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The oceanographic toolbox for the collection of sinking and suspended marine particles

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ABSTRACT

Marine particles play a central role in controlling the transport, cycling, and inventories of many major elements and trace elements and isotopes throughout the oceans. Studies seeking to elucidate the biogeochemical roles of marine particles often require reliable ways to collect them from the ocean. Here, we review the oceanographic toolbox of techniques and instrumentation that are employed to collect both suspended and sinking particles. With these tools, it is possible to determine both the concentrations and vertical fluxes of important elements and individual particle types. We describe the various methods for quantifying the concentrations of particulate matter with in situ pumps, towed sampling devices, bottle collectors, and large volume capture devices. The uses of various types of flux collection platforms are discussed including surface tethered, neutrally buoyant, and bottom moored devices. We address the issues of sediment trap collection biases and the apparent inconsistencies that can arise due to differences in the temporal and spatial scales sampled by the various methodologies. Special attention is given to collection considerations made for the analysis of trace metals and isotopes, as these methodologies are of high importance to the ongoing GEOTRACES program which seeks to identify the processes and quantify fluxes that control the distributions of key trace elements and isotopes in the ocean. With the emergence of new particle collection methodologies and the continued reliance on traditional collection methods, it is imperative that we combine these multiple approaches in ways that will help improve their accuracy and precision while enhancing their utility in advancing understanding of the biogeochemical and ecological roles of marine particles.

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Introduction

Marine particles (Fig. 1) play a critical biogeochemical role in determining the distribution and concentration of carbon, nutrients, and many trace elements and isotopes (TEIs) throughout

the oceans. They serve as a vehicle for transporting material both vertically and horizontally throughout the oceans and act as oases of chemical and biological activity. For these reasons, the careful study and physical collection of particles is an important component of any oceanographic investigation attempting to identify the processes and quantify the fluxes that control the oceanic distributions of the elements.

Particle concentrations, compositions, and basic dynamics are crucial parameters for understanding the scavenging and removal of particle-reactive TEIs. Particles can be direct sources of TEIs to the water column at ocean interfaces (e.g., the atmospheric deposition of mineral dust, or the input of sedimentary material from the ocean margins) as well as agents for their removal, by

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providing surfaces for the adsorption and subsequent removal of particle-reactive TEIs. Indeed, particles are central to the internal cycling of many TEIs via processes of active biological uptake and remineralization (Morel et al., 2003), passive scavenging and desorption (Bacon and Anderson, 1982), and transformations of particles between the suspended and sinking classes through processes of aggregation and disaggregation (Clegg and Whitfield, 1990; Nozaki et al., 1987). Total and acid-leachable concentrations of TEIs can provