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Cross-flow filtration of dissolved and colloidal nitrogen and phosphorus in seawater: results from an intercomparison study

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Abstract

A cross-flow filtration (CFF) intercomparison study was conducted to evaluate the effectiveness of a variety of CFF systems in fractionating and recovering ≥ 1 -kD (kilodalton) molecular weight seawater organic matter. Inorganic nutrients and total and organic nitrogen and phosphorus results are presented for CFF-processed, 0.2- μ m-filtered seawater representative of both shallow coastal (Woods Hole) and deep open-ocean (Hawaii) environments. Concentrations of $\text{NO}_3^- + \text{NO}_2^-$, NH_4^+ , PO_4^{3-} and $\text{Si}(\text{OH})_4$ all showed evidence of contamination or scavenging within individual CFF systems at one time or another. When adequate precautions were taken, however, nutrients displayed predicted conservative behavior in all systems.

Organic N was generally observed to be less of a potential contaminant in CFF systems than was organic C. Contamination by inorganic and organic P was relatively common. Due to the low natural abundances of P in these and other natural seawater samples, even slight P contamination may confound interpretation of colloidal P recoveries. Those CFF systems that recovered significant quantities of colloidal (≥ 1 -kD molecular weight) organic N generally recovered significant quantities of colloidal organic C as well. Recoveries of colloidal organic N ranged from 0 to $\sim 50\%$ of total seawater organic N. High variability in colloidal organic N recovery ($\sim \pm 20\%$) was characteristic of identical or nearly identical CFF systems. High variability was also observed in the recovery of colloidal organic P (range = 20–80% of total seawater organic P) from coastal Woods Hole seawater. Using open-ocean Hawaii seawater, in which no total seawater organic P was detected, CFF systems that recovered significant quantities of colloidal organic C and N showed recovery of an apparent colloidal organic P fraction. This finding suggests that scavenging of P into the colloidal fraction may occur during CFF processing.

C/N elemental ratios of CFF-processed organic fractions showed several differences between Woods Hole and Hawaii seawater. In general, C/N values for coastal Woods Hole seawater organic matter were relatively similar in the various fractions compared to the unfractionated, starting seawater. In contrast, the high-molecular-weight (≥ 1 kD) fraction of open-ocean Hawaii seawater had highly elevated C/N values relative to both unfractionated seawater and low-molecular-weight (≤ 1 kD) organic matter. It was not possible to adequately assess C/P ratios at this time due to potential artifact-associated ambiguities in organic P data.

These results emphasize the need for greater controls and calibration both among and within different makes of CFF systems. Excessive variability in both quantitative recoveries and qualitative characterization of organic matter isolated by

similar or identical systems suggests that the performance of CFF systems may be sensitive to subtle differences in clean-up protocols or operating parameters, or to differences in manufacturing quality control.

Keywords: colloids; organic matter; nitrogen; phosphorus; cross-flow filtration

1. Introduction

Cross-flow filtration (CFF) has recently become increasingly popular among marine and aquatic geochemists as a tool for understanding the cycling of both inorganic and organic elements and materials. The advent of CFF has allowed for the concentration of dissolved organic matter (DOM) and subsequent analysis of a variety of associated parameters that were previously not measurable due to the extremely dilute quantities in which DOM occurs in many marine and other aquatic environments. To date, CFF has been used most extensively for studies of carbon, radionuclide, and trace-metal cycling (Benner et al., 1992; Moran and Buesseler, 1992; Santschi et al., 1995; Powell et al., 1996-this issue), but it has not been similarly employed in studies of nutrient element cycling.

Previous analyses of the carbon content of organic material retained by various CFF systems suggest that anywhere from 5% to ~35% of the dissolved organic carbon (DOC) in seawater may be comprised of so-called “high-molecular-weight” (HMW) colloidal organic carbon (Whitehouse et al., 1986; Whitehouse et al., 1990; Benner et al., 1992; Guo et al., 1994). In those few cases where highly concentrated colloidal organic matter has been analyzed (usually in a lyophilized, solid state) for organic nitrogen content (Sigleo et al., 1983; Benner et al., 1992), low nitrogen relative to carbon contents [molar C/N of (20–25):1] have generally been observed. The high C/N ratios of this HMW or colloidal organic matter have been taken as an indication that it is enriched in carbohydrates or carbohydrate-like material (Benner et al., 1992; Pakulski and Benner, 1992).

One of the disadvantages of studies in which only the final lyophilized concentrate is examined is that a mass balance of the nitrogen in all fractions [total, “colloidal”, and low-molecular-weight (LMW)] is not routinely performed, because the low nitrogen contents of the starting DOM and LMW fractions are often difficult to measure due to methodological

constraints. However, the implication of elevated C/N ratios of the HMW fraction relative to an “assumed” Redfield stoichiometry for bulk organic matter (i.e. DOM of ~7–10) is that there must, by mass balance, exist a LMW fraction that is highly enriched in nitrogen. In those few studies where C/N ratios of unfractionated, bulk DOM have been determined, values in the deep ocean (~ ≥ 100 m) range from ~8 to ~25, with most values clustering between ~10 and ~17 (Hansell, 1993; Hansell et al., 1993). Surface water C/N values of DOM are generally higher and more variable than those in deep waters (Hansell, 1993; Hansell et al., 1993). In the only previous known study where carbon and nitrogen contents of all three fractions (total, “colloidal”, and LMW) of ultrafiltered DOM have been measured directly (Bauer et al., 1994), the presence of a nitrogen-depleted (C/N ≈ 20–22) colloidal organic fraction and a highly nitrogen-enriched (C/N ≈ 2–5) LMW organic fraction have been observed in several open-ocean samples. The molecular composition of this LMW, low-C/N material (both deduced and measured) is unknown, but must be dominated by molecules similar in C/N to urea and small amino acids. To date, no such data are available on the distribution of phosphorus in seawater organic fractions. Independent measurement of elemental compositions of all fractions in CFF studies can also bring to light the existence of potential problems and artifacts in the processing of different fractions by ultrafiltration.

As part of an intercomparison study of the isolation of colloids by CFF conducted at Woods Hole Oceanographic Institution and the National Energy Laboratory of Hawaii in August 1994 and January 1995, respectively, we measured carbon, nitrogen and phosphorus contents of: (1) total starting DOM prior to processing by CFF; (2) HMW or “colloidal” organic matter retained by CFF; and (3) LMW organic matter that comprises the permeate or filtrate. The concomitant measurement of C, N and P serves to complement and refine CFF studies that would otherwise use C analyses as the main analytical

parameter (cf. Buesseler et al., 1996-this issue). In addition, an examination of elemental ratios allows potential differences in the elemental and molecular composition of the component fractions separated by different CFF technologies to be further elucidated.

2. Materials and methods

A summary of the CFF systems and sampling techniques used in this study, as well as background and theoretical considerations of CFF, are presented in Buesseler et al. (1996-this issue). All samples (original seawater, permeates and retentates) that were collected and analyzed for organic carbon by high-temperature catalytic oxidation (HTC-OC; see methods description in Buesseler et al., 1996-this issue) were also analyzed simultaneously for total nitrogen (HTC-TN) at Woods Hole (using Vineyard Sound coastal seawater samples SW1 and SW2) and Hawaii (using 600-m-deep oligotrophic seawater samples SW3 and SW4) shortly after sample collection. The 0.2- μm -filtered (using MEMTRES-PC polycarbonate filters in Woods Hole, and MEMTRES-PS polysulfone filters in Hawaii) source seawater was monitored at regular intervals for nutrients and total and organic N and P, as well as for DOC, for a period of ~ 3 h in Woods Hole and ~ 4 h in Hawaii (i.e. the period during which samples were distributed to the various CFF systems). In addition to seawater samples, Milli-Q water was processed by all CFF systems, and the same fractions (i.e. permeates and retentates) were analyzed as a check on the potential introduction of blank HTC-TN, nitrate, nitrite and ammonium and of inorganic and organic phosphorus (see below) to the processed waters. Inorganic N and P as well as $\text{Si}(\text{OH})_4$ were all determined by autoanalyzer. Inorganic P was also independently measured by spectrophotometric techniques in studies of total and organic P (see below).

For HTC-TN, 50- or 100- μl aliquots of 0.2- μm -filtered starting water, permeate and retentate water produced from CFF processing of either seawater samples or Milli-Q water were injected into a high-temperature catalytic oxidation unit at 680°C. The HTC-TN is oxidized to nitric oxide (NO) which is subsequently measured by an Antek (Houston, Texas) chemiluminescence detector (Hansell, 1993; Hansell et al., 1993; Williams et al., 1993). The system was

calibrated using known liquid organic and inorganic nitrogen standards as well as NO gas standards to check recovery and to correct for any incomplete combustion losses. Peak output was monitored and integrated using a MacIntosh computer equipped with MacIntegrator peak integration software (Rainin, Inc., Emeryville, California). The sum of NO_3^- , NO_2^- and NH_4^+ was subtracted from HTC-TN values to obtain high-temperature catalytically oxidizable organic nitrogen (HTC-ON). As emphasized by Hansell et al. (1993), since ON estimates are based on the difference between several independently measured parameters (TN and each of the inorganic N species), the uncertainty in ON estimates is subject to the uncertainty in each of the separate measurements. A small under- or over-estimate (e.g., $\sim 10\%$) in TN or nutrient N could potentially result in a very large (up to 80%; Hansell et al., 1993) over- or under-estimate in ON depending on the absolute magnitudes of the concentrations. Triplicate injections of each sample were typically made. The standard deviation for replicate HTC-TN injections averaged less than $\pm 1 \mu\text{M N}$, and the detection limit for the method was $\sim 0.5 \mu\text{M N}$.

