 | | | n.c. | | |
| F4 | −6 | | | 0 | 119 | 0 | −1 | | |
| O1 | 0 | 63 | 0 | −1 | | | n.c. | | |
| O2 | −3 | | | 0 | 57 | 0 | n.c. | | |
| O3 | −3 | | | 0 | 57 | 0 | 1 | 44 | 4 |
| X1 | 0 | 43 | 0 | 0 | 40 | 0 | −1 | | |
| Z1 | n.c. | | | n.c. | | | n.c. | | |

n.c. = not collected. Sum and %COC values are not given if calculated colloidal OC < 0.
[a] Colloidal OC concentration calculated from average permeate OC and Eq. 4. All data can be found in Tables 2 and 3.
[b] Sum of colloidal OC and average permeate OC concentrations.
[c] Colloidal OC/source OC.
[d] Average source OC concentration as appropriate for SW1, SW2, SW3, and SW4.
[e,f,g] As for [a, b, c], respectively, except the "integrated" permeate sample OC concentration is used in the calculations.

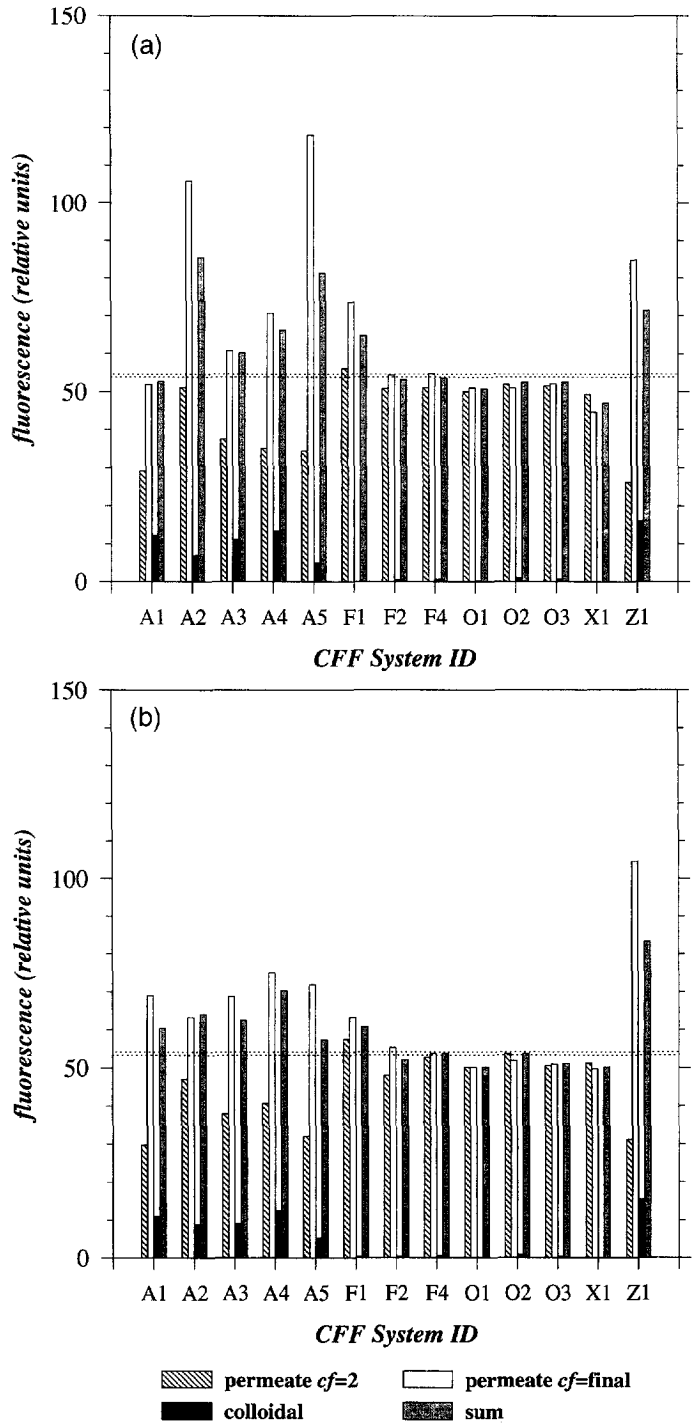


Fig. 2. Intercomparison of bulk fluorescence results: (a) Woods Hole sample SW1; (b) Woods Hole sample SW2; (c) Hawaii sample SW3; and (d) Hawaii sample SW4. Details and ID's as described in Fig. 1.

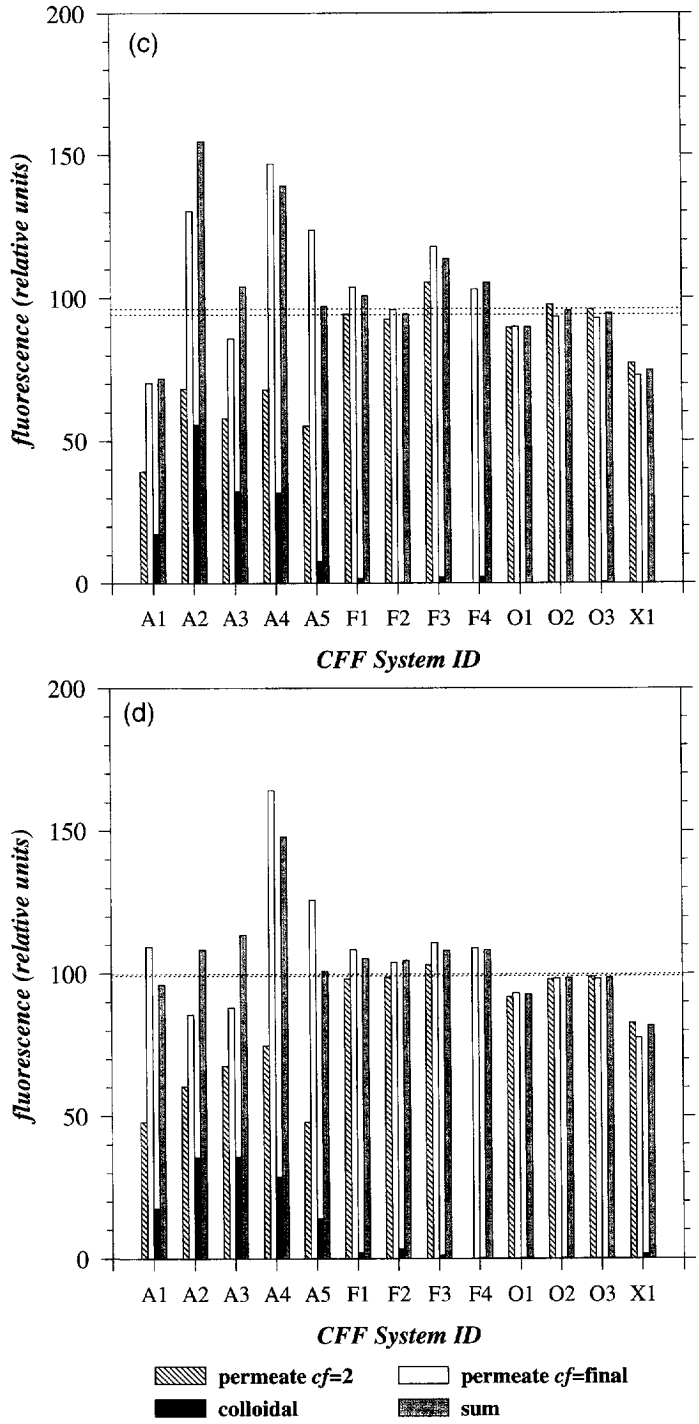


Fig. 2 (continued).

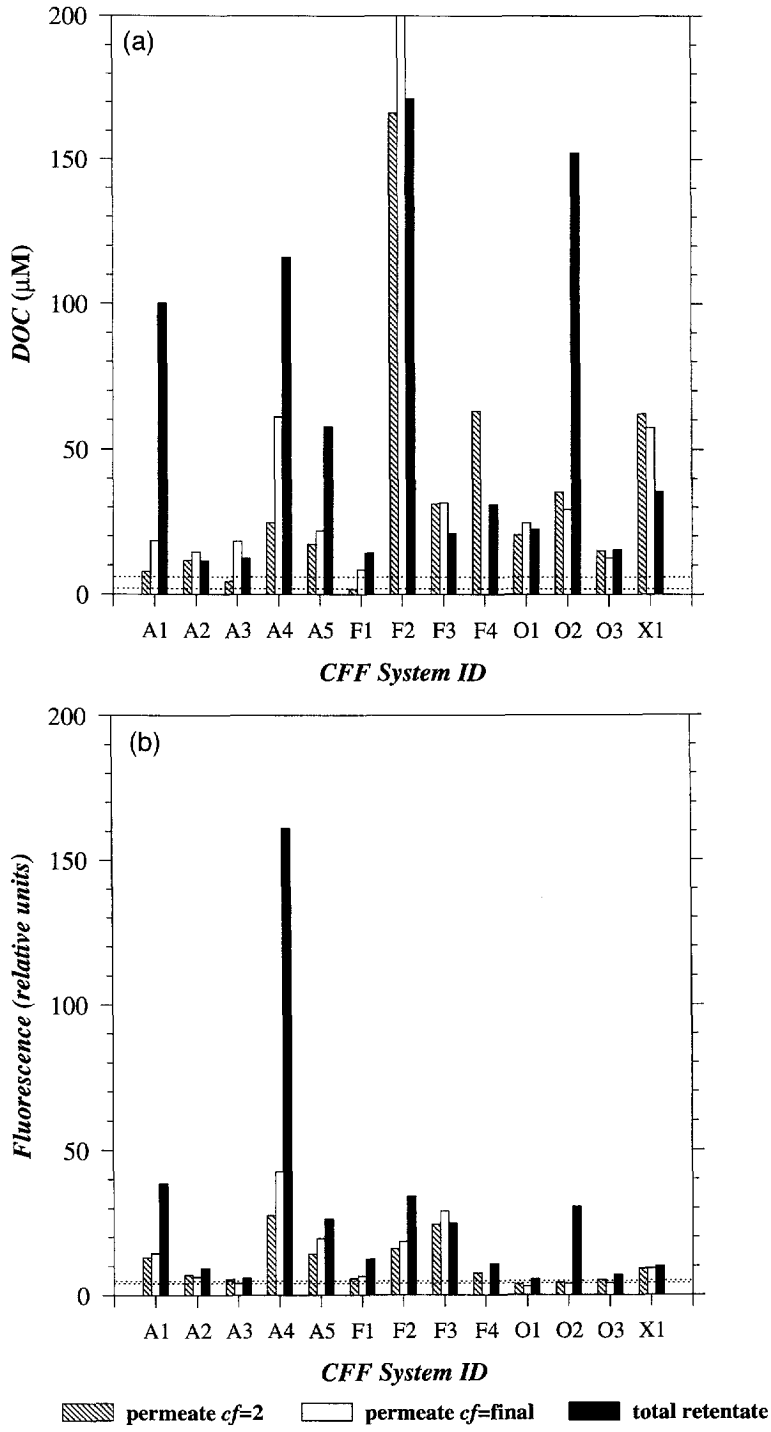


Fig. 3. Intercomparison of Q-water blanks for the different cross-flow filters systems grouped by CFF ID (see Table 1) and according to manufacturer: (a) Hawaii sample Q2 results for organic carbon; and (b) Hawaii sample Q2 results for fluorescence. CFF ID's are shown on lower $x$-axis. Data are shown for each system for the permeate concentration at $cf = 2$ (*diagonal fill*), permeate at $cf$ = final (*open fill*), and for the total retentate concentration (*solid fill*).

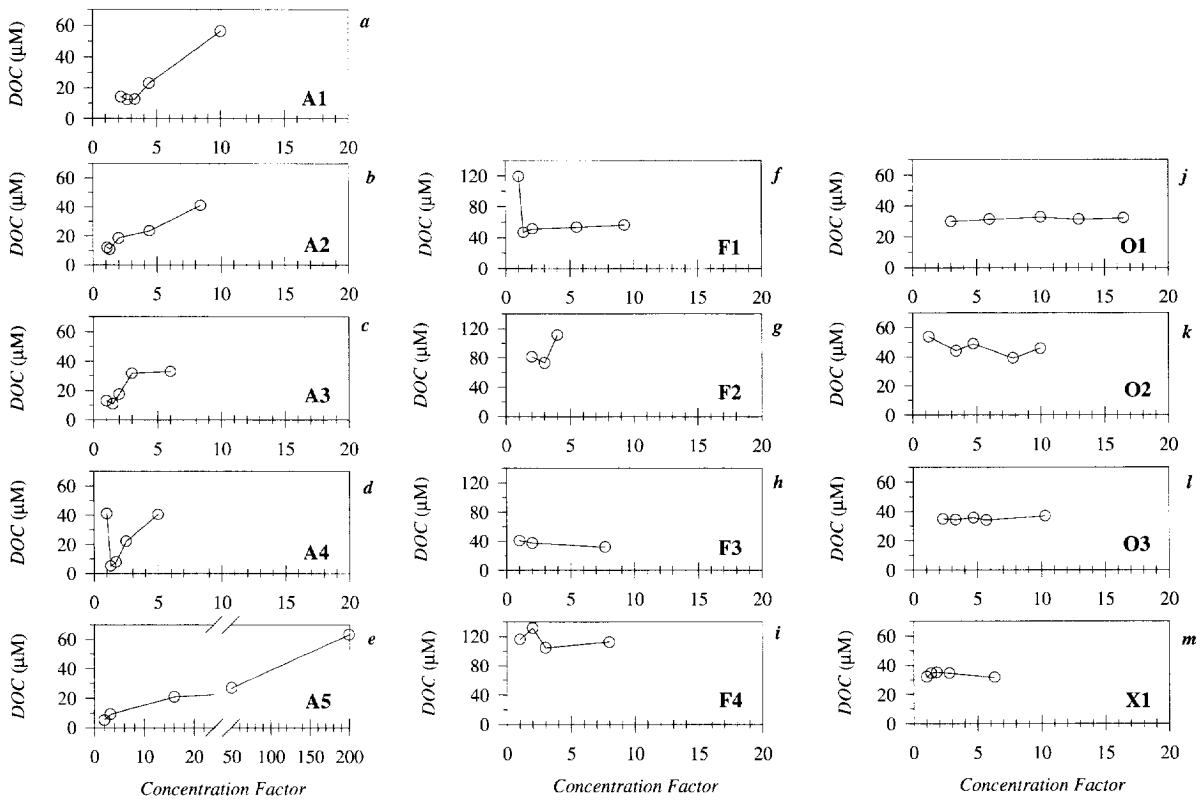


Fig. 4. Time-series of permeate OC vs. concentration factor for SW4. Data for each CFF system are plotted separately in (a)–(m), and CFF systems are identified as in Table 1. Note change in *x*-axis scale for (e) (0–200) rather than *cf* range of 0–20 used for all others. The measured permeate OC concentration of each sample is shown by *open circles* on a scale of 0 to 70 $\mu M$, except for (f)–(i) (Filtron systems), where a 0 to 130 $\mu M$ *y*-axis is used.

rapidly as a sample is processed. An alternative explanation is that the decrease represents early sorptive losses of OC onto the CFF. A smaller and slower decrease in OC was seen in two of the systems that had elevated OC concentration relative to the source waters (F4, O2).

The Amicon CFF systems had both the highest overall retention of colloidal OC and exhibited the strongest trend of increasing OC concentration with increasing *cf*. This trend was seen starting at a *cf* as low as 1.5–3 (prior OC levels were decreasing or relatively constant) and in many cases OC concentrations increased thereafter in a quasi-linear fashion. The slopes of these curves differed substantially, for example, system A1 showed a three-fold increase in permeate OC at a $cf = 10$, and a similar increase was not reached until $cf = 200$ for system A5.

The non-Amicon systems generally had a very flat, or non-changing permeate concentration with time. CFF systems F3, O1, O3 and X1 all had a mean permeate OC concentration of 45 $\mu M$ which was, on average, a few $\mu M$ less than the source water OC concentration as measured by this second HTC-OC instrument. This is consistent with the very low retention of colloidal OC in these CFF systems, but slightly at odds with the previous OC concentration results for SW4 (Fig. 1d), where a trend of higher OC concentration was found for some of these same systems between the permeate at $cf = 2$ and $cf =$ final. Both OC sample sets were collected, stored and analyzed in slightly different manners on different HTC-OC instruments. There appears to be close to a $+8$ $\mu M$ offset in the time-series OC results from the standard OC concentration data that

cannot be resolved within this intercomparison exercise. The effect of the changing permeate OC concentration on the calculated colloidal OC percentages will be discussed below, and is addressed specifically in Guo and Santschi (1996-this issue), Gustafsson et al. (1996-this issue), and Wen et al. (1996-this issue).

## 5. Discussion

Marine scientists use CFF with the intent to operationally separate seawater samples into dissolved and colloidal fractions. The central assumptions are: (1) that the CFF system is behaving in a well-defined and operationally-reproducible and consistent manner for each sampling; and (2) that the separation process does not significantly alter the physicochemical nature or size distribution of natural substances in the original sample. The goal of this intercomparison exercise was to examine the first of these assumptions by comparing the relative performance of different CFF systems used in marine sciences with respect to the bulk separation of organic and inorganic colloidal matter from seawater. The interpretation of these results is presented below, beginning with a discussion of CFF system blanks, followed by an analysis of mass balances and sorptive losses. In addition, time-series data and the results of one standard molecule experiment will be addressed.

### *5.1. Operational blanks for* CFF *systems*

As for all chemical analyses, it is essential that a procedural blank be determined. In the case of CFF, evidence of contamination can be seen either by the detection of elevated concentrations in Q-water blanks, or by an assessment of the chemical mass balance. Both of these approaches were taken during this intercomparison study. Note that both organic and inorganic blanks can be important regardless of the measured contaminant. For example, it is possible that bulk OC contamination of even a few $\mu M$, may lead to an alteration of the apparent trace-metal or specific organic compound speciation, particularly at the low (nmol/l to sub-pmol/l) ambient concentrations of common trace constituents. Likewise, metal contamination may lead to precipitation of colloidal oxyhydroxides during sample processing which, in turn, could alter the natural size distribution of bulk OC or specific organic and inorganic substances by sorption to the inorganic colloid surfaces. Quantification of both organic and metal contamination is therefore important for all marine CFF applications.

#### *5.1.1. Q-water blanks for organic carbon and fluorescence*

Q-water blanks can be useful in identifying large contamination problems; however, these Q-water values cannot be applied directly to correct for procedural blanks in seawater CFF data. One reason is that there are large pH and compositional differences between the seawater and Q-water media such that contamination and sorptive processes are not necessarily the same. The Q-water results in Hawaii (Fig. 3a; Table 3) and Woods Hole (Table 2) indicate that many of the CFF systems have OC blanks that are greater than the total ambient seawater OC levels. By comparing the Hawaii Q-water OC blank (Fig. 3a) with the Hawaii seawater OC data (Fig. 1c and d), it is also clear that the patterns and absolute magnitude of the individual Q-water blanks are not simply reflected in the seawater OC distributions. Since these same CFF systems are regularly used for studies of colloidal OC and trace-metal and organic compound speciation in marine samples, these OC Q-water blanks point to the possibility of random artifacts in such studies. Optimistically, it appears that at least one system of every type can be treated to obtain OC blanks as low as a few to 10 $\mu M$ relative to Q-water (in Hawaii: A2, F1, O3). In some applications of CFF to coastal waters or estuaries, where total OC levels are much higher ($> 100\ \mu M$), a small OC blank may not pose as significant a problem compared to open-ocean deep waters where total OC levels closer to 40 $\mu M$ are found.

Ironically, our attempt to provide each participant with a new CFF membrane prior to the Woods Hole experiment brought the OC blank issue immediately to light. It was thought that new membranes should be used in this intercomparison to avoid complications due to membrane fouling or other artifacts related to membrane lifetime. Many of the participants (including all the Filtron and system Z1 users)

received their membranes only shortly before the WHOI sampling and therefore could not undertake their normal cleaning procedures. In most cases, this cleaning entails processing > 100 l of Q-water, acidic, basic, solvent and salt solutions through the CFF membrane (Table 1). Some participants have found that the use of methanol or detergents for these cleaning steps can cause lingering OC blanks, though in the case of Filtron membranes, an initial rinse with 10% MeOH lowered the OC blank considerably. The OC blank decreased between Woods Hole and Hawaii, demonstrating that with continued use, many of these systems can be rendered appreciably "cleaner". Nonetheless, some systems which displayed very low OC blanks at WHOI showed appreciable OC contamination 5 months later in Hawaii, indicating that alterations in CFF OC blanks can occur upon repeated use and with prolonged storage (as documented in Gustafsson et al., 1996-this issue).

The Q-water fluorescence blanks are relatively smaller than the bulk OC blanks. Nevertheless, many systems with a higher than ambient fluorescence blank also displayed an elevated OC blank, though this was not always the case. This result implies that the compounds which contribute to the bulk OC blank can at times be aromatic, perhaps associated with the membrane materials which vary between manufacturers. This difference between the pattern and magnitude of the bulk OC blank and the fluorescence blank indicates that some fractionation of the total organic carbon pool is possible among these systems. A more exact determination of the organic composition of the Q-water blanks would allow for the identification of the specific materials and components in these systems which contribute significantly to the blank.

