



PERGAMON

Deep-Sea Research II 50 (2003) 655–674

DEEP-SEA RESEARCH
PART II

www.elsevier.com/locate/dsr2

Determining true particulate organic carbon: bottles, pumps and methodologies

Wilford D. Gardner^{a,*}, Mary Jo Richardson^a, Craig A. Carlson^b, Dennis Hansell^c, Alexey V. Mishonov^a

^aDepartment of Oceanography, Texas A&M University, College Station, TX 77843, USA

^bUniversity of California Santa Barbara, Santa Barbara, CA 93106, USA

^cRosenstiel School of Marine and Atmospheric Science, Miami, FL 33149, USA

Accepted 3 October 2002

Abstract

The primary means of determining particulate organic carbon (POC) concentrations in aquatic environments is by filtering from water bottles or by in situ filtration with pumps and analyzing the filters. The concentrations measured by these two methods, however, can differ by a factor of 1.2–5 in temperate waters, and by factors as large as 200 in cold, high-latitude waters. Here we report that the ratio of bottle POC to pump POC ranged between 20 and 200 in the Ross Sea during early spring and between 5 and 50 during summer. In the Antarctic Polar Front the ratio ranged between 2 and 25 in spring. A new approach to constraining POC concentrations is to use high-temperature combustion (HTC) of water samples (rather than filters), POC being the difference between measurements of total and dissolved organic carbon. POC concentrations determined by bottle filtration are in reasonable agreement with the POC concentrations obtained by HTC, independent biomass measurements, and beam-attenuation/bottle POC ratios that are similar to previous studies, thus lending credibility to the bottle POC values. Data from several studies suggest that the most likely reasons for differences between bottle and pump POC are the use of slightly larger pore-size filters with in situ pumps and higher pressure differentials across the filter during in situ pump filtration, resulting in particulate carbon being pulled through the filters. The one-to-two orders of magnitude differences in high-latitude, cold-water environments needs further investigation. If accurate measurements of POC can be obtained for calibration, beam attenuation profiles using transmissometers offer a way to quantify rapidly the distribution of POC. The JGOFS protocols for POC filtration must be modified to include a blank that accounts for DOC adsorption onto filters. The largest impact of DOC adsorption will be when POC concentrations are below $\sim 2 \mu\text{mol/l}$, which includes most sub-euphotic zone waters. These findings have important ramifications for any programs involving the particulate portion of the carbon cycle.

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1. Introduction and background

In the 1960s, methods were developed to measure particulate organic carbon (POC) in small samples of seawater (Menzel and Vaccaro, 1964),

*Corresponding author. Fax: +1-979-845-6331.

E-mail address: wgardner@ocean.tamu.edu (W.D. Gardner).

making it possible to measure POC throughout the water column (Wangersky and Gordon, 1965; Menzel, 1967; Gordon, 1971). Methods varied, but 1–271 of water were filtered through 47 mm, silver filters (pore sizes of 0.45–5 μm), rinsed with 5 ml distilled water, and analyzed by combustion at 750–800°C, and the resulting CO_2 detected (Wangersky and Gordon, 1965; Gordon, 1971). Eventually most methods used 25-mm glass fiber filters (nominal pore size of 0.7 μm) and one to several liters were filtered.

Later, in situ pumps were developed to filter large volumes of water (100s–1000s of liters) to obtain larger particulate samples for chemical and biological analysis, to increase the chances of collecting the rare, large particles in the ocean, and to decrease the chances of sample contamination through exposure to air and ship conditions (e.g., Bishop and Edmond, 1976; Bishop et al., 1985; Buesseler et al., 1998; Bacon et al., 1996; Moran et al., 1999). Bishop and Edmond (1976) noted that total particulate matter (PM) concentrations measured from Niskin bottles were roughly 30% less than the PM concentrations measured with in situ pump filtration at the same depth and time. Their explanation was that in situ pumps filtering hundreds to thousands of liters collected the rare, large particles that were under-sampled by Niskin bottles collecting only 5–30 l. While this may account for a small portion of the difference, Gardner (1977) demonstrated that rapidly sinking particles settle below the spigots of a Niskin bottle and are seldom sampled (the dregs). Inclusion of the dregs can increase the PM concentration by 10–100% (Gardner, 1977; Calvert and McCartney, 1979; Gardner et al., 1993), which easily accounts for the lower PM concentrations in bottles.

Results from recent studies, however, indicate that POC and particulate organic nitrogen (PON) concentrations measured on samples filtered aboard ship from small-volume water bottles are greater than (not less than, as with PM) those using in situ large-volume filtration systems (Altabet et al., 1992; Dunne et al., 1997; Moran et al., 1999; Bishop, 1999; Bishop et al., 1999). Moran et al. (1999) reported differences in excess of a factor of 4, but differences in later studies cited here exceeded a factor of 100. Given the

importance of POC in biogeochemical processes from micro to global scales, these differences need to be explained.

In this paper, we explore several hypotheses and seek to understand the causes of the discrepancy between POC values measured with “small-volume” bottles and “large-volume” in situ pumps. Properly calibrated transmissometers can then be used to obtain rapid estimates of POC in aquatic environments. We will briefly report results from experiments we have conducted and data comparisons using independent means of POC assessment, as well as compare results from existing literature.

2. Methods

2.1. Bottle and pump POC data

Possible reasons for the differences in POC concentration include spatial patchiness, artificial creation of POC, contamination, volumes sampled, filter loading, method of POC analysis, adsorption of DOC onto filters, particle retention of filters, and differences in pressure drop (ΔP) across the filter. Table 1 lists the major characteristics of the two sampling methods.

In addition to considering the bottle/pump POC comparisons reported by Altabet et al. (1992), Dunne et al. (1997), Moran et al. (1999), Bishop (1999), and Bishop et al. (1999), we compare bottle and pump POC concentrations collected during the US Joint Global Ocean Flux (JGOFS) programs in the Equatorial Pacific (EqPac), Arabian Sea, Antarctic Polar Front Zone (APFZ) and the Ross Sea (<http://usjgofs.whoi.edu/jg/dir/jgofs/>). In most cases, bottle POC was obtained by collecting between a fraction of a liter (in the Ross Sea) and up to 6 l (in EqPac deep water), filtering the water at <0.25 atm through pre-combusted 25-mm GF/F filters (nominal pore size 0.7 μm) by inverting the bottle into a standard funnel set up, drying the filter, and later analyzing carbon with an elemental analyzer. Samples are usually acid fumed to remove carbonate, which is generally less than 6% of the particulate carbon in surface waters (Gordon, 1971). POC from pump samples

Table 1
Characteristics of sampling with water bottles and in situ pumps

Parameters	Bottle filtration	In situ filtration pumps
Filter type and pore size	GF/F—0.7 μm nominal cutoff Silver filters—0.45 μm	Quartz fiber—1.0 μm nominal cutoff or glass fiber filters—0.70 μm
Filter diameter	25 mm	142 or 292 mm
Filter area	$\sim 4 \text{ cm}^2$	~ 150 or $\sim 600 \text{ cm}^2$
Mass collected	0.1–0.5 mg	2.5–250 mg
Volume	0.2–6 l; 2–4 l common	100s–1000s of liters
Filter loading	0.02–0.20 mg/l	0.02–2.0 mg/l
ΔP across filter	$< \sim 0.25 \text{ atm}$	$> 0.75 \text{ atm}$ (seldom reported)

is often separated by sieving at 53 or 70 μm and analyzing a subsample of both size fractions (Table 1) in the same manner as bottle samples. Buesseler et al. (1995) found that in EqPac the $< 53\text{-}\mu\text{m}$ size fraction was $< 8\%$ carbonate carbon, and the $> 53\text{-}\mu\text{m}$ fraction had a maximum value of 20%.

Bacon et al. (1996) filtered water using a large-volume in situ pump during two time-series cruises on the equator during the EqPac program, and subsamples of the filters were analyzed for POC. The in situ pump constructed at WHOI was equipped with a flow sensor but the pressure differential across the filter was not measured. Bishop (1999) used his Large-Volume Filtration System to filter water at stations between 12°N and 12°S during EqPac. Subsamples of filters were analyzed for POC and compared with beam c_p from a transmissometer attached to the pump. Buesseler et al. (1995) used custom-built in situ pumps on a series of NOAA cruises during EqPac. Rather than taking discrete samples at different depths, Buesseler developed a profiling mode where he filtered continuously while lowering and raising the pump in order to obtain an integrated value over the top 100 m, thus saving considerable wire and analysis time. In addition, some discrete samples were taken at 5 and 100 m. During the Arabian Sea study, Buesseler et al. (1998) used a new custom in situ pump (a precursor to the McLane Labs pumps), similar to the pumps his group used in the EqPac program and made integrating profiles and discrete measurements at 5 and 100 m.

