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Marine Chemistry 67 (1999) 33–42

MARINE CHEMISTRY

Differences in seawater particulate organic carbon concentration in samples collected using small- and large-volume methods: the importance of DOC adsorption to the filter blank

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Received 20 August 1998; accepted 11 May 1999

Abstract

Particulate organic carbon (POC) data collected by small-volume (~ 1–2 l) bottle filtration and large-volume (~ 100–600 l) methods are compared for samples from the central Arctic, Equatorial Pacific, Equatorial and South Atlantic, Gulf of Maine, and Narragansett Bay. Small-volume samples were collected using Niskin® and Go-Flo® bottles and large-volume samples were collected using in situ pumps and large-volume bottle filtration. Results indicate that small-volume bottle POC data are often greater than large-volume results, by as much as 2–4 times, in regions with low POC concentration ($< \sim 5$ μM). The implication is that POC concentrations determined by small-volume bottle filtration in regions characterized by low POC concentrations, i.e., in the majority of surface open ocean and deep waters, may be erroneously high. We suggest the most likely explanation is adsorption of DOC to the filter, which is rarely quantified yet can significantly increase the filter blank. The magnitude of DOC adsorption was assessed using coastal seawater by determining the *y*-intercept of a plot of the organic carbon retained by a glass-fiber filter against the volume filtered. The intercept was approximately two-fold greater than the precombusted filter blank, which we attribute to DOC adsorbed to the filter. Thus, when seawater POC concentrations are similar to, or less than, the precombusted filter blank, not correcting for the true in situ blank can result in erroneously high POC concentrations. To avoid this artifact, we recommend using large-volume sampling methods, which result in a greater quantity of POC per unit area of the filter relative to the filter blank. When large-volume filtration is not possible, we recommend a simple method to evaluate the true in situ filter blank. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: seawater POC concentration; DOC adsorption; filtration

1. Introduction

There are two primary methods used to collect suspended particulate matter in oceanic waters for the determination of particulate organic carbon (POC) concentration. The most widely used method involves deploying a water bottle on a hydrowire or CTD rosette at a fixed depth to collect a discrete water sample for subsequent filtration. With this method, small sample volumes of ~ 1–2 l are typically filtered under mild vacuum through a 25-mm diameter, 0.7-μm pore-size, precombusted glass-fiber

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PII: S0304-4203(99)00047-X

filter. The second method involves the use of in situ pumps, which typically filter several 100–1000 l of seawater from a fixed depth through a 142- or 292-mm diameter precombusted glass-fiber filter of similar pore size. In both cases, POC concentrations are quantified by high-temperature combustion. Provided that the same pore-size filter is used, the principal difference between the two sampling techniques is the volume of water filtered and hence the amount of POC collected per unit area of the filter.

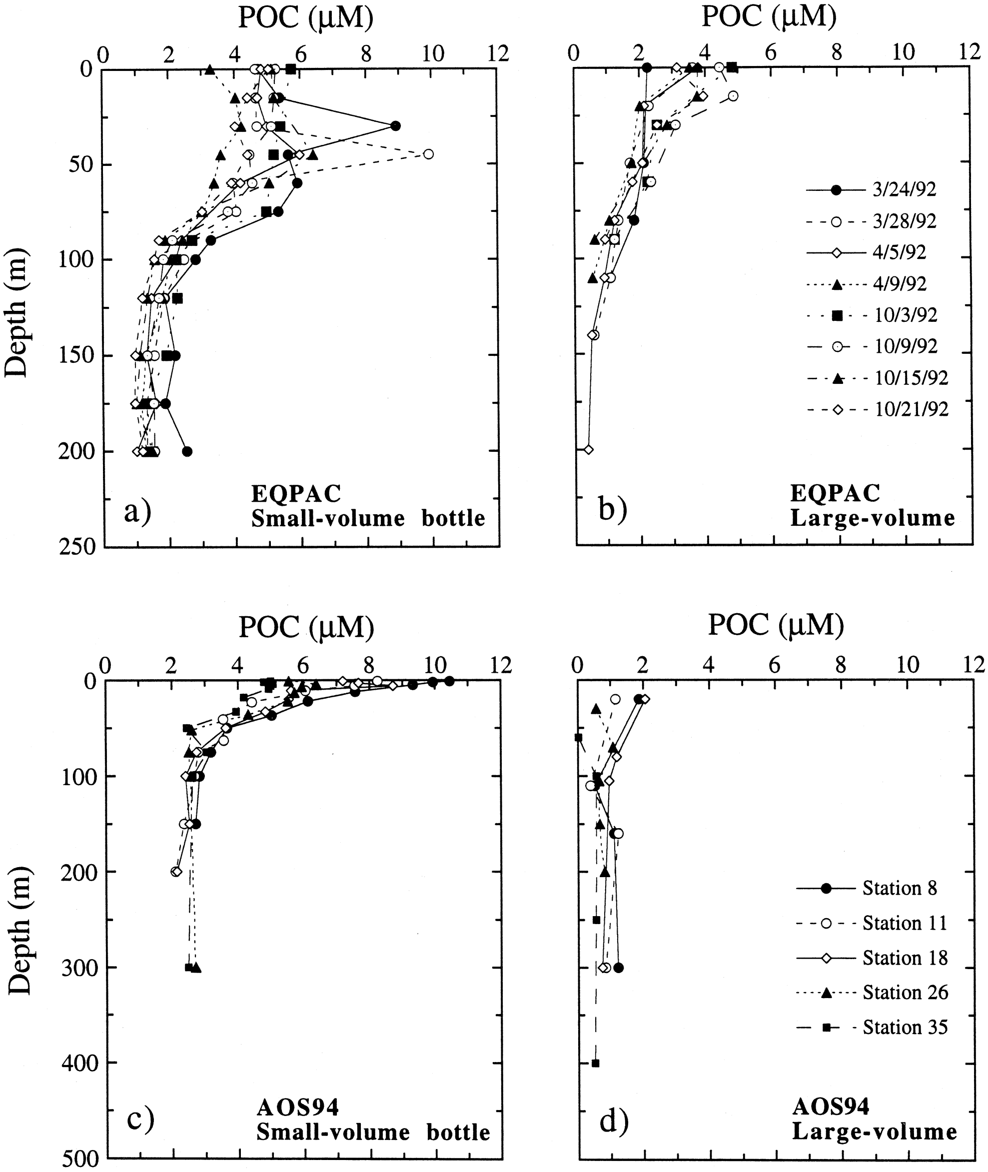

Fig. 1. POC depth profiles. (a) JGOFS EQPAC bottle data (Ducklow, 1994); (b) JGOFS EQPAC large-volume in situ pump data (Bacon et al., 1996); (c) AOS94 bottle data (Wheeler et al., 1997); (d) AOS94 large-volume in situ pump data (Moran et al., 1997). The JGOFS time-series data were collected at the equator at 140°W. The AOS94 small-volume samples were collected aboard the *USCGC Polar Sea* and the large-volume samples were collected aboard the *CCGS Louis S. St. Laurent*; samples were collected while both ships were in close proximity to each other. The AOS94 large-volume station locations are: St. 8 (75°27′N, 170.35′W), St. 11 (76°38′N, 173°19′W), St. 18 (80°09′N, 173°15′W), St. 26 (84°04′N, 175°04′W), St. 35 (90°00′N).

Samples collected from the same water mass using these methods should, ideally, yield the same result.

Results from several recent studies indicate that POC concentrations in samples collected by small-volume bottle filtration are often greater than those collected using large-volume methods. For example, the JGOFS Equatorial Pacific (EQPAC) program and the 1994 Arctic Ocean Section (AOS94) expedition reported bottle POC concentrations that are greater than determined using large-volume in situ pumps (Fig. 1). The large difference between small- and large-volume POC data evident from these recent studies warrants further investigation, particularly given the importance of accurate POC data to global ocean carbon flux studies.

In this paper, we investigate the importance of sampling technique, specifically small- (bottles) and large-volume (in situ pumps and large-volume bottles) methods, on the accuracy of POC data. We report: (1) a comparison of POC data collected by bottles and in situ pumps during several recent oceanographic expeditions; (2) experimental data comparing the two sampling methods in a mesocosm environment; (3) an assessment of the effect of DOC adsorption on the true in situ filter blank; and (4) a recommendation to avoid filter blank artifacts due to DOC adsorption.

2. Methods

2.1. Oceanic POC data

Table 1 lists POC data obtained from recent field studies in which samples were collected by small-volume bottle and large-volume filtration methods at the same location and time. In this study, ‘‘large-volume’’ refers to the collection of large-volume (>100 l) samples using either in situ pumps or bottles. This is an important point because, as discussed below, we suggest that differences in POC concentration are not due to differences between pumps vs. bottles but rather to the concentration of POC per unit area of the filter relative to the filter blank. All samples were collected using precombusted 0.7-μm glass-fiber filters, either Whatman GF/F or 0.7 μm Poretics® GF-75 filters (25-mm diameter for small-volume filtration; 142-mm diameter for large-volume filtration), and stored frozen until CHN analysis. Pike and Moran (1997) reported that GF-75 and GF/F filters yield comparable POC blanks and concentrations.

Small-volume samples were collected by bottle filtration using conventional sampling bottles (Niskin®, Go-Flo®) deployed either on a hydrowire or a CTD rosette. For the small-volume samples not processed in this study (AOS94, EQPAC), commonly used sample collection and CHN analysis methods were employed (Ducklow, 1994; Wheeler et al., 1997). Note that Wheeler et al. (1997) did not acidify their AOS94 small-volume bottle samples to remove inorganic carbon. This would result in slightly higher particulate carbon concentrations, although inorganic carbon is typically only 10% of the total particulate carbon (e.g., Wangersky, 1994 and references therein). Also, Wheeler et al. (1997) did not dry their filters, and hence there may be an additional source of (dissolved) carbon in their data. All other small-volume samples were processed in this lab by draining unfiltered seawater into acid-

Table 1
Small- and large-volume POC data used in this study

Cruise	Location[a]	Filter	Method of large-volume sampling[b]
EQPAC	Equatorial Pacific	Whatman® GF/F	In situ pump
AOS94	Arctic Ocean	Whatman® GF/F	In situ pump
GOM1-95	Gulf of Maine	Whatman® GF/F	Surface pump (<25 m), all other depths in situ pump
GOM2-95	Gulf of Maine	Poretics® GF-75	Surface pump (<25 m), all other depths in situ pump
GOM3-95	Gulf of Maine	Poretics® GF-75	Surface pump (<25 m), all other depths in situ pump
WA95	Western Arctic	Poretics® GF-75	Surface pump (<25 m), all other depths in situ pump
IOC96	South Atlantic	Poretics® GF-75	Surface pump (<20 m), all other depths by CTD-rosette

[a] Sources of data are: Equatorial Pacific (Ducklow, 1994); Arctic Ocean (Moran et al., 1997; Wheeler et al., 1997); Gulf of Maine (Charette et al., 1996); Western Arctic (Moran and Smith, 1999); South Atlantic (Charette and Moran, 1999).

[b] Small-volume POC data was collected by bottle filtration as discussed in the text.

leached Nalgene bottles (3 l) and filtering ~0.5–2 l through a precombusted, 25 mm, 0.7-μm glass-fiber filters held in a clean polysulfone filter chimney under mild vacuum, typically within 1 h of sample collection (Pike and Moran, 1997). Filters were stored frozen in petri dishes for subsequent CHN analysis.

Large-volume samples (~100–600 l) were collected using either in situ pumps (in all cases Challenger Oceanic Systems and Services, UK, except Dr. M.P. Bacon's pumps were used during EQPAC) or by filtering ~200–400 l directly from Niskin® bottles on a CTD-rosette (IOC-96; Charette and Moran, 1999). Large-volume samples were collected by filtering seawater at a flow-rate of ~2–5 l min^{-1} sequentially through a 53-μm (142 mm) Nitex screen and a precombusted 0.7-μm (142 mm) glass-fiber filter held in a PVC filter holder. The Nitex screen and glass-fiber filters do not come into contact in the 142 mm filter holder. Two 25-mm subsamples were cut from the 142-mm glass-fiber filters using a stainless steel punch (Moran et al., 1997). Samples were stored frozen in polycarbonate petri dishes for POC analysis. Nitex screens were immersed in 0.7-μm glass-fiber filtered seawater in an ultrasonicator for ~1 min to resuspend particulate matter. The large particle-seawater suspensions were immediately filtered through precombusted 25-mm glass-fiber filters and stored frozen in petri dishes for subsequent analysis (Moran et al., 1997).

POC was quantified in the small- and large-volume samples by first drying the 25-mm filter samples in a 60°C oven for a minimum of 12 h, followed by acid-fuming of the samples and CHN analysis using a Carlo-Erba CHN EA1108 Elemental Analyzer (Pike and Moran, 1997). After POC analysis, the > 53-μm POC fraction was added to the 0.7-μm size-fraction. Filter blanks for all samples collected from these cruises were in the range 0.6–2 μmole C for a 25-mm filter.

2.2. Marine Ecosystems Research Laboratory experiment

Seawater with a relatively high POC concentration (~30 μM) was sampled by small-volume bottle filtration and using a large-volume in situ pump under controlled conditions at the Marine Ecosystems Research Laboratory (MERL), Graduate School of Oceanography (Wicklund, 1996). During filtration, work areas were covered with aluminum foil and rinsed with acetone. Acetone-rinsed stainless steel tweezers and scissors were used to handle the filters. None of the MERL filter samples were stored frozen.

Small-volume samples were collected in triplicate from three separate bottle casts using a 5-l Niskin® bottle deployed at a depth of 1.5 m. Approximately 500 ml of seawater from each cast were transferred into separate acid-cleaned Nalgene bottles. Samples were filtered through 53-μm Nitex screen to remove large aggregates. Particulate matter was filtered onto precombusted 25-mm Whatman® GF/F filters under mild vacuum (5–10 psi). Filters were transferred to plastic petri dishes and dried in a 60°C oven for approximately 12 h.

Large-volume samples were collected from the same depth using an in situ pump with a 142-mm PVC filter holder. Three separate pump casts were conducted in triplicate to filter 5-, 10- and 15-l samples each. Due to the high particulate concentrations of Narragansett Bay (~10 mg l^{-1}), larger volumes were not pumped to avoid filter breakage due to high particle loading (Sheldon and Sutcliffe, 1969; Sharp, 1974). Seawater was pumped sequentially through a 53-μm Nitex screen (to remove large aggregates) and a 0.7-μm glass-fiber filter held in a 142-mm PVC filter holder. Two 25-mm diameter subsamples were cut from each filter using a stainless steel punch, placed in plastic petri dishes, and then dried in a 60°C oven for approximately 12 h.

Samples from the MERL tanks were used to attempt to quantify the effect of DOC adsorption on the filter blank. Seawater samples were collected using Niskin® bottles and increasing volumes (approximately 100, 250, 500 ml) of seawater were filtered separately and in triplicate through 25-mm precombusted GF/F filters held in polysulfone filter holders under mild vacuum. Filters were transferred to plastic petri dishes and dried in a 60°C oven.

After drying the filter samples from the MERL experiment, subsamples (~15–20% by weight of the total filter) were cut using acetone-cleaned scissors and tweezers. Subsamples from unused precombusted GF/F filters were processed in the same manner and used as procedural blanks. The filter samples were acid-fumed followed by CHN analysis using a Carlo-Erba CHN EA1108 Elemental Analyzer (Pike and Moran, 1997). Filter blanks from the MERL experiment averaged 2 ± 0.3 μmole C per 25-mm filter.

3. Results

Results from field studies conducted with parallel small-volume bottle filtration and large-volume sampling clearly indicate that the concentration of POC determined in the small-volume bottle samples is often greater than the large-volume samples, by as much as 2–4 times (Fig. 2). This discrepancy is most evident in samples having < ~ 5 μM POC that were collected by large-volume sampling. Also, whereas there are many large-volume POC data in the range ~ 0.2–2 μM, there are almost no small-volume bottle POC data with < 2 μM. By comparison, results from the MERL experiment, in which POC concentrations were ~ 30 μM, indicate good agreement between the small-volume bottle and large-volume data (Fig. 2). Note that ~ 40 l filtered through a 142-mm diameter filter is equivalent to filtering ~ 1 l through a 25-mm filter in terms of C per unit filter area. For large-diameter filtration methods to be effective, it is important to filter at least > 100 l.