To summarize these findings, the Q-water blanks provide a broad view of the contamination of CFF systems but themselves are not reliable indicators of the behavior of these systems when processing seawater. The variation in Q-water blanks with time (i.e. between WHOI and Hawaii) shows that the OC blank is not fixed. Also, the variability in the blank between CFF systems of a given type is large, suggesting that individual cleaning and handling protocols are critical. It is therefore important that procedural blanks be routinely evaluated and documented prior to the application of CFF to individual seawater samples. Ultimately, Q-water OC blanks of the magnitude found here will be a major obstacle for getting reliable CFF results in open-ocean settings, where total OC levels are only 40–70 $\mu M$.

*5.1.2. Mass-balance approach*

In the mass-balance approach a comparison is made between the sum of the measured colloidal and permeate fractions and an independent sample that has not been ultrafiltered (ideally the pre-filtered source waters). If the two quantities are equal, then it is generally assumed that both contamination and sorptive losses during CFF processing are negligible. The advantage of this approach over the Q-water blank lies primarily in the direct comparison of the behavior of a realistic sample medium, i.e. seawater, within the CFF system. In addition to testing for leaching from the CFF system, determination of mass balance also tests for the net removal of natural substances by sorption to the system; something that Q-water blanks cannot indicate. However, with the mass-balance approach, the signal to noise ratio of the contaminant relative to the ambient concentration is much poorer compared to the Q-water blanks.

In the results shown in Figs. 1 and 2, one can easily compare the source waters (horizontal dashed lines) to the individual fractions and the sum of the colloidal and permeate concentrations. In Table 4 we also list the sum of the calculated colloidal OC and permeate results and the source OC concentrations. Overall, the apparent OC mass balance improved when the CFF systems were used the second time in the low-OC setting off Hawaii. These data suggest that with repeated use, and in seawater media, bulk OC contamination from the CFF system components generally decreases, although there are some exceptions. In Hawaii however, total OC levels are only 41 $\mu M$, so the difference between the sum and the source OC is often as large or larger than the calculated colloidal OC concentration. It is also evident, that while some systems are more prone to OC contamination, the same type of CFF systems can have higher or lower blanks, similar to the Q-water results. This depends presumably upon the cleaning, preconditioning, and sample handling steps used by the individual operator.

Fluorescence balances were much closer for many

CFF systems. However, a few of the Amicon systems plus system Z1 had elevated permeate concentrations relative to the source solution (Fig. 2). In contrast to bulk OC concentration, a net loss of fluorescence was found in at least one seawater sample for three systems (A1, O1 and X1). The humic and fulvic fractions are thought to represent a major component of colored DOM, at least in coastal waters, and would have a high fluorescence signal (open-ocean OC is thought to be made up of more aliphatic compounds). The source of bulk OC contamination does not generally appear to release OC with fluorescing properties, at least for the wavelengths examined. Seawater Al is similar to bulk OC with respect to the mass balances; as in many cases, there is a clear excess of Al relative to the source waters (Reitmeyer et al., 1996-this issue). On the other hand, iron shows significant sorptive losses, and was the only compound measured where a general decrease was found in concentration in the permeate with time. Furthermore, the CFF results of Wen et al. (1996-this issue) provide additional evidence for fractionation by CFF of certain trace metals.

There are three major caveats with respect to the mass-balance approach. The first concern is that, at best, most CFF mass balances are considered "reasonable" if the sum and total agree within 10–20%. If the colloidal fraction represents only 20% of the total, then the total error on the magnitude of the colloidal pool could be $\pm 50$–100%. This concern is not unique to CFF, but holds in general when one size class or fraction represents only a small fraction of the total. Some investigators report both the colloidal fraction as measured and as determined by difference, while others assume that the lack of a mass balance can be attributed specifically to sorption of colloidal compounds or dissolved solutes, and the difference is added to the specified fraction (Baskaran et al., 1992; Liang et al., 1996).

The second caveat when examining mass-balance data is that when measuring bulk properties such as OC concentration, a mass balance strictly implies that sorptive losses and contamination sources are in balance. The observed bulk OC recovery is therefore the result of a combination of unknown losses and contamination. Selective losses of specific organic compounds would result in fractionation of the sample during the CFF process which would not be detectable in the mass balance. Some evidence for fractionation between systems in this intercalibration can be seen in the absorbance results (Mopper et al., 1996-this issue).

A final caveat is that since the permeate concentration may be changing over time, the calculated colloidal concentration will vary as a function of the processing time or concentration factor. In effect, the attainment of mass balances is only possible if the calculated colloidal and permeate concentrations are accurate relative to the starting phase distributions (see discussion below of the time-series permeate OC results). For Figs. 1 and 2 the average of the two permeate samples was used to calculate the sum concentration. Mass balances can be best compared when an integrated permeate was collected for SW4; and, in this case the mass balances ranged from 41 to 60 $\mu M$, or up to 19 $\mu M$ greater than the source OC (calculated for A1–A5, Table 4).

In summary, the Q-water and mass-balance approaches have advantages and disadvantages. Both methods should be used to elucidate contamination and/or major sorptive losses to CFF systems during ultrafiltration. One alternative to separating contamination from sorptive losses includes adding standard molecules at realistic concentrations to the sample, and then following their behavior in both the retentate and permeate with time. Using this approach, Gustafsson et al. (1996-this issue) have found that sorptive losses are kinetically controlled, and time series sampling is needed to reach a quasi-equilibrium between the added compound and the CFF system. Finally, it may also be possible to analyze the cleaning solutions used between CFF processing, to assess sorbed losses. In this case, if a significant fraction of the compound of interest is identified, then it is still unclear if the sorbed species were originally dissolved or colloidal; however, closure of the mass balance assures to a first approximation that the system can be cleaned between samples, and that carryover is minimal.

### 5.2. *Retention characteristics of* CFF *systems in marine applications*

One of the primary features of this intercomparison is the large difference in apparent retention

characteristics of the different CFF systems when used on natural seawater samples. Despite the range of operating conditions (Table 1), the retention characteristics of the CFF systems group according to the manufacturer of the membrane. At both sites, the concentration of colloidal OC retained by the CFF systems follows the order:

Amicon > Filtron ≥ Osmonics > Membrex

This holds for bulk OC concentration (Fig. 1a–d), fluorescence (Fig. 2a–d), Fe and Al (Reitmeyer et al., 1996-this issue), organic nitrogen, organic phosphorus (Bauer et al., 1996-this issue), Cu, Ni and Cd (Greenamoyer and Moran, 1996-this issue), and optical properties (Mopper et al., 1996-this issue). System Z1 (Desal) also had high retention, similar to the Amicons at Woods Hole (Table 4), but the high OC mass balances and limited study of this system preclude further discussion at this time.

Given these large differences in apparent cut-offs, a CFF experiment was conducted with a standard molecule of known size (3-kD). The details of this experiment are described in the companion paper by Gustafsson et al. (1996-this issue). A fluorescing dextran carbohydrate standard was added in sub-*M* carbon equivalent concentrations to the prefiltered Hawaii samples. The same qualitative pattern of high retention by the Amicon systems was observed, with the two Amicon systems tested retaining 33% (A4) and 75% (A1) of the 3-kD standard using the 1-kD membrane. Retention of the 3-kD standard was only 21%, 14% and 5% on average, for the Filtron, Osmonics and Membrex CFF systems, respectively. This experiment also pointed out the potential for large sorptive losses by each of the CFF systems (ranging from 5% to 70%; see discussion in Gustafsson et al., 1996-this issue). One additional study conducted outside of this intercomparison using standard molecules suggested that the retention characteristics of the Amicon membrane are more consistent with the rated 1-kD cut-off (Guo and Santschi, 1996-this issue), although different protocols were used than in Gustafsson et al. (1996-this issue). As seen in other CFF studies, there is also evidence (Guo and Santschi, 1996-this issue) for the retention of standard molecules with a molecular weight smaller than the rated cut-off.

The 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. For example, Amicon defines the membrane cut-off using globular proteins and a 90% retention criteria, while Osmonics uses dextran standards and a loosely-applied 80% rejection criterion. In all cases, it is clear that the manufacturers' testing procedures reflect the needs of their major users in the industrial and biomedical communities. Retention coefficients are determined at high transmembrane pressure (50–100 psi or 345–690 kPa) and very high standard concentrations (3 g/l for Osmonics). The behavior of the same membrane for compounds at $\leq \mu M$ levels is expected to be different (e.g., Buffle et al., 1992). Theoretical and experimental data suggest that some compounds will react with the membrane, thus leading to chemical fractionation for a natural sample composed of a heterogeneous assembly of macromolecules and trace-metal ligands (Gustafsson et al., 1996-this issue; Wen et al., 1996-this issue). Ionic strength effects and tertiary molecular structure play a role as well (Staub et al., 1984; Küchler and Miekeley, 1994).

The retention characteristics and behavior of CFF systems in seawater media clearly must be better understood, prior to making any determination of the true sample size distribution based upon CFF data. Defining the cut-off properties of a given membrane in seawater with realistic standard molecules presents a challenge (Guo and Santschi, 1996-this issue; Gustafsson et al., 1996-this issue). Given the evidence of batch to batch variations in membrane characteristics (Buffle et al., 1992), and the potential for fouling or aging effects on these membranes, progress in this area is critical. The characterization of new membranes for marine applications is also needed, as well as the standardization of each system as frequently as is practical, including perhaps the addition of an internal standard to each sample.

### 5.3. Changes in permeate concentration with time

When the permeate was sampled at a concentration factor of 2 and at the end of the ultrafiltration run we often detected an increase in permeate OC concentration (see $cf = 2$ and $cf =$ final permeate data in Fig. 1a–d). One implication is that as the sample is processed, fractionation is occurring, as

macromolecules initially retained by the membrane are passing through the membrane at higher concentration factors. This feature is more clearly demonstrated in our time-series permeate experiment (Fig. 4a–m). Any compound with a retention coefficient between zero (i.e. passes completely through the CFF membrane) and slightly less than one (fully retained) will be affected by this process. To maintain a mass balance, the concentration in the permeate must increase as the concentration in the retentate loop increases. This process might be expected to be most obvious for those systems with the highest retention (i.e. Amicon). The breakthrough process is not an artifact per se, but a consequence of CFF processing that needs to be included in our interpretation of CFF results.

The changing permeate concentration as a function of *cf* has received considerably more attention in the CFF membrane sciences literature and freshwater applications than in marine studies. For single LMW molecules with a constant permeation coefficient of $< 1$ (permeation coefficient $= 1 - RC$), the time varying breakthrough of compounds in the permeate can be predicted, if sorption is negligible and the retention characteristics at the membrane remain constant (Logan and Jiang, 1990; Kilduff and Weber, 1992). When these conditions hold, the true initial concentration of single LMW solutes can be calculated from appropriate time-series permeate data. Guo and Santschi (1996-this issue) apply such a simple permeation model to standard molecule and bulk OC data from their Amicon system. These researchers conclude that the increase in OC is related to the retention of LMW compounds, and that CFF experiments should be concluded at high concentration factors ($> 100$), in order to obtain a more accurate estimation of the true in situ colloid abundances. However, with a high *cf*, the assumption of a constant RC is not likely and other artifacts may occur (Buffle et al., 1992; Kilduff and Weber, 1992).

It is obvious that time-series permeate results, such as shown here in Fig. 4a–m, are needed to understand permeation dynamics. Although higher frequency sampling would be desirable, one can already see a number of different permeation patterns in the Amicon time-series data that cannot be predicted from the simple permeation models of Logan and Jiang (1990) or Kilduff and Weber (1992). For example, some permeate OC concentrations first decrease, then increase (A4); alternatively, there is no change in OC concentration in some portion of the permeation curve (below $cf = 3.5$ for A1, and above $cf = 3$ for A3); and overall, there are significant differences in the slopes of these curves as well (A5 vs. rest). Given these time-series data, one cannot be confident that RC remains constant or that sorption/contamination is negligible in these CFF systems, a required condition for applying these existing models.

Measurements such as HTC-OC represent the average properties of a wide variety of organic compounds with differing physicochemical properties and sizes. These separate compounds would be expected to respond in different ways to the build up of OC concentration in the retentate loop and on the CFF membrane. Logan and Jiang (1990) point out that for a mixture of compounds, the concentration of material smaller than the membrane cut-off will be underestimated if a standard permeation model with a composite permeation coefficient is used. It is therefore not clear how well the observed concentration changes in the permeate of bulk properties, such as OC, can be used to accurately predict the original size distribution of the original sample, even in an ideal CFF system.

CFF systems with a sharper cut-off in the retention characteristics of both HMW and LMW compounds would tend to minimize breakthrough effects. In addition, concentration breakthrough may be minimized in those set-ups (O1, O2, O3 and A5) where a fixed volume retentate loop is continually topped-off with the larger volume of sample solution. This technique is essentially a modification of difiltration processing to remove salts, in which the sample volume is maintained by the continuous addition of fresh waters during ultrafiltration. Such techniques will minimize the effects of concentration polarization (Kilduff and Weber, 1992) and eliminate the need for secondary storage containers.

### *5.4. Calculation of colloidal abundances*

If the permeate concentrations are changing with *cf* then it must be acknowledged that the apparent colloidal/dissolved partitioning can be strongly affected by the manner in which the permeate stream

is sub-sampled. In other words, the final *cf*, and whether or not the permeate is sampled at a discrete point in time or as the volume-integrated average permeate, will alter the calculated colloidal concentrations. In this study, there was only a 0–3 $\mu M$ difference if the colloidal OC concentrations were calculated from the average of the two discrete permeate samples (collected at $cf = 2$ and $cf =$ final) or from the integrated permeate sample (Table 4, SW4). In practice, if only a single permeate sample can be collected, then an integrated permeate sample is preferred (Guo and Santschi, 1996-this issue). For large volume processing (> 100 l) it is not always practical to collect the entire permeate fraction in an appropriately clean vessel; hence, at a minimum, subsamples must be taken over time to determine the integrated, or volume-adjusted permeate concentrations. An additional approach suggested by Mopper et al. (1996-this issue), would be continuous monitoring of the permeate stream, which may be possible for at least fluorescence and absorbance properties.

In many previous studies, colloidal abundances have been calculated by difference. Using the measured source water OC concentration minus the integrated permeate OC concentration for the Amicon systems for SW4 results in colloidal OC concentrations of 1–13 $\mu M$, or as much as 10–19 $\mu M$ lower than concentrations calculated using the measured integrated permeate and retentate data. Essentially, when either the permeate or retentate concentration and the measured total concentration plus *cf* are known, colloidal concentrations can be estimated using a difference approach:

$$[X]_{\text{total}} = [X]_{\text{perm}} + [X]_{\text{coll}}$$
$$= [X]_{\text{perm}} + ([X]_{\text{ret}} - [X]_{\text{perm}})/cf$$

Unfortunately, if one fraction is calculated by difference, this precludes the mass-balance check for contamination.

## 6. Recommendations

### 6.1. Cleaning and preconditioning

It is clear from the intercomparison results, that OC contamination from the CFF membranes and associated ultrafiltration hardware is initially quite high, but can be reduced by flushing with copious quantities of solution. A single set of cleaning conditions and solutions cannot be recommended for every system; however, warm or room temperature dilute solutions of sodium hydroxide, inorganic acids, laboratory detergents, organic solvents and 1–2 *M* salt solutions and seawater have all been used. In the initial cleaning of any CFF membrane, > 10 l of cleaning solution per square foot of membrane must be flushed through the system. It is important to check the specific manufacturers cleaning recommendations, as exceeding the pH limits or using incompatible chemicals during cleaning can permanently alter the retention characteristics of the membrane. It must be emphasized that high-OC or Fe blanks may alter the distribution of other trace elements such that, at a minimum, a system should be shown to be clean for major OC and trace-metal contaminants. Though not tested in detail here, other investigators have found evidence of continuous leaching of contaminants, which necessitates continuous monitoring of the CFF system blanks and regular cleaning between samples, even after short-term storage (Gustafsson et al., 1996-this issue). For long-term storage, cartridges should remain wet, preferably filled with Q-water and a bacteriostat such as 0.2% sodium azide, or stored at high or low pH and if possible under refrigeration to reduce bacterial growth.

Preconditioning with the prefiltered sample solution is also recommended, both to reduce contamination of extractables from the system, and potentially to minimize sorptive losses to the membrane and other surfaces. The details of preconditioning were not studied however, and the effect of preconditioning on the build-up of the concentration polarization layer is not well understood. Using time-series sampling, one may be able to evaluate the preconditioning volume required for a given application. As shown by Gustafsson et al. (1996-this issue) however, the approach to a steady-state condition may require more time, and hence volume, depending upon the specific chemistry of the compound of interest. Following preconditioning, the CFF system should be completely drained, and CFF processing should begin immediately.

At the end of processing, some of the participants

suggested that the permeate line should be closed off and the retentate solution rapidly recirculated to enhance recovery of colloidal material off the CFF membrane. The system should be drained as well as possible. Failure to drain the CFF system completely can lead to cross contamination between samples and inaccurate accounting of volumes needed for determining the concentration factor and mass balances.

Mass balances and Q-water blanks are required to identify major contamination artifacts. However, the Q-water blank cannot be applied directly for correcting for OC contamination when processing seawater. The demonstration of a mass balance, particularly when the colloidal abundances are low, is not a sensitive indicator of contamination, and it must be remembered that contamination and sorptive losses may be co-occurring. However, a negative result for the mass balance indicates a large artifact somewhere in the processing steps, which may be reduced with proper preconditioning or cleaning. For future studies, a low or near-zero OC artificial or UV-irradiated seawater medium would prove quite useful in quantifying CFF blanks.

### 6.2. Time-series sampling

Many of the artifacts associated with CFF only become apparent with time-series sampling. This includes the determination of appropriate cleaning and preconditioning volumes and the characterization of the extent of apparent breakthrough. Time-series experiments are required to determine the best sampling window within which to operate for a given set of conditions and compounds of interest. In addition, for mass balances and for the correct determination of the dissolved solute and colloidal fractions, time-series sampling of the permeate, or the collection of a volume-integrated permeate sample is required (Guo and Santschi, 1996-this issue). Though not tested here, time-series sampling of the retentate, such as performed by Gustafsson et al. (1996-this issue) for bulk OC, specific hydrocarbons and colloid standards, is also encouraged, particularly for compounds which can be analyzed in small volumes. Retentate concentrations higher than those predicted from the concentration factor can indicate contamination within the retentate loop which is masked in the final calculation of colloidal abundances and mass balances. Any permeation model applied to natural systems must be reconciled with both standard molecule results and natural abundance measurements, using time-series sampling from both the permeate and retentate lines. At a minimum, researchers should state explicitly in each application of CFF how and when the permeate and retentate lines were sampled.

### 6.3. Standard molecule experiments

Though not a focus of this intercomparison exercise, the tracer experiment using a dextran colloid standard confirmed the field data with respect to the relative cut-offs of the membranes and in addition identified sorptive losses (Gustafsson et al., 1996-this issue). Since the manufacturers test and rate the effective cut-offs of each CFF membrane under conditions that are not comparable to natural environmental applications, each CFF system should be tested for its ability to retain standard molecules of known size and chemical properties under realistic operating conditions (Guo and Santschi, 1996-this issue; Gustafsson et al., 1996-this issue). These tests should be conducted using prefiltered seawater or appropriate carrier medium, and the standards should be added at ambient concentration levels. A range of naturally occurring compound classes should ideally be tested, as specific interactions with the membrane may affect the retention characteristics. A wide variety of fluorescent labeled compounds are available, and in many applications may prove suitable. Once the retention characteristics of a given CFF system are documented, it may be possible to monitor changes with time under differing operating conditions using the addition of single or multiple standards to each sample or between applications.

### 6.4. Better documentation of operating conditions

A final recommendation for each and every application of CFF to natural samples is that the user should carefully document and report the experimental design and operating conditions used. These variables should include a record of: transmembrane pressure; permeate flow with time and total recirculation flows; sample volumes; the sequence and specifics of any time-series sampling; detailed de-

scription of all CFF system materials and reservoir volumes; results of any Q-water blanks or mass balances; total processing time and temperature; cleaning and preconditioning steps; and prefiltration details. Replication in the field should be encouraged when using a single membrane and especially when switching membranes during field sampling.

## 7. Summary and conclusions

CFF has been increasingly used to isolate marine colloids, and the results of these investigations suggest that marine colloids are an abundant and potentially important component in marine biogeochemical cycles. The challenge today is to move towards a more detailed understanding of the quantity and qualitative characteristics of colloids in an effort to better understand their behavior. As a first step in this direction, we set out to test whether CFF systems behaved in a well-defined and operationally reproducible manner using natural seawater. The results suggest that there are large differences in the quantity of colloidal material isolated by CFF systems, depending upon the specific membrane used, and to a lesser extent, on the operating protocols. At present, the consistency of results between samples within any single system is often good. However, even between nearly identical systems from the same manufacturer, the variability in the quantity of colloidal OC isolated can be as high as a factor of $\geq 3$. Even greater differences were found between different manufacturers' CFF systems. For example, data from the Amicon systems indicated relatively high colloidal OC abundances in the intermediate waters off Hawaii (15–67% COC), whereas data from any of the other CFF systems indicated essentially no colloidal OC in these same samples ($< 4\%$ COC).

No consensus was reached regarding a single system that could be recommended for all users, although some systems seemed to be plagued with generally higher OC blanks and low retention relative to the membrane's rated cut-off. Within a single group of systems, there were clearly operational practices that improved performance and minimized blanks and other obvious artifacts. There is some indication that the composition of the colloidal material also varied among CFF systems, so fractionation is considered likely, at least with respect to trace constituents with differing chemical properties. Time-series sampling demonstrated that variations in permeate concentration need to be considered.

CFF will continue to be used in marine studies as it remains the only practical method for processing large volume samples in order to extract colloidal material for chemical analyses or biological experimentation. The results of this intercomparison show that caution is in order. Work must continue to better characterize the properties of CFF systems before they are more broadly applied in oceanographic studies (Guo and Santschi, 1996-this issue; Gustafsson et al., 1996-this issue; Wen et al., 1996-this issue). This should include careful studies with standard compounds at ambient concentration in seawater media. Permeation models applicable to natural compound assemblages need to be developed and tested. Future studies are also required to determine the effect of manipulating operating parameters on the separation process. Much can be learned from previous experiments and studies outside of oceanography. However, given the low concentration of colloids and solutes and high salinity conditions of marine samples, independent confirmation of the applicability of these results to marine studies is needed. Comparison of time-series CFF results to other techniques (ultracentrifugation; field-flow fractionation) might lend more confidence in these methods. Scientists will need to ask themselves if CFF is an appropriate tool to answer the questions they pose in their research. Ultimately, intercomparison studies must give way to true intercalibration work. The experiment outlined here and the results represented in this issue are one step in this direction.

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## References

Amon, R.M.W. and Benner, R., 1994. Rapid cycling of high-molecular-weight dissolved organic matter in the ocean. Nature (London), 369: 549–552.

Baskaran, M., Santschi, P.H., Benoit, G. and Honeyman, B.D., 1992. Scavenging of thorium isotopes by colloids in seawater of the Gulf of Mexico. Geochim. Cosmochim. Acta, 56: 3375–3388.

Bauer, J.E., Williams, P.M. and Druffel, E.R.M., 1992. $^{14}C$ activity of dissolved organic carbon fractions in the central North Pacific and Sargasso Sea. Nature (London), 357: 667–670.

Bauer, J.E., Ruttenberg, K., Wolgast, D., Monaghan, E. and Schrope, M.K., 1996. Cross-flow filtration of dissolved and colloidal nitrogen and phosphorus in seawater: Results from an intercomparison study. In: K. Buesseler (Guest Editor), The Use of Cross-flow Filtration for the Isolation of Marine Colloids. Mar. Chem., 55: 33–52.

Benner, R., Pakulski, J.D., McCarthy, M., Hedges, J.I. and Hatcher, P.G., 1992. Bulk chemical characteristics of dissolved organic matter in the ocean. Science, 255: 1561–1564.

Benoit, G., Oktay-Marshall, S.D., Cantu, A., Hood, E.M., Coleman, C.H., Corapcioglu, M.O. and Santschi, P.H., 1994. Partitioning of Cu, Pb, Ag, Zn, Fe, Al and Mn between filter-retained particles, colloids, and solution in six Texas estuaries. Mar. Chem., 45: 307–336.

Bertine, K.K. and VernonClark, R., 1996. Elemental composition of colloidal phase in WHOI seawater sample. In: K. Buesseler (Guest Editor), The Use of Cross-flow Filtration for the Isolation of Marine Colloids. Mar. Chem., 55: 189–204.

Brownawell, B.J. and Farrington, J.W., 1986. Biogeochemistry of PCB's in interstitial waters of a coastal marine sediment. Geochim. Cosmochim. Acta, 50: 157–169.

Bruland, K.W., Donat, J.R. and Hutchins, D.A., 1991. Interactive influences of bioactive trace metals on biological production in oceanic waters. Limnol. Oceanogr., 36: 1555–1577.

Buffle, J., Perret, D. and Newman, M., 1992. The use of filtration and ultrafiltration for size fractionation of aquatic particles, colloids, and macromolecules. In: J. Buffle and H.P. van Leeuwen (Editors), Environmental Particles, Vol. 1. Lewis, Boca Raton, FL, pp. 171–230.

Carlson, C.A., Ducklow, H.W. and Michaels, A.F., 1994. Annual flux of dissolved organic carbon from the euphotic zone in the northwestern Sargasso Sea. Nature (London), 371: 405–408.

Carlson, D.J., Brann, M.L., Mague, T.H. and Mayer, L.M., 1985. Molecular weight distribution of dissolved organic materials in seawater determined by ultrafiltration: a re-examination. Mar. Chem., 16: 155–171.

Chin, Y.P. and Gschwend, P.M., 1992. Partitioning of polycyclic aromatic hydrocarbons to marine porewater colloids. Environ. Sci. Technol., 26: 1621–1626.

Dai, M., Martin, J.-M. and Cauwet, G., 1995. The significant role of colloids in the transport and transformation of organic carbon and associated trace metals (Cd, Cu and Ni) in the Rhône delta, France. Mar. Chem., 51: 159–175.

de Mora, S.J. and Harrison, R.M., 1983. The use of physical separation techniques in trace metal speciation studies. Water Res., 17: 723–733.

Druffel, E.R.M. and Williams, P.M., 1990. Identification of a deep marine source of particulate organic carbon using bomb $^{14}C$. Nature (London), 347: 172–174.

Druffel, E.R.M., Williams, P.M., Bauer, J.E. and Ertel, J.E., 1992. Cycling of dissolved and particulate organic matter in the open ocean. J. Geophys. Res., 97: 15,639–15,659.

Giddings, J.C., 1988. Field-flow fractionation. Chem. Eng. News, 66: 34–45.

Greenamoyer, J.M. and Moran, S.B., 1996. Evaluation of a spiral wound cross-flow filtration system for size-fractionation of Cu, Ni and Cd in seawater. In: K. Buesseler (Guest Editor), The Use of Cross-flow Filtration for the Isolation of Marine Colloids. Mar. Chem., 55: 153–163.

Guo, L. and Santschi, P.H., 1996. A critical evaluation of cross-flow ultrafiltration techniques for sampling colloidal organic carbon in seawater. In: K. Buesseler (Guest Editor), The Use of Cross-flow Filtration for the Isolation of Marine Colloids. Mar. Chem., 55: 113–127.

Guo, L., Coleman, Jr., C.H. and Santschi, P.H., 1994. The distribution of colloidal and dissolved organic carbon in the Gulf of Mexico. Mar. Chem., 45: 105–119.

Guo, L., Santschi, P.H., Cifuentes, L.A., Trumbore, S. and Southon, J., 1996. Cycling of high molecular weight dissolved organic matter in the middle Atlantic Bight. Limnol. Oceanogr., in press.

Gustafsson, O., Buesseler, K.O. and Gschwend, P.M., 1996. On the integrity of cross-flow filtration for collecting marine organic colloids. In: K. Buesseler (Guest Editor), The Use of Cross-flow Filtration for the Isolation of Marine Colloids. Mar. Chem., 55: 93–111.

Hedges, J.I., Bergamaschi, B.A. and Benner, R., 1993. Comparative analyses of DOC and DON in natural waters. Mar. Chem., 41: 121–134.

Johnson, B.D. and Kepkay, P.E., 1992. Colloid transport and bacterial utilization of oceanic DOC. Deep-Sea Res. I, 39(5): 855–869.

Kilduff, J. and Weber, W.J., 1992. Transport and separation of organic macromolecules in ultrafiltration processes. Environ. Sci. Technol., 26: 569–577.

Koike, I.S., Hara, S., Terauchi, K. and Kogue, K., 1990. Role of sub-micron particles in the ocean. Nature (London), 345: 242–244.

Küchler, I.L. and Miekeley, N., 1994. Ultrafiltration of humic compounds through low molecular mass cut-off level membranes. Sci. Total Environ., 154: 23–28.

Liang, Y., Murray, J.W. and Balistrieri, L.S., 1996. Behavior of colloidal $^{234}$Th in Puget Sound, WA. J. Mar. Res., submitted.

Logan, B.E. and Jiang, Q., 1990. Molecular size distributions of dissolved organic matter. J. Environ. Eng., 116(6): 1046–1062

Longhurst, A.R., Koike, I., Li, W.K.W., Rodriguez, J., Dickie, P., Kepkay, P., Partensky, F., Bautista, B., Ruiz, J., Wells, M. and Bird, D.F., 1992. Sub-micron particles in Northwest Atlantic Shelf water. Deep-Sea Res. I, 39(1): 1–7.

Mopper, K., Feng, Z., Bentjen, S.B. and Chen, R.F., 1996. Effects of cross-flow filtration on the absorbance and fluorescence properties of seawater. In: K. Buesseler (Guest Editor), The Use of Cross-flow Filtration for the Isolation of Marine Colloids. Mar. Chem., 55: 53–74.

Moran, S.B., 1991. The application of cross-flow filtration to the collection of colloids and their associated metals in seawater. In: Marine Particles: Analysis and Characterization. Geophys. Monogr., 63: 275–280.

Moran, S.B. and Buesseler, K.O., 1992. Short residence time of colloids in the upper ocean estimated from $^{238}$U–$^{234}$Th disequilibria. Nature (London), 359: 221–223.

Moran, S.B. and Buesseler, K.O., 1993. Size-fractionated $^{234}$Th in continental shelf waters off New England: Implications for the role of colloids in oceanic trace metal scavenging. J. Mar. Res., 51: 893–922.

Moran, S.B. and Moore, R.M., 1989. The distribution of colloidal aluminum and organic carbon in coastal and open ocean waters off Nova Scotia. Geochim. Cosmochim. Acta, 53: 2519–2527.

Moran, S.B., Yeats, P.A. and Balls, P.W., 1996. On the role of colloids in trace metal solid–solution partitioning in continental shelf waters: A comparison of model results and field data. Cont. Shelf Res., 16: 397–408.

Niven, S.E.H., Kepkay, P.E. and Boraie, A., 1995. Colloidal organic carbon and colloidal $^{234}$Th dynamics during a coastal phytoplankton bloom. Deep-Sea Res. II, 42(1): 257–273.

Peltzer, E.T. and Hayward, N.A., 1996. Spatial and temporal variability of total organic carbon along 140°W in the equatorial Pacific Ocean in 1992. Deep-Sea Res. II, EQPAC Vol. II, in press.

Qian, J. and Mopper, K., 1996. An automated, high performance, high temperature combustion dissolved organic carbon analyzer. 1996 Ocean Sci. Meet., Abstr., Eos (Trans. Am. Geophys. Union), 76(3), Jan. 1996, Suppl.

Reitmeyer, R., Powell, R.T., Landing, W.M. and Measures, C.I., 1996. Colloidal Al and Fe in seawater: An intercomparison between various cross flow ultrafiltration systems. In: K. Buesseler (Guest Editor), The Use of Cross-flow Filtration for the Isolation of Marine Colloids. Mar. Chem., 55: 75–91.

Rue, E.L. and Bruland, K.W., 1995. Complexation of iron(III) by natural organic ligands in the central North Pacific as determined by a new competitive ligand equilibration/adsorptive cathodic stripping voltammetric method. Mar. Chem., 50(1): 117–138.

Sansone, F.J., Smith, S.V., Price, J.M., Walsh, T.W., Daniel, T.H. and Andrews, C.C., 1988. Long-term variation in seawater composition at the base of the thermocline. Nature (London), 332(6166): 714–717.

Santschi, P.H., Guo, L., Baskaran, M., Trumbore, S., Southon, J., Bianchi, T.S., Honeyman, B. and Cifuentes, L., 1995. Isotopic evidence for the contemporary origin of high-molecular weight organic matter in oceanic environments. Geochim. Cosmochim. Acta, 59(3): 625–631.

Sharp, J.H., 1993. The dissolved organic carbon controversy: An update. Oceanography, 6(2): 45–50.

Staub, C., Buffle, J. and Haerdi, W., 1984. Measurement of complexation properties of metal ions in natural conditions by ultrafiltration: Influence of various factors on the retention of metals and ligands by neutral and negatively charged membranes. Anal. Chem., 56: 2843–2849.

Stordal, M.C., Gill, G.A., Wen, L.-S. and Santschi, P.H., 1996. Mercury phase speciation in the surface waters of three Texas estuaries: Importance of colloidal forms. Limnol. Oceanogr., in press.

van den Berg, C.M.G., 1995. Evidence for organic complexation of iron in seawater. Mar. Chem., 50(1): 139–158.

Wells, M.L. and Goldberg, E.D., 1991. Occurrence of small colloids in seawater. Nature (London), 353: 342–344.

Wells, M.L. and Goldberg, E.D., 1994. The distribution of colloids in the North Atlantic and southern oceans. Limnol. Oceanogr., 39: 286–302.

Wen, L.-S., Stordal, M.C., Gill, G.A. and Santschi, P.H., 1996. An ultraclean cross-flow filtration technique for the study of trace metal processes in the coastal environment. In: K. Buesseler (Guest Editor), The Use of Cross-flow Filtration for the Isolation of Marine Colloids. Mar. Chem., 55: 129–152.

Whitehouse, B.G., Petrick, G. and Ehrhardt, M., 1986. Crossflow filtration of colloids from Baltic Sea water. Water Res., 20(12): 1599–1601.

Whitehouse, B.G., Yeats, P.A. and Strain, P.M., 1990. Cross-flow filtration of colloids from aquatic environments. Limnol. Oceanogr., 35(6): 1368–1375.

Williams, P.M. and Druffel, E.R.M., 1987. Radiocarbon in dissolved organic matter in the central North Pacific Ocean. Nature (London), 330: 246–248.

Williams, P.M., Bauer, J.E., Robertson, K.J., Wolgast, D.J. and Ocelli, M.L., 1993. Report on DOC and DON measurements made at Scripps Institution of Oceanography, 1988–1991. Mar. Chem., 41: 271–281.