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Determination of particulate organic carbon (POC) in seawater: The relative methodological importance of artificial gains and losses in two glass-fiber-filter-based techniques

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Abstract

Particulate matter in aquatic systems is an important vehicle for the transport of particulate organic carbon (POC). Its accurate measurement is of central importance for the understanding of marine carbon cycling. Previous work has shown that GF/F-filter-based bottle-sample-derived concentration estimates of POC are generally close to or higher than large-volume in-situ-pump-derived values (and in some rare cases in subzero waters are up to two orders of magnitude higher). To further investigate this phenomenon, water samples from the surface and mid-water Northeast Atlantic and the Baltic Sea were analyzed. Our data support a bias of POC concentration estimates caused by adsorption of nitrogen-rich dissolved organic material onto GF/F filters. For surface-ocean samples the mass per unit area of exposed filter and composition of adsorbed material depended on the filtered volume. Amounts of adsorbed OC were enhanced in the surface ocean (typically 0.5 μmol cm^{-2} of exposed filter) as compared to the deep ocean (typically 0.2 μmol cm^{-2} of exposed filter). These dependencies should be taken into account for future POC methodologies. Bottle/pump differences of samples that were not corrected for adsorption were higher in the deep ocean than in the surface ocean. This discrepancy increased in summer. It is shown that POC concentration estimates that were not corrected for adsorption depend not only on the filtered volume, true POC concentration and mass of adsorbed OC, but also on the filter area. However, in all cases we studied, correction for adsorption was important, but not sufficient, to explain bottle/pump differences. Artificial formation of filterable particles and/or processes leading to filterable material being lost from and/or missed by sample-processing procedures must be considered. It can be deduced that the maximum amounts of POC and particulate organic nitrogen (PON) that can be artificially formed per liter of filtered ocean water are $\sim$3–4 μM OC (5–10% of dissolved OC) and $\sim$0.2–0.5 μM ON (2–10% of dissolved ON), respectively. The relative sensitivities of bottle and pump procedures, and of surface- and deep-ocean material, to artificial particle formation and the missing/losing of material are evaluated. As present procedures do not exist to correct for all possible biasing effects due to artificial particle formation and/or miss/loss of filterable material, uncertainties

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of filtration-based estimates of POC concentrations need further testing. The challenge now is to further constrain the magnitude of the biasing effects that add to the adsorption effect to reduce the uncertainties of estimates of POC concentrations, inventories and fluxes in the ocean.

1. Introduction

Particulate matter (PM) in aquatic systems is an important vehicle for the transport, dispersion and redistribution of many chemical elements, particularly carbon (C). In comparison to the pool sizes of other C constituents in the ocean [especially dissolved organic and inorganic carbon (DOC and DIC)] the particulate-organic-carbon (POC) pool comprises a rather small amount of C. However, because of the significance of sinking particles for the transport of C from the surface into the deep ocean and sediments, POC plays a crucial role in the marine and global carbon cycle despite its small pool size (e.g., Prentice et al., 2001). Hence, for the determination of C fluxes and residence times in the ocean accurate determination of POC concentration is of central importance.

Particulate and dissolved material is often operationally defined as material which does not, and which does, pass a filter of typically 0.7 μm pore size (the nominal GF/F glass-fiber-filter pore size; there is, however, a range of operational definitions with pore sizes from 0.2 μm up to 1.0 μm). In marine environments PM samples are usually collected using large-volume in situ pumps (filtered volume: typically hundreds up to a few thousand liters) or small-volume bottles attached to CTDs (filtered volume: typically within the range of 0.1–10 L). Recently, a number of publications have indicated that often there is a difference between measured POC concentrations derived from samples collected by in situ pumps and measured POC concentrations derived from samples collected by bottles: In almost all cases the bottle-derived results were higher (1–5 times, with rare cases up to ∼200 times in subzero waters) than pump-derived results (Moran et al., 1999; Gardner et al., 2003; Liu et al., 2005).

Reasons for the discrepancy that have been discussed in the literature include use of filters with different pore sizes for bottle and pump samples (Altabet et al., 1992), seawater patchiness (Wangersky, 1974), contamination of bottle samples (Altabet et al., 1992; Gardner et al., 2003; Liu et al., 2005), higher pressure differences across the filter in large-volume pumps (Gardner et al., 2003), artificial particle formation during processing of bottle samples (Liu et al., 2005), more quantitative collection in bottles of actively swimming zooplankton, improper or missing blanks to correct for adsorption of dissolved material onto the filters, and PM washout from pump filter holders (Gardner et al., 2003; Liu et al., 2005) (a more detailed discussion of these reasons follows in Section 3.1).

To further constrain the range of and possible reasons for the discrepancies and their spatio-temporal variability we conducted adsorption experiments and present a comprehensive dataset of bottle- and pump-derived pairs of POC-concentration measurements comprising samples from the Baltic Sea and seasonal samples from the surface and deep Northeast Atlantic. We support the earlier finding that adsorption of dissolved organic matter (DOM) onto glass-fiber filters (GF/F filters of 0.7 μm nominal pore width) plays an important role (Menzel, 1966; Moran et al., 1999; Gardner et al., 2003; Liu et al., 2005). However, in virtually all cases, correction for adsorption was not sufficient to explain bottle/pump differences completely. Artificial formation of filterable particles or processes leading to originally-filterable material being lost from and/or missed by sample-processing procedures must be considered. Given the large volume of the ocean and its resulting significance as a global biogeochemical compartment, the high uncertainties of oceanic inventories of particle-associated constituents such as POC and PON are "unacceptably large" (Gardner et al., 2003). In this paper we provide new information on the magnitude, spatio-temporal variability and 'direction' of the bottle/pump biases which we hope will help improve future measurements of POC.

2. Materials and methods

2.1. Bottle POC and PON

2.1.1. Open-ocean waters — Northeast Atlantic

To assess the effect of adsorption onto filters on the estimated concentration of POC and PON an experiment was conducted using different volumes of filtered deep-ocean water (intercept approach: see Section 3.1 for

details; and Menzel, 1966; Moran et al., 1999; Liu et al., 2005). Water samples were taken on cruise M60/1 of RV Meteor with a CTD rosette in mid-water in the Northeast Atlantic (1975 m depth; ∼1600 m above the seafloor; 3.6 °C; salinity 34.92) at station 677, 46.39°N, 16.57°W, 16 Nov. 2003. Different volumes (0.5, 1, 2, 5, 10, 15 and 20 L) from the same depth were filtered through pre-combusted 25 mm-diameter GF/F filters at a vacuum of ∼200 mbar using the same filtration device. Also, one 8 L sample of water that had been filtered through a 142 mm-diameter polycarbonate filter of 0.4 µm pore width was re-filtered through a pre-combusted 25 mm-diameter GF/F filter. Filters were analyzed for POC and PON as outlined in the last paragraph of this Section 2.1.1.

Additional bottle samples were collected with CTD-mounted bottles in the surface, mid-water and near-bottom waters near the Sedlo and Seine seamounts in the Northeast Atlantic. The Sedlo seamount (summit depth ∼750 m; depth in surrounding valleys ∼2000–2600 m) is located at 40°25′N, 26°55′W on the Mid Atlantic Ridge near the Azores whereas the Seine seamount (summit depth ∼170 m; depth of surrounding seafloor ∼4400–4500 m) is located at 33°50′N, 14°20′W between Madeira and the Iberian peninsula. A detailed description of PM characteristics and distributions at these seamounts is provided by Vilas et al. (in review) and Kiriakoulakis et al. (in review). Samples at the Seine seamount were obtained during cruises 295 (20 March–1 April 2003) and 309 (25 March–08 April 2004) of RV Poseidon, cruise M60/1 of RV Meteor (11 Nov.–6 Dec. 2003), and cruise 282 of RRS Discovery (30 June–01 Aug. 2004). Samples at the Sedlo seamount were obtained during cruise M60/1 of RV Meteor and during cruise 282 of RRS Discovery. Sample bottles with a space below the spigot were used. Water from below the spigot was not sampled. Typically 5 or 8 L (range: 1.5–10 L) of water were filtered through pre-combusted (500 °C for 12 h) and pre-weighed 25 mm-diameter Whatman GF/F filters. During filtration the vacuum was held at ∼200 mbar. As it was attempted to use GF/F filters also for the determination of total particulate matter (TPM) the 25 mm-diameter GF/F filters were rinsed with a single wash of 10 mL of 0.2 µm-filtered Milli-Q water to remove sea salt from the filters. Most likely the salt removal was not quantitative. Therefore, the TPM data are not reported. Although the volume of Milli-Q water used to rinse the samples was small there is the possibility of osmotic cell rupture which could result in slight underestimates of the amounts of POC, PON and other PM constituents.

Until analysis the filters were deep-frozen and stored individually in sealed plastic petri-dishes. The filters were dried at 60 °C for 12 h. In order to remove carbonates the filters were kept in fumes of hydrochloric acid (37% w/w) for 12 h, rinsed with Milli-Q water and dried. Unused pre-combusted GF/F-filters were treated in the same way (these filters provide mere filter blanks without adsorbed DOM). Filters were folded in tin foil and analyzed for POC and PON in a Carlo-Erba CHN-Analyzer according to Verardo et al. (1990) with slight modifications. Acetanilide was used as the calibration standard. Organic-carbon (OC) filter blanks were within the range of 0.7–1.6 µmol C per 25 mm-diameter GF/F filter. Nitrogen was not detectable on 25 mm-diameter filter blanks.

2.1.2. Coastal waters — Baltic Sea

To assess the effect of adsorption on the estimated concentration of POC and PON in coastal sea water, an adsorption experiment was conducted for the coastal Baltic Sea using the intercept approach (see Section 3.1 for details). Water was sampled with CTD-mounted bottles on cruise 44-01-02 of R/V Alexander von Humboldt in the southwestern Baltic Sea at 4.5 m depth (∼14.5 m above the seafloor; 6.5 °C; salinity 11.37) at station 233350, 54.20°N, 11.90°E, 25 April 2001. Due to the design of the bottles (no space beneath the spigot) the sample water could be drained completely through the spigot. That is, there is no danger of biased results due to missed particles that accumulated in the space below the spigot (see Gardner, 1977). Different volumes (0.1, 0.25, 0.5, 1 and 2 L) were filtered through pre-combusted 25 mm-diameter GF/F filters at a vacuum of ∼200 mbar. Also, water was filtered through a 47 mm-diameter GF/F filter into a cleaned glass flask and different volumes (0.1, 0.25, 0.5, 1 and 2 L) of this pre-filtered water were re-filtered through pre-combusted 25 mm-diameter GF/F filters at a vacuum of ∼200 mbar. Filters were analyzed for POC and PON as outlined in Section 2.1.1.

2.1.3. Coastal waters — Gran Canaria

To assess the effect of adsorption on the concentration of POC and PON in coastal sea water, five adsorption experiments were conducted with near-shore waters from Gran Canaria using the intercept approach (see Section 3.1 for details) and the in-line approach (see below). Water was directly pumped into an acid-cleaned 50 L polypropylene container. Duplicates or triplicates of different aliquot volumes (0.5–8 L) were dispensed and filtered using an in-line single-place system: A second in-line filter was placed downstream of the sample filter. Material collected on the second filter was assumed to represent material adsorbing to the GF/F

filters. Water was filtered through pre-combusted (450 °C, 12 h) 25 mm-diameter Whatman GF/F filters. Filters were wrapped in pre-combusted aluminium foil and stored at −20 °C until processed. Before analysis filters were placed in acid-cleaned glass vials and oven-dried overnight at 50–60 °C. After drying, samples were kept in a desiccator with HCl fumes for 12 h to remove inorganic C in carbonates. Afterwards the samples were placed in a desiccator with silica gel and dried overnight. A minimum of 4 acetanilide standards were run every analysis day and two system blanks after each set of 5–10 samples. Average filter blanks were 0.51 ± 0.08 µmol C and 0.04 ± 0.02 µmol N per 25 mm-diameter GF/F filter. The respective ranges for filter blanks were 0.42–0.64 µmol C and 0.01–0.06 µmol N per 25 mm-diameter GF/F filter.

2.2. POC and PON from in situ pumps

For the comparison of bottle-derived and pump-derived results, in-situ-pump samples were obtained at identical or similar sampling depths as the bottle samples (see station information for the seamount samples in Section 2.1.1). One set of pump samples was collected and processed as follows. PM was collected on pre-combusted 293 mm-diameter GF/F filters using a large-volume Challenger Oceanic in situ pump. From all filters sub-sample-disks with a diameter of 23 mm were punched out (to match the effective filter area of a 25 mm-diameter GF/F filter). Except for not rinsing with Milli-Q water, these sub-samples were processed in the same way as the 25 mm-diameter filters with the bottle-derived sample material (see Section 2.1.1). To determine filter blanks, three blank filters of 293 mm diameter were weighed and cut in quarters. From two quarters of each of the three filters, 23 mm-diameter disks were punched out ($N = 17, 17, 18, 21, 22, 21$). These disks were processed in the same way as the sample disks and an average blank value was subtracted from the sample values: 1.2 µmol C and 0.4 µmol N per 23 mm-diameter sub-sample disk. These disks provide mere filter blanks without adsorbed DOM. To translate from the amount of material per 23 mm-diameter filter disk to the whole pump filter, an effective filtration area of 615.44 cm^2 was assumed. Given an effective area of 4.154 cm^2 of the 23 mm-diameter sub-sample disks the conversion factor was 148.16.

Another set of pump samples was collected and processed as follows. During the four seamount cruises mentioned above, PM was collected on pre-combusted (400 °C; >4 h) 293 mm-diameter GF/F filters using large-volume Challenger Oceanic in situ pumps. To

correct these samples for adsorption of OC and ON the in-line method was used: For each sampling depth two 293 mm-diameter GF/F filters were used in-line and the amount and composition of the material retained on the second filter was assumed to be representative of the adsorbed material. All filters were kept frozen at −70 °C during the cruises and freeze-dried upon arrival at the laboratory. POC and PON analyses were carried out on freeze-dried sub-sample disks of a known area punched from the GF/F filters. Four punched filter disks (133 mm^2) were transferred into silver capsules (pre-extracted in a 1:1 mixture of acetone and hexane and heated in a muffle furnace at 250 °C for 14 h). At the same time aliquots (∼2 mg) of pure CaCO$_3$ standard were weighed into separate Teflon cups. Two of the filter aliquots were analysed without decarbonation to avoid possible effects on the total nitrogen determination. The two remaining aliquots were decarbonated according to the acid vapour method of Yamamouro and Kayanne (1995). The decarbonated samples were then dried (∼60 °C; 4–6 h) in order to drive off the water and excess acid and analysed (CE Instruments NC 2500 CHN analyser) for OC and ON. There was no clear difference between nitrogen results with and without decarbonation (data not shown). For comparability of bottle- and pump-derived data we used the pump-derived nitrogen results after decarbonation. Average blanks of pre-combusted filters were 0.50 ± 0.04 µmol OC and 0.17 ± 0.04 µmol N per 23 mm-diameter sub-sample disk equivalent.

2.3. General methodological remarks on POC and PON data

All OC blanks are very similar to the blanks reported by other researchers (e.g., Moran et al., 1999: 0.6–2 µmol C per 25 mm-diameter GF/F filter). There was only one unusually high average filter blank of 5.7 ± 0.2 µmol C for samples from cruise 309 of RV Poseidon which could be due to contamination.

The temperature and duration of pre-combustion of GF/F filters differed slightly between the labs contributing to this study. Since filter backgrounds were quantified, any bias caused by differing filter backgrounds can be ruled out. Another bias could be due to differential changes of filter texture caused by differences in duration and temperature of combustion. However, some of the filters for the bottle and pump sample pairs were treated by the same duration of combustion and temperature. These sample pairs qualitatively showed the same pattern of differences between bottle and pump results as the sample pairs whose bottle and pump sample were processed in different labs. Because of the

overall reproducible patterns we are confident that, despite some differences of sample treatment among the labs, the reported patterns are real. We know of no published results on the effect of slight differences of temperature and duration of combustion on blank values.

Throughout this paper, when using the terms "volume filtered per cm^2 of exposed filter" and amount of a given material "adsorbed per cm^2 per exposed filter" we are referring to the exposed (effective) area of the filter through which water is drawn. The respective units are "L cm^{-2}" and "amount of a given substance per cm^2". At this stage it remains unclear whether or not the part of filters through which water does not flow, but still gets wet, contributes to adsorbed OC. This is not an issue if plugs are taken from the center of large in-situ pump filters, but it could have a small effect if a 25 mm-diameter filter is totally combusted. (The total area of a 25 mm-diameter filter is larger than its effective filter area by a factor of about 1.18. Therefore, assuming a homogeneous distribution of adsorbed organic material on 25 mm-diameter filters, the impact due to a missing correction for adsorption could be overestimated by a maximum of about 18%.)

Unfortunately, there are no replicate samples for POC and PON in this study. Therefore, there is no direct information on overall uncertainties including uncertainties due to spatial heterogeneity on the sampling scale of decimeters and meters. However, replicate POC and PON samples (for which the same volume of water was filtered) from within the bottommost 250 m of the water column at various locations in the deep Arabian Sea were characterized by typical ±1S.D. uncertainties of ±6% and ±20% for POC and PON, respectively. Additionally, replicate analyses of particulate ^{234}Th in the mid-water of the Arabian Sea resulted in an overall uncertainty of ±10.8% (±1S.D.) (Turnewitsch and Springer, 2001). Analytical uncertainties are generally better than these values which comprise uncertainty due to spatial heterogeneity on the sampling scale of decimeters up to meters. As this overall uncertainty is the most relevant one we use the ±6% and ±20% precision values as typical uncertainties of POC and PON.

2.4. Chlorophyll

To assess the effect of filtration of different volumes of filtered sea water on the estimated concentration of chlorophyll *a* and phaeopigments, another volume experiment was conducted during cruise 322 of R/V Poseidon (14 May–01 June 2005). Samples were obtained from just above the seafloor of the Seine seamount summit (165 m depth). After sample filtration, filters were rinsed with pre-filtered salt water. Chlorophyll *a* was extracted from frozen (−20 °C) non-combusted 25 mm-diameter GF/F filters in 9 mL 90% acetone in a cell mill with glass beads (Edler, 1979). After centrifugation for 30 min at 4 °C, chlorophyll *a* was measured in the supernatant with a Turner Design Fluorometer (TD 700) using the acidification method of Holm-Hansen et al. (1965). Phaeopigments and chlorophyll pigment equivalents (CPE) were analyzed and measured fluorometrically with calculations of concentrations based on the JGOFS protocol (UNESCO, 1994).

3. Results and discussion

3.1. Conceivable reasons for bottle versus pump discrepancies

In the study of Liu et al. (2005) and in this study differences between bottle- and pump-derived POC concentration estimates were observed despite the use of the same glass-fiber-filter type (GF/F) for both bottle and pump samples. Therefore, filter type cannot be the sole reason for the observed discrepancies. Spatial variability of POC distribution in natural seawater is also becoming a less likely reason as already pointed out by Liu et al. (2005): If spatial variability was the dominant cause of the discrepancy, ratios of bottle- and pump-derived POC concentration estimates, R^{POC}, would deviate from, but also scatter around, unity. (A list of symbols frequently used in this paper can be found in Table 1.) However, an increasing number of studies from various kinds of environments show a clear trend towards $R^{POC} > 1$. So far, no obvious and systematic contamination problems with bottle samples could be identified (see overviews by Gardner et al., 2003; Liu et al., 2005). As very similar procedures with almost completely closed and cleaned systems for the processing of bottle samples were used in this study it seems safe to assume that contamination can be ruled out as a major reason for bottle/pump differences in this study as well. This notion is supported by filter blanks which are similar to the filter blanks of other labs (see Section 2). For Challenger Oceanic in situ pumps used in this study, a typical pressure differential across the filter of ∼0.6 atm (∼600 mbar) is reported by Liu et al. (2005). As no clear reproducible effect of different pressure differentials within the vacuum range of ∼100–900 mbar across filters for bottle- and pump-derived samples could be found so far we follow Liu et al. (2005) and assume that variability in "the pressure difference across the filter cannot readily explain the differences between bottles and pumps".

Table 1
Definition of symbols frequently used in this paper

Symbol	Definition
C_{AB}^{X}, C_{AP}^{X}	Apparent (subscript A) concentration (main-text-font C) of constituent X in the particulate phase of a bottle (subscript B) and pump (subscript P) sample if no correction for 'adsorption' of X from the dissolved phase onto the filter is applied (µM or µg L^{-1})
C_{C}^{X}	Estimated concentration (main-text-font C) of constituent X in truly (subscript C) particulate material after correction for 'adsorption' of X from the dissolved phase onto the filter (µM or µg L^{-1})
C_{B}^{X}, C_{P}^{X}	Concentration (main-text-font C) of constituent X lost (−) or gained (+) from bottle (subscript B) and pump (subscript P) samples in addition to the adsorbed material (µM or µg L^{-1})
V_{B}, V_{P}	Volume (main-text-font V) of filtered water obtained from bottle (subscript B) and pump (subscript P) samples (L)
M_{adsB}^{X}, M_{adsP}^{X}	Total amount (main-text-font M) of constituent X adsorbed onto the filter used for filtration of bottle (subscript adsB) and pump (subscript adsP) sample water (µmol or µg)
M_{B}^{X}, M_{P}^{X}	Total amount (main-text-font M) of constituent X lost (−) or gained (+) from bottle (subscript B) and pump (subscript P) samples in addition to the adsorbed amount (µmol or µg)
M_{TB}^{X}, M_{TP}^{X}	Total amount (main-text-font M) of constituent X in the truly particulate plus adsorbed phase (subscript T) for a bottle (subscript B) and pump (subscript P) sample (µmol or µg)
R^{X}	Ratio of C_{AB}^{X} divided by C_{AP}^{X}
R_{C}^{X}	Ratio of C_{AB}^{X} corrected for M_{adsB}^{X} divided by C_{AP}^{X} corrected for M_{adsB}^{X}
α, β, γ	First (µmol L^{-2} or µg L^{-2}), second (µmol L^{-1} or µg L^{-1}) and third (µmol or µg) constant in the second-order polynomial describing the relationship between the total amount of constituent X on the filter (y-axis) and the volume of filtered water (x-axis). β is the estimated concentration corrected for adsorption (γ) and other biasing effects (α).

Small-volume samples are bottle samples; large-volume samples are in situ pump samples.

Previous work has shown that artificial creation of filterable particles from DOM during sample processing remains a possible reason for discrepancies between estimated bottle- and pump-derived POC concentrations (Kepkay and Johnson, 1989; Kepkay, 1991, 1994; Altabet et al., 1992; Mopper et al., 1995; Liu et al., 2005). Results of this study support this notion. Selective (not quantitative) particle capture by pumps, and passive hydrodynamic particle sorting and particle modification (disaggregation) through artificially changed hydrodynamics at the pump inlet need to be considered. Moreover, Liu et al. (2005) suggest mobile zooplankton might be able to escape before being drawn into the large-volume pump, while not being able to escape from being trapped in a bottle. In several pump designs, the pump inlet remains open all the time, so the possibility of particle washout from the filter holder of the pump also needs to be considered as a possible reason for the observed discrepancies between estimated bottle- and pump-derived POC concentrations (Liu et al., 2005).

Finally, adsorption of DOM onto the filter may influence the estimate of the concentration of POC and other truly particulate constituents. Menzel (1966), Moran et al. (1999) and Liu et al. (2005) reported that, on contact with water, a seemingly more or less constant amount of DOC (i.e., independent of filtered volume) rapidly adsorbed to and rapidly saturated the filter. If sample filters are not corrected for DOC adsorption, POC concentrations become dependent on the volume of filtered water. This relationship between apparent (subscript A) POC concentration (C) in a bottle sample (subscript B), C_{AB}^{POC} (µM), and respective filtered volume, V_{B} (L), can be described by

$$C_{AB}^{POC} = \frac{C_{C}^{POC} V_{B} + M_{adsB}^{POC}}{V_{B}} = \frac{M_{TB}^{POC}}{V_{B}} \qquad (1)$$

where C_{C}^{POC} (µM) is the true POC concentration (subscript C), and M_{adsB}^{POC} (µmol) is the total amount (M) of OC adsorbed to the small-diameter filter used for filtration of bottle samples (subscript adsB). M_{adsB}^{POC} equals the y-axis intercept of the relationship between the total amount of OC on the small filter, M_{TB}^{POC}, and the volume filtered: $M_{TB}^{POC} = C_{C}^{POC} V_{B} + M_{adsB}^{POC}$. This is the intercept approach, first used by Menzel (1966), for determining the amount of adsorbed DOC on the filter. According to Eq. (1), to theoretically arrive at or close to C_{C}^{POC}, one either has to correct for the adsorption [by determining the y-axis intercept (intercept approach) or the organic carbon on a second in-line filter (in-line approach)], or to filter a high volume of water to, at least, minimize the effect of DOC adsorption. In Eq. (1) it is assumed that DOM adsorbs to and saturates the filter virtually instantaneously upon contact with water. Because of the potential significance of this adsorption phenomenon for reliable estimates of POC concentration, a correction for DOC adsorption should always be applied (e.g., Moran et al., 1999; Turnewitsch and Graf, 2003).

To further constrain the range of and possible reasons for the discrepancies and their spatio-temporal variability we present a comprehensive dataset of bottle- and pump-derived pairs of POC-concentration estimates comprising summer and late-autumn/winter/spring samples from the surface and deep Northeast Atlantic and also data from the Baltic Sea.

3.2. DOM adsorption onto GF/F filters

3.2.1. Open ocean — Northeast Atlantic

Results of the bottle adsorption experiment with late-autumn waters from the mid-water Northeast Atlantic are shown in Fig. 1. M_{TB}^{POC} and M_{TB}^{PON} on the 25 mm-

diameter filters increased with increasing V_B (Fig. 1a). Except for the 2 L-sample, for $V_B < \sim 6$ L, the M_{TB}^{POC}–V_B and M_{TB}^{POC}–V_B relationships were approximately linear. The M_{TB}^{POC}–V_B and M_{TB}^{PON}–V_B relationships up to $V_B = 20$ L were not linear but could be best described by a second-order polynomial (Fig. 1a). For the corresponding concentration estimates the following equation can be written:

$$C_{AB}^{POC} = \frac{\alpha V_B^2 + \beta V_B + \gamma}{V_B} \qquad (2)$$

where α (μmol L^{-2}), β (μmol L^{-1}) and γ (μmol) are constants (Fig. 1b). (An analogous equation can be written for PON.) Here, α reflects the influence of processes such as methodologically related loss of material from ($\alpha < 0$; the curve bends down at higher volumes), or methodologically related addition of material to ($\alpha > 0$; the curve bends up at higher volumes), the filtered mass; β is the true POC concentration; and γ is the V_B-independent amount of OC on the filter resulting from OC sources other than filterable POC (probably initial DOM adsorption).

For mid-water samples with $V_B > 6$ L, increasingly less POC per additional liter of water was retained on the filter with increasing V_B ($\alpha < 0$). This could result from less freshly filtered material being retained on and/or more previously deposited material detaching and passing through the filter. PON seems to behave in the opposite sense: At higher volumes increasingly more PON per additional liter of filtered water is retained on the filter ($\alpha > 0$). The amount of OC adsorbed per cm^2 of exposed filter as a function of volume filtered per cm^2 of exposed filter (see upper x-axis) will be discussed below in the context of the non-linear relation between M_{TB}^{POC} and V_B.

Estimated 'true' POC and PON concentrations (β) were 0.90 μM and 0.02 μM, respectively (Fig. 1a,b). This corresponds to a very high 'true' molar C/N ratio of 56.3 for the bottle-sampled particulate organic material (POM). This C/N ratio is higher than any of the measured C/N ratios estimated using data that were not corrected for DOM adsorption (Fig. 1c). (Throughout the rest of the paper the terms "ads-corrected" and "ads-uncorrected" will be used to denote values that were, and were not, corrected for DOM adsorption, respectively.) Unfortunately we have only one such estimate for the C/N ratio of 'true' mid-water PM. At this stage it is not possible to judge how representative this value is and we refrain from speculating about possible biogeochemical reasons and implications.

For both M_{TB}^{POC} and M_{TB}^{PON} there was a y-axis intercept $\gamma > 0$ (Fig. 1a). If the POC and PON data are not corrected

for the material causing the intercept, a pronounced negative and non-linear relationship between measured POC (PON) concentrations [C_{AB}^{POC} (C_{AB}^{PON})] and V_B is observed [Eq. (2); Fig. 1b]. These y-axis intercepts cannot be explained by DOM and dissolved inorganic nutrients in the small volume of water which is retained in the filter after filtration (Liu et al., 2005). Therefore,
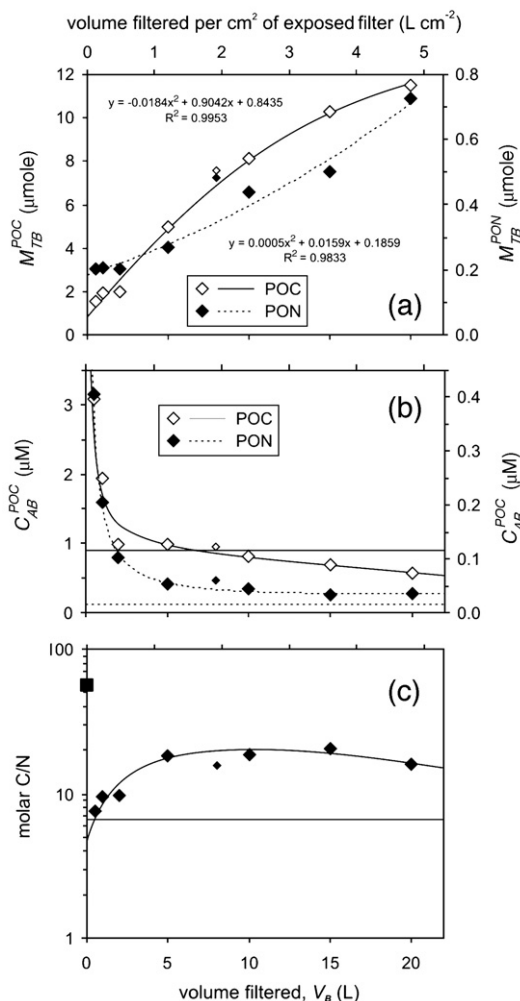

Fig. 1. Results of the bottle adsorption experiment with water from the interior ocean (1975 m depth) of the Northeast Atlantic. Small symbols are values for 8 L of pre-filtered water that were re-filtered. Each diagram also has an upper x-axis indicating the volume filtered per cm^2 of exposed filter area. (a) Mass of particulate organic carbon (POC), M_{TB}^{POC}, and particulate organic nitrogen (PON), M_{TB}^{PON}, on the filters versus the filtered volume, V_B. Fit functions are indicated. (b) Ads-uncorrected POC and PON concentrations (C_{AB}^{POC} and C_{AB}^{PON}) plotted versus V_B. Fit curves which derive from the equations in (a) are indicated. Solid and dashed horizontal line: 'true' POC and PON concentrations. (c) Molar C/N ratios of ads-uncorrected material plotted versus V_B. Fit curve which is derived from the equations in (a) is indicated. Horizontal line: Redfield C/N ratio. Square: estimate of the C/N ratio of 'true' particulate matter. See text for details.

the notion is supported that DOM adsorption onto the filter needs to be invoked to explain the positive y-axis intercepts of the $M_{TB}^{POC}-V_B$ and $M_{TB}^{PON}-V_B$ relationships (Menzel, 1966; Moran et al., 1999; Gardner et al., 2003; Liu et al., 2005).

The y-axis intercepts for the $M_{TB}^{POC}-V_B$ and $M_{TB}^{PON}-V_B$ relationships were 0.84 µmol OC per 25 mm-diameter filter and 0.19 µmol nitrogen per 25 mm-diameter filter, respectively. The corresponding molar C/N ratio is 4.4 (Fig. 1c). Given a molar C/N ratio of DOM of ~16 in the North Atlantic (Hopkinson and Vallino, 2005), instantaneously saturating adsorption of bulk DOM onto the filter cannot explain the positive y-axis intercepts. Rather initial adsorption of a nitrogen-rich fraction of bulk DOM seems to be responsible for the y-axis intercepts.

Evidence that the OC and ON y-axis intercepts are actually due to adsorption of dissolved material was supported by the fact that there was no detectable positive y-axis intercept in the relationships between filtered volumes and mass of chlorophyll a and phaeopigment on the filters (Fig. 2). As these pigments are believed to be associated with filterable particles (not "dissolved" components) the near-zero intercepts support the notion of actual adsorption of DOM onto the filters as opposed to other possible explanations for the positive y-axis intercepts.

In Fig. 3 more information on the adsorbed open-ocean material is presented as derived from large-volume pump samples from the two seamount systems. Material that presumably adsorbs to GF/F filters was sampled on the second of two 293 mm-diameter filters operated in-line. The figure shows mass of OC adsorbed

Fig. 3. (a) Mass of adsorbed organic carbon (OC) per cm^2 of exposed filter plotted versus the volume of water filtered by large-volume in situ pumps (V_P) in the surface and deep ocean. Lower horizontal line (BV: from bottle samples): amount of adsorbed OC per cm^2 of exposed filter from Fig. 1a (y-axis intercept). Upper horizontal line: typical mass of adsorbed OC per cm^2 of exposed filter from the Gran Canaria small-volume experiment (Fig. 5a). (b) Molar C/N ratios of material adsorbed to filters versus V_P. Upper, middle and lower horizontal lines: molar C/N ratios of bulk dissolved organic matter in the deep North Atlantic (Hopkinson and Vallino, 2005), Redfield ratio and molar C/N ratio of adsorbed material from Fig. 1c, respectively. Some extremely high or negative C/N ratios are not shown in (b) as they result from estimates of adsorbed carbon or nitrogen that are below the detection limit. Both diagrams (a) and (b) also have an upper x-axis indicating the volume filtered per cm^2 of exposed filter.
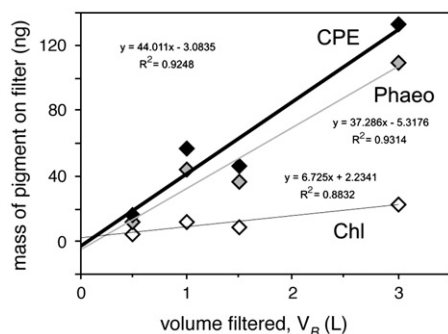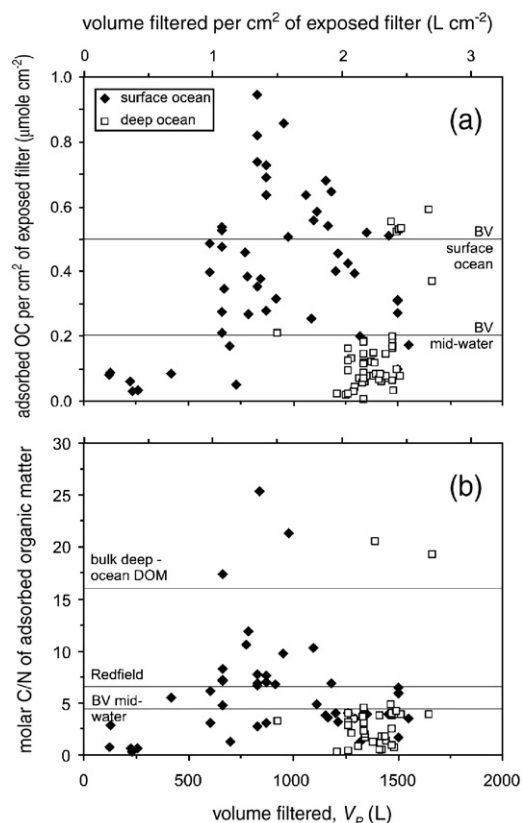

Fig. 2. Pigment results from a bottle adsorption experiment using samples from the near-bottom water column of the Seine Seamount summit. Mass of chlorophyll a (Chl), phaeopigments (Phaeo) and chlorophyll pigment equivalents (CPE) are plotted versus the volume of filtered seawater, V_B. Linear fit functions are indicated, with all intercepts close to zero.

per cm^2 of exposed filter (Fig. 3a), and molar C/N ratios of the adsorbed material (Fig. 3b), plotted versus the large volumes of water filtered by the pumps (subscript P), V_P. To facilitate comparison with bottle-derived data, a second x-axis is shown expressing the filtered volume as volume per cm^2 of exposed filter.

In the surface ocean (≤ 250 m depth) adsorbed OC increased from ~0.05 µmol cm^{-2} at ~100 L (~0.16 L cm^{-2}) up to ~0.9 µmol cm^{-2} at ~800 L (~1.3 L cm^{-2}). There is some evidence for a reversed (negative) relationship at $V_P > 800$ L (~1.3 L cm^{-2}). This volume

dependence of adsorbed OC suggests that DOM adsorption onto filters might not always be instantaneously saturating as assumed for Eqs. (1) and (2). The range of V_P for samples from water depths >250 m is small and no clear trend between adsorbed OC and V_P is detectable. Here amounts of adsorbed OC were mostly between 0.0 and 0.2 μmol cm^{-2} (only a few samples were 4–5 times that amount), the upper limit being very close to the value of 0.2 μmol cm^{-2} as determined for bottle samples using the intercept approach (cf. Fig. 1a). In the surface (≤250 m depth) and deep (>250 m depth) ocean the in-situ-pump-derived average amounts of OC adsorbed per cm^2 of exposed filter were 0.47±0.52 μmol cm^{-2} and 0.16± 0.17 μmol cm^{-2}, respectively (Table 2).

The majority of molar C/N ratios of adsorbed OM was <16 (Fig. 3b) which is the average molar C/N ratio of bulk DOM in the North Atlantic (Hopkinson and Vallino, 2005). Many C/N ratios of adsorbed material were even <6.6 (Redfield ratio), particularly in the mid-

water. This strongly supports the finding from the bottle adsorption experiment that a nitrogen-rich fraction of bulk DOM adsorbs to the filters.

For surface-ocean samples (water depth ≤250 m) C/N ratios of adsorbed material and the range of these ratios increased with increasing V_P up to ∼800 L (∼1.3 L cm^{-2}). At higher V_P the C/N ratios and their range decreased again. Because of the narrow range of V_P for deep-ocean samples (water depth >250 m) no trend of C/N ratios with V_P was detectable. Most deep-ocean C/N ratios lay in a range similar to the surface-ocean ratios in the respective V_P range.

3.2.2. Coastal waters — Baltic Sea and Gran Canaria

Another bottle y-axis intercept experiment was conducted with water from the coastal Baltic Sea. Qualitatively many results were similar to the results from the open-ocean experiment. However, in contrast to M_{TB}^{PON}, which increased linearly over the whole volume range,

Table 2
Amounts of organic carbon (OC) 'adsorbed' to GF/F filters expressed as OC per unit of effective filter area (μmol cm^{-2})

Study site	'Adsorbed' OC (μmol cm^{-2})	Approach	Reference
Gulf of Mexico, bottom nepheloid layer	0.15, 0.23	A: Four 25 mm diameter filters in-line; little variation on bottom 3 filters; first and second value for 1 L and 4 L samples, respectively	Feely (1974)
Narragansett Bay, NW Atlantic, surface ocean	∼0.48	B: ∼0.1, 0.25 and 0.55 L bottle samples filtered through 25 mm diameter filters; filter samples remained unfrozen; filter blank: 2.0± 0.3 μmol C per 25 mm diameter filter; high particle load: ∼10 mg TPM L^{-1}, ∼30 μM POC	Moran et al. (1999)
South Atlantic (IOC 96 cruise), surface ocean	∼0.63	A: two 142 mm diameter filters stacked in-line; OC determined for second filter; filter blank: 2.0 μmol C per area of 25 mm diameter filter	Moran et al. (1999)
NW Mediterranean, surface ocean	0.19±0.07	A: 1 L bottle samples from 25, 50 and 100 m filtered through two in-line 25 mm diameter filters	Liu et al. (2005)
NW Mediterranean, surface ocean	∼0.48	A: 1 L bottle samples from 2, 45, 75, 100, 150 and 200 m, and 0.5 L from 20 m filtered through two in-line 25 mm diameter filters	Liu et al. (2005)
NW Mediterranean, surface ocean	<0.64	B: 0.05–2 L bottle samples from 45 m filtered through two in-line 25 mm diameter filters	Liu et al. (2005)
NW Mediterranean, surface ocean	0.54	A: 0.05–2 L bottle samples from 45 m filtered through two in-line 25 mm diameter filters	Liu et al. (2005)
NE Atlantic, ocean interior	0.20	B: 0.5, 1, 2, 5, 10, 15 and 20 L bottle samples from ∼2000 m filtered through 25 mm diameter filters	This study (Fig. 1)
Coastal Baltic Sea	∼0.11–0.77	B: 0.1, 0.25, 0.5, 1, and 2 L bottle samples from ∼5 m filtered through 25 mm diameter filters	This study (Fig. 3)
NE Atlantic, coastal Gran Canaria	0.58±0.36	B: 0.5–8 L bottle samples filtered through 25 mm diameter filters	This study (Fig. 4)
NE Atlantic, coastal Gran Canaria	0.43±0.17	A: 0.5–8 L bottle samples filtered through two in-line 25 mm diameter filters	This study (Fig. 4)
NE Atlantic, Seine and Sedlo Seamounts, whole water column	0.32±0.23	A: 122–1661 L from within the depth range of 50–4443 m filtered through two in-line 293 mm diameter SAPS filters (N=84)	This study
NE Atlantic, Seine and Sedlo Seamounts, ≤250 m depth	0.47±0.52	A: 122–1549 L from within the depth range of 50–200 m filtered through two in-line 293 mm diameter SAPS filters (N=42); increase with increasing volume filtered	This study (Fig. 3)
NE Atlantic, Seine and Sedlo Seamounts, >250 m depth	0.16±0.17	A: 925–1661 L from within the depth range of 450–4443 m filtered through two in-line 293 mm diameter SAPS filters (N=42)	This study (Fig. 3)

mab: meters above bottom. A: In-line approach. B: Intercept approach. SAPS: Stand-alone pumping system (in-situ pump). See text for details.

$M_{\mathrm{TB}}^{\mathrm{POC}}$ increased nonlinearly (Fig. 4a). The y-axis inter-
cepts derived from second-order polynomial fits are
positive for both POC (0.45 μmol per 25 mm-diameter
filter; Table 2) and PON (0.21 μmol per 25 mm-diameter
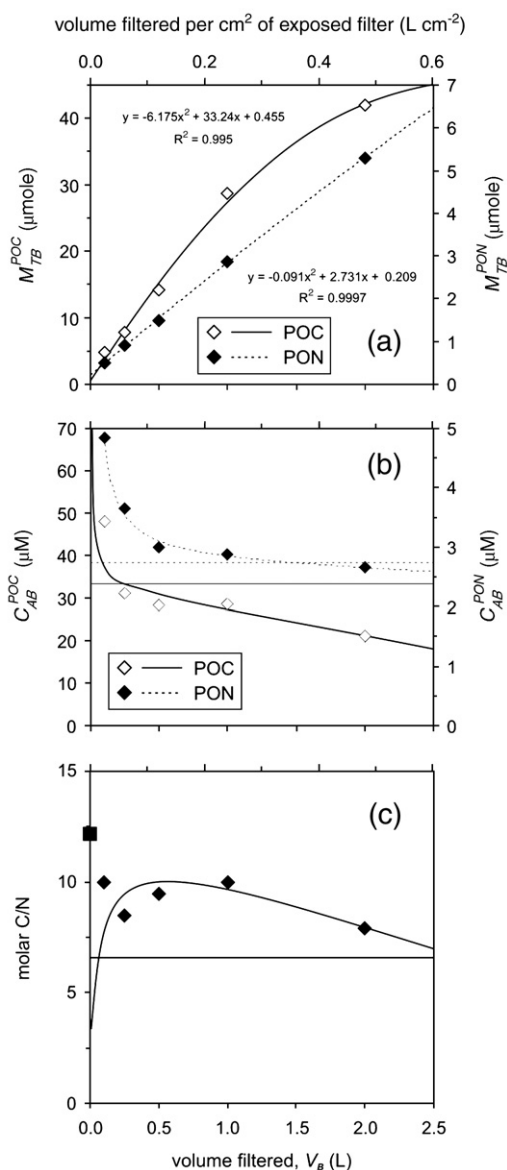filter). (A third-order polynomial yields a POC intercept

of ∼3 μmol per 25 mm-diameter filter. Given typical
uncertainties of POC and PON data it has to remain
unclear which fit is most appropriate.)

There are examples of $M_{\mathrm{TB}}^{\mathrm{POC}}$–$V_{\mathrm{B}}$ relationships from
the coastal ocean (Moran et al., 1999) and the surface
ocean (Liu et al., 2005) which exhibit linearity for the
small-volume range ≤2 L. Our Baltic-Sea data, however,
suggests that this linearity may not be a general feature for
samples from coastal and surface-ocean settings.

As with the mid-water samples from the Northeast
Atlantic, estimates of POC and PON concentrations from
the Baltic Sea depend heavily on V_{B} if not corrected for
adsorption (Fig. 4b). The values for ads-corrected POC
and PON concentrations are 33.2 μM and 2.7 μM, res-
pectively (Fig. 4a,b; β in the second-order polynomials).

In addition to the ads-uncorrected concentration esti-
mates, C/N ratios also varied with changing V_{B} (Fig. 4c).
Again, the molar C/N ratio of the 'true' PM (as derived
from the equations in Fig. 4a) is higher than any of the
measured C/N ratios estimated using ads-uncorrected
data. And, again, with a value of 2.2, the estimated molar
C/N value of the adsorbed material was low indicating
initial adsorption of a nitrogen-rich fraction of bulk DOM.
[The non-linear curve in Fig. 4c originates from the fit
curves in Fig. 4b (which in turn originate from the fit
curves in Fig. 4a). The discrepancy between the C/N fit
curve and the measured C/N values at small V_{B} results
from increasing analytical uncertainty of the small values
for total mass of OC and ON on the filters at small filtered
volumes (Fig. 4a). The reason to show the fit curve is that,
as the fit curve in Fig. 4c is based on five OC and five ON
values, we believe it is a better reflection of actual patterns
than an interpretation of individual data points.]

Another adsorption experiment was conducted using
coastal waters from Gran Canaria (Fig. 5). Five conse-
cutive experiments were carried out and there was some
scatter among replicates and individual experiments.
However, $M_{\mathrm{TB}}^{\mathrm{POC}}$ and $M_{\mathrm{TB}}^{\mathrm{PON}}$ clearly increased with in-
creasing V_{B} (Fig. 5a,b). The y-axis intercepts were >0
for both OC and ON. Average mass of adsorbed OC
and ON per cm^{-2} of exposed filter – based on the
intercept approach – were 0.58 ± 0.36 μmol OC cm^{-2}
and 0.07 ± 0.04 μmol N cm^{-2}, respectively. Adsorp-
tion was also quantified by the in-line approach: The
corresponding values for the mass of adsorbed OC and
ON were 0.43 ± 0.17 μmol OC cm^{-2} of exposed filter
and 0.06 ± 0.02 μmol N cm^{-2} of exposed filter, respec-
tively (Table 2).