During EqPac, bottle POC and simultaneous beam c_p measurements were made for comparison

during the cruises when Bacon et al. (1996) and Bishop (1999) made pump measurements, but not during the NOAA cruises with the work of Buesseler et al. (1995). In the Arabian Sea, bottle samples of POC were obtained in fairly close proximity in time (hours) and space to the pump profiles of Buesseler et al. (1998), though the match was not preplanned and was less than ideal. In addition to discrete bottle samples at 5 and 100 m, we integrated the bottle POC values over the 0–100 m range for comparison with the integrating pump values.

During the US JGOFS program in the Ross Sea and APFZ, Cochran et al. (2000) and Buesseler et al. (2001) used Challenger Oceanic Systems and Services, Inc. and McLane Labs in situ filtration pumps to collect PM and thorium at discrete depths. These pumps were operated by battery power and these independent units were attached to a hydro wire for synchronous sampling. The McLane pumps tended to be used at shallow depths (J.K. Cochran, 2002, personal communication). Both the Challenger pumps and McLane pumps used a mechanical flow meter to calculate volume filtered because the volumes modeled by the McLane pump software were not sufficiently reliable. After passing through the microquartz filter, the water flowed through Mn sorbing cartridges for removal of dissolved Th.

2.2. Beam c_p as a function of POC

Employing data from JGOFS and other programs, POC concentrations measured from Niskin bottle samples have been correlated with the beam

Table 2
Beam c_p /POC slopes from selected geographic regions

Area	Cruise	Slope c_p /POC ($\times 10^{-3}$)	SD of slope ($\times 10^{-3}$)	References
<i>Bottles</i>				
NABE	Atlantis II 119/4-5	39.38	0.9	Gardner et al. (1993)
EqPac	TT007	25.60	1.1	this paper
	TT008	11.91	0.4	this paper
	TT011	48.97	2.1	this paper
	TT012	21.73	0.5	this paper
	French	23.90	—	Claustre et al. (1999)
Arabian Sea	TN043	31.01	0.9	Gundersen et al. (1998)
	TN045	24.39	0.7	Gundersen et al. (1998)
	TN049	24.79	0.6	Gundersen et al. (1998)
	TN054	23.62	0.8	Gundersen et al. (1998)
Ross Sea	NBP 96-4A	20.24	0.7	Gardner et al. (2000)
	NBP 97-1	18.93	0.5	Gardner et al. (2000)
	NBP 97-8	23.12	0.4	Gardner et al. (2000)
Polar front	RR Kiwi 7	29.11	0.8	Gardner et al. (in prep.)
	RR Kiwi 9	22.53	0.8	Gardner et al. (in prep.)
<i>In situ pumps</i>				
EqPac	TT007	63.40	0.003	Bishop (1999)
	TT008	21.67	2.7	Bacon et al. (1996); this paper
	TT011	60.90	0.003	Bishop (1999)
	TT012	27.21	4.6	Bacon et al. (1996); this paper
Ross Sea	NBP 96-4A	*400–4000		Calculations—(1996); this paper; data from Cochran et al. (2000)
	NBP 97-1	*100–1000		Calculations—this paper; data from Cochran et al. (2000)
Polar front	RR Kiwi 7	*30–700		Calculations—this paper; data from Buesseler et al. (2001)

*Based on POC_{bottle}/POC_{pump} , not c_p/POC

attenuation coefficient due to particles (beam c_p) measured in situ at the depth of the Niskin bottle sample (Gardner et al., 1993, 2000, 2001; Gundersen et al., 1998; Claustre et al., 1999) (Table 2). The robustness of the correlations in a given area and time have made it possible to estimate the standing stock of POC in the upper water column based on CTD/transmissometer profiles. It is important to compare the beam c_p from the up-cast of a CTD with bottle POC because bottles are tripped on the up-cast and internal waves and spatial variability can significantly change the beam c_p value at a specific depth between the down and up casts. Bishop (1999) and Bishop et al. (1999) found good correlation between POC from large-volume in situ filtration pump samples and beam c_p from a transmissometer attached to the pump.

2.3. HTC estimates of POC

An independent method for estimating POC in water samples was tested during the US JGOFS study in the Ross Sea where POC concentrations were very high. During two cruises (NPB 97-1 Summer; NBP 97-8 Spring) high-temperature combustion (HTC) was used to measure both total organic carbon (TOC) and dissolved organic carbon (DOC) on samples of water (Carlson et al., 2000). POC was estimated as the difference between TOC (unfiltered water) and DOC (gravity filtered in-line through a precombusted GF/F filter) and is here referred to as HTC-POC. Initially, 15 ml of sample water were passed through the filter before the filtrate was collected in order to saturate any active sites of the GF/F

filter with DOC and to prevent further DOC removal by adsorption onto the filter. Unfiltered water samples of 20–40 ml were sonicated to break up and homogenize particles prior to TOC analysis. Individual injection volumes for TOC analysis were 0.1 ml. Values of POC determined by this method are likely to underestimate true POC concentrations collected during bloom conditions due to the still heterogeneous distribution of particles in the sonicated sample and the small injection volume used. Nonetheless, comparing HTC-POC to bottle POC from the same bottles provides an independent means of testing for the true POC concentrations.

2.4. Vacuum experiment

To test for the effects of different levels of vacuum during filtration we intended to filter water at three vacuum levels for measurement of POC and PM. For logistical reasons POC was filtered only at 0.5 atm, but PM was filtered at three vacuums and the results are insightful. Total PM was measured from samples drawn through 0.4- μm Poretics polycarbonate membrane filters at vacuums of 0.17, 0.5 and 0.83 atm. Samples were obtained from three different depths on two casts in the axis of the Mississippi Canyon (bottom depth of 300 m at the site) in the Gulf of Mexico. Water was drawn through in-line filter holders placed between the Niskin bottles and glass carboys evacuated to specific maximum values. Filters were washed ten times with filtered, distilled water within a laminar flow hood to remove salts, then dried and sealed in Petri dishes and returned to the laboratory for reweighing.

3. Results

3.1. Bottle POC versus pump POC and c_p /POC

3.1.1. EqPac

When the pump POC concentrations measured by Bacon et al. (1996) were regressed against the beam c_p data closest in time and space, the slope was 22×10^{-3} during El-Niño conditions (TT008) and 27×10^{-3} during non-El Niño conditions

(TT012; Fig. 1, Table 2) with significant scatter, but the total number of samples was only 22 and 18, respectively. By comparison, the c_p /POC slopes for the bottle samples during those two periods were about 12×10^{-3} and 22×10^{-3} (Fig. 2, Table 2). This matches well the comparison made by Moran et al. (1999) of the pump POC measured by Bacon et al. (1996) with the bottle POC, where they found that most bottle POC concentrations ranged from equal, to a factor of 2 higher than pump samples.

Comparing the c_p /POC slopes for bottle POC (POC from JGOFS data base, c_p from unpublished CTD bottle files for up-cast data) with the

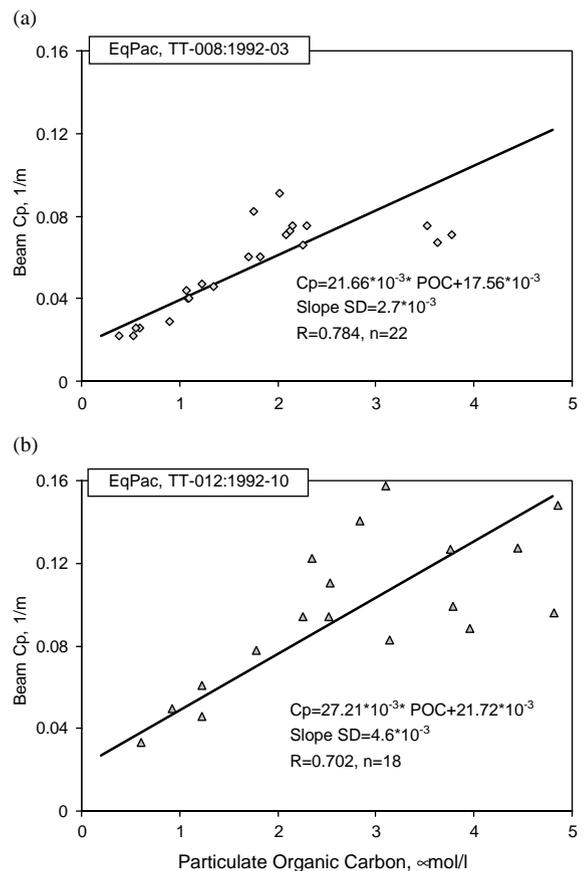


Fig. 1. Beam c_p as a function of POC concentration measured using in situ pumps during the US JGOFS EqPac program by Bacon et al. (1996) at 0° , 140°W (a) during El-Niño conditions, (b) during non-El-Niño conditions. Cruise numbers and year-month of data acquisition are given in boxes on top of each plot.