Samples for total, inorganic, and organic phosphorus (TP, IP, and OP, respectively) analyses were frozen at -20°C immediately after collection and stored frozen in acid-cleaned polypropylene bottles until immediately before analysis. As a test of sample deterioration during storage, IP was analyzed in selected samples both at Woods Hole and at Hawaii immediately following CFF processing, and again at the time of sample thawing prior to TP analysis (~ 12 and ~ 6 months elapsed time for Woods Hole and Hawaii, respectively). Phosphate concentrations in the Hawaii samples, analyzed by autoanalyzer in Hawaii and spectrophotometrically at WHOI, agreed to within $\pm 4\%$, indicating minimal sample deterioration over the 6-month storage period and good agreement between the two laboratories. Phosphate concentrations in the Woods Hole samples, analyzed by autoanalyzer at the University of Rhode Island analytical facility and spectrophotometrically at WHOI, were significantly lower upon re-analysis at WHOI. It is unlikely that this apparent discrepancy for the two independent analyses of SW1 and SW2 is due to rapid sample deterioration during the second 6 months' storage given the small discrepancy ob-

served for the Hawaii samples after being frozen for 6 months. Sample deterioration alone is also unlikely to explain the different discrepancies observed for SW1 (21%) and SW2 (42%). It is more probable that differences in analytical calibration and sample handling contributed to the observed offsets. In any case, the reproducibility and analytical precision within the existing data sets still renders the relevant comparisons valid.

Selected samples were analyzed for TP (the sum of organic plus inorganic P) using the ashing method of Solorzano and Sharp (1980). Briefly, after samples had thawed and reached room temperature, 10-ml aliquots were transferred to glass vials and spiked with 200 μl of MgSO_4 (0.17 M) and taken to dryness in a 95°C oven. After drying, samples were muffled at 500°C for 2 h, taken up in dilute HCl, and hydrolyzed at 80°C for 30 min [see Solorzano and Sharp (1980) for details]. After cooling to room temperature, phosphate concentrations were determined spectrophotometrically using the molybdate blue method of Koroleff (1976). The mean procedural blank for TP analyses was 0.08 μM P for seawater samples ($n = 11$), and 0.08 μM P for Milli-Q water samples ($n = 5$). TP was determined in duplicate for all samples with a mean relative error of 1.9%. The detection limit for this method was found to be $\sim 0.11 \mu\text{M}$ P.

We performed concurrent IP concentration measurements on all samples for which TP determinations were made. Separate 10-ml aliquots of each sample were transferred to reaction vessels, at the same time that aliquots were transferred to vials for TP determination. The IP aliquots were reacted immediately, according to the molybdate blue method of Koroleff (1976), and analyzed for IP. The mean relative error of duplicate IP analyses of seawater samples was 1.5%. Organic P was calculated as the difference between TP and IP. Since OP estimates are derived from the difference between two independently measured parameters (TP and IP), the uncertainty in OP estimates, as with ON estimates, is subject to the uncertainty in both TP and IP measurements, and may be large. We note that the method

we have employed includes polyphosphates, linear polymers of orthophosphate ions which may or may not be organically bound, in the TP pool (Solorzano and Strickland, 1958). Thus any inorganic polyphosphate will be included in the OP reservoir.

3. Results and discussion

3.1. Cross-flow filtration of seawater inorganic nutrients

As in Buesseler et al. (1996-this issue), CFF systems are grouped according to manufacturer (A = Amicon, F = Filtron, O = Osmonics, X = Membrex, and Z = Desalination Systems), and 1-kD (kilodalton) filtration cut-offs were used in all systems. All filtration membranes were made of polysulfone with the exception of system Z1 which used a polyethylene membrane. For details and operating parameters of each of the CFF systems, refer to table 1 in Buesseler et al. (1996-this issue).

Inorganic nutrient solutes should behave in a conservative manner over the course of CFF sample processing since these solutes are much smaller than the 1-kD filtration cut-off. Exceptions to conservative behavior could arise as a result of several factors, including: (1) contamination of the sample by different components of the various CFF systems, (2) the presence of contamination levels of certain species contained in CFF cleaning reagents (see Buesseler et al., 1996-this issue) that have not been adequately flushed from the system prior to sample processing, (3) adsorptive or other removal of charged species by certain components of the CFF systems, or (4) in the case of inorganic P, sorption by organic or inorganic (e.g., Fe- or Mn-oxyhydroxides) colloids during sample processing.

Results of autoanalyzer $\text{NO}_3^- + \text{NO}_2^-$, NH_4^+ , PO_4^{3-} and Si(OH)_4 nutrient concentrations in starting seawater and in CFF processed permeates and retentates are shown in Tables 1 and 2. Permeate samples were collected at a concentration factor (CF) of two (CF = 2) and again when the sample had been concentrated to its final volume (CF = final). The final CFs

Notes to Table 1:

n.a. = not applicable; n.d. = not determined. All values in μM .

Table 1
Inorganic nutrients determined by autoanalyzer in Woods Hole SW1 and SW2 samples for initial and CFF-processed seawater

CFF ID	Type	SW1					SW2				
		CF	NO ₃ ⁻ + NO ₂ ⁻	NH ₄ ⁺	PO ₄ ³⁻	Si(OH) ₄	CF	NO ₃ ⁻ + NO ₂ ⁻	NH ₄ ⁺	PO ₄ ³⁻	Si(OH) ₄
Init. (t = 0)	< 0.2 μm	n.a.	3.09	1.27	1.01	4.04	n.a.	2.93	1.23	1.28	4.06
Init. (t = 1 h)	< 0.2 μm	n.a.	3.15	1.30	1.01	4.05	n.a.	2.96	1.11	1.28	4.06
Init. (t = 2 h)	< 0.2 μm	n.a.	3.20	1.54	1.01	4.05	n.a.	2.83	1.04	1.30	4.10
Init. (t = 4 h)	< 0.2 μm	n.a.	n.d.	n.d.	n.d.	n.d.	n.a.	2.71	1.08	1.27	4.07
A1	permeate	2	2.55	0.50	0.94	3.40	2	n.d.	n.d.	n.d.	n.d.
A1	permeate	13.0	2.95	0.56	1.71	3.95	13.0	2.95	0.67	2.01	4.09
A1	retentate	13.0	3.21	0.62	3.63	4.52	13.0	2.95	0.66	2.61	4.15
A2	permeate	2	3.15	1.43	0.99	4.12	2	2.85	1.15	1.19	3.95
A2	permeate	15.7	3.25	4.74	1.16	4.21	5.5	2.98	2.70	1.29	4.10
A2	retentate	15.7	3.27	1.61	1.18	4.41	5.5	2.99	1.06	1.25	4.13
A3	permeate	2	3.17	0.48	0.96	4.12	2	2.95	5.49	1.20	3.93
A3	permeate	16.0	3.44	0.72	1.10	4.22	18.0	3.14	7.64	1.25	4.02
A3	retentate	16.0	3.43	0.70	1.16	4.40	18.0	3.31	9.38	1.21	4.06
A4	permeate	2	3.15	0.44	0.96	4.18	2	2.88	0.63	1.05	3.92
A4	permeate	15.7	2.37	0.78	0.81	3.05	16	2.97	0.94	1.46	4.13
A4	retentate	15.7	2.30	0.57	0.88	3.09	16	3.03	1.04	1.35	4.30
A5	permeate	2	2.20	0.50	0.68	2.89	2	2.67	0.59	1.08	3.87
A5	permeate	150	3.09	1.49	1.21	4.42	165	n.d.	n.d.	n.d.	n.d.
A5	retentate	150	3.19	1.41	1.81	5.04	165	n.d.	n.d.	n.d.	n.d.
F1	permeate	2	3.19	1.07	0.99	4.24	2	2.94	0.97	1.14	3.93
F1	permeate	11.1	3.51	1.34	1.04	5.20	13.6	3.00	0.81	1.30	4.08
F1	retentate	11.1	3.28	1.46	1.05	2.39	13.6	2.37	0.48	0.92	3.40
F2	permeate	2	3.19	1.27	0.98	9.13	2	2.85	1.00	1.20	13.11
F2	permeate	11.0	3.23	1.29	1.01	18.81	20.0	2.92	0.55	1.22	50.05
F2	retentate	11.0	3.12	1.16	1.01	18.23	20.0	2.86	0.54	1.10	50.50
F4	permeate	2	3.17	1.30	0.98	4.97	2	2.87	0.88	1.13	4.58
F4	permeate	20.0	3.14	1.25	0.96	5.60	12.0	2.70	0.55	1.33	6.32
F4	retentate	20.0	3.09	1.16	1.03	5.72	12.0	2.88	0.49	1.08	6.58
O1	permeate	2	3.23	1.25	0.97	4.22	2	2.78	0.76	1.10	4.01
O1	permeate	15.3	3.10	1.67	1.02	4.14	17.0	2.54	0.86	1.31	4.07
O1	retentate	15.3	3.14	1.28	0.99	4.08	17.0	2.46	0.76	1.12	4.09
O2	permeate	2	3.21	1.09	1.01	4.69	2	2.99	1.17	1.21	4.13
O2	permeate	3.5	3.15	1.01	0.98	4.44	4.3	2.97	1.01	1.26	4.19
O2	retentate	3.5	3.08	1.24	1.01	4.46	4.3	2.90	1.04	1.24	4.30
O3	permeate	2	3.21	1.44	1.02	6.54	2	2.80	0.75	1.21	5.07
O3	permeate	3.8	3.20	1.27	1.01	6.11	3.9	2.88	0.80	1.29	4.79
O3	retentate	3.8	3.14	2.12	1.02	5.58	3.9	2.86	0.76	1.26	4.83
X1	permeate	2	3.14	1.19	0.98	4.10	2	2.88	0.86	1.22	3.94
X1	permeate	49.7	3.22	1.27	0.99	4.14	12.9	3.00	0.78	1.29	4.02
X1	retentate	49.7	3.56	1.44	0.99	4.44	12.9	2.95	0.56	1.27	3.92
Z1	permeate	1.2	6.38	1.16	0.86	3.97	2	3.62	0.49	1.18	4.03
Z1	permeate	26.0	11.97	0.56	1.32	6.41	25.0	6.29	0.68	1.54	5.05
Z1	retentate	26.0	8.18	0.88	1.63	6.83	25.0	4.21	2.06	1.84	6.38

Table 2
Inorganic nutrients determined by autoanalyzer in Hawaii SW3 sample for initial and CFF-processed seawater

CFF ID	Type	CF	SW3			
			NO ₃ ⁻ + NO ₂ ⁻	NH ₄ ⁺	PO ₄ ³⁻	Si(OH) ₄
Init. (t = 0)	< 0.2 μm	n.a.	41.44	0.13	3.11	86.16
Init. (t = 1 h)	< 0.2 μm	n.a.	41.30	0.13	3.10	85.86
Init. (t = 1 h)	< 0.2 μm	n.a.	41.33	0.11	3.10	85.82
Init. (t = 2 h)	< 0.2 μm	n.a.	41.51	0.13	3.12	86.58
Init. (t = 2 h)	< 0.2 μm	n.a.	41.47	0.13	3.11	86.54
Init. (t = 4 h)	< 0.2 μm	n.a.	41.72	0.16	3.12	87.69
A1	permeate	2	41.79	0.03	2.81	84.58
A1	permeate	20.0	41.55	0.16	3.80	87.37
A1	retentate	20.0	41.82	0.16	5.34	90.09
A2	permeate	2	41.21	0.05	3.15	86.13
A2	permeate	5.2	41.74	0.28	3.56	87.9
A2	permeate	5.2	41.68	0.28	3.84	89.12
A3	permeate	2	41.10	0.28	2.96	84.3
A3	permeate	8.3	41.41	0.31	3.25	85.68
A3	retentate	8.3	41.80	0.34	3.77	87.58
A4	permeate	2	41.33	0.50	3.11	86.71
A4	permeate	20.2	42.13	0.54	3.48	88.45
A4	retentate	20.2	42.18	0.46	3.86	89.39
A5	permeate	2	41.39	0.13	2.91	87.2
A5	permeate	204	42.03	0.28	3.37	88.59
A5	retentate	204	41.88	0.23	4.15	90.48
F1	permeate	2	41.11	0.13	3.12	84.75
F1	permeate	9.2	41.22	0.16	3.21	85.3
F1	retentate	9.2	41.37	0.19	3.38	85.47
F2	permeate	2	40.92	0.23	3.10	85.95
F2	permeate	16.0	41.45	0.28	3.14	87.23
F2	retentate	16.0	41.49	0.16	3.08	86.18
F3	permeate	2	41.06	0.16	3.01	83.41
F3	permeate	12.8	41.32	0.16	3.24	84.96
F3	retentate	12.8	41.32	0.16	3.28	66.34
F4	permeate	2	n.d.	n.d.	n.d.	n.d.
F4	permeate	4.0	41.22	0.16	3.14	85.64
F4	retentate	4.0	41.47	0.16	3.29	86.13
O1	permeate	2	41.25	0.13	3.15	85.47
O1	permeate	16.0	41.47	0.13	3.14	87.79
O1	retentate	16.0	41.70	0.19	3.22	87.93
O2	permeate	2	41.12	0.08	3.15	85.09
O2	permeate	6.8	41.53	0.16	3.13	85.51
O2	retentate	6.8	41.58	0.13	3.10	87.29
O3	permeate	2	41.06	0.13	3.07	84.3
O3	permeate	6.3	41.21	0.13	3.18	85.19
O3	retentate	6.3	41.10	0.16	3.09	85.66

Table 2 (continued)

CFF ID	Type	CF	SW3			
			NO ₃ ⁻ + NO ₂ ⁻	NH ₄ ⁺	PO ₄ ³⁻	Si(OH) ₄
X1	permeate	2	41.06	0.03	3.14	84.85
X1	permeate	20.1	41.28	0.19	3.11	84.78
X1	retentate	20.1	41.22	0.16	3.16	85.11

n.a. = not applicable; n.d. = not determined. All values in μM.

for the individual CFF systems tested ranged from ~ 4 to ~ 200. Retentate samples were collected at CF = final only.

Average concentrations of the various nutrient species for the starting 0.2-μm-filtered seawater samples from Woods Hole coastal seawater (SW1 and SW2) and Hawaii deep (600 m), oligotrophic seawater (SW3) are given in Tables 1 and 2. For Woods Hole SW1, both NO₃⁻ + NO₂⁻ and NH₄⁺, underwent slight increases over ~ 2-h time while the reverse trend was noted for SW2 over ~ 4 h. PO₄³⁻ and Si(OH)₄ showed no changes for the time periods over which SW1 and SW2 were collected. Small but significant changes were noted between SW1 and SW2 for NO₃⁻ + NO₂⁻, NH₄⁺, and PO₄³⁻ but not for Si(OH)₄.

Inorganic nutrient concentrations in both permeates and retentates of SW1 and SW2 (Woods Hole) during CFF processing can be seen on the whole to have displayed minimal differences from starting seawater values in the majority of CFF systems (Table 1). Dramatic exceptions to this general rule can be seen, however, especially in individual nutrient-CFF system combinations where there is evidence of both contamination (most noticeably for NO₃⁻ + NO₂⁻ and Si(OH)₄) and of scavenging [most commonly for NH₄⁺, but also to some extent for PO₄³⁻ and Si(OH)₄]. It is interesting to note that while contamination or scavenging of a specific nutrient may have been found in permeates and/or retentates for a given system at certain times, this was not inevitably true in all instances. Cases of gross contamination were usually manifested in all fractions collected [e.g., system Z1 for NO₃⁻ + NO₂⁻ and system F2 for Si(OH)₄] and often carried over between SW1 and SW2. The more subtle cases of minor contamination often corrected themselves between SW1 and SW2, presumably a result of the

effects of continued flushing of the CFF system. Much more enigmatic and deserving of further study are those cases in which one or more of the nutrient solutes were scavenged (e.g., NH_4^+ in systems A1, A3, A4 and Z1). All of these non-conservative patterns can present a considerable challenge for conducting elemental mass balances.

Autoanalyzer nutrient determinations for the Hawaii seawater samples were performed only for SW3 (Table 2). All of the starting 0.2- μm -filtered seawater samples had significantly elevated concentrations of $\text{NO}_3^- + \text{NO}_2^-$, PO_4^{3-} and $\text{Si}(\text{OH})_4$ and lower values of NH_4^+ relative to Woods Hole SW1 and SW2, and the values for individual nutrients did not change in any predictable or significant manner over the time course of collection. For the CFF-processed samples (Table 2), it is of greatest interest to note that the nutrient concentrations of both permeates (CF = 2 and CF = final) and the final retentate did not generally differ significantly from the starting 0.2- μm -filtered seawater. Exceptions to this were noted for several of the Amicon systems (A1–A5) in which both NH_4^+ and PO_4^{3-} were scavenged in CF = 2 permeates but were in excess in CF = final permeates and retentates. These opposing patterns of apparent nutrient scavenging and contamination in the course of the same processing run are not fully understood at present. The reasons for the generally conservative behavior of nutrients in the other CFF systems during processing of Hawaii seawater, and the more problematic behavior of inorganic nutrients in seawater from Woods Hole, are also not readily apparent. However, this may be related to the more extensive cleaning (and intervening use) of the CFF systems prior to their use in Hawaii. At a minimum, these nutrient data emphasize that care must be taken to avoid artifacts even with presumably conservative solutes, by performing frequent checks of concentrations of the species of interest both prior to and during sample processing by CFF.

3.2. Cross-flow filtration of seawater organic nitrogen

3.2.1. Woods Hole results

The HTC-TN and organic N (HTC-ON) contents of the permeates and retentates of CFF-processed samples, as well as of 0.2- μm -filtered starting seawater, are given in Table 3 and Fig. 1a and b for

Woods Hole SW1 and SW2. Results for the 0.2- μm -filtered starting seawater at Woods Hole indicate that ON had a range of $\sim 5\text{--}9 \mu\text{M N}$ (mean = $6.4 \pm 2.0 \mu\text{M N}$) for SW1 and a range of $\sim 7\text{--}8 \mu\text{M N}$ (mean = $7.3 \pm 0.7 \mu\text{M N}$) for SW2 (Fig. 1a and b). Variability in the ON content of the source water may be due to sampling or storage artifacts of SW1 and SW2 [see Buesseler et al. (1996-this issue) for details of the sampling set-up] or to tidal influences on the source water at the intake (a shallow subtidal pipe).

A general feature of the ON results for Woods Hole SW1 and SW2 during CFF processing (Fig. 1a and b) was that the range in ON values for all permeates and retentates relative to the starting seawater ON was considerably less (factor of 2–8) than the range observed in OC values (factor of 50–1000; Buesseler et al., 1996-this issue). This indicates that in addition to colloidal (i.e. $\geq 1 \text{ kD}$) organic matter becoming concentrated, contamination, when it occurred, was due to carbon-rich, nitrogen-poor material. Most of the manufacturers' systems showed at least periodic contamination artifacts (i.e. permeate and/or "sum" values were above the range of starting seawater values), most often in final permeate ON (Fig. 1a and b). Evidence of elevated permeate ON was observed for several systems with relatively low CFs ($\sim 4\text{--}20$): A2, F1, and O1 for SW1 (Fig. 1a), and for systems F2 and O3 for SW2 (Fig. 1b). Systems with moderate to high CFs showed permeate ON contamination artifacts similar to low-CF systems: A5 (CF = 150–165) for SW1 and SW2 and Z1 for SW2 (CF = 25) (Table 3; Fig. 1a and b). Contamination of system permeate streams was not accompanied by contamination of system colloidal ON values.

Similar to the OC results (Buesseler et al., 1996-this issue), we observed an increase in permeate ON between CF = 2 and CF = final in nearly all CFF systems for both Woods Hole SW1 and SW2 (Fig. 1a and b). For those systems employing the highest CFs (A5, X1 and Z1), the difference in permeate ON between CF = 2 and CF = final was often, but not always, greatest. Permeate ON thus exhibited a general trend similar to OC, and likewise may show elevated concentrations that increase as a function of both time and CF due to contamination and/or retentate "breakthrough" at increasing CF (i.e. at

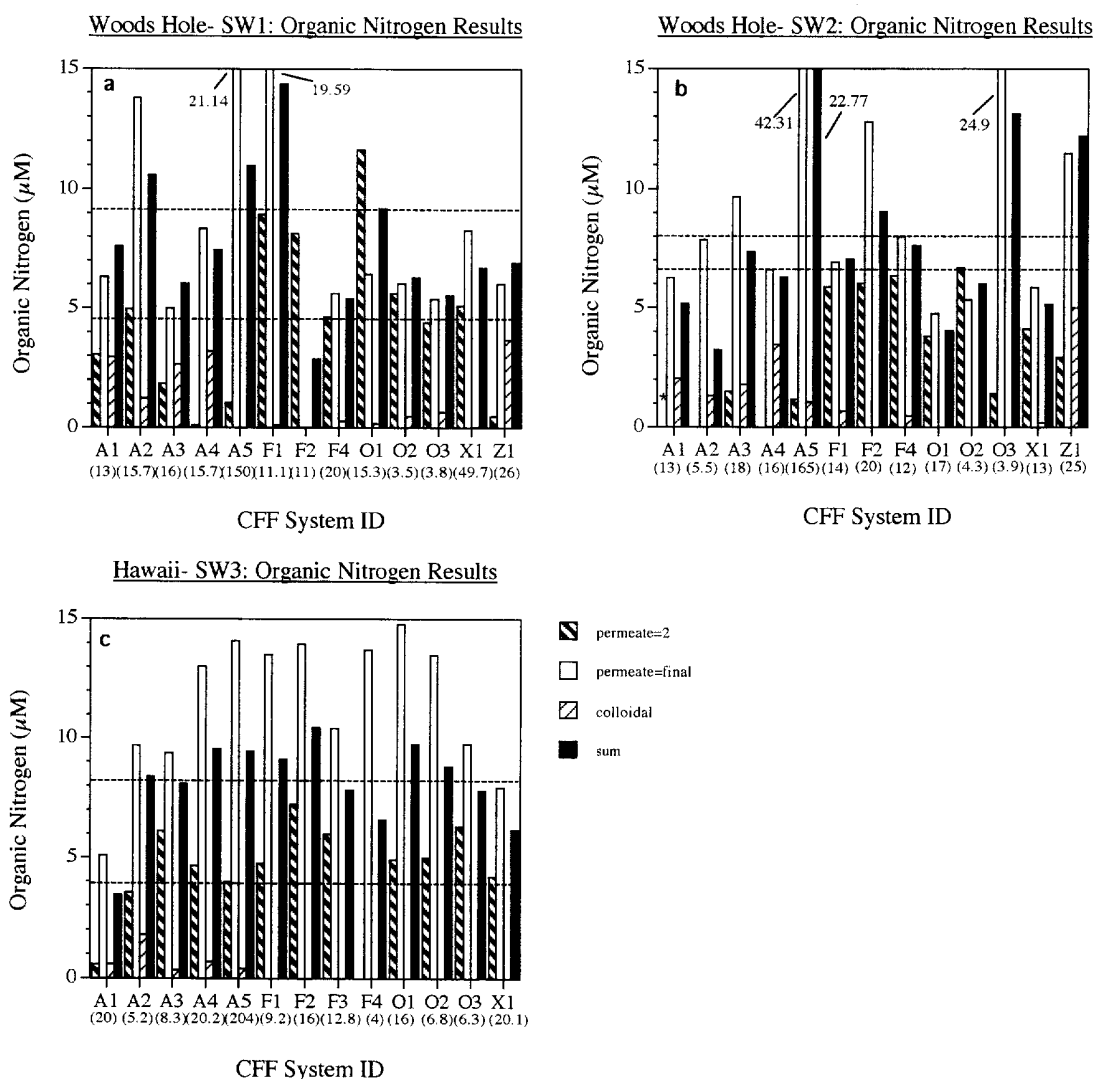


Fig. 1. Intercomparison of seawater organic nitrogen (HT-ON) results for different CFF systems grouped by CFF-ID and manufacturer [see table 1 in Buesseler et al. (1996-this issue), for details]: (a) Woods Hole sample SW1; (b) Woods Hole sample SW2; and (c) Hawaii sample SW3. CFF-ID's are presented on the x -axis and final concentration factors are listed in parentheses below CFF-ID's. Data are shown for each system for permeate ON concentration at $\text{CF} = 2$ (heavy diagonal fill), permeate ON concentration at $\text{CF} = \text{final}$ (open fill), colloidal ON concentration (light diagonal fill) and for the sum of the colloidal and average permeate ON concentrations (dark fill). Colloidal ON concentration was calculated using the average of permeate ON at $\text{CF} = 2$ and $\text{CF} = \text{final}$, where colloidal ON = [(retentate ON) - (average permeate ON)]/ CF_{final} . The 0.2- μm -filtered starting seawater ON ranges are shown by the two horizontal dashed lines in each subfigure. Asterisks indicate where data are not available; otherwise, categories (permeates, colloidal and sum) where no bar appears were not significantly different from 0 μM .

$\text{CF} = \text{final}$ (Kilduff and Weber, 1992; Guo and Santschi, 1996-this issue).

The recoveries of colloidal ON (see Fig. 1 caption for how this was calculated) were on the whole greatest for the Amicon systems (systems A1–A5)

when compared with other manufacturer's systems (Fig. 1a and b) for Woods Hole SW1 and SW2. This is in general agreement with the OC results (Buesseler et al., 1996-this issue). The Desalination Systems unit (Z1) also recovered a significant amount

Table 3

Total and organic nitrogen in Woods Hole SW1 and SW2 samples for initial and CFF-processed seawater – also shown are results for Milli-Q water

CFF ID	Type	Q1		SW1		SW2			
		CFTN	CF	TN	ON	CF	TN	ON	ON
Init. (t = 0)	< 0.2 μm	n.a.	n.d.	n.d.	10.0	5.6	n.a.	12.2	8.0
Init. (t = 1 h)	< 0.2 μm	n.a.	n.d.	n.d.	10.6	6.2	n.a.	10.7	6.6
Init. (t = 2 h)	< 0.2 μm	n.a.	2.1	n.d.	9.4	4.6	n.a.	11.8	7.9
Init. (t = 4 h)	< 0.2 μm	n.a.	0.0	n.d.	9.2	9.2	n.a.	10.6	6.8
A1	permeate	2	1.3	2	6.1	3.0	2	6.3	n.d.
A1	permeate	final	1.6	13.0	9.8	6.3	13.0	9.9	6.3
A1	retentate	final	1.6	13.0	46.7	42.9	13.0	33.2	29.6
A2	permeate	2	0.7	2	9.6	5.0	2	n.d.	0.0
A2	permeate	final	0.2	15.7	21.8	13.8	5.5	13.5	7.9
A2	retentate	final	2.6	15.7	33.4	28.5	5.5	13.1	9.1
A3	permeate	2	n.d.	2	5.5	1.8	2	9.9	1.5
A3	permeate	final	2.0	16.0	9.1	5.0	18.0	20.4	9.7
A3	retentate	final	6.8	16.0	49.7	45.6	18.0	50.3	37.6
A4	permeate	2	2.5	2	3.7	0.1	2	2.6	0.0
A4	permeate	final	8.8	15.7	11.5	8.4	15.7	10.5	6.6
A4	retentate	final	12.7	15.7	57.4	54.5	15.7	61.1	57.1
A5	permeate	2	1.1	2	3.7	1.0	2	4.4	1.2
A5	permeate	final	2.2	150	25.7	21.1	165	42.3	42.3
A5	retentate	final	5.7	150	n.d.	0.0	165	193.9	193.9
F1	permeate	2	7.0	2	13.2	9.0	2	9.8	5.9
F1	permeate	final	9.4	11.1	24.4	19.6	13.6	10.7	6.9
F1	retentate	final	3.7	11.1	20.1	15.3	13.6	18.2	15.3
F2	permeate	2	232.2	2	12.6	8.1	2	9.9	6.0
F2	permeate	final	48.4	11.0	3.5	0.0	20.0	16.3	12.8
F2	retentate	final	10.4	11.0	n.d.	0.0	20.0	5.7	2.3
F4	permeate	2	n.d.	2	9.1	4.6	2	10.1	6.3
F4	permeate	final	6.5	20.0	10.0	5.6	12.0	11.2	8.0
F4	retentate	final	4.6	20.0	14.7	10.5	12.0	16.2	12.8
O1	permeate	2	n.d.	2	16.1	11.7	2	7.3	3.8
O1	permeate	final	0.0	15.3	11.2	6.4	17.0	8.2	4.8
O1	retentate	final	0.2	15.3	16.0	11.6	17.0	3.5	0.3
O2	permeate	2	4.0	2	9.9	5.6	2	10.9	6.7
O2	permeate	final	3.1	3.5	10.2	6.0	4.3	9.3	5.3
O2	retentate	final	1.8	3.5	11.8	7.4	4.3	10.0	6.0
O3	permeate	2	n.d.	2	9.0	4.4	2	5.0	1.4
O3	permeate	final	0.3	3.8	9.8	5.4	3.9	28.6	24.9
O3	retentate	final	n.d.	3.8	12.6	7.3	3.9	16.7	13.1

Table 3 (continued)

CFF ID	Type	Q1		SW1		SW2			
		CF	TN	CF	TN	ON	CF	TN	ON
X1	permeate	2	0.2	2	9.4	5.1	2	7.9	4.1
X1	permeate	final	0.7	49.7	12.8	8.3	12.9	9.6	5.8
X1	retentate	final	0.7	49.7	12.3	7.3	12.9	10.8	7.2
Z1	permeate	2	6.1	1.2	8.0	0.5	2	7.0	2.9
Z1	permeate	final	1.7	26.0	18.5	6.0	25.0	18.5	11.5
Z1	retentate	final	3.1	26.0	108.0	98.9	25.0	138.5	132.2

n.a. = not applicable; n.d. = not determined. All values in μM.

colloidal ON fraction, but had permeate and “sum” values for SW2 that were in excess of those required for a net mass balance; this was also noted in the OC results (Buesseler et al., 1996) suggesting that contamination of the retentate (and hence colloidal) portion of this system was pronounced for both ON and OC. This is in contrast to the other systems which generally showed a greater degree of OC than ON contamination [see fig. 1a and b of Buesseler et al. (1996-this issue)]. For the Amicon systems, colloidal ON represented 0–50% of the total sample ON (mean = $29 \pm 17\%$) for SW1 and SW2 combined. All other CFF systems (with the exception of Z1) recovered much lower, and in some cases undetectable, quantities of colloidal ON (Fig. 1a and b). It should be noted that Filtron systems F1 and F4 and Osmonics systems O2 and O3 sometimes showed reasonable mass balances (as indicated by “sum” values in Fig. 1a and b) and recovered small quantities of colloidal ON for at least one of the two Woods Hole samples. For these systems, colloidal ON represented $\sim \leq 9\%$ of total sample ON. Our reported recoveries for colloidal ON may be conservative estimates since they are based on the average of the two permeate ON values (CF = 2 and CF = final; see Fig. 1 legend). If actual permeate ON values remain closer to those for CF = 2, then calculated quantities and percentages of colloidal ON would increase accordingly.

