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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 ∼3–4 μM OC (5–10% of dissolved OC) and ∼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.

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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

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