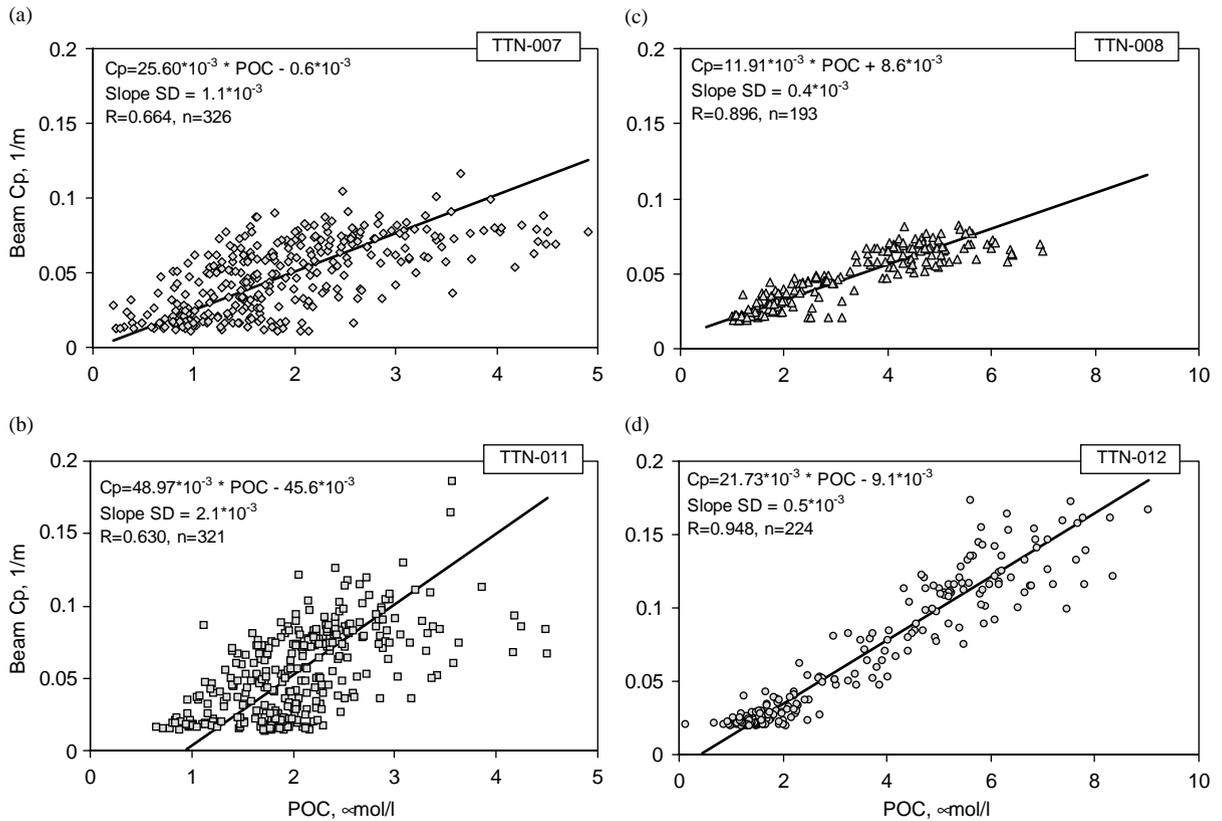


Fig. 2. Beam c_p as a function of POC concentration from water bottles during the US JGOFS EqPac program; (a,b) along two transects from 12°N to 12°S at 140°W (c,d) at 0° , 140°W during El-Niño conditions (a,c) and non-El-Niño conditions (b,d). Cruise numbers are given in boxes on top of each plot.

Bishop (1999) and Bacon et al. (1996) pump POC suggests bottle POC concentrations are a factor of 1.2–2.5 larger than those obtained using large volume pumps in the EqPac during the US JGOFS EqPac program (Table 2).

3.1.2. Arabian Sea

A comparison of bottle and pump POC values at 5m, 100m, and integrated from 0 to 100m reveals better agreement between the two methods during the NE and SW monsoons than during the intermonsoon (Fig. 3). Most of the monsoon period data indicated that bottle POC was 1–5 times greater than pump POC, although some pump values were greater than bottle values. During the intermonsoon period there was usually a subsurface maximum that may have caused more

scatter in data from the two collection systems. There was no prior plan to compare data from these two sampling systems, so samples were often taken hours apart, thus degrading the likelihood of agreement.

3.1.3. APFZ, Ross Sea

The POC concentrations plotted versus depth were vastly different for bottle and pump samples collected closest in time and space to the pump samples (Fig. 4). When bottle POC concentrations were plotted against pump POC concentrations, the ratio of POC determined using the two methods varied by a factor of 2–25 in the APFZ (Fig. 5a) and 5–200 in the Ross Sea (Figs 5b and c). The regression of c_p/POC for pump POC had little correlation (not shown), whereas the regression

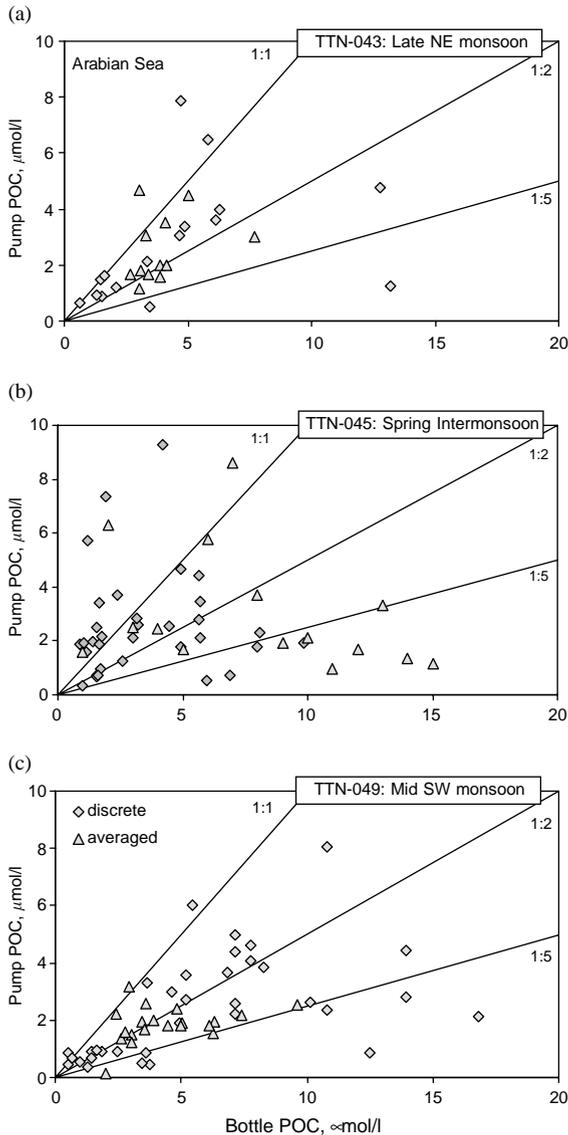


Fig. 3. Pump versus bottle POC from all pump stations during three cruises of the US JGOFS program in the Arabian Sea. Bottle data were averaged where pump samples were integrated from 0 to 100 m. Lines are constant ratios of 1:1 to 1:5.

between c_p and POC from the bottle data had a correlation coefficient of 0.90–0.95 (Fig. 6). The beam c_p data fit the bottle POC profiles much better than the pump profiles (Fig. 7). For a carbon-focused program like JGOFS, a discrepancy of this magnitude in POC measurements is a serious uncertainty that needs resolution.

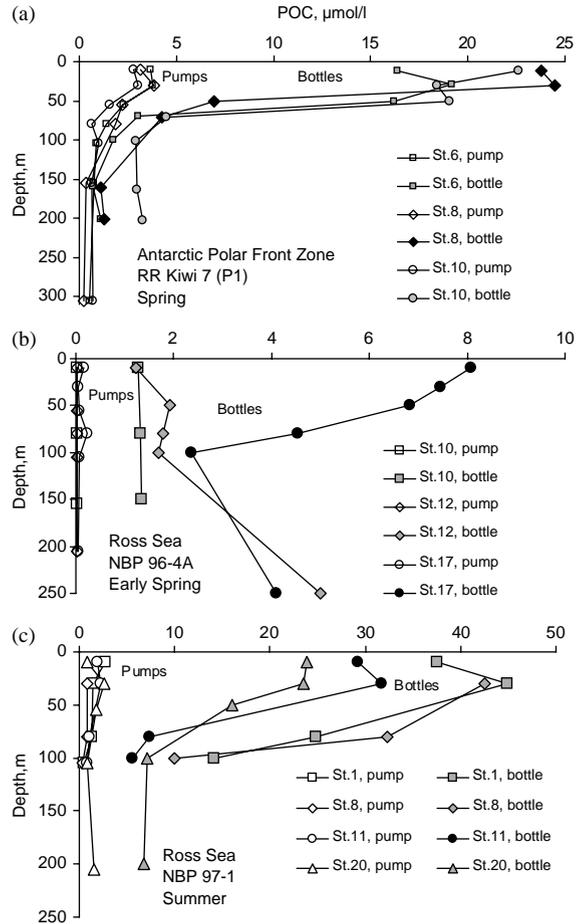


Fig. 4. Depth profiles of POC concentrations from bottle filtration (Gardner et al. 2000; JGOFS database) and in situ pumps (Cochran et al., 2000; Buesseler et al., 2001) in (a) the APFZ, (b) the Ross Sea during Process Cruise 1 (October 1996), (c) the Ross Sea during Process Cruise 2 (January–February 1997).