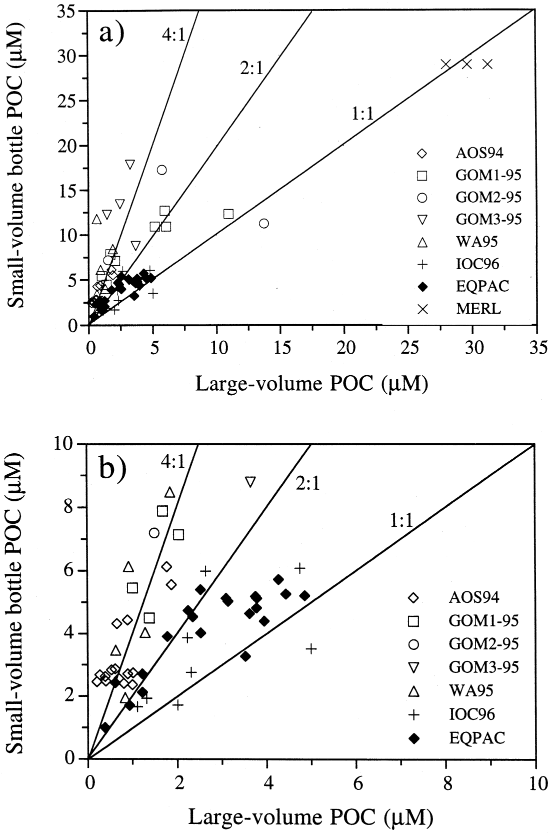

Fig. 2. Comparison of POC concentrations in samples collected using small-volume bottle filtration and large-volume methods. Small-volume bottle data: AOS94 (Wheeler et al., 1997); GOM1-3,95 (Charette et al., 1996); WA95 (Beaufort Sea; Moran and Smith, 1999); IOC96 (Charette and Moran, 1999); EQPAC (Ducklow, 1994); MERL (this study). Large-volume data: AOS94 (Moran et al., 1997); GOM1-3,95 (Charette et al., 1996); WA95 (Beaufort Sea; Moran and Smith, 1999); IOC96 (Charette and Moran, 1999); EQPAC (Bacon et al., 1996); MERL, average of three separate samples each collected in triplicate (this study). (a) All POC data; (b) POC data in the range 0–10 μM.

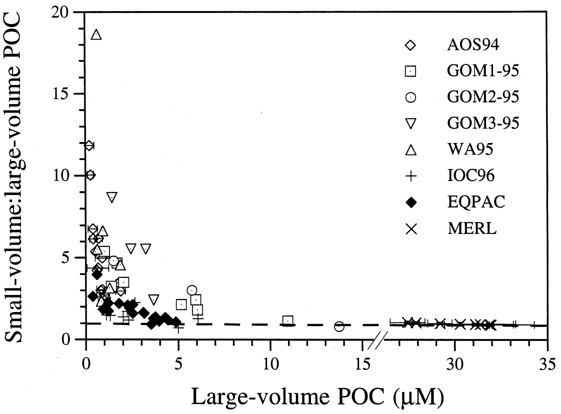

Fig. 3. Ratio of POC concentrations in samples collected using small-volume bottle filtration and large-volume methods plotted against POC concentration determined by large-volume sampling. Dashed line represents the ideal 1:1 ratio for the two sampling methods. Error bars are the standard deviation of replicate samples.

The ratio of small-volume to large-volume POC concentration decreases with an increase in large-volume POC (Fig. 3). We assume that the large-volume data are more accurate, due to the larger sample size and hence greater POC concentration on the filter relative to the filter blank. For POC concentrations greater than ~ 5 μM, the small-volume: large-volume POC ratio approaches a value equal to 1; all of the MERL data (~ 30 μM) have ratios equal to 1. For POC concentrations below ~ 5 μM, however, the small-volume:large-volume POC ratio

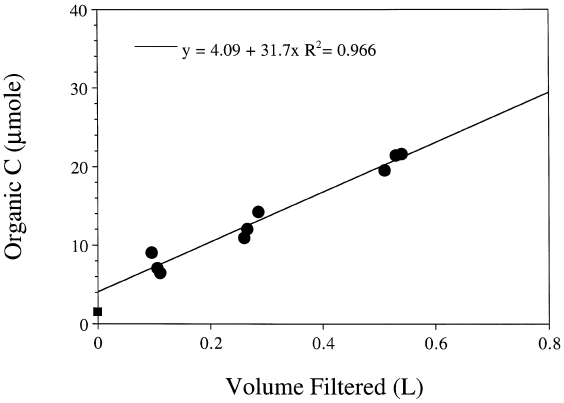

Fig. 4. Plot of organic carbon retained on GF/F filters against the volume filtered for samples collected from the MERL experiment. The data point at zero volume filtered (■) is the precombusted GF/F filter blank.

increases dramatically, due to the much lower POC concentration in the small-volume samples. For POC concentrations $< \sim 5$ μM, the majority of the data are above the 1:1 small:large volume POC ratio.

There is a linear correlation between the organic carbon retained on the filter and volume filtered in the MERL experiment (Fig. 4). The intercept is clearly non-zero and greater than the precombusted filter blank.

4. Discussion

4.1. Differences in POC collected using small- and large-volume techniques

Discrepancies in POC data collected by small- and large-volume methods have been known to exist over the past several decades and there have been a number of discussions of this issue (Wangersky, 1974; Bishop, 1991; Feely and Trefry, 1991; Altabet et al., 1992; King et al., 1998). Traditional explanations for differences between POC collected by bottles and in situ pumps include: (1) differences in analytical technique; (2) presence of large, rare, aggregates not effectively sampled by bottles; (3) differences in filter type; (4) a low signal:noise ratio for POC analysis; and (5) a filter blank that does not consider adsorption of DOC to the filter. There has not, however, been a consensus as to the primary reasons for this apparent discrepancy and, while recognized as important (Bishop, 1991; Feely and Trefry, 1991), this issue has largely been disregarded. Results presented in this study provide a clear demonstration of how serious this discrepancy can be.

Before discussing possible reasons for the apparent discrepancies, it is important to consider the study of Altabet et al. (1992), which reported differences in particulate nitrogen (PN) and δ^{15}N in samples collected using bottles and large-volume pumps in Gulf Stream warm core rings and the Sargasso Sea. They observed large differences in PN and δ^{15}N collected using bottles and pumps from warm core rings and suggested the following additional possible explanations: (1) different retention of particles by different particle filtration systems; (2) filter loading; (3) rinsing samples with distilled water; and (4) sample handling methodology. However, they could account for only a fraction of the discrepancies in PN and δ^{15}N. Altabet et al. (1992) suggested that the most important factors appeared to be artifacts associated with differences in sample collection and handling and differences in the size-distribution of sub-micron particles. Differences in sample handling methodology may also be important in our comparison, however, as discussed further below we suggest this is unlikely to account for the large differences observed at low POC concentrations. With respect to differences in the size-distribution of sub-micron particles, Altabet et al. (1992) used different filter media, which may indeed explain some of the differences in their data.

Retention of particles by different filtration systems will be dependent on the pressure drop across the filter, nominal retention size, and mean loading of the particles (Altabet et al., 1992). Differences in pressure drop would be insignificant for the small- and large-volume sampling techniques used in this study, as they were for Altabet et al. (1992). Differences in filter loading does not provide an explanation because the large-volume samples have higher loading, yet lower POC concentrations, than the small-volume samples; Altabet et al. (1992) reported a similar result for PN and δ^{15}N. Unlike the results reported by Altabet et al. (1992), filtered samples were never rinsed with distilled water in this study and is therefore not a factor.

It is unlikely that differences between small- and large-volume POC data are due to analytical technique. A recent intercomparison involving 10 laboratories reported a ±8% standard error of the mean for the POC concentration of marine sediments and sediment trap material due solely to differences in analysis (King et al., 1998). Differences due to analysis would also be expected to be scattered about the 1:1 line for the small-volume bottle and large-volume samples. We would not expect data to be skewed towards high values for bottle samples with low POC concentration, as is evident in Fig. 2.

Discrepancies in POC data collected by small- and large-volume methods are unlikely to be related to the presence of large aggregates included in the large-volume samples by collection on 53-μm Nitex screen. Aggregates can be missed by bottles and they can settle below the bottle spigot prior to filtration (Bishop and Edmond, 1976; Gardner, 1977). However, large aggregates typically represent a small fraction (< 10–20%) of the suspended POC concentration (Bishop et al., 1977, 1986; Altabet, 1988; Altabet et al., 1992; Moran et al., 1997). It would seem quite unlikely that the presence of aggregates could shift the small-volume:large-volume POC ratio from the 1:1 value to the extent observed in Fig. 2. Aggregates captured on the 53-μm Nitex screen commonly used in large-volume pumping are typically a relatively small subset of the total aggregate population. For example, aggregate concentrations in the surface waters during EQPAC were on the order of 10's per liter based on the aggregate imaging data, which was considerably greater than aggregate numbers from in situ pumping (Walsh et al., 1997).

Differences in filter type cannot be a contributing factor in this study because in all cases the glass-fiber filters had the same nominal pore-size (0.7 μm). The comparison by Altabet et al. (1992) used filters with different nominal pore-size and/or materials. They compared PN and δ^{15}N values in samples collected using 0.7-μm Whatman GF/F glass-fiber filters, 1-μm Gelman A/E filters, and 1-μm quartz fiber Microquartz filters. We suggest that differences in their bottle and large-volume pump data are due, in part, to the different filter media and filter pore-size used.

Obtaining a high signal:noise ratio is an important consideration in collecting small-volume bottle samples in regions with low POC concentration. When the concentration of carbon collected per unit filter area approaches the filter blank, the blank can become a significant fraction of the total carbon detected and will increase the uncertainty in the POC measurement. For example, the small-volume bottle data from the central Arctic Ocean (AOS94) were collected by filtering 1 l of seawater through precombusted 25-mm GF/F filters (Wheeler et al., 1997). The concentration of particulate carbon in samples from > 100 m are in the range ∼ 2–3 μM (Fig. 1). By comparison, the AOS94 large-volume in situ pump POC data below 100 m are ∼ 0.25–1 μM (Fig. 1), approximately 4 times lower than the small-volume bottle data (Fig. 2). The AOS94 small-volume blank was 0.6 ± 0.1 μmole C per 25 mm filter (Wheeler et al., 1997), which is comparable to the large-volume filter blank of 0.8 ± 0.3 μmole C normalized to a 25-mm filter (Moran et al., 1997). If the large-volume pump data are considered more accurate due to the greater sample size, then clearly the small-volume data of Wheeler et al. (1997) would be close to the detection limit, even considering that their measurements included inorganic and organic carbon. That is, there would barely be sufficient carbon on the 25-mm filter after filtering just 1 l of seawater for CHN analysis compared to the blank; this may explain why Wheeler et al. (1997) never reported a particulate carbon concentration less than ∼ 2 μM (Figs. 1 and 2).

If the difference between the small-volume bottle and large-volume POC concentrations was due only to a detection limit problem, however, then we might expect a large uncertainty with data scattered about a 1:1 line. As evident from Figs. 2 and 3, this is clearly not the case. We suggest that there must be other factor(s) that contribute to the systematically higher POC data in samples collected using small-volume techniques at low POC concentrations ($< \sim 5$ μM).

4.2. Blank artifacts due to DOC adsorption to glass-fiber filters

An important consideration in attempting to explain the difference in POC data from samples collected using small- and large-volume methods is that the filter blank does not include adsorption of DOC to the filter. It is well-known that DOC adsorbs to glass-fiber filters (Menzel, 1966; Loder and Hood, 1971; Banoub and Williams, 1972; Gordon and Sutcliffe, 1974; Uno, 1976; Johnson and Wangersky, 1985) and silver filters (Sondergaard and Middleboe, 1993). Although subsequent studies have debated the magnitude of DOC adsorption to filters (Gordon and Sutcliffe, 1974; Johnson and Wangersky, 1985), DOC clearly adsorbs to solid surfaces in seawater and most likely to filtered POC (Johnson and Wangersky, 1985; Sondergaard and Middleboe, 1993). Of particular relevance to this study is the implication based on these previous findings that the true blank for a filter exposed to seawater may be greater than the precombusted glass-fiber filter blank.

The MERL experiment was designed to directly address the hypothesis that DOC adsorption significantly increases the in situ filter blank. The plot of the organic carbon retained on the GF/F filters plotted against the volume filtered shows a linear correlation with an intercept that is clearly non-zero, and most importantly, greater than the precombusted filter blank (Fig. 4). After correcting for the precombusted filter blank (2 μmole C), the magnitude of the intercept is ~ 2 μmole C. Menzel (1966) conducted similar experiments and reported an intercept of 1.7–2.1 μmole C (after correcting for the filter blank of ~ 2 μmole C), which was attributed to adsorption of DOC on the filter. The implication from our data and Menzel (1966) is that DOC adsorption can significantly increase the true in situ filter blank.

During the IOC96 cruise, we filtered seawater using two GF/F filters stacked in-line in a 142 mm PVC filter holder and measured the POC content of each filter using the procedures described above. In this case, the second glass-fiber filter indicated an organic carbon content of 4.6 μmole C (normalized to a 25-mm filter), which was approximately two-fold higher than the precombusted filter blank of 2 μmole carbon. It is intriguing that the second in-line filter had a POC content similar to the in situ blank from the MERL tank and reported by Menzel (1966). These data lead us to speculate that this may be indicative of an initial rapid uptake of DOC (including macromolecular colloidal organic matter) onto the filter, which saturates the available adsorption sites, followed by slower DOC uptake.