As in the Baltic Sea, ads-uncorrected POC and PON
concentration estimates decreased substantially with
increasing V_{B} (Fig. 5c,d). Estimates of ads-corrected
POC and PON concentrations were derived as for the

Fig. 4. Bottle adsorption experiment in the coastal Baltic Sea. Each
diagram has an upper x-axis indicating the volume filtered per cm^2 of
exposed filter and a lower axis of filtered volume, V_{B}. (a) Mass of POC,
$M_{\mathrm{adsB}}^{\mathrm{POC}}$, and PON, $M_{\mathrm{adsB}}^{\mathrm{PON}}$, versus V_{B}. Fit functions are indicated. (b) Ads-
uncorrected $C_{\mathrm{AB}}^{\mathrm{POC}}$ and $C_{\mathrm{AB}}^{\mathrm{PON}}$ versus V_{B}. Fit curves which are derived
from the equations in (a) are indicated. Solid and dashed horizontal lines:
'true' POC and PON concentrations. (c) Molar C/N ratios of ads-
uncorrected material versus V_{B}. Fit curve which was derived from the
equations in (a) is indicated. Horizontal line: molar Redfield C/N ratio.
Square: molar C/N ratio of 'true' particulate matter. See text for details.
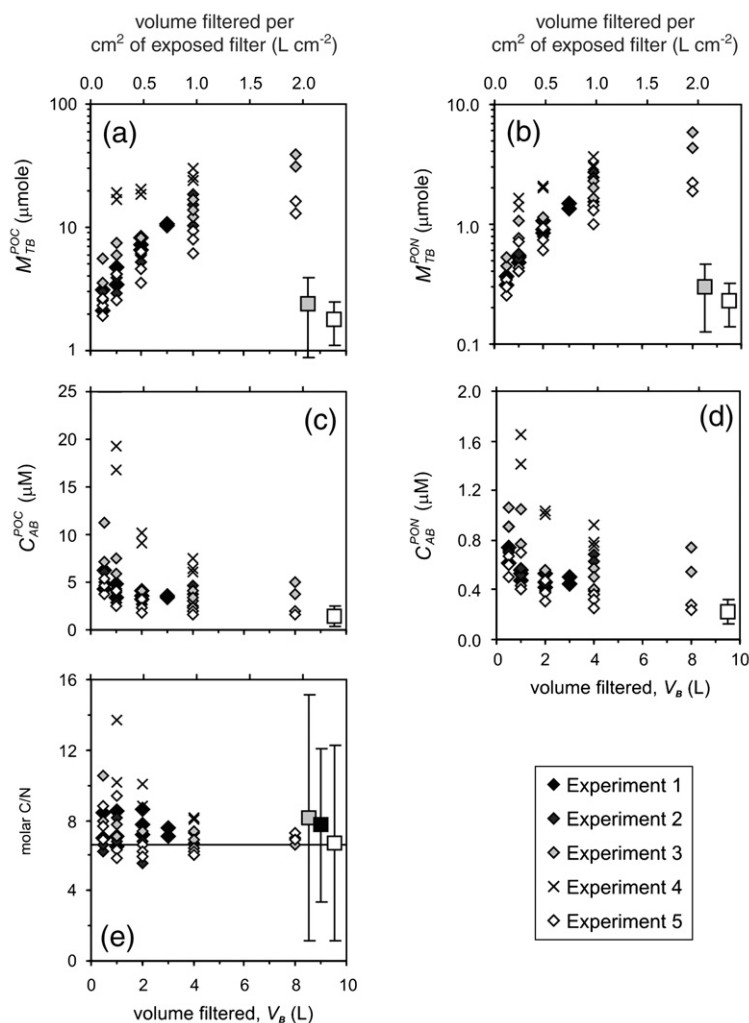
Fig. 5. Bottle adsorption experiment with coastal water from Gran Canaria, Northeast Atlantic. Each diagram also has an upper x-axis indicating the volume filtered per cm^2 of exposed filter. (a) M_{TB}^{POC} and (b) M_{TB}^{PON} versus V_B. Gray and white squares: average±1S.D. estimates of the mass of adsorbed OC and ON as determined by the intercept and in-line approaches, respectively. (c) C_{AB}^{POC} and (d) C_{AB}^{PON} versus V_B. Squares: estimates of average±1S.D. ads-corrected POC and PON concentrations. (e) Molar C/N ratios versus V_B. Horizontal line: Redfield ratio. Gray, black, white square: average±1S.D. estimates for the molar C/N of adsorbed material based on the intercept and in-line approach, and for the ads-corrected particulate material, respectively. Results from experiment 4 were omitted for the calculation of all averages. See text for details.

open-ocean and Baltic-Sea experiments and amounted to 1.5 ± 1.1 μM and 0.22 ± 0.10 μM, respectively. (For all average estimates from the Gran Canaria experiment results from experiment 4 in Fig. 5 have been excluded because of its unusually high values.)

In contrast to the open-ocean and Baltic-Sea experiments (Figs. 3b and 4c), C/N ratios of the Gran-Canaria experiment (Fig. 5e) did not increase with V_B but either showed no clear trend or tended to decrease with increasing V_B. The estimated average ads-corrected molar C/N ratio of PM was 6.7 ± 5.6. Average molar C/N ratios of the adsorbed material as determined by the intercept and in-line approaches were 8.1 ± 7.0 and 7.7 ± 4.4,

respectively. All these ratios for the adsorbed material are low and indistinguishable from the Redfield ratio of 6.6. This supports the aforementioned notion that the initially adsorbed substances consist of nitrogen-rich material.

3.2.3. Conclusions of adsorption experiments

Four main conclusions can be derived from the adsorption experiments: (1) The results support previous evidence for DOM adsorbing to GF/F filters. (2) Fig. 3a shows that, for samples from the surface ocean, the assumption of a constant mass of adsorbed material per unit area of exposed filter (i.e., independent of the

volume filtered) does not seem to be generally valid. (3) For the surface ocean there is evidence for dependence of the composition of adsorbed material on filtered volume. (4) The combined information from in-line and intercept approaches indicates that the adsorbing material consists of a nitrogen-rich fraction of bulk DOM.

3.3. POC concentration estimates — pump versus bottle samples

3.3.1. Effect of DOC adsorption and filter diameter — theoretical considerations

In Section 3.2 we presented evidence that DOM adsorption onto GF/F filters plays an important role in the determination of POC and PON concentrations. In

this section theoretical considerations will show that the importance of adsorption for estimated POC concentrations depends not only on the volume of filtered seawater, the true POC concentration and the amount of adsorbed OC per unit area of exposed filter, but can also depend on total filter area if no adequate correction for adsorbed OC is applied.

For the theoretical consideration, the possibility of non-linearity in the relationship between the total mass of OC on the filter and the filtered volume has to be considered. The procedure for assessing the possible importance and for the introduction in the theoretical calculations of non-linearity was as follows.

(I) The best quantitative evidence for non-linearity in the relationship between the total mass of OC on the
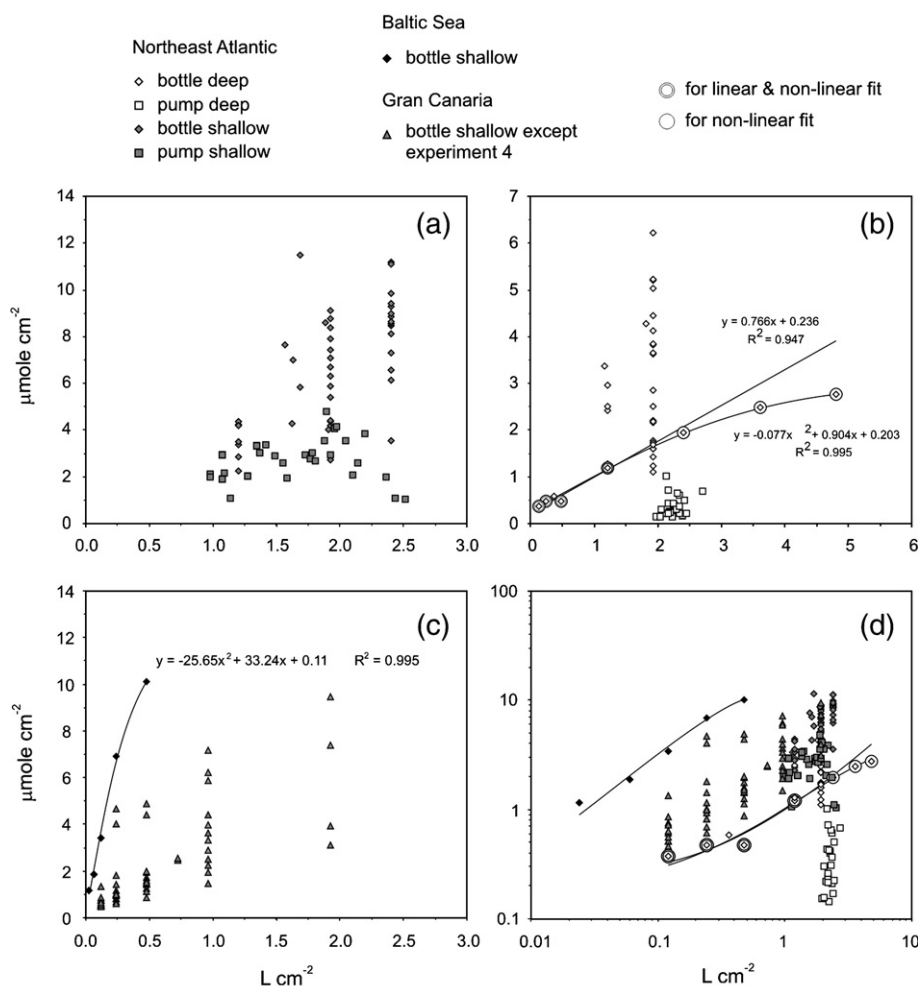

Fig. 6. Total organic carbon per cm^2 of exposed filter versus volume filtered per cm^2 of exposed filter. (a) Bottle and pump samples from the topmost 250 m of the open Northeast Atlantic. (b) Bottle and pump samples from the open Northeast Atlantic at depths >250 m. Encircled symbols are from the mid-water adsorption experiment (Fig. 1). The data encircled twice were fitted linearly; the data encircled once and twice were fitted with a second-order polynomial. (c) Bottle samples from the coastal Baltic Sea and Gran Canaria. The Baltic Sea samples are fitted with a second-order polynomial. (d) All data from (a)–(c) on logarithmic y- and x-axes. See text for details.

filter and the filtered volume was obtained from the Northeast Atlantic mid-water (Fig. 1a) and Baltic-Sea (Fig. 4a) adsorption experiments. In Fig. 6 these data are plotted again. However, in contrast to Figs. 1a and 4a, total mass of OC is now expressed as OC per cm^2 of exposed filter (rather than the total amount of OC per filter) and plotted versus volume filtered per cm^2 of exposed filter (rather than the total filtered volume). All other data from our complete bottle and pump dataset were then plotted in the same way for comparison (Fig. 6a–d). Why was this kind of plot chosen? The non-linearity is probably due to changes in properties of the filters and/or filter-retained material in the course of filtration: The more water was filtered and the longer the filtration, the more 'strain' was imposed on the filter and the filter-retained material that was filtered earlier during the filtration. To be able to compare small- and large-diameter filters in terms of this strain, our data were plotted as OC per cm^2 of exposed filter (rather than the total amount of OC per filter) versus volume filtered per cm^2 of exposed filter (rather than the total filtered volume).

(II) An analysis of the pattern of values in Fig. 6 reveals that the Baltic-Sea (Fig. 6c) and the Northeast-Atlantic mid-water (Fig. 6b) datasets seem to delimit the natural range of scenarios at the upper and lower ends of the overall dataset, respectively (Fig. 6d), with Gran-Canaria and upper-open-ocean data being mid-range examples (Fig. 6a,c,d). It also becomes clear that almost all bottle and pump samples (except for the samples for the adsorption experiments) were filtered within the narrow range of ∼1–2.5 L cm^{-2} of exposed filter (Fig. 6a,b,d). It can therefore be concluded that, regarding the relative volumes of filtered water (L cm^{-2}) (which is interpreted as a measure of the aforementioned 'strain'), bottle and pump samples are very similar. The range of volumes filtered per cm^{-2} of exposed filter for ordinary samples was much narrower than the range for the samples of the adsorption experiments. The latter showed non-linearity over the full range. However, within the narrow range of volumes filtered per cm^{-2} of exposed filter for ordinary samples, non-linearities can be neglected (Fig. 6d). Consequently, non-linearities such as the ones shown in Figs. 1a and 4a for OC are an unlikely explanation for the bottle/pump discrepancies. However, the phenomenon of non-linearities warrants more detailed study including an experiment where both pumps *and* bottle procedures process a range of identical volumes filtered per cm^{-2} of exposed filter. If bottle and pump samples from a given study are to be compared filtered volumes should be chosen so that volumes filtered per cm^{-2} of exposed filter do not differ much between bottle and pump approaches.

(III) In contrast to our real-world samples, the volumes filtered per cm^{-2} of exposed filter will vary over at least two orders of magnitude for the theoretical considerations. Because the deep ocean below the euphotic zone comprises a major compartment of the world ocean, an open-ocean mid-water scenario was chosen for the theoretical calculations. The Northeast-Atlantic mid-water data from the adsorption experiment (encircled data in Fig. 6b,d) were used to parameterize the non-linearity. To do so, the ratio of a linear fit to the four smallest values (encircled twice in Fig. 6b,d) and a second-order polynomial fit to all seven values (encircled once or twice in Fig. 6b,d) was used. Here, each ratio is allocated to a specific volume filtered per cm^2 of exposed filter (filter strain). This relationship was derived from a small-volume experiment, but because of the relative nature of the relationship (both OC and volume are normalized to cm^2 of exposed filter) this relationship should be valid for both bottle and pump samples. Consequently, to correct a given value of the total amount of OC per filter for non-linearity, the correction ratio was chosen based on the respective volume filtered per cm^2 of exposed filter.

We assume that the POC distribution in the filtered water remains constant and homogeneous over the duration of the filtration. We also assume that the sorptive behavior of a filter used for bottle-sample filtration equals the sorptive behavior of a filter used for pump-sample filtration. Furthermore, it was assumed that the amount of adsorbed OC per cm^2 of exposed filter was constant, i.e., independent of the filtered volume. This assumption was made because, in contrast to surface-ocean data, no clear relationship between the amount of adsorbed OC and the filtered volume could be detected in the pump data from the mid-water ocean (Fig. 3a).

To demonstrate the potential effect of filter area on ads-uncorrected data for the mid-water ocean, the 'true' POC concentration is assumed to be 1 μM and the amount of adsorbed OC per cm^2 of exposed filter to be 0.20 μmol cm^{-2} (cf. Fig. 1 and Table 2).

Under these conditions, upon initial contact with sample water and virtually no water having been filtered, the OC on the filter is adsorbed carbon and the total amount of adsorbed OC has to increase with increasing filter size (*y*-axis intercepts in Fig. 7a). The relative change in total OC loading with increasing filtered volume is most intense for the smaller filters because the relative contribution of adsorbed OC is initially smaller on the smaller filters. This is also reflected in the amount (*I*) of OC per cm^2 of exposed filter: $I_{\text{TB}}^{\text{POC}} = (C_{\text{C}}^{\text{POC}} V_{\text{B}} + M_{\text{adsB}}^{\text{POC}})/F_{\text{s}}$, or $I_{\text{TP}}^{\text{POC}} = (C_{\text{C}}^{\text{POC}} V_{\text{P}} + M_{\text{adsP}}^{\text{POC}})/F_{\text{l}}$, where F_{s} and F_{l} is the exposed filter area of a small- and large-diameter filter used for filtration of bottle and
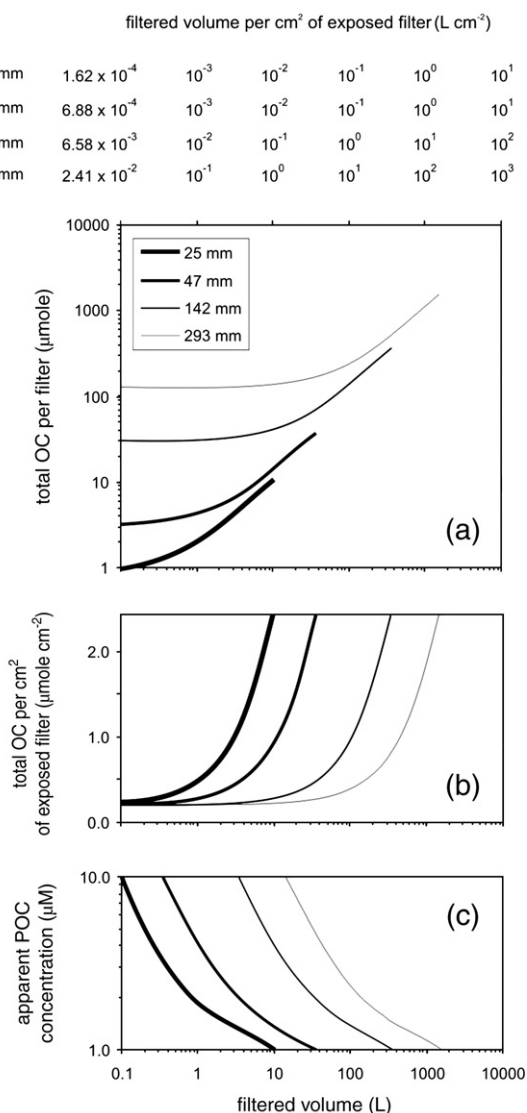
Fig. 7. Assessing the influence of adsorption on ads-uncorrected POC concentrations within the parameter space of filter diameter (25, 47, 142 and 293 mm) and filtered volume. The legend in (a) applies to all plots (a)–(c). Each diagram has an upper *x*-axis indicating the volume filtered per cm^2 of exposed filter for four filter diameters. Mass of adsorbed OC per 4.15 cm^2 (the effective filter area of a 25 mm-diameter filter) is 1 μmol; true POC concentration is 1 μM. The dependence on volume of filtered water of (a) the total (adsorbed + truly particulate) amount of OC on the filters, (b) the total amount of OC per cm^2 of filter area, and (c) ads-uncorrected POC concentration is shown.

pump samples, respectively (Fig. 7b). Consequently, for a given volume of filtered water, the apparent POC concentrations derived from small-diameter filter samples (C_{AB}^{POC}) are closer to the true POC concentration than apparent POC concentrations derived from large-diameter filter samples (C_{AP}^{POC}) (Fig. 7c). The deviation of the

apparent POC concentration from the true POC concentration decreases towards higher volumes of filtered water as the ratio of truly particulate OC to adsorbed OC increases. For a given volume of filtered water, the deviation also increases with increasing amounts of adsorbed OC (curves shifted horizontally towards higher volumes in Fig. 7c) and decreasing true POC concentrations (curves shifted vertically towards lower concentrations of ads-uncorrected POC in Fig. 7c). Hence, if there is no correction for adsorbed OC the apparent POC concentration depends on four parameters: volume of filtered water, amount of OC adsorbed per cm^2 of exposed filter, true POC concentration, and filter diameter (area).

These theoretical considerations indicate that, if no adequate correction for DOC adsorption onto filters is applied, there is the possibility that differences between bottle-derived and pump-derived POC estimates could partly result from unfavorable combinations of filter diameter, volume filtered, true POC concentration and amount of adsorbed OC. Given typical volumes filtered for bottle and pump samples, a difference of ads-uncorrected POC concentration estimates by up to a factor of two caused by such an unfavorable combination of filtration parameters is conceivable. It also becomes evident that the mere equality of ads-uncorrected bottle-derived and pump-derived concentration estimates is no guarantee for accuracy. In this study corrections for adsorption have been applied and it is, therefore, safe to assume that in this study different filter diameters cannot be the reason for any observed bottle/pump discrepancies.

3.3.2. Differences between ads-uncorrected bottle- and pump-derived results

Here, we present more data on pairs of values of ads-uncorrected bottle- and pump-derived POC concentrations. Results were compiled from four cruises to two seamounts in the Northeast Atlantic. Samples were collected by pumps and bottles at virtually the same time at identical or very similar depths. For bottle samples typically 5 L or 8 L (range: 1.5–10 L) of seawater were filtered (filter diameter: 25 mm; filter time typically ~2 h, but in rare cases up to ~5 h) whereas 122–1661 L of seawater were filtered by the pumps (filter diameter: 293 mm; filter time 2 h).

At both study sites, bottle and pump samples show a trend of decreasing C_{AB}^{POC} and C_{AP}^{POC} with increasing depth (Fig. 8a). C_{AB}^{POC} from the summer cruise (RRS Discovery 282) tended to be higher than on the other cruises, which took place in late autumn, winter or spring. Bottle-derived values were always greater than pump-derived values. The difference between C_{AB}^{POC} and C_{AP}^{POC} was greater at depth (>250 m) than in the surface
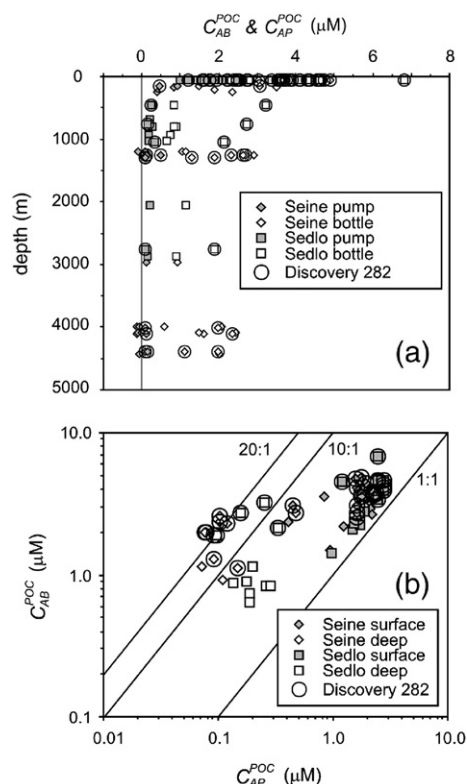
Fig. 8. (a) Ads-uncorrected POC concentration in bottle, C_{AB}^{POC}, and pump, C_{AP}^{POC}, samples collected from various depths at the Seine and Sedlo seamounts. (b) C_{AB}^{POC} plotted versus C_{AP}^{POC} for samples collected in the topmost 250 m of the water column ("surface") and at depths >250 m ("deep"). Isolines of 1:1, 10:1 and 20:1 concentration ratios are indicated. Encircled data in (a) and (b): samples obtained in summer during RRS Discovery cruise 282; other samples were obtained in late autumn, winter or spring.

ocean (≤250 m) (Fig. 8b). This trend was particularly pronounced during the summer. Can these differences be resolved by correcting for DOC adsorption onto the filters?

3.3.3. POC and PON after correction for adsorption — the need for additional gain and/or loss terms

In this section we will attempt to further constrain possible reasons for the observed differences between ads-uncorrected pump- and bottle-derived results. The first step is to assess the significance of adsorption. Data in Fig. 8 were not ads-corrected. All bottle and pump data in this study were then corrected for DOC adsorption onto the filters. For 25 mm-diameter filter samples from depths <250 m an amount of adsorbed OC of 0.47 μmol cm^{-2} of exposed filter and an amount of adsorbed ON of 0.12 μmol cm^{-2} of exposed filter were applied. These values were chosen as they are typical for surface-ocean environments (see compilation of published and new OC

data in Table 2). Constant amounts of adsorbed OC of 0.20 μmol cm^{-2} of exposed filter (Fig. 1a; Table 2) and of adsorbed ON of 0.04 μmol cm^{-2} of exposed filter (Fig. 1a) were assumed for all 25 mm-diameter GF/F filters with samples from depths >250 m. All pump samples were individually corrected for adsorbed OC as determined by the in-line approach (Fig. 3a).

Average amounts of adsorbed OC were higher in the surface ocean than in the ocean mid-water (Table 2). This depth dependence in the more eutrophic Northeast Atlantic contrasts with the reported absence of a depth dependence in the more oligotrophic Sargasso Sea (Menzel, 1966). During our study the average DOC concentration within the topmost 250 m of the water column was 66.0±5.4 μM (calculated from 128 samples from the Seine and Sedlo seamount) whereas between 300 m and 3000 m depth the average DOC concentration was 49.2±1.1 μM (calculated from 252 samples from the Seine and Sedlo Seamount) (Vilas et al., in review). Despite the considerable scatter of the values of the amounts of adsorbed OC it can be suggested that the adsorbed amount increases with increasing DOC concentrations in the more eutrophic Northeast Atlantic. However, despite enhanced DOC concentrations in the surface ocean of the Sargasso Sea (Hansell et al., 2004) Menzel (1966) did not find increased amounts of adsorbed OC on surface-ocean filters (assuming that vertical DOC distribution did not change between these two studies). This supports the notion that DOC concentration is one, but not the only, controlling parameter for amounts of adsorbed OC per cm^2 of exposed filter. We have shown earlier that a nitrogen-rich fraction of the bulk DOM adsorbs to the filters first. Therefore, the chemical composition of the bulk DOM may also play an important role for the presence or absence of a depth dependence of the amount of adsorbed DOC. The combination of the volume filtered and the amount of total PM per unit area of exposed filter could also play a role. These issues need further study.

In Fig. 9 bottle- and pump-derived POC concentrations that were corrected for OC adsorption are compared with each other, and with ads-uncorrected values. In Fig. 9a C_{AB}^{POC} and C_{AP}^{POC} (on the right y-axis) are plotted versus the respective ads-corrected values (on the x-axis). The uncorrected values plot just above the 1:1 line. Because of the higher adsorption correction surface-ocean data (gray symbols) plot slightly higher above the 1:1 line than deep-ocean data (white symbols). On the left y-axis of Fig. 9a the ratio of ads-corrected and ads-uncorrected POC is plotted versus the respective ads-corrected POC concentrations on the x-axis. At low ads-corrected concentrations there was an
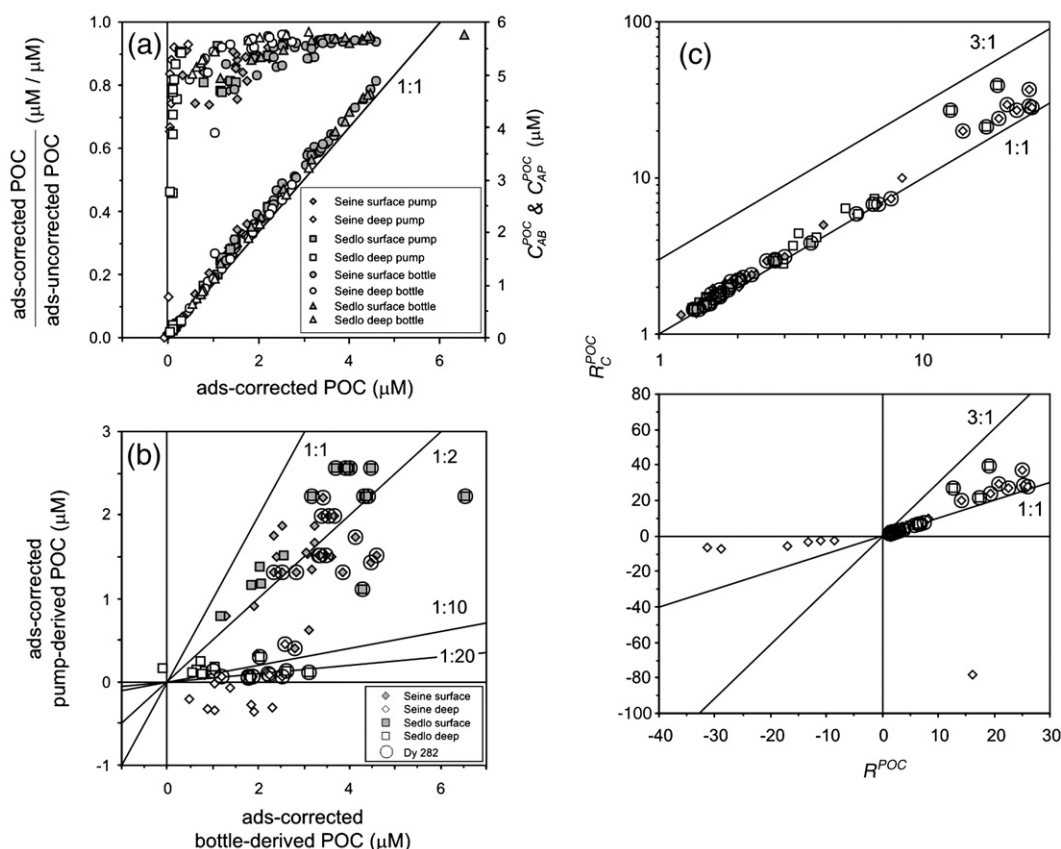
Fig. 9. (a) Ratio of ads-corrected to ads-uncorrected POC concentration (left *y*-axis) versus ads-corrected POC concentration (*x*-axis) (boomerang-shaped cloud of values in upper left of diagram). A few values > 1 are not shown (they are due to negative estimates of the amount of adsorbed OC). Also shown is ads-uncorrected POC concentration (right *y*-axis) versus ads-corrected POC concentration (*x*-axis). These data fall just above the 1:1 line. (b) Ads-corrected pump-derived POC concentrations versus ads-corrected bottle-derived POC concentrations. Isolines for 1:1, 1:2, 1:10 and 1:20 ratios are indicated. (c) The ratio, R_C^{POC}, of bottle- and pump-derived ads-corrected POC concentrations versus the ratio R^{POC} which is not corrected for adsorption. Isolines for 3:1 and 1:1 ratios are indicated. Lower plot: same as upper plot but on linear axes also showing negative values resulting from negative estimates of ads-corrected POC. Legend in (b) also applies to (c). (b) and (c): data from summer cruise 282 of RRS Discovery encircled.

extremely steep increase of the ratio with increasing ads-corrected concentration. This increase continued, but leveled off, at ads-corrected concentrations > 1–2 μM. For pump samples from the deep ocean adsorption correction can have a very strong effect with corrected values being as low as ∼ 10% of uncorrected values. Above ads-corrected concentrations of 1 μM, correction for adsorption leads to a reduction of estimated concentrations of only ∼ 30% or less. Here, for a given ads-corrected concentration, the effect of adsorption correction was slightly higher for surface-ocean samples, particularly pump samples. In virtually all cases ads-corrected bottle estimates were higher than ads-corrected pump estimates, with differences in samples from the deep ocean reaching more than one order of magnitude (Fig. 9b). (The few negative values in Fig. 9b are due to estimates of amounts of adsorbed OC being higher than estimates of amounts of total OC on the filters.)

Another way of looking at the effect of adsorption on the bottle versus pump problem is to compare the ratio of ads-uncorrected bottle- and pump-derived POC concentrations, R^{POC}, with the ratio of ads-corrected (subscript C) bottle- and pump-derived POC concentrations, R_C^{POC}. R^{POC} and R_C^{POC} can be written as

$$R^{POC} = \frac{C_{TB}^{POC}}{C_{TP}^{POC}} = \frac{\dfrac{C_C^{POC} V_B + M_{adsB}^{POC}}{V_B}}{\dfrac{C_C^{POC} V_P + M_{adsP}^{POC}}{V_P}} \qquad (3a)$$

and

$$R_C^{POC} = \frac{\dfrac{C_{TB}^{POC} V_B - M_{adsB}^{POC}}{V_B}}{\dfrac{C_{TP}^{POC} V_P - M_{adsP}^{POC}}{V_P}} \qquad (3b)$$

where $M_{\text{adsP}}^{\text{POC}}$ is the total amount of organic carbon adsorbed to the large-diameter filter used for pump filtration (subscript adsP). For surface-ocean samples $R_{\text{C}}^{\text{POC}} \approx R^{\text{POC}}$ (Fig. 9c). For summer samples from the deep ocean, however, there was some evidence for an increase of $R_{\text{C}}^{\text{POC}}$ with increasing R^{POC}; i.e., after correction for adsorption the discrepancy between bottle- and pump-derived estimates was even larger by up to a factor of ~ 2 than in ads-uncorrected samples. (A few $R_{\text{C}}^{\text{POC}}$ values from the deep water column at the Seine seamount were negative: bottom diagram in Fig. 9c. These negative values result from the negative ads-corrected pump data shown in Fig. 9b.)

It can be concluded that correction for adsorption of DOC onto filters is important, but not sufficient, to explain bottle/pump discrepancies. To investigate this issue in more detail Eq. (3a) is modified to include the terms $M_{\text{B}}^{\text{POC}}$ and $M_{\text{P}}^{\text{POC}}$ for gains or losses of material in addition to adsorption in bottle and pump samples:

$$R^{\text{POC}} = \frac{C_{\text{AB}}^{\text{POC}}}{C_{\text{AP}}^{\text{POC}}} = \frac{\dfrac{C_{\text{C}}^{\text{POC}}V_{\text{B}} + M_{\text{adsB}}^{\text{POC}} \pm M_{\text{B}}^{\text{POC}}}{V_{\text{B}}}}{\dfrac{C_{\text{C}}^{\text{POC}}V_{\text{P}} + M_{\text{adsP}}^{\text{POC}} \pm M_{\text{P}}^{\text{POC}}}{V_{\text{P}}}} \qquad (4)$$

Eq. (4) can be rearranged to give $M_{\text{B}}^{\text{POC}}$ and $M_{\text{P}}^{\text{POC}}$:

$$\pm A_{\text{B}}^{\text{POC}} = C_{\text{AB}}^{\text{POC}}V_{\text{B}} - C_{\text{C}}^{\text{POC}}V_{\text{B}} - M_{\text{adsB}}^{\text{POC}} \qquad (5a)$$

$$\pm A_{\text{L}}^{\text{POC}} = C_{\text{AL}}^{\text{POC}}V_{\text{L}} - C_{\text{C}}^{\text{POC}}V_{\text{L}} - M_{\text{adsL}}^{\text{POC}} \qquad (5b)$$

Eqs. (5a) and (5b) can be multiplied by $1/V_{\text{B}}$ and $1/V_{\text{P}}$, respectively, to give estimates of the respective concentrations, $C_{\text{B}}^{\text{POC}}$ and $C_{\text{P}}^{\text{POC}}$, of the lost/missed/gained material:

$$\pm C_{\text{B}}^{\text{POC}} = \frac{M_{\text{B}}^{\text{POC}}}{V_{\text{B}}} = \frac{C_{\text{AB}}^{\text{POC}}V_{\text{B}} - C_{\text{C}}^{\text{POC}}V_{\text{B}} - M_{\text{adsB}}^{\text{POC}}}{V_{\text{B}}} \qquad (6a)$$

$$\pm C_{\text{P}}^{\text{POC}} = \frac{M_{\text{P}}^{\text{POC}}}{V_{\text{P}}} = \frac{C_{\text{AP}}^{\text{POC}}V_{\text{P}} - C_{\text{C}}^{\text{POC}}V_{\text{P}} - M_{\text{adsP}}^{\text{POC}}}{V_{\text{P}}} \qquad (6b)$$

These equations can also be used analogously for nitrogen yielding estimates of $C_{\text{B}}^{\text{PON}}$ and $C_{\text{P}}^{\text{PON}}$.

For a given $C_{\text{C}}^{\text{POC}}$, $M_{\text{B}}^{\text{POC}}$ and $M_{\text{P}}^{\text{POC}}$ are linked through R^{POC}. Consequently, there are still two unknowns ($C_{\text{C}}^{\text{POC}}$ and the combination of $M_{\text{B}}^{\text{POC}}$ and $M_{\text{P}}^{\text{POC}}$) in Eq. (4) and it is still not possible to determine $C_{\text{C}}^{\text{POC}}$. However, the sensitivity of $M_{\text{B}}^{\text{POC}}$ ($C_{\text{B}}^{\text{POC}}$) and its corresponding $M_{\text{P}}^{\text{POC}}$ ($C_{\text{P}}^{\text{POC}}$) for different assumed $C_{\text{C}}^{\text{POC}}$ can be assessed. For each sample a range of estimates of $C_{\text{B}}^{\text{POC}}$ and corresponding $C_{\text{P}}^{\text{POC}}$ was derived by using the measured values for $C_{\text{AB}}^{\text{POC}}$, $C_{\text{AP}}^{\text{POC}}$, V_{B}, V_{P}, $M_{\text{adsB}}^{\text{POC}}$ and $M_{\text{adsP}}^{\text{POC}}$, and by using
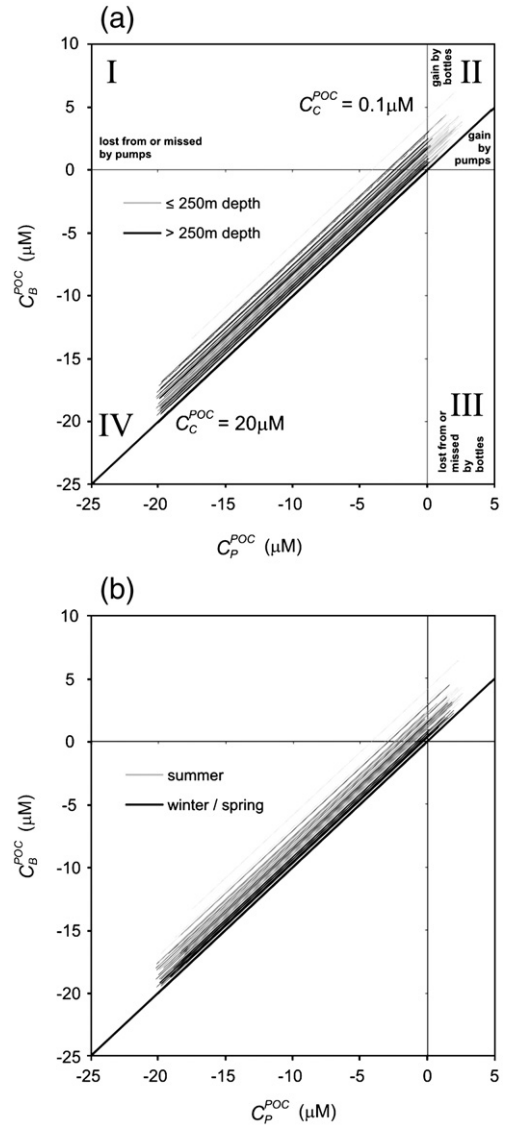

Fig. 10. (a) Concentrations of particulate organic carbon (POC), $C_{\text{B}}^{\text{POC}}$, gained by (positive y-axis) or lost from (negative y-axis) bottles versus POC concentration, $C_{\text{P}}^{\text{POC}}$, gained by (positive x-axis) or lost from (negative x-axis) pumps for each bottle/pump pair of Fig. 8 assuming a range of true POC concentrations ($C_{\text{C}}^{\text{POC}}$) of 0.1–20 μM. Quadrants I–IV are explained in Section 3.3.3. Samples from ≤250 m depth: gray lines; samples from depths >250 m: black lines. (b) Same as (a) but highlighting samples from late autumn/winter/spring (black lines) and summer (gray lines; cruise 282 of RRS Discovery).

a range of assumed $C_{\text{C}}^{\text{POC}}$ of 0.1–20 μM. For $C_{\text{B}}^{\text{PON}}$ and corresponding $C_{\text{P}}^{\text{PON}}$ the measured values of $C_{\text{AB}}^{\text{PON}}$, $C_{\text{AP}}^{\text{PON}}$, V_{B}, V_{P}, $M_{\text{adsB}}^{\text{PON}}$ and $M_{\text{adsP}}^{\text{PON}}$, and a range of assumed $C_{\text{C}}^{\text{PON}}$ of 0.01–3 μM were used.

The sensitivity results for OC are shown in Fig. 10. Each sample is represented by a line. The line represents the range of assumed $C_{\text{C}}^{\text{POC}}$ (Fig. 10a). In these diagrams

there are four quadrants: (I) upper left: $+C_B^{POC}$ and $-C_P^{POC}$, i.e., artificial gain of filterable material in bottle samples and artificial loss from and/or miss by pumps; (II) upper right: $+C_B^{POC}$ and $+C_P^{POC}$, i.e., artificial gain of filterable material in bottle and pump samples; (III) lower right: $-C_B^{POC}$ and $+C_P^{POC}$, i.e., artificial loss from and/or miss by bottles and artificial gain of filterable material by pumps. (IV) lower left: $-C_B^{POC}$ and $-C_C^{POC}$, i.e., artificial loss from and/or miss by bottles and pumps.

The results of the sensitivity analysis (Fig. 10) provide information on the relative likeliness of artificial particle formation and missing/losing of material in bottle and pump procedures. For the surface ocean the whole bundle of lines is shifted further towards the upper right and into quadrant II. Hence, it can be concluded that deep-ocean material is less prone to artificial particle formation and more prone to being missed by and/or lost from samples than surface-ocean material. Moreover, the sample lines are parallel to the 1:1 line but shifted towards quadrant I. The fact that all these lines, covering the same C_C^{POC} range, plot above the 1:1 line indicates that generally pumps are more prone to missing and/or losing material whereas bottle samples are more prone to artificial particle formation.

In Fig. 10b the same data as in Fig. 10a are plotted. However, in Fig. 10b summer data (gray lines) and late-autumn/winter/spring data (black lines) are compared. This seasonal comparison indicates that in the summer the proneness of bottle samples for artificial particle formation is somewhat higher than in late autumn, winter and spring. This holds for both the surface and the deep ocean. Interestingly, no such seasonal pattern occurred in pump data. The nitrogen data show the same general patterns (not shown).

Because $C_C^X \geq 0$ we can constrain the upper possible limit for artificial POC and PON formation from dissolved material to be $\sim 3–4\ \mu M$ OC (Fig. 10a) and $\sim 0.2–0.5\ \mu M$ N (not shown). Typical DOC and DON concentrations in the topmost 200 m of the Northeast Atlantic are $50–70\ \mu M$ and $5–10\ \mu M$, respectively; concentrations in the interior Northeast Atlantic are $44\ \mu M$ DOC and $5–10\ \mu M$ DON (Kähler and Koeve, 2001; Vilas et al., in review). That is, our data indicate that a maximum of 5–10% of DOC and 2–10% of DON in a water sample can coagulate into filterable particles during sampling and/or sample processing using GF/F filters and the sampling and laboratory procedures of this study.

The rate of coagulation of large molecules and/or colloids into larger filterable entities depends on the concentration and 'stickyness' of the particles (e.g., Engel et al., 2004). Both concentration and stickiness tend to be higher in the surface ocean, and during and after phyto-

plankton blooms (e.g., Passow, 2002). This is consistent with the more positive C_B^X and C_P^X in bottle and pump samples from the surface ocean. In contrast to bottle samples it does not seem that pump samples from the deep ocean can be affected by artificial particle creation. The way of sampling and/or sample processing of bottle samples seems to favor artificial particle formation. During the various steps of bottle-sample processing hydrodynamics and temperature regime differ to varying degrees from the natural regime at the sampling location and this could result in artificial particle formation. Interestingly, high amounts of filterable apparent POC and PON were retained on the filter when 8 L of pre-filtered water from the mid-water Northeast Atlantic were re-filtered (Fig. 1a). This experiment resulted in apparent POC and PON concentrations that would have been expected for 8 L of water that was not pre-filtered (Fig. 1b) (a similar effect was observed for samples from the coastal Baltic Sea; data not shown). It seems that, during or shortly after the first filtration, PM was artificially produced, a phenomenon that had been described before (e.g., Chin et al., 1998; Geibert and Usbeck, 2004). The estimated concentration of this artificially produced POC from the mid-water would be $\sim 1\ \mu M$ and, therefore, well within the range of $0\ \mu M$ up to $3–4\ \mu M$ of POC that could be artificially produced from coagulating DOM (see previous paragraph).

Because theoretically C_C^X could have any value >0 it is more difficult to constrain the upper limit of PM that can be lost from or missed by bottles and pumps (cases of negative C_B^X and C_P^X). As for bottle samples, incomplete removal of sample water from the bottles could lead to artificial loss of PM. Rapidly settling particles in the bottles could accumulate below the spigot used to drain the water. If the water below the spigot is not sampled and the proportion of rapidly settling particles is high C_C^X would be underestimated (Gardner, 1977). Because of the use of bottles with spigots above the bulged bottom of the bottle and because the water between the spigot and the bottommost part of the bottle was not sampled this is a potentially relevant factor for Northeast-Atlantic samples in this study. However, this effect would only decrease the bottle/pump discrepancy and cannot be a reason for bottle-derived data to be higher than pump-derived ones. In fact, bottle/pump discrepancies as observed in this study might have even been underestimated because water between the spigot and the bottommost part of the bottle was not sampled.

The advantage of in situ pumps is that there are fewer procedural steps (particularly fewer ones involving hydrodynamic biases) and no temperature changes until the PM comes to sit on the filter. Results reported by

Gardner et al. (2003) however suggest that bottle-derived data might be less biased than pump-derived results: The bottle-derived values for POC concentration during two cruises were only 45% and 87% larger than the values derived from the high-temperature combustion (HTC) method. The disadvantage of the in situ pumps we used is the inlet of the filter holder which remained open during pump retrieval. The possibility of washout of collected material from the filter holder during pump retrieval, leading to underestimated POC and PON concentrations, cannot be ruled out. The potential importance of PM washout from in situ pump filter holders was already mentioned by Liu et al. (2005). The possible significance of PM washout from pumps is supported by increases of the absolute values of R^{POC} and particularly R_C^{POC} with increasing depth (Fig. 9c): Retrieval times of the pumps were short (time scale of minutes) for the surface-ocean in comparison to the deep-ocean deployments (up to more than an hour). The longer the retrieval times the more time there is for material to be washed out of the filter holder.

It has also been suggested that, due to the hydro-dynamics at the water inlet, particles could be modified (disaggregation) and/or selectively sampled (i.e., undersampled) by pumps, potentially leading to underestimated POC and PON concentrations. This type of bias would also include active avoidance by motile zooplankton of being drawn into pumps (Liu et al., 2005). Samples for POC may include heterotrophic bacteria, pico-, nano- and microphytoplankton, micro-zooplankton, detritus, and occasionally some mesozoo-plankton (e.g., Legendre and Michaud, 1999). After correction for adsorption, the bottle-derived POC concentration estimates are higher than pump-derived POC concentration estimates by typically 0.5–2.5 μM. As suggested by Liu et al. (2005) specific members of the micro- and mesozooplankton category could be suffi-ciently mobile to avoid being drawn into the pumps. However, based on studies such as the ones by Tanaka and Rassoulzadegan (2002) and Ramaiah et al. (2005) the total average biomass of these organisms often seems to be less than 1.5 μM POC in the surface ocean and less than 0.5 μM POC in the interior ocean. More-over, sufficiently mobile micro- and mesozooplankton can be expected to constitute only a fraction of this biomass. We, therefore, tentatively conclude that, based on the absolute values of micro- and mesozooplankton biomass estimates and based on the decrease of this biomass from the surface towards the deep ocean, active avoidance of pumps by mobile micro- and mesozoo-plankton is often quantitatively insufficient to explain the differences we see between bottle-derived and pump-derived samples. This statement has to remain specula-tive though because at this stage we do not have suitable plankton data to address this issue within the context of our dataset.

4. Summary and conclusions

Concentrations of particulate material and its con-stituents in seawater have been determined mostly by filtration-based bottle and in-situ-pump approaches. For POC measurements usually glass-fiber (GF/F) filters have been used. It has been known that, typically, bottle-derived POC concentration estimates are higher than pump-derived POC concentration estimates. Almost all of the data previously published in this context originate from the surface ocean. By adding a comprehensive set of surface- *and* deep-ocean data we show that there is an increasing divergence between bottle- and pump-derived estimates from the surface towards the deep ocean with bottle-derived values being up to more than one order of magnitude higher than pump-derived ones.

A number of possible reasons for such discrepancies have been proposed. In this study, we provide evidence to support the significance of adsorption of DOM onto filters and indicate that the adsorbing material is a ni-trogen-rich fraction of the bulk DOM. We found en-hanced amounts of adsorbed OC in the surface ocean (often ~ 0.5 μmol cm^{-2} of exposed filter) as compared to the deep ocean (often ~ 0.2 μmol cm^{-2} of exposed filter). It is shown that ads-uncorrected POC concentra-tion estimates depend not only on the filtered volume, true POC concentration and amount of adsorbed OC, but also on the filter area. The mere equality of ads-uncorrected bottle-derived and pump-derived concen-tration estimates is no guarantee of accuracy of either measurement.

In virtually all cases studied correction for adsorption was important, but not sufficient, to explain bottle/pump differences. Artificial formation of filterable particles or processes leading to originally-filterable material being lost from and/or missed by sample-processing proce-dures must be considered. Deep-ocean material is less prone to artificial particle formation and more prone to being missed by and/or lost from samples than surface-ocean material. Pump procedures tend to be more prone to missing and/or losing material whereas bottle pro-cessing procedures are more prone to artificial particle formation. Bottle procedures also seem to be more sea-sonally sensitive throughout the oceanic water column than pump procedures. We can constrain the maximum amount of POC and PON that can be artificially formed from DOC and DON per liter of filtered ocean water to

be $\sim$3–4 μM OC and $\sim$0.2–0.5 μM ON (5–10% of bulk DOC and 2–10% of bulk DON). The challenge now is to further constrain the magnitude of the biasing effects that add to the adsorption effect, and to find time-efficient methods to quantify these effects. Also a standardization of procedures among labs is advisable.

Biasing effects seem to be particularly crucial in the deep ocean where, as indicated by optical seawater characteristics, particulate-matter concentrations are definitely smaller than in the surface ocean. Given the large volume of the deep ocean it is expected to store a sizeable amount of carbon in the particulate phase despite its comparatively low concentrations. The uncertainties of oceanic POC concentrations, inventories and corresponding fluxes translate into increased uncertainties of biogeochemical models and their predictions. Because of this crucial link "it is imperative that we come to closure on the methods used to measure particulate carbon" in natural waters as pointed out by Gardner et al. (2003) and that the methods become standardized.

Acknowledgements

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