3.2. HTC-POC

There were two cruises in the Ross Sea when both bottle POC and HTC-POC were measured. During these cruises, the POC:(HTC-POC) regression slopes were 1.45 (Cruise NBP 97-1 in January 1997) and 1.87 (Cruise NBP 97-8 in November 1997) (Fig. 8). While these slopes are higher than unity, we noted that the HTC-POC values are likely underestimates of the true POC because of under-sampling of large particles and aggregates in 0.1 ml. Thus the regressions are upper estimates.

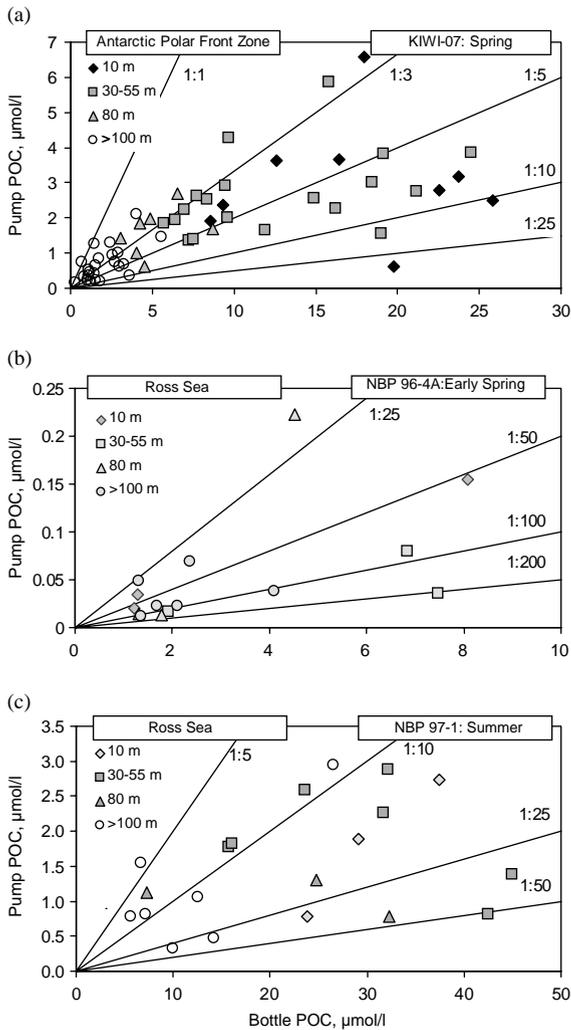


Fig. 5. POC concentrations (stations used in Fig. 4 plus extra stations in a) from in situ pumps versus bottles at the closest time and space position in (a) the APFZ, (b) the Ross Sea during Process Cruise 1 (October 1996) (c) the Ross Sea during Process Cruise 2 (January–February 1997). Lines are constant ratios of 1:1 to 1:200

More important, the ratio of pump POC to HTC-POC from the bottles is on the order of 0.02 for these cruises, suggesting that these particular pumps greatly underestimated POC in these conditions.

3.3. Vacuum experiment

The vacuum level had little effect on the concentration of Mississippi Canyon PM for

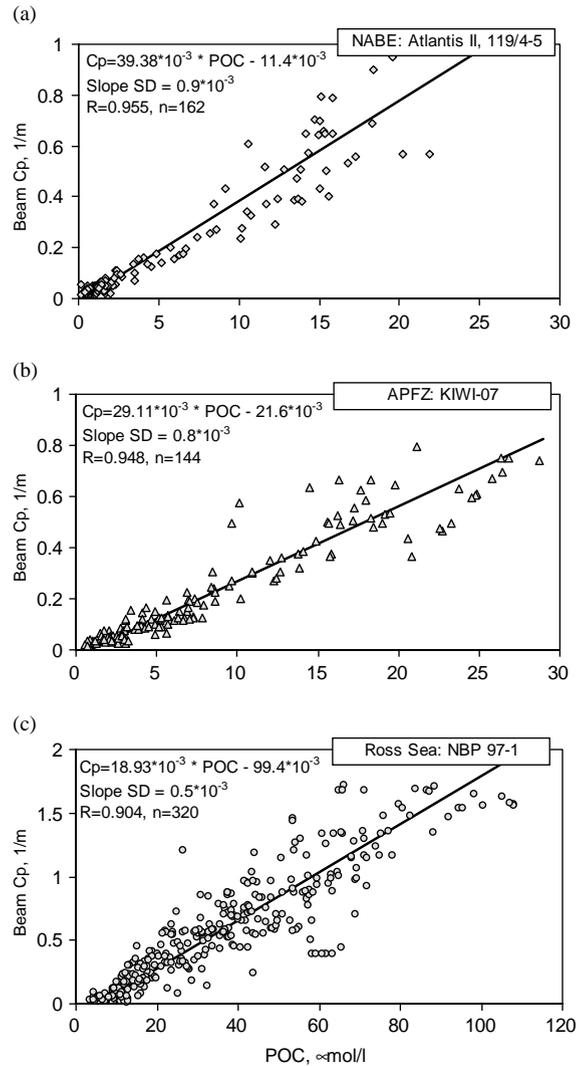


Fig. 6. Beam c_p as a function of POC concentration from bottle filtration during (a) the US JGOFS North Atlantic Bloom Experiment (revised from Gardner et al., 1993), (b) the APFZ, and (c) the Ross Sea. Project and cruise numbers are given in boxes on top of each plot.

samples between 80 and 270 m and, in fact, at 115 and 270 m, PM increased 15% and 25%, respectively, with increasing vacuum (Fig. 9). However, at 25 and 55 m the PM concentration decreased by 2–10 times at the greater vacuum of 0.83 atm. The sample from 55 m was taken at the thermocline, and the beam attenuation profile showed a large particle peak right above that depth. The samples

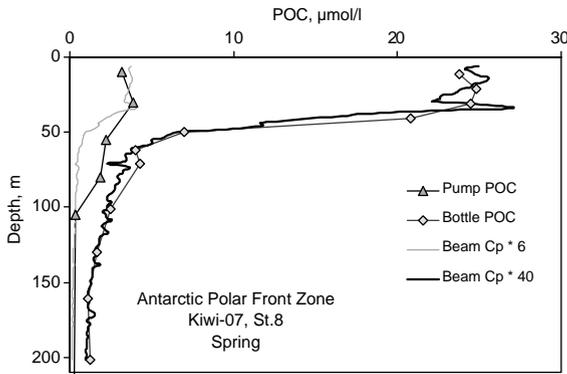


Fig. 7. Bottle and pump POC versus depth from station 8 of the APFZ, cruise RR-KIWI 7 (December 1997). Beam c_p is arbitrarily multiplied by 40 to optimize the fit with bottle POC data and by 6 to best match the pump POC data.

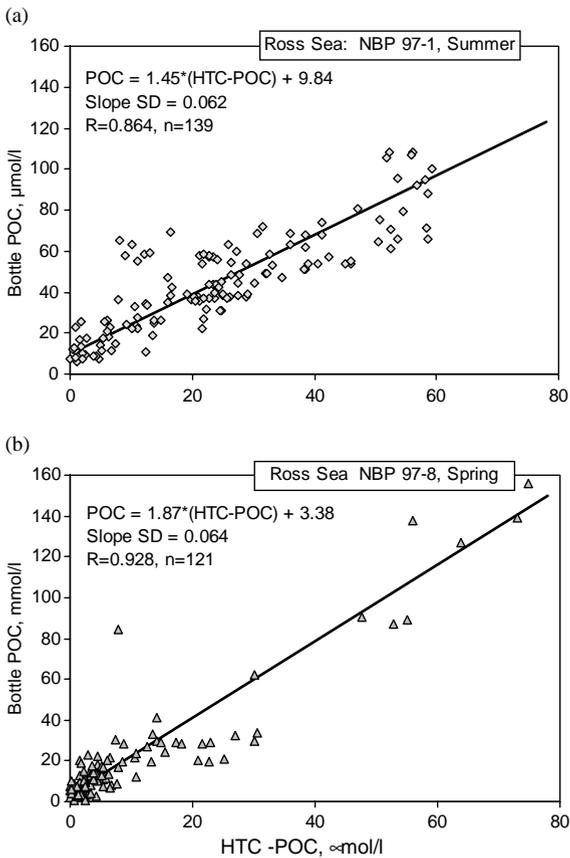


Fig. 8. Bottle POC versus HTC-POC in the Ross Sea for (a) cruise NBP 97-1 (January–February 1997) (b) cruise NBP 97-8 (November 1997).

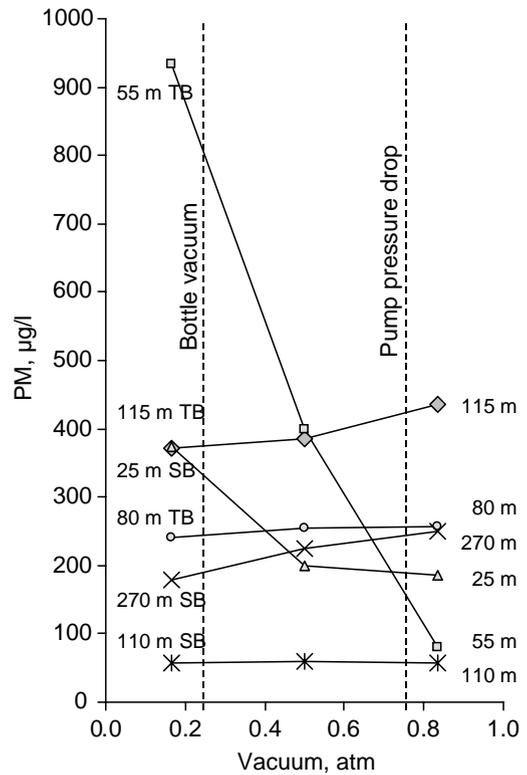


Fig. 9. PM concentration as a function of the vacuum at which the samples were filtered in-line from a Niskin bottle. Depths marked TB used triplicate-tripped bottles at that depth for the three different filtration vacuums. Depths marked SB were from the single bottle from which samples were filtered simultaneously using tubing splitters. The vertical dashed line at 0.25 atm indicates the vacuum at which most POC samples are filtered and the dashed line at 0.75 atm is the pressure drop across Bishop pumps (Altabet et al., 1992).

were taken from three different bottles tripped at the same depth less than a minute apart, but we cannot rule out the possibility that some of the PM difference resulted from collecting water with truly different particle content. The samples at 25 m were collected from the same bottle and filtered in-line simultaneously using tubing splitters.

4. Discussion

We find that there are two classes of discrepancies in bottle POC versus pump POC determinations: one specific to the very cold waters

Table 3
 $\text{POC}_{\text{bottle}}/\text{POC}_{\text{pump}}$ slopes from selected geographic regions

Area	Cruise	Ratio $\text{POC}_{\text{bottle}}/\text{POC}_{\text{pump}}$ ($\mu\text{mol/l}$)		References
		Most data	Full range	
MERL tanks		1		Moran et al. (1999)
Arabian Sea	TN043	1–2	0.5–10	this paper
	TN045	0.5–6	0.2–10	this paper
	TN049	1–5	1–10	this paper
EqPac	TT007, 011	1.2–2.5		Bishop (1999); Dunne et al. (1997)
	TN008, 012	1.3–1.8		Moran et al. (1999); this paper
Gulf of Maine	GOM	3–5		Moran et al. (1999)
West Arctic	WA95	3–5		Moran et al. (1999)
Arctic	AOS94	3–5		Moran et al. (1999)
Ant. Polar Front	Kiwi 7	2–10	1–25	Gardner et al. (2000); this paper
Ross Sea	NBP 96-4, 97-1	8–200	5–200	Gardner et al. (2000); this paper

experienced in the Southern Ocean and the other common to all of the waters sampled. We believe that the order-of-magnitude differences between pump and bottle POC in the Ross Sea and Polar Front are caused by reasons different from the factor of five or less difference observed in the Arabian Sea and EqPac. Each of these classes of discrepancy will be discussed here.

4.1. Discrepancy increase with colder temperatures/ higher latitude

Moran et al. (1999) carefully compared POC from bottle samples and an in situ pump submerged in one of the large environmental monitoring tanks at the University of Rhode Island. Concentrations were around $30 \mu\text{mol/l}$ for both bottles and pumps, filtering <11 with both methods. They also reported data from similar bottle and pump collections from field experiments at several other sites. The discrepancy between bottle and pump POC collated in Table 3 tends to increase as surface water temperature (based on latitude) decreases. This trend is most notable when we add the data from the APFZ and the Ross Sea. The differences between pump and bottle POC are a factor of 1.2–5 in the EqPac and Arabian Sea, increase to 3–5 in the Arctic, and are 2–25 in the Antarctic Polar Front and 5–200 in the Ross Sea. Note that the same or similar pumps

were used in the Arabian Sea, Polar Front, and Ross Sea.

Several pieces of evidence argue that the bottle POC values in the Southern Ocean are closer to true POC than pump POC. First, the beam c_p /POC relationships are close to those measured in the Arabian Sea, EqPac and NABE for both bottles and pumps (Table 2); i.e., the optics predict much higher POC concentrations in the Southern Ocean than measured with pumps. The vertical profile of c_p fits the bottle data much better than pump data (e.g. Fig. 7). The c_p profile in Fig. 7 is arbitrarily multiplied by 6 to optimize the maximum and minimum value of pump POC and by a factor of 40 to optimize the fit with bottle POC. Furthermore there is a close correlation between c_p and bottle POC, (Fig. 6), but not between c_p and pump POC. Second, the independently determined values of HTC-POC are much closer to the bottle POC values than pump values (Fig. 8). Third, Landry et al. (2002) counted numerous classes of plankton in water samples in the Ross Sea and Polar Front and converted the counts to carbon biomass. Their estimates (which did not include detritus) far exceeded the POC concentrations measured by pumps, and equaled about 40% of the POC measured from bottles, providing evidence that the bottle POC values are closer to true POC concentrations. There was also a reasonable correlation between bottle POC and biomass ($r^2 = 0.54$). Finally, the summary in

Cochran et al. (2000) noted that the pump ^{234}Th deficiency estimate of carbon export in the Ross Sea was 30–50% of the decrease in POC inventory calculated from bottle POC, with the difference likely accounted for by remineralization. Had they made a comparison with their own pump POC, their export estimate would have exceeded the decrease in POC by an order of magnitude, thus supporting the bottle POC values.

We cannot conceive of how this magnitude of discrepancy ($5\text{--}200\times$) can result from any of the errors typically considered—contamination, pressure differentials, etc. We have carefully examined the POC data for errors in reporting the values and units in which they were compared, and have found none. Buesseler and Cochran (2002, personal communication) have examined their pump data looking for similar errors and have found none. The operation of the pumps was similar in each area. The primary environmental differences between the southern ocean region and the “equatorial” region are water and air temperature and POC concentration. These types of in situ pumps have been operated in cold water (deeper than 1000 m) in warmer regions (Buesseler et al., 1998) without indication of problems or such drastic differences. However, in the Ross Sea the air temperature was usually below (often well below) 0°C , and the water was below 0°C throughout the water column on all but one cruise. Therefore, Cochran and co-workers did not prime the pump with distilled water as recommended in the McLane manual. The filters and Mn cartridges were saturated before deployment. The question arises as to whether the filter retention is different in very cold water or if the pumps or flow meters malfunctioned for any reason. To achieve low POC concentrations, the amount of water filtered would have to be much less than recorded by the flow meter, which argues against a frozen or sluggish flow meter. A temperature effect is consistent, however, with the fact that the pump POC values in the Ross Sea showed a larger discrepancy with bottle POC values than in the Polar Front where air and surface temperatures were still near freezing, but less often sub-zero.

Cochran et al. (2000) note that a check on the accuracy of the flow volumes is whether the ^{234}Th collected was in equilibrium with the expected ^{238}U in the water. They note that equilibrium could not be reached if volumes were off by a factor of >10 , and equilibrium was usually achieved. However, they also noted that about 50% of the Mn sorber cartridges had unusually low efficiencies, which they attribute to the formation of ice crystals when distilled water-saturated cartridges contacted cold air or sea water. They note that the ice crystals could have prevented water from contacting the Mn and adsorbing Th. They estimate corrections for efficiency, but when the efficiency was too low, they have discarded the data.