3.2.2. Hawaii results

Total ON content of 0.2-μm-filtered starting seawater in Hawaii ranged from 4–8 μM N (mean = $5.5 \pm 2 \mu\text{M N}$) for SW3 (Table 4; Fig. 1c). These total ON values are in the same general range as

Table 4
Total and organic nitrogen in Hawaii SW3 sample for initial and CFF-processed seawater

CFF ID	Type	SW3		
		CF	TN	ON
Init. (<i>t</i> = 0)	< 0.2 μm	n.a.	45.6	4.0
Init. (<i>t</i> = 1 h)	< 0.2 μm	n.a.	45.5	4.1
Init. (<i>t</i> = 1 h)	< 0.2 μm	n.a.	46.3	4.9
Init. (<i>t</i> = 2 h)	< 0.2 μm	n.a.	45.6	4.0
Init. (<i>t</i> = 2 h)	< 0.2 μm	n.a.	49.7	8.1
Init. (<i>t</i> = 4 h)	< 0.2 μm	n.a.	50.0	8.1
A1	permeate	2	42.4	0.6
A1	permeate	20.0	46.8	5.1
A1	retentate	20.0	56.8	14.8
A2	permeate	2	44.8	3.5
A2	permeate	5.2	51.7	9.7
A2	retentate	5.2	57.9	15.9
A3	permeate	2	47.5	6.1
A3	permeate	8.3	51.1	9.4
A3	retentate	8.3	52.7	10.6
A4	permeate	2	46.5	4.7
A4	permeate	20.2	55.7	13.0
A4	retentate	20.2	65.4	22.8
A5	permeate	2	45.5	4.0
A5	permeate	204	56.4	14.1
A5	retentate	204	134.9	92.8
F1	permeate	2	46.0	4.8
F1	permeate	9.2	54.9	13.5
F1	retentate	9.2	50.4	8.8
F2	permeate	2	48.4	7.3
F2	permeate	16.0	55.7	14.0
F2	retentate	16.0	49.8	8.2
F3	permeate	2	47.2	6.0
F3	permeate	12.8	51.9	10.4
F3	retentate	12.8	45.0	3.5
F4	permeate	2	n.d.	n.d.
F4	permeate	4.0	55.1	13.7
F4	retentate	4.0	47.4	5.8
O1	permeate	2	46.3	4.9
O1	permeate	16.0	56.4	14.8
O1	retentate	16.0	50.1	8.2
O2	permeate	2	46.2	5.0
O2	permeate	6.8	55.2	13.5
O2	retentate	6.8	48.0	6.3
O3	permeate	2	47.5	6.3
O3	permeate	6.3	51.1	9.8
O3	retentate	6.3	47.8	6.5

Table 4 (continued)

CFF ID	Type	SW3		
		CF	TN	ON
X1	permeate	2	45.3	4.2
X1	permeate	20.1	49.4	7.9
X1	retentate	20.1	49.5	8.1

Total N results for CFF-processed Milli-Q water were below the limit of detection for all systems and thus not shown. n.a. = not applicable; n.d. = not determined. All values in μM.

Woods Hole samples SW1 and SW2 (Table 3) and are comparable to ON values for similar depths (~ 600 m) in other open-ocean environments (Armstrong et al., 1966; Walsh, 1989; Hansell, 1993; Hansell et al., 1993; Koike and Tupas, 1993). For SW3, ON concentrations of the starting seawater source appeared to increase by ~ 3–4 μM N over the period of collection (Table 4).

In contrast to the Woods Hole data, there was less apparent random spurious contamination of the various CFF systems by extraneous ON in the Hawaii seawater samples (Fig. 1c). This is evident in the more tightly grouped ON data across all systems for the Hawaii samples. The majority of CFF systems achieved reasonable mass balances for SW3 (as indicated by “sum” values; see Fig. 1 caption). For several of the CFF systems (A4, A5, F1, F2, F4, O1 and O2) permeate ON contents at CF = final lay far above the upper bound of the starting 0.2-μm-filtered seawater. The greater ON contents of the permeates at CF = final were also considerably greater than those at CF = 2, suggesting either that: (a) contamination by LMW (< 1 kD) N-containing organics increased in the CFF system recirculation loops with extent of sample processing (i.e. by the time of CF = final), or (b) sample retentate ON had reached high enough concentrations to result in breakthrough into the final permeate stream. The differences in permeate ON content between CF = 2 and CF = final for nearly all CFF systems are in direct contrast with OC results for Hawaii samples, where little difference in permeate OC concentration was found except in CFF systems that recovered significant amounts of colloidal OC (Buesseler et al., 1996).

Significant quantities of colloidal ON were again recovered by Amicon systems (A1–A5; Fig. 1c) using SW3. This is similar to findings for Woods

Hole SW1 and SW2 colloidal ON contents (see above) and for Hawaii colloidal OC contents (Buesseler et al., 1996-this issue). The range of colloidal ON recovery for the Amicon systems with Hawaii SW3 were 6–33% (mean = $14 \pm 11\%$) of the starting seawater total ON. Apart from the Amicon systems, little or no recovery of colloidal ON was observed for any of the other CFF systems using Hawaii seawater (Fig. 1c).

It is apparent that even though the Amicon systems recovered substantially more colloidal ON in general, there is a high degree of variability within these nearly identical systems (using Amicon model DC-10 and S10N1 spiral-wound filtration cartridges; see table 1 in Buesseler et al., 1996-this issue) and for replicate samples (e.g., Woods Hole SW1 vs. SW2). As with the OC values (Buesseler et al., 1996-this issue), the recovery of colloidal ON does not appear to be related to the concentration factors used. CFF system A5 achieved the greatest concentration factors (CF \approx 150–200) for both the Woods Hole and Hawaii samples, yet generally had one of the lowest colloidal ON recoveries among the five Amicon systems. The other four Amicon systems had CFs that were considerably lower than system A5, and were comparable to CFs for all other CFF systems.

Among the various CFF systems, it is evident that fewer systems recovered measurable colloidal ON from Hawaii than from Woods Hole seawater (compare Fig. 1c with Fig. 1a and b). Those systems (i.e. Amicons) that did recover colloidal ON from both Woods Hole and Hawaii, generally recovered smaller amounts of colloidal ON from Hawaii seawater. These observations may be explained by qualitative differences (e.g., molecular weight distributions of organic-N compounds) in the total ON contained in Woods Hole vs. Hawaii seawater. Note also that system Z1 (Desalination Systems), which recovered significant quantities of colloidal ON from Woods Hole seawater, was not part of the Hawaii intercomparison.

3.3. Cross-flow filtration of seawater total and organic phosphorus

3.3.1. Woods Hole results

Concentrations of total and inorganic phosphorus (TP and IP, respectively) were determined for Woods

Hole SW1 0.2- μ m-filtered starting seawater and CFF-processed permeates and retentates, and the concentration of organic phosphorus (OP) was calculated by difference (Table 5). Concentrations of TP and IP in CF = 2 and CF = final permeates and in the calculated colloidal TP and IP fractions are shown in Fig. 2a and b, respectively. The calculated OP contents (= TP – IP) of the permeates and of the colloidal fractions are shown in Fig. 2c.

Concentrations of TP in both CF = 2 and CF = final permeate streams generally exhibited close agreement with TP in starting seawater in most CFF systems, though gross contamination was noted in some (e.g., A1 and A5; Fig. 2a). Colloidal TP appeared to become most concentrated in all Amicon systems (A1–A5) and in system Z1, while small amounts of IP were concentrated in the colloidal fraction by systems A1 and Z1 only (which were also the only two systems to show IP contamination; Fig. 2b). The reasons for the observed differences in TP vs. IP, especially among similar systems (i.e. Amicons), are unknown, but may be related to the system-specific CF or to the use of specific pre-processing cleaning procedures such as P-based detergents or reagents containing trace amounts of contaminant P (see Buesseler et al., 1996-this issue).

In contrast to the relatively conservative behavior of TP and IP in the various CFF systems, OP exhibited a large degree of variability among different systems (Fig. 2c), with both apparent contamination and scavenging. Part of this increased variability is expected since OP is a derived value and is subject to errors in both TP and IP determinations. Reasonable mass balances of OP were demonstrated by several systems (A3, A4, F2, F4, O1 and O3). Amicon systems A1–A5, along with system Z1, showed the highest apparent recoveries of colloidal OP ranging from \sim 20–80% of average total starting seawater OP, but 6 of the 13 systems (A1, A2, A5, F1, O2 and Z1) suffered from apparent OP contamination.

3.3.2. Hawaii results

Sample SW4 from Hawaii was processed by selected CFF systems for determination of TP, IP and OP in 0.2- μ m-filtered starting seawater as well as in CFF final permeates and retentates (Table 6). Concentrations in CF = final permeates and in the calcu-

Table 5

Total, inorganic and organic phosphorus determined spectrophotometrically in Woods Hole SW1 sample for initial and CFF-processed seawater — also shown are results for Milli-Q water

CFF ID	Type	Q1				SW1			
		CF	TP	IP	OP	CF	TP	IP	OP
Init. ($t = 0$)	< 0.2 μm	n.a.	-0.04	-0.01	-0.04	n.a.	1.00	0.83	0.18
Init. ($t = 1$ h)	< 0.2 μm	n.a.	-0.05	0.00	-0.05	n.a.	1.14	0.85	0.29
Init. ($t = 2$ h)	< 0.2 μm	n.a.	0.20	0.01	0.20	n.a.	0.99	0.82	0.17
Init. ($t = 4$ h)	< 0.2 μm	n.a.	0.11	0.01	0.10	n.a.	1.03	0.87	0.17
A1	permeate	2	-0.06	0.01	-0.07	2	1.25	0.95	0.31
A1	permeate	final	0.07	0.11	-0.03	13.0	2.13	1.52	0.61
A1	retentate	final	0.58	0.40	0.18	13.0	4.93	2.18	2.74
A2	permeate	2	-0.03	0.01	-0.05	2	0.99	0.83	0.16
A2	permeate	final	-0.06	0.01	-0.07	15.7	1.38	0.93	0.45
A2	retentate	final	0.10	0.00	0.10	15.7	2.25	1.05	1.20
A3	permeate	2	-0.04	0.00	-0.04	2	0.86	0.82	0.04
A3	permeate	final	-0.05	0.01	-0.06	16.0	1.00	0.80	0.20
A3	retentate	final	0.19	0.00	0.19	16.0	2.79	0.93	1.85
A4	permeate	2	0.07	0.03	0.04	2	0.85	0.75	0.10
A4	permeate	final	-0.03	0.03	-0.06	15.7	0.90	0.88	0.02
A4	retentate	final	0.19	0.03	0.16	15.7	3.21	1.01	2.20
A5	permeate	2	0.71	0.01	0.70	2	1.49	0.81	0.68
A5	permeate	final	0.03	0.04	-0.01	150	1.46	0.90	0.56
A5	retentate	final	0.11	0.00	0.12	150	17.32	1.71	15.61
F1	permeate	2	0.06	0.02	0.05	2	1.03	0.78	0.24
F1	permeate	final	0.41	0.02	0.39	11.1	1.12	0.73	0.39
F1	retentate	final	0.21	0.00	0.21	11.1	1.57	0.79	0.78
F2	permeate	2	1.22	0.02	1.20	2	0.79	0.74	0.04
F2	permeate	final	0.21	0.01	0.21	11.0	0.99	0.71	0.28
F2	retentate	final	0.33	0.00	0.32	11.0	1.28	0.86	0.42
F4	permeate	2	0.07	0.06	0.01	2	0.99	0.81	0.17
F4	permeate	final	-0.01	0.00	-0.01	20.0	1.00	0.79	0.21
F4	retentate	final	0.18	0.03	0.15	20.0	1.57	0.86	0.71
O1	permeate	2	0.52	0.02	0.05	2	1.08	0.79	0.29
O1	permeate	final	0.09	0.01	0.08	15.3	1.04	0.77	0.27
O1	retentate	final	0.21	0.00	0.21	15.3	1.45	1.04	0.41
O2	permeate	2	-0.01	0.02	-0.03	2	0.86	0.84	0.02
O2	permeate	final	1.02	0.01	1.01	3.5	1.47	0.74	0.73
O2	retentate	final	n.d.	n.d.	n.d.	3.5	1.24	0.83	0.41
O3	permeate	2	n.d.	n.d.	n.d.	2	n.d.	n.d.	n.d.
O3	permeate	final	0.35	-0.01	0.36	3.8	0.96	0.83	0.14
O3	retentate	final	0.27	-0.01	0.28	3.8	1.20	0.87	0.32
X1	permeate	2	0.05	0.01	0.06	1.2	0.98	0.82	0.15
X1	permeate	final	-0.06	0.01	-0.06	49.7	0.98	0.75	0.24
X1	retentate	final	0.10	0.12	-0.02	49.7	0.99	0.87	0.12
Z1	permeate	2	0.16	0.02	0.14	2	0.90	0.74	0.16
Z1	permeate	final	-0.03	-0.01	-0.03	26.0	1.29	1.06	0.23
Z1	retentate	final	0.23	0.04	0.19	26.0	6.23	1.85	4.38

lated colloidal fraction are shown in Fig. 3a–c. For comparison, the TP content of seawater collected from ~600-m depth at US-JGOFS Station Aloha was previously found to range from ~2.7 to ~3.1 $\mu\text{M P}$ (Karl et al., 1993) and is virtually identical to that found here (mean = 3.0 $\mu\text{M P}$). It is not possible to ascertain whether permeate TP, IP or OP contents changed over the course of CFF processing since P data for permeates at CF = 2 are not available.

The IP content of all fractions analyzed is assumed to be comprised of soluble reactive phosphate (PO_4^{3-}). As discussed above, in the absence of contamination or scavenging, PO_4^{3-} should behave conservatively in CFF systems. In the Amicon systems, elevated concentrations of both TP and IP were noted in all final retentates and in at least one of the final permeates (Table 6). In system A1, which showed apparent P contamination in the Woods Hole SW1 sample, this likely results in part from the presence of contaminant P. The trace P contamination of all Amicon systems was greater than all of the other systems (except F4 and O2) in this portion of the study (Fig. 3a and b).

If it is indeed the case that there is no detectable OP in starting SW4 (Table 6; Fig. 3 caption), then we would predict that there should also be negligible colloidal OP collected by the various CFF systems. We observed, however, non-zero quantities of OP both in CFF permeates and retentates (Table 6). This leads to the calculation, in Amicon systems A2–A5, as well as in Filtron system F4, of small but “measurable” quantities of colloidal OP (Fig. 3c). It is possible that trace amounts of OP contained in starting SW4 were adequately concentrated during CFF processing to allow for its subsequent detection in the final retentate. However, the elevated quantities of OP in CFF permeates (Fig. 3c) are more enigmatic, especially because contamination of the permeate streams was not indicated during CFF processing of Milli-Q water blanks (see below and Table 6). In summary, the Amicon systems, which also showed elevated recoveries of both OC (Buesseler et al., 1996-this issue) and ON (this study) are the only

ones to systematically show excess TP and IP and colloidal OP.

Although it is possible that the apparent colloidal OP fraction may derive from concentration of low level, naturally occurring colloidal OP, it is also possible that this fraction is artificially produced during the concentration process. Several concurrent or synergistic processes may be acting to generate the observed OP results, including: (1) the effects of ionic strength in “producing” contaminant P via leaching from various surfaces within each of the CFF systems during seawater processing; (2) potentially significant adsorption and desorption of the various forms of seawater P within the CFF system components; (3) scavenging of inorganic P via sorption during CFF concentration of trace metals, especially Fe (Powell et al., 1996-this issue; Reitmeier et al., 1996-this issue); and (4) potential artifactual production of “colloidal” OP during CFF processing via the association of IP with true colloidal organic molecules as they become concentrated. Other workers have observed a similar phenomenon, the apparent “creation” of colloidal OP during concentration of colloidal organic matter from a fresh water lake by tangential flow ultrafiltration (Nanny and Minear, 1996). These authors argue that the colloidal OP results from association of phosphorus with aggregates that form during the concentration process. From our data, it is not possible to unequivocally demonstrate which, if any, of the above factors is of greatest importance. The data do, however, illustrate the caution that must be exercised in interpreting results of “colloidal” element distributions without adequately understanding their behavior in CFF systems. It is obvious in this case that phosphorus behaves quite differently than either C or N in these systems.

3.4. Evaluation of N and P blanks during cross-flow filtration

Milli-Q water was processed by CFF systems prior to seawater at both Woods Hole and Hawaii. “Q”-water was used in an attempt to evaluate CFF

Notes to Table 5:

n.a. = not applicable; n.d. = not determined. All values in μM .

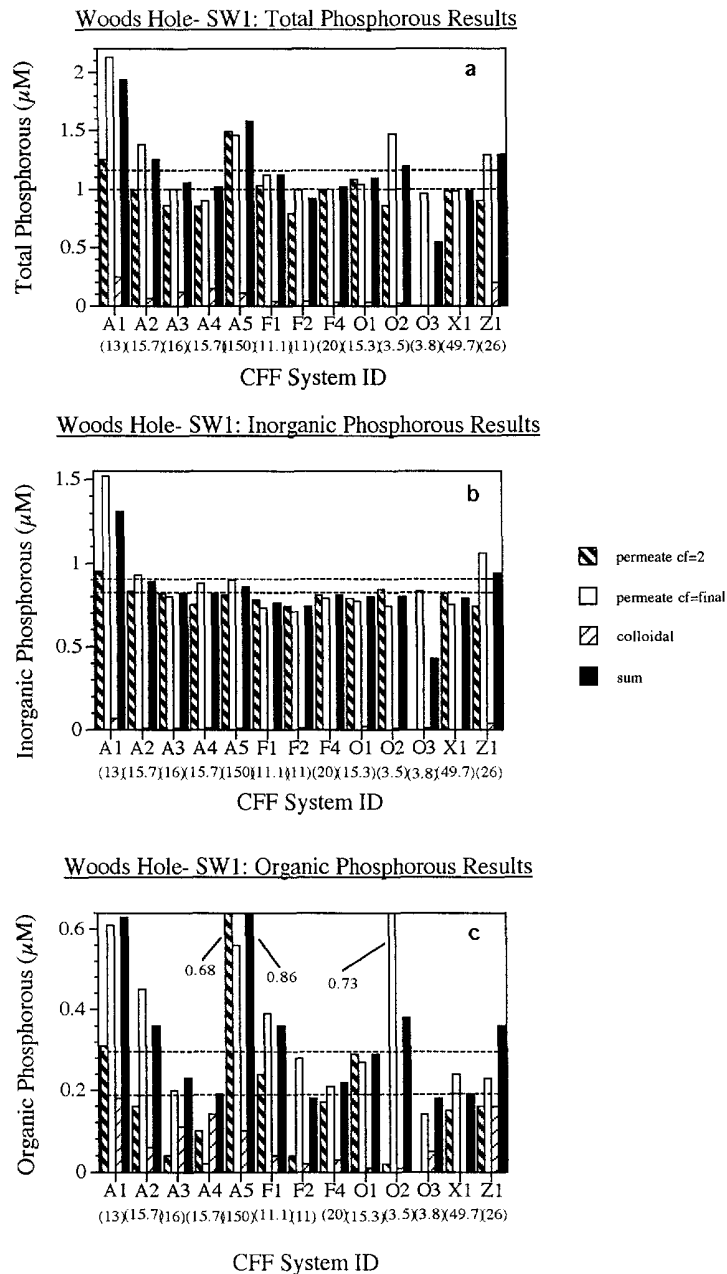


Fig. 2. Intercomparison of seawater total phosphorus (TP), inorganic phosphorus (IP), and organic phosphorus (OP) for Woods Hole SW1 sample: (a) TP; (b) IP; and (c) OP. Conventions used are given in Fig. 1 caption. Colloidal P concentrations were calculated using the average of permeate P at CF = 2 and CF = final, where colloidal P = [(retentate P) - (average permeate P)]/CF_{final}. The 0.2- μ m-filtered starting seawater TP, IP and OP ranges are shown by the horizontal dashed lines in each subfigure. Asterisks indicate where data are not available; otherwise, categories (permeates, colloidal and sum) where no bar appears were not significantly different from 0 μ M.

system blanks in a manner that was independent of mass balances (indicated as ‘‘sum’’ values) presented in Figs. 1–3. Q-water blanks were measured

for total N, total P and inorganic P, and are shown in Tables 3 and 5 and 6, respectively. Total N is not reported for Q-water blanks from Hawaii because these values were below the limit of detection for all CFF systems. As pointed out by Buesseler et al. (1996-this issue), blanks determined through the use of Q-water are not necessarily representative of blanks that arise during the processing of seawater due to differences in ionic strength and other considerations. For this reason, mass balances are likely to be the most appropriate means of blank evaluation during the processing of seawater samples. Nonetheless, Q-water or other high-purity water processing blanks are often helpful in evaluating CFF system contaminants prior to the processing of true samples.

As can be seen from Woods Hole (Table 3), Q-water total N system blanks were usually found to exceed background (i.e. undetectable) levels in nearly all cases, yet mass balances generated from CFF processing of Woods Hole seawater indicated that, for the most part, CFF systems generally did not exceed the range of concentrations present in starting seawater, at least for ON (Fig. 1a and b). With phosphorus, CFF systems that did not show elevated TP or IP in Q-water blanks (e.g., SW1 permeates of A1, permeates and retentate of A2 and CF = final permeates and retentate of A5; Table 5) could subsequently have seawater TP and/or IP concentrations that were in excess of starting seawater values (Tables 5 and 6; Fig. 2a–c). Until the particular contamination or scavenging characteristics of an individual CFF system are known, it is advisable to evaluate blanks as comprehensively as possible by means of both high-purity water and mass balances of a given seawater sample.

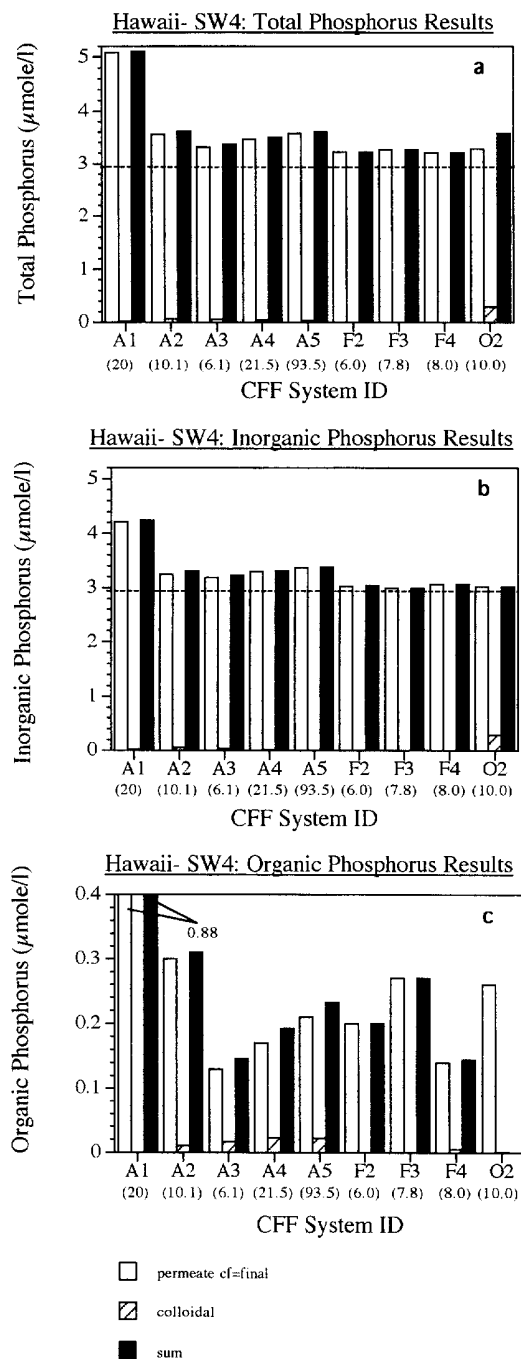


Fig. 3. Intercomparison of seawater total phosphorus (TP), inorganic phosphorus (IP), and organic phosphorus (OP) for Hawaii SW4 sample for selected CFF systems: (a) TP; (b) IP; and (c) OP. Conventions used are given in Fig. 1 caption. Colloidal P concentration was calculated using the average of permeate P at CF = 2 and CF = final, where colloidal P = [(retentate P) – (final permeate P)]/CF_{final}. CF = 2 permeates were not measured for P contents. The 0.2-μm-filtered starting seawater TP and IP ranges are shown by the horizontal dashed lines in each subfigure. Asterisks indicate where data are not available; otherwise, categories (permeates, colloidal and sum) where no bar appears were not significantly different from 0 μM. Starting OP concentration was not significantly different from 0 μM P.

3.5. Elemental ratios of organic matter separated by cross-flow filtration

The availability of both OC (Buesseler et al., 1996-this issue) and ON data from this intercomparison study permits us to calculate organic molar C/N elemental ratios in CFF-processed permeates and retentates relative to starting, unfractionated seawater. These ratios are valuable for understanding whether differences in the composition and charac-

teristics of CFF-processed fractions are real or artificial. They are also useful as a tool for evaluating the relative contributions of C- and N-containing contaminants during CFF processing. Due to the ambiguity and relatively small amount of P data available from this study, P will not be incorporated as part of the discussion of elemental ratios in the various organic fractions. It is evident that additional work is necessary in order to resolve the complex behavior of P in CFF systems before confidence can

Table 6

Total, inorganic and organic phosphorus determined spectrophotometrically in Hawaii SW4 sample for initial and CFF-processed seawater — also shown are results for Milli-Q water

CFF ID	Type	Q2				SW4			
		CF	TP	IP	OP	CF	TP	IP	OP
Init. (<i>t</i> = 0)	< 0.2 μm	n.a.	0.01	0.01	0	n.a.	2.98	3.07	−0.09
Init. (<i>t</i> = 1 h)	< 0.2 μm	n.a.	0.01	−0.01	0.02	n.a.	2.94	2.95	−0.01
Init. (<i>t</i> = 1 h)	< 0.2 μm	n.a.	0.01	0.03	−0.02	n.a.	2.97	2.99	−0.02
Init. (<i>t</i> = 2 h)	< 0.2 μm	n.a.	0.46	0.04	0.42	n.a.	n.d.	n.d.	n.d.
Init. (<i>t</i> = 4 h)	< 0.2 μm	n.a.	0.02	0.07	−0.05	n.a.	n.d.	n.d.	n.d.
A1	permeate	20.0	n.d.	n.d.	n.d.	20.0	5.09	4.21	0.88
A1	retentate	20.0	n.d.	n.d.	n.d.	20.0	5.55	4.77	0.78
A2	permeate	5.2	−0.01	0.22	−0.23	10.1	3.56	3.25	0.3
A2	retentate	5.2	n.d.	n.d.	n.d.	10.1	4.21	3.8	0.41
A3	permeate	8.3	−0.01	0.06	−0.07	6.1	3.32	3.19	0.13
A3	retentate	8.3	n.d.	n.d.	n.d.	6.1	3.66	3.43	0.23
A4	permeate	20.2	n.d.	n.d.	n.d.	21.5	3.47	3.3	0.17
A4	retentate	20.2	n.d.	n.d.	n.d.	21.5	4.36	3.7	0.65
A5	permeate	204	0	0.03	−0.03	93.5	3.58	3.37	0.21
A5	retentate	204	0.06	−0.01	0.07	93.5	6.58	4.29	2.29
F1	permeate	9.2	−0.02	0.07	−0.09	9.2	n.d.	n.d.	n.d.
F1	retentate	n.d.	n.d.	n.d.	n.d.	9.2	n.d.	n.d.	n.d.
F2	permeate	16.0	n.d.	n.d.	n.d.	6.0	3.23	3.03	0.2
F2	retentate	16.0	n.d.	n.d.	n.d.	6.0	3.14	3.11	0.03
F3	permeate	12.8	n.d.	n.d.	n.d.	7.8	3.27	2.99	0.27
F3	retentate	12.8	n.d.	n.d.	n.d.	7.8	2.89	2.8	0.09
F4	permeate	4.0	n.d.	n.d.	n.d.	8.0	3.21	3.07	0.14
F4	retentate	4.0	n.d.	n.d.	n.d.	8.0	3.23	3.06	0.18
O2	permeate	6.8	0.09	0	0.09	10.0	3.29	3.02	0.26
O2	retentate	6.8	0.17	0.02	0.15	10.0	3.05	3.04	0.01
O3	permeate	6.3	n.d.	n.d.	n.d.	10.3	n.d.	n.d.	n.d.
O3	retentate	6.3	0	0.09	−0.09	10.3	n.d.	n.d.	n.d.
X1	permeate	20.1	0.14	0.41	−0.27	12.8	n.d.	n.d.	n.d.
X1	retentate	20.1	0.01	−0.01	0.01	12.8	n.d.	n.d.	n.d.

n.a. = not applicable; n.d. = not determined. All values in μM.

be placed in its quantitative and qualitative significance in colloidal fractions.

C/N ratios of organic matter separated from Woods Hole SW1 and SW2 and Hawaii SW3 samples using CFF are shown in Fig. 4a–c. For Woods Hole samples, C/N values of starting seawater ranged from 9.4 to 26 (mean = 17.3 ± 5.6) for both SW1 and SW2 (dashed lines in Fig. 4a and b). The

majority of CFF systems produced CF = 2 permeates that were significantly elevated in C/N relative to final permeates and retentates. This is likely due to the flushing of contaminant carbon from the plastic tubing and other components of these systems during the early stages of sample processing. Several of the systems (in particular Amicons A4 and A5, Filtrons F1 and F4, and Millipore Z1) showed initially high

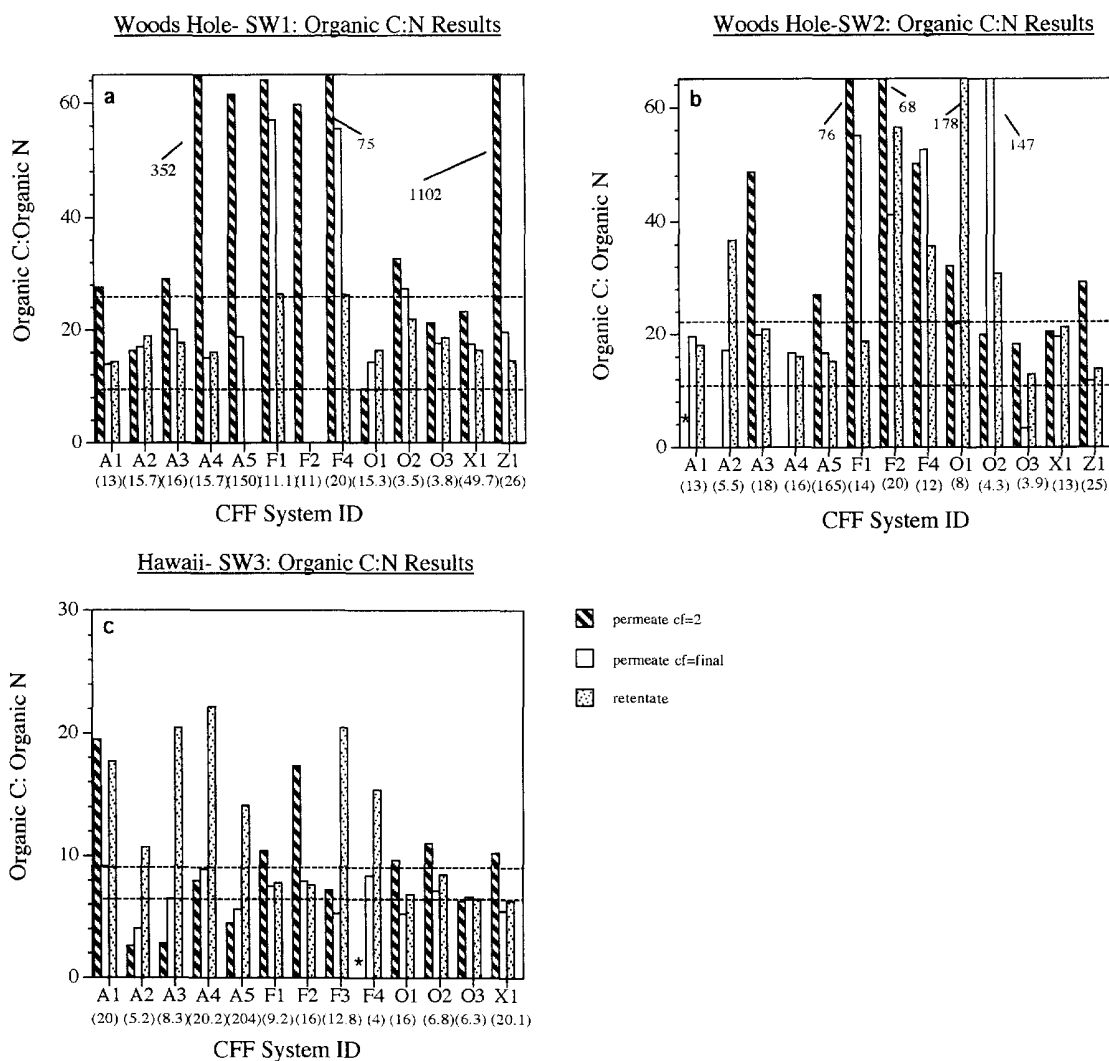


Fig. 4. Intercomparison of seawater C/N values of permeates and retentates from CFF systems for Woods Hole SW1 and SW2 and Hawaii SW3 samples: (a) Woods Hole sample SW1; (b) Woods Hole sample SW2; and (c) Hawaii sample SW3. Conventions used are given in Fig. 1 caption. Asterisks indicate where data are not available; otherwise, categories (permeates, colloidal and sum) where no bar appears were not significantly different from $0 \mu M$. The $0.2\text{-}\mu\text{m}$ -filtered starting seawater C/N ranges are shown by the two horizontal dashed lines in each subfigure.

C/N's that in most cases (but not all, e.g. F1 and F4) had decreased to the range of starting seawater by the time of the CF = final permeate (Fig. 4a and b). These elevated C/N ratios persisted for all the Filtron systems from SW1 to SW2 and were also observed for Osmonics systems O1 and O2 during processing of SW2. Elevated C/N values can in most cases probably be attributed to the high overall levels of contaminant OC observed in these systems (refer to Buesseler et al., 1996). The remaining systems that did not show unusual levels of contamination, revealed C/N values of final permeates and retentates that were similar to starting seawater values (Fig. 4a and b). This suggests that in this coastal seawater sample, C and N were in general not differentially partitioned on the basis of molecular weight.

For Hawaii sample SW3 (Fig. 4c), C/N ratios were notably different from those observed for Woods Hole seawater. Starting SW3 C/N values were significantly lower (range = 6.5–9.0) than SW1 and SW2. In general, CF = 2 permeate C/N values were still the highest among the various fractions analyzed during SW3 processing. In accordance with the overall lower levels of OC contamination observed for Hawaii samples relative to Woods Hole samples (see Buesseler et al., 1996-this issue), far fewer instances of extremely elevated C/N values were also observed in Hawaii compared with Woods Hole samples.

For Hawaii SW3 samples, those systems that recovered significant quantities of colloidal OC and ON, final retentates (with the exception of system A1 permeates due to apparent contamination) had significantly higher C/N ratios than CF = 2, final permeates, and starting seawater (in particular, Amicon systems A1–A5, but also Filtron systems F3 and F4; Fig. 4c). For SW3, final retentate C/N values in these systems were ~ 1.5–3 times higher than starting seawater C/N ratios (Fig. 4c).

The most striking features of the C/N values reported here are for those systems (i.e. Amicons A1–A5) that systematically isolated significant colloidal C and N, and include: (1) minimal differences in C/N values of HMW retentates vs. final permeates and total seawater ON for coastal Woods Hole seawater (except system A2 for SW2); and (2) significantly elevated C/N values of retentates vs. final permeates and total seawater ON observed for open-

ocean Hawaii seawater. It is possible that qualitative differences in the N content of organic matter in coastal vs. open-ocean settings are real and that these differences are reflected in dissimilar proportions of total ON partitioning into distinct molecular weight classes.

It has been reported that $\geq 50\%$ of the HMW material isolated from pelagic waters may be comprised of carbohydrate-rich material (Benner et al., 1992), and this is supported by the elevated C/N values seen in this study for the HMW fraction of Hawaii seawater. The molecular composition of the LMW fraction has not yet been examined, but the data presented here suggest that if CFF processing artifacts are significant (see below), this material may be enriched in N relative to the HMW fraction in certain marine waters, at least for open-ocean environments. Enrichment of LMW organic matter in N relative to its HMW counterpart has also been suggested previously on the basis of microbial degradation experiments (Amon and Benner, 1994). Direct measurements of lower C/N ratios in the LMW fraction have also been made in eastern North Pacific seawater (Bauer et al., 1994).

C/N values for all Amicon systems except A1 increased from CF = 2 to CF = final permeates for Hawaii SW3 (Fig. 4c). These data suggest that in these systems, which isolated the greatest amounts of both colloidal OC and ON, active fractionation of organic N and C maybe occurs throughout the course of CFF processing. Fractionation may result from: (a) sorptive removal of N-rich compounds within CFF systems, or (b) selective breakthrough into the permeate stream of N-rich organic matter relative to organic C at the CFs used here. At very high CF values (greater than those used in most CFF systems in the present study), it is possible that fractionation between C and N stabilizes as C retention by the CFF membranes becomes less efficient (Kilduff and Weber, 1992; Guo and Santschi, 1996-this issue). Thus, qualitative and quantitative characterizations of isolated, HMW organic matter (as well as the LMW permeate fraction) may vary as a function of the magnitude of CF, even if blanks and molecular weight cut-offs are well defined. Further methodological investigation of the effects of both processing time and CF are needed in order to determine whether fractionation is a general consequence of

CFF. It is therefore not possible at present to exclude the possibility of fractionation artifacts during the CFF processing of seawater organic matter. Additional work is needed to validate the use of CFF as a tool for elucidating the characteristics of seawater organic matter and the importance of different dissolved and colloidal fractions to the seawater microbial community.

4. Summary and conclusions

Findings on the effectiveness of a variety of CFF systems in processing seawater inorganic nutrients and organic N and P indicate that there exists large variability in the performance and reported recoveries of systems not only on the basis of manufacturer, but among individual units of a specific model. The magnitude of this variability makes comparisons of data arising from different CFF systems (or even from the same CFF unit used at different times) difficult at this stage of development. Depending on the particular application, precautions must be taken in the cleaning of CFF systems prior to sample processing, and care must be exercised in accounting for contamination and scavenging effects both prior to and during sample processing. Although a particular CFF system may be used primarily or even exclusively for studying the cycling of a specific element or substance, it is reasonable to hypothesize that contamination or scavenging of non-target elements or substances may affect the quantities of the target substance observed at different stages of CFF processing. The preliminary findings presented here on nutrient element distributions within different molecular weight fractions of seawater organic matter suggest that sub-fractions of total seawater organic matter may be dissimilar with respect to the cycling of these elements. Additional work is necessary, however, before the full potential of CFF as a tool in biogeochemical studies is realized. Future work that examines nutrient and trace-element distributions in marine organic colloids in conjunction with carbon is likely to contribute significantly to our understanding of organic matter cycling in the oceans.

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