Could a blank artifact due to DOC adsorption to the filter account for the difference between small- and large-volume POC data evident at low POC concentrations? Assuming an upper ocean DOC concentration of 80 μM and filtration of 1 l of seawater, adsorption of only a few percent of seawater DOC to a glass-fiber filter would result in an apparent ''POC'' concentration of 2–3 μM. Presumably, one would expect a similar DOC adsorption artifact in the deep ocean. If we further assume a ''true'' POC concentration of 0.25–1 μM, such as the large-volume POC data indicate below 100 m in the central Arctic (Fig. 1), then the small-volume bottle data (1 l in AOS94; Wheeler et al., 1997) could be significantly overestimated by adsorption of a few percent of ambient seawater DOC. In this regard, Wheeler et al. (1997) minimum signal:blank ratio was approximately $(2+0.6)/0.6$, or ~ 4:1. It is possible that they had sufficient carbon on the filter to detect but that a significant fraction of this was adsorbed DOC. We suggest that the EQPAC and other small-volume bottle POC data may be similarly biased. Such an artifact would of course be greatly minimized by filtering large-volumes (>100 l), and is a primary justification for our assumption that the large-volume POC data are more accurate. Thus, a significant amount of reported POC may in fact be DOC adsorbed to the precombusted glass-fiber filter.

There are additional factors that likely affect the efficacy of DOC adsorption to filters and contribute to the scatter in the plot of the small-volume vs. large-volume POC data (Fig. 2). These include, for example, depth variations in the concentration and adsorption characteristics of DOC, the volume of water processed, and the exposure time of the filter in seawater. We contend that differences due to sample handling would also contribute to the scatter in these data (Altabet et al., 1992), though this is unlikely to explain the large offset observed in Figs. 1 and 2 between the small- and large-volume POC data at low POC concentration.

4.3. Recommendations

While the problem of determining the reason(s) for the difference between the small- and large-volume POC data is a difficult one, there are some straightforward solutions. First, we recommend filtering more water. Large-volume POC data are more accurate than small-volume results because they are less affected by artifacts of low sample size and hence a low signal:noise ratio. Although DOC will adsorb to large-volume filters, the much greater concentration of POC in the large-volume samples reduces this artifact to a relatively insignificant percent of the total POC concentration. The use of pumps does not necessarily produce more accurate POC data than bottles, just larger sample size. This is an important point given that many investigators do not have access to large-volume in situ pumping systems. Filtering large-volumes of seawater, either from large-volume bottle samples or in situ pumps, reduces artifacts associated with filter blanks and results in more accurate POC data.

A drawback to filtering more water is that in many cases water obtained from bottle casts is at a premium and therefore filtering larger volumes of seawater is simply not possible. For example, this was the case for the bottle samples collected during the AOS94 program, where only 1 l of seawater was available from the CTD rosette for POC sampling. Nevertheless, if POC determinations are conducted with little modification or documentation to control the DOC adsorption blank artifact, there will be the potential for significant errors in the small-volume POC data. It is important that POC determinations take into account the blank artifact due to DOC adsorption on the filter.

We recommend that POC sampling should include an evaluation of the true in situ filter blank using the same experimental protocol used in the MERL tank experiment. In cases where samples are collected from discrete depths using bottles, samples should be also collected to conduct the successive volume filtration experiment, such as illustrated in Fig. 4. By conducting such experiments in specific oceanographic locations, one could subtract a true in situ filter blank that would include the contribution to the blank due to DOC adsorption. It is likely that only a few experiments conducted using seawater collected over the depth range sampled would be sufficient for a given station. This would result in a small increase in the number of samples analyzed per station.

5. Summary

Almost 25 years ago, Gordon and Sutcliffe (1974) provided the following recommendation for collecting POC samples: ''...1 l will suffice for coastal water, 5 l for surface ocean water, and 10 l for deep ocean water.'' This recommendation is in the EQ-PAC protocol, however, we suggest this should include an evaluation of the filter blank-including adsorbed DOC. Although the volume of seawater that should be filtered will vary for different oceanographic regimes, results reported here indicate that the most accurate data will be obtained by filtering large-volumes of seawater. It is essential to filter a sufficient sample volume to ensure that DOC adsorption or other blank artifacts do not significantly affect POC data. We recommend evaluating the in situ filter blank, particularly for oceanographic regimes characterized by $<\sim 5$ μM POC. This in situ filter blank should be used to correct POC data collected for each station occupied. This study indicates that large-volume filtration, either by in situ pumping or large-volume bottle sampling, provides more accurate POC data than small-volume bottle filtration.

Acknowledgements

This paper benefited from the comments made by Ian Walsh, Bob Collier and an anonymous reviewer. Funding for this work was provided by the Gulf of Maine Regional Marine Research Program (UM-S244), the NSF (OCE-9408945), and an ONR Young Investigator Award (N0014-96-1-0685) to SBM.

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