There is also a strong increase in the percent of ^{234}Th collected in the pump particulate phase as temperature increases. In the Ross Sea ($T < 0^\circ\text{C}$) the cruise averages of particulate ^{234}Th were 3–6% of total ^{234}Th collected (JGOFS data base) and there was little variation in the profiles with depth (Cochran et al., 2000). In an Arctic polynya ($T \leq 0^\circ\text{C}$), particulate ^{234}Th was 5–10% of the total ^{234}Th (Cochran et al., 1995). Cruise averages at stations in the Polar Front ($T = -1.6^\circ\text{C}$ to 5°C) were 13–16% particulate ^{234}Th , but in the Arabian Sea ($T = 23\text{--}27^\circ\text{C}$) cruise averages of particulate ^{234}Th increased to 24–46% (JGOFS data base). Are these real regional differences in ^{234}Th partitioning or is this evidence that in the coldest environments the pump filters were less effective at collecting particulate ^{234}Th and POC for some reason? For example, if the filters cracked or water somehow by-passed the filter, particles would not be collected, but the ^{234}Th could be collected by Mn cartridges. Buesseler (2002, personal communication) noted that if filters were cracked and allowed water to pass unfiltered, it would show up as a stain on the fritted filter support and the sample would have been discarded. Cochran et al. (2000) noted that even if the pump POC values are too low, it would not affect their carbon export estimates using the ^{234}Th deficit method as long as all ^{234}Th is collected in either particulate or dissolved state (filters and Mn cartridges) and the $\text{POC}/^{234}\text{Th}$ ratio is unbiased on their filters.

A second possible reason for larger differences between bottle and pump POC in the Ross Sea is

the presence of different plankton communities. Most stations in the Ross Sea were dominated by *Phaeocystis antarctica* colonies. Perhaps these were collected with different efficiencies. The optical data, however, did not reveal any difference between POC and community types in the Ross Sea. There were several stations in the Ross Sea dominated by diatoms, but the c_p /PM ratio from these stations was indistinguishable from those at stations dominated by *Phaeocystis antarctica* (data in Fig. 6c are not differentiated by phytoplankton type, but there are no aberrations in the data that could cause order-of-magnitude increases in the c_p /PM slope). In the Polar Front there was a slight difference in the c_p /PM ratio north and south of the front, but no difference in the c_p /POC data (POC in Fig. 6b). Buesseler and Cochran (2002, personal communication), Cochran et al. (1995) and Moran et al. (1999) report other data sets in cold, high-latitude waters with bottle/pump discrepancies of a factor of 4–10. Plankton in the southern ocean tends to be much larger (diatoms, *Phaeocystis*) than plankton in the EqPac, yet the largest bottle/pump differences are in the cold regions. If filter size cutoff was the reason for differences in POC collected, one would expect smaller differences in the Southern Ocean where plankton are larger.

At this point we can not adequately explain why the pump values are relatively low, so the problem needs further investigation. We will set aside the large discrepancies between pumps and bottles in the Southern Ocean and focus now on the 1.2–5-fold differences in POC observed in other data sets. While factors of 1.2–5 seem small compared to factors of 2–200, they are still unacceptably large for a program like JGOFS.

4.2. Reasons for smaller differences at lower latitudes

4.2.1. Adsorption of DOC onto filters and volumes filtered

Determining proper blanks and testing for adsorption of DOC onto filters has been a concern since the first measurements of POC. In an attempt to determine blanks for POC measurements, Menzel (1966) filtered 0.5–4 l of water from

different environments, plotted POC mass as a function of liters filtered and accepted the positive intercept on the carbon axis as the blank. For three very different water types the intercept was 25 $\mu\text{g C}$ (2.1 μmol) for glass fiber filters. He recommended this procedure for the determination of filter blanks to include adsorption of DOC during filtration. Menzel also filtered 1 l of water 15 times with separate filters and found that the carbon on each filter was about 15–20 $\mu\text{g C}$ (1.25–1.67 μmol). Cumulatively the amount of DOC lost during the filtration was roughly equivalent to the amount of POC measured on the 15 filters.

Using paired filters Loder and Hood (1971) determined that the adsorption of DOC onto glass fiber filters ranged from 0 to 10 $\mu\text{g C}/\text{filter}$ (0–0.82 $\mu\text{mol C}/\text{filter}$). Feely (1974) used four layers of 25 mm GF/F filters to test for DOC adsorption and found little variation of organic carbon on the bottom 3 filters. He calculated adsorption of 7.5 $\mu\text{g C}/\text{filter}$ (0.63 $\mu\text{mol C}$) when filtering 1 l, and 11.4 $\mu\text{g C}/\text{filter}$ (0.95 $\mu\text{mol C}$) when filtering 4 l, suggesting that saturation is not complete after 1 l has been passed through the filter.

Hickel (1984) tested for adsorption of DOC onto GF/C filters and concluded that adsorbed DOC does not add weight to the seston (POC) measured with GF/C. Abdel-Moati (1990) also evaluated the adsorption of DOC onto GF/C filters using both eutrophic and oligotrophic waters. However, his measurements indicated that DOC added 3.5–15 $\mu\text{g C}/\text{filter}$ (0.29–1.25 $\mu\text{mol C}/\text{filter}$), which equaled 21–33% of the POC load on the filter. He reported that the problem of DOC interference in POC determinations was greater in oligotrophic than eutrophic waters.

In a manner similar to Menzel (1966), Moran et al. (1999) filtered 0.1–0.55 l of water with high POC concentration (40–70 $\mu\text{mol C}/\text{l}$) and plotted POC mass as a function of volume filtered. They found a linear correlation between mass and volume with an intercept of about 2 μmol above the blank value of an unused filter using 25-mm circular subsamples from the 142-mm filter. While this may be a way to check for DOC adsorption, as long as there is a non-zero intercept on the y -axis, the same data plotted as concentration versus volume filtered show that concentration is a

function of volume filtered. Moran et al. (1999) suggested that one could also use double filters, with the underlying filter as the correction for DOC adsorbed onto sample filters. Smith et al. (1996) have traditionally used this method to obtain a POC blank that includes DOC adsorption, determining both surface and deep-water blanks. A similar method recommended by John Martin (<http://usjgofs.whoi.edu/eqpac-docs/proto-18.html>) is to pass filtered seawater through an unused, precombusted filter to obtain a blank. The above factors strongly suggest that, one of the latter two methods replace the JGOFS POC protocols, which presently call for selecting 3 unused filters per cruise from a lot of precombusted filters as a blank, without any exposure to filtered seawater (Knap et al., 1994).

DOC adsorption does not explain the much higher bottle POC values in colder water (higher latitude), but it could be important in other environments where POC concentrations are only a few $\mu\text{mol/l}$. For areas where the bottle-pump differences are not large, Moran et al. (1999) noted that the POC discrepancy may not be a matter of bottles versus pumps, but small volumes (bottles) versus large volumes (pumps) because of the different signal to noise ratio; a point made by others as well in reference to contamination as well as DOC adsorption. Therefore, it is important (1) to use a proper blank to correct for adsorption and (2) to filter enough water (per unit area of filter) to have a distinct signal for POC. There are many data suggesting that POC should be $\sim 1 \mu\text{mol/l}$ below the euphotic zone (Wangersky and Gordon, 1965; Menzel, 1967; Gordon, 1971), yet much of the JGOFS data shows POC values $> 1 \mu\text{mol/l}$ below the euphotic zone.

4.2.2. Spatial patchiness and replication

To test for small-scale patchiness of POC in the ocean, Wangersky (1974) tripped 5 Niskin bottles simultaneously at a single depth using a specially configured CTD rosette. He then sampled and filtered the contents of each Niskin for POC using standard methods. He calculated a standard deviation of $1.3 \mu\text{g C/l}$ (i.e. $\sim 0.11 \mu\text{mol C/l}$) and stated that no samples $< 5 \mu\text{g C/l}$ (i.e. $0.42 \mu\text{mol C/l}$) apart should be considered to be really different.

He attributed the small variations in samples that he found to patchiness in the ocean.

Reproducibility from duplicate samples of POC is seldom reported. In the Southern Ocean the replicate variation was reported as $\pm 5\%$ (Gardner et al., 2000) and $\pm 7\%$ in the Arabian Sea (Richardson, unpublished data). It appears that neither patchiness nor reproducibility is sufficiently large to account for a significant portion of the difference (up to 5-fold) between pump and bottle samples outside of cold surface waters.

We know of no tests where duplicate POC water samples were collected from the same bottles and sent to different laboratories for analysis and comparison. However, our group at Texas A&M University has collected in excess of 200 samples on different cruises from the same region of the ocean and sent them to different labs for analysis. We then correlated c_p with POC. While a comparison of POC concentrations at different times reveals nothing about accuracy, a comparison of the c_p/POC ratios is relevant. The slopes of the correlations differed by only 10%, suggesting no large difference in POC analysis from different labs, assuming particles were similar in size, shape and composition. King et al. (1998) reported that during an intercomparison evaluating ten laboratories the standard error of the mean for POC concentrations in marine sediments and sediment trap material was only $\pm 8\%$, which is much less than the magnitude of differences between bottle and pump samples.

4.2.3. Contamination during handling

It is highly desirable to minimize contamination by keeping water enclosed from the time of collection through filtration using in-line tubing. However, JGOFS protocols (Knap et al., 1994) prescribe sampling of POC using the funnel filtration described above in Methods. Water samples were exposed to air during collection from Niskin bottles and as they were poured into the funnels during filtration. A study that compared particulate organic nitrogen (PON) filtration in open and closed systems was carried out by Altabet et al. (1992). Water from the bottles was emptied into large, pre-cleaned vats and then filtered. To test for contamination artifacts, a set

of bottle samples was processed without the use of vats. The PON concentrations were not significantly different over a range of PON from 0.1 to 1.0 $\mu\text{mol/l}$. The authors pointed out that samples with low concentrations are more likely to be affected by contamination.

Altabet et al. (1992) also compared PON concentrations measured from water bottles and in situ pumps. Concentrations of PON filtered from water transferred from Niskin bottles were found to be as much as eight times greater than PON obtained through in situ filtration at the same location and at about the same time in a Gulf Stream ring. Differences were large throughout the water column and varied from station to station.

The same authors made a similar bottle/pump comparison at the OFP station (nominally located at 31°50'N, 64°10'W) near Bermuda, using a different in situ pump. The differences between bottle and pump PON were not as large as in the Gulf Stream ring, but were still significant (factor of 2–4). To explain the differences the authors considered the effects of different retention sizes for the filter types used by the two techniques and the lack of large particles in Niskin bottles, but these accounted for only a fraction of the discrepancies in one set of samples. They seemed to attribute most of the concentration difference to sample handling and loss of sub-micron particles because of different filter types. When PON concentrations were low, as in deep water, contamination obviously would have a larger impact than, when natural PON concentrations were high. Contamination artifacts are always a concern, but the lack of a significant difference between bottle samples processed with and without transfer vats (described above) demonstrated that the vats were not the primary source of difference between the bottle and pump POC concentrations. Larger filter “pore cutoffs” and larger pressure drops across the pump filters are more likely causes for the differences.

During the US JGOFS North Atlantic Bloom Experiment cruises, POC was sampled from bottles and filtered in a closed system by directly transferring water to a closed carboy through a tube and then pressure filtering all the water in the carboy via a tube at the base of the carboy. In all

subsequent JGOFS process studies bottle POC was determined from water samples collected in Nalgene bottles that were then inverted into funnel filtration racks. When POC was regressed against beam c_p using POC data obtained from both open (EqPac, Arabian Sea, Ross Sea, APFZ) and closed systems (NABE), the regression slopes were similar (Table 2). Furthermore, if the open sampling method introduced a constant mass error due to contamination, the % error should decrease as POC values increased. This would cause larger errors at low concentrations than at high concentrations. No such pattern was observed in the data collected. If the contamination errors were random, this should decrease the c_p /POC correlation. Again, no such trend was obvious.

4.2.4. Artificial creation of POC from DOC during processing

Sutcliffe et al. (1963) and Riley et al. (1964, 1965) suggested that passing small air bubbles through seawater could convert DOC into POC, with bubbles providing nucleation sites for DOC. A commonly used method for filtering water from Niskin bottles is to fill (after 3 rinses) a dark bottle, and then pour the water into a funnel system holding a 25-mm GF/F filter. The dark bottle is turned upside down and rests on the funnel lip. As the water filters below the bottle opening, large air bubbles rise through the bottle releasing more water into the funnel system. One might suspect that during the bubbling, DOC is converted to POC and is collected on the filter.

A later re-evaluation by Menzel (1966) suggested that “bubbling is an unlikely mechanism for the production of carbon-producing particles.” However, Batoosingh et al. (1969) pointed out that, by first filtering the water, Menzel (1966) had removed the larger colloidal and particulate materials necessary for further particle formation by surface coagulation. These authors and others (Johnson et al., 1986; Kepkay and Johnson, 1989) showed that the rate of particle coagulation at bubble surfaces depends on the distribution of dissolved, colloidal, and larger particles, and that the process of coagulation with bubbling is real. Its importance relative to the question addressed here

remains unquantified. Note, however, that the bubbles evaluated by the latter authors were fine and numerous, while those created when draining the bottles used for POC analysis are large and few.

4.2.5. Particle retention as a function of particle and filter type

We have long known that the boundaries between particulate, colloidal and dissolved organic matter are arbitrary, based primarily on mechanical and material limitations (Sharp, 1973). However, as we learn more about the structure of organic carbon at the fine end of the spectrum, we find that particle size may be even more difficult to define because there is evidence that organic carbon may be more of a continuum (Azam, 1998) and that polymers in seawater form a gel with ephemeral bonds (Chin et al., 1998). A gel-like structure would make it much easier for organic carbon to pass through all types of filters, but it is reasonable that the pressure drop across a filter is a controlling factor on the amount of carbon retained (Goldman and Dennett, 1985).

Bishop and Edmond (1976) tested the filtration efficiency of Mead 935-BJ glass fiber filters in their pump system using a Coulter Counter to measure the percentage of particles retained by the filter. They found that “relative to Whatman GF/F filters, one Mead glass fiber filter retained 65% of the particles counted in the 1–1.25 μm size range and 74% of those in the 0.8–1 μm range. Similarly, two layers of glass fiber filters retained 95% and 96% of the particles in these two size classes, respectively”. In absolute values, the single glass fiber filter retained 83% and 55% of these two size classes. Bishop and Edmond (1976) argued that the retention percentage of glass fiber relative to GF/F was more appropriate than absolute values because of the high noise levels in the two smallest sizes of the Coulter Counter. Thus they concluded that two layers of glass fiber filters removed 95% of the particles down to 0.8 μm .

Regardless of whether one accepts the relative versus absolute values from the tests of Bishop and Edmond (1976), the real uncertainty lies in the type of particles used in these filtration tests.

Rather than making tests with natural populations found in seawater, they used Peerless No. 2 kaolinite clay (R.T. Vanderbilt Co., N.Y.) provided by one of the authors of this paper (WDG). Using a subsample from the same container of Peerless No. 2 kaolinite used by Bishop and Edmond (1976), the clay size distribution was determined recently after wet sieving (removing particles $> 63 \mu\text{m}$) and Coulter-Counter analysis (Fig. 10). More than 90% (by volume) of the clay was $> 5 \mu\text{m}$ and contained little carbon. Thus, while two layers of the Meade filters may remove 95% of the clay particles $> 0.8 \mu\text{m}$ in their test, the removal efficiency of natural marine particles, most of which are $< 5 \mu\text{m}$ and are carbon-rich, remains untested for Meade glass fiber filters. Furthermore, pump programs later employed MicroQuartz filters, with a stated minimum cutoff size of 1.0 μm (Bishop et al., 1985; Cochran et al., 2000; Buesseler et al., 2001). While the difference between 0.7 (GF/F cutoff) and 1.0 μm is small, many marine particles are in this size range (Koike et al., 1990). Altabet (2002, personal communication) analyzed by flow cytometry filtrate from sea water passed through a microquartz filter and another sample that had passed through a glass fiber filter, finding that more particulate material had indeed passed through the microquartz filter than the glass fiber filter.

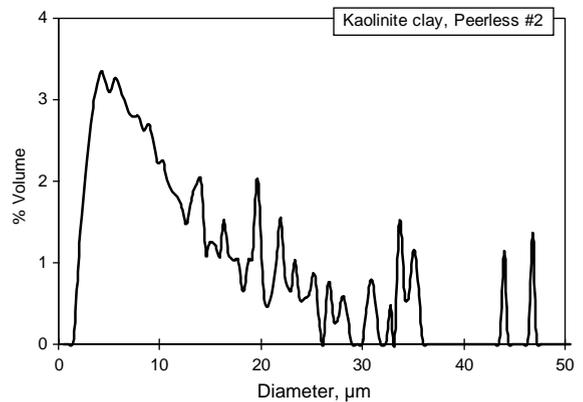


Fig. 10. Coulter-Counter-derived size distribution of Peerless no. 2 kaolinite clay used by Bishop and Edmond (1976) for calibration of filtration efficiency of Mead glass fiber filters. The sample was wet-sieved at 63 μm before analysis.

Another important factor that may be responsible for lower pump POC values is that the [Bishop and Edmond \(1976\)](#) calibration of in situ pump filtration using robust kaolinite particles may have led to the false sense that pumps were collecting all marine organic particles at a high efficiency (up to 95%). If natural surface seawater with a typical plankton community had been used in these experiments rather than inorganic clay minerals, we suggest that much lower efficiencies would have been determined. Experiments should be made to test this. Shifting from the use of Meade glass fiber filters (0.8 μm cutoff) to micro quartz filters (1.0 μm cutoff) increased the window size of POC being missed compared to GF/F filters (0.7 μm cutoff).

[Dunne et al. \(1997\)](#) noted that bottle POC concentrations in the EqPac program were greater than pump POC concentrations. They compared collection of chlorophyll and ^{234}Th from bottle and pump pairs and concluded that pump POC concentrations had to be increased by factors of 1.12–2.32 for accurate comparison with the bottle POC, the difference being attributed to loss of fine POC because of the larger pore size of pump quartz filters. [Bishop \(1999\)](#) made no reference to this when analyzing the same data, but our assessment from c_p /POC comparisons ([Table 3](#)) closely matches that of [Dunne et al. \(1997\)](#).

4.2.6. Pressure drop across the filter

We are not aware of any published experiments where POC was filtered under different vacuums, but we have some carefully controlled experiments where total PM was measured from samples drawn through 0.4- μm Poretics polycarbonate membrane filters at three different vacuums ([Fig. 9](#)). The vacuum level had little effect on the concentration of PM for samples taken from depths between 80 and 270 m. Although at 25 and 55 m depths the PM concentration decreased by 2 and 10 times, respectively, at a vacuum of 0.83 atm as opposed to 0.17 atm, we cannot be certain that the three bottles tripped at 55 m collected the same water since they were just below a large particle maximum seen on the down trace of c_p . The samples at 25 m were all filtered simultaneously from the same bottle, so the factor

of 2 difference is likely to be real. [Cochran \(2002, personal communication\)](#) reported that he and colleagues have filtered POC from samples from Stony Brook Harbor (New York) and cultures of robust diatoms at the three vacuums used in [Fig. 9](#) and found no difference in POC concentrations.

While not evaluating POC specifically, [Goldman and Dennett \(1985\)](#) found that vacuum pressure differentials > 25–100 mm Hg (0.037–0.148 atm) across polycarbonate filters caused cell breakage in fragile phytoplankton species that led to the accumulation of recently fixed ^{14}C in the filtrate. GF/F filters were much less problematic in this regard. For most in situ pumping systems the pressure differential has not been reported (e.g., [Bacon et al., 1996](#); [Buesseler et al., 2001](#); [Sherrell et al., 1998](#)).

Little was mentioned by [Altabet et al. \(1992\)](#) about the pressure drop (ΔP) across the filters, but data were provided in their [Table 1](#). The in situ pressure drop across the filters in Bishop's pumps began at 0.75–1.05 atm. The pressure differential for the bottle samples was reported incorrectly in units of atm, and should have been in units of psi ([Altabet, 2001, personal communication](#)), yielding a ΔP of only 0.2–0.4 atm. The different in situ pumps used at the OFP site had no ΔP listed while the bottle samples there had a 0.4–0.7 atm ΔP reported. Most filtration of POC from bottles is done at <0.25 atm (e.g. [Sharp, 1974](#); [Gardner et al., 2000](#)). In light of the large decrease in mass concentration at the high pressure differentials reported in our experiments earlier in this paper, it is certainly possible that differences in pressure differentials across the filters contributed significantly to the difference in PON concentrations reported by [Altabet et al. \(1992\)](#). The fact that PON concentrations showed better agreement at the OFP site may result from [Altabet et al. \(1992\)](#) using higher ΔP for the bottle samples, or the ΔP for the pump may have been lower (ΔP was not reported).

Even the bottle POC concentrations may be too low based on detailed studies at the OFP site by [Altabet \(1990\)](#). He tested different filter types and found that of the POC retained on a 0.2 μm Anopore aluminum filter, 40% had passed through a GF/F filter (0.7 μm size cutoff). He

found that the passage of POC through quartz fiber filters (QM-A), like those commonly used in pumps, was 55%. Waterbury et al. (1986) found that 50–80% of *Synechococcus* pass through 1- μm membrane filters and that 80–85% of all bacteria pass through 0.6- μm filters in Sargasso Sea waters. According to Turley et al. (1986) and Fuhrman et al. (1989), bacteria may be the most important components of the 0.2–0.7- μm fraction. Thus, a significant portion of bacteria and viruses are drawn through filters at high vacuum, perhaps even at low vacuum. Furthermore, plankton without skeletons might be deformed and pulled through the fiber. At a higher pressure differential, cells may be disrupted or shredded (Goldman and Dennett, 1985), allowing large amounts of POC to be drawn through the filters. Organic matter associated with frustules (i.e. cell walls or debris) could also be stripped off and drawn through the filter under large pressure differentials. Thus, the much larger pressure difference across the filters generated by at least some pumps may contribute to some of the 1.2–5-fold higher POC concentrations for bottles than in situ pumps.

Pressure differences are likely to increase as a filter is loaded with POC. This overloading appears to occur at much lower volumes of water filtered than previously thought. Carlson et al. (2002) found that retention of carbon-14 labeled POC was reduced on 25-mm GF/F filters at volumes greater than 30 ml in waters where a *Phaeocystis* bloom was in progress. This is an issue that needs further investigation, keeping in mind that mass loading per unit filter area is the important variable, not total volume or mass filtered.

4.3. Other evidence for true POC concentration

Using the HTC method of analyzing POC produced values much closer to bottle than pump values in the Ross Sea. We note, however, that the POC:(HTC-POC) ratio was 1.45 on one cruise and 1.87 on the other (Fig. 7). The zero intercepts for filter POC are about 10 and 3 $\mu\text{mol C/l}$, respectively. One might argue that the intercepts are the adsorption blanks and that if the HTC method yields the true POC, then bottle filter POC values

are too high. The earlier caveats about the HTC method, however, noted the very small volume collected (20–40 ml) and analyzed (0.1 ml) and the fact that the HTC technique was being used as a quick estimate of POC, not a rigorously developed method.

Overall, the c_p /POC ratios published from bottle samples are of similar value, though they vary some by season and location (Table 2, Gardner et al. 1993, 2000, 2001; Gundersen et al. 1998; Claustre, 1999). Bishop (1999) and Bishop et al. (1999) also report high correlation coefficients in their c_p /POC relationships, but their equation applies only to POC > 1 μm (their filter size cutoff). Furthermore, if large pressure differences across the filter results in POC from particles > 1 μm being drawn through the filter, the c_p /POC relationship from pumps must be used with great caution. Dunne et al. (1997) and our data suggest that pump POC in EqPac was low by a factor of 1.12–2.5, so POC estimates based on the c_p /POC equation in Bishop (1999) will underestimate the true POC concentration in aquatic environments. Equations using c_p /POC relationships from bottle data without accounting for adsorbed DOC may over-estimate POC when concentrations are low (< $\sim 2 \mu\text{mol/l}$).

5. Conclusions

The data suggest that the discrepancy between bottle and pump POC increases with decreasing surface temperature based on latitude. The disagreement is largest in the Polar Front and Ross Sea. Independent methods of estimating POC—optics, HTC on water samples, and organism counts converted to POC, ^{234}Th deficiency estimates of carbon export—are in much closer agreement with bottle than pump POC values at high latitudes. There is no unambiguous explanation for this difference, though we suggest the difference is more likely methodological than physiological.

Bottle-pump POC differences are much smaller at lower latitudes, but still significant (1.2–5 times higher bottle POC). In situ pumps have the advantage of filtering large volumes of water and

collecting large samples of PM; however, this advantage is counter-balanced by the fact that more fine organic matter is drawn through the filters because of the larger effective pore size of the filters typically used with pumps and perhaps because of the larger pressure drop across the filters. These two factors seem to be the primary cause for differences between bottle and pump POC when POC greater than $\sim 2 \mu\text{mol/l}$. Using GF/F filters with pumps and lowering the pressure drop across the filter should increase POC retention and lessen the discrepancy with bottle POC.

It appears that the JGOFS bottle POC measurements have not had proper blank corrections that included adsorption of DOC onto the filters, but there is not a simple correction that can be made without knowing the adsorption blank (which could only be estimated) as well as the volume filtered (data are available). Errors would be largest at low concentrations ($< \sim 2 \mu\text{mol/l}$), which includes most sub-euphotic waters. It is important to change JGOFS protocols to include a blank exposed to seawater.

We have presented various tests and comparisons that have been made at different times comparing different pumps and bottle methods in different environments. The data presented and cited in this paper explain many of the differences in POC measured with bottles and pumps. We suggest, however, that a carefully planned suite of experiments is needed using pumps, bottles and identical filter types in warm and sub-zero waters where POC is known to have a wide range of concentrations. Coincident measurements should be made of as many parameters as possible—pumps with known and controllable pressure drop across the filter, bottle samples taken at the same time and depths and analyzed with standard filtration methods, HTC analysis of the water, simultaneous measurements of in situ beam c_p , organism counts, C:N ratio determination, and measurements of total PM and chlorophyll. Since carbon is the “coin of the realm” for JGOFS and many future programs seeking to understand biogeochemical processes, it is imperative that we come to closure on the methods used to measure particulate carbon.

Acknowledgements

We thank Sarah Searson, and Christopher Nugent for data processing and graphics assistance and many JGOFS PIs for lively discussions. Comments from Mark Altabet, Ken Buesseler, Kirk Cochran and Mike Bacon as well as from two anonymous reviewers were helpful, though we take responsibility for our conclusions. This research was supported by NSF grants OCE 95-30837 to W.D.G. and M.J.R. and OCE 95-30845 to D.H. and C.A.C. This is US JGOFS contribution number 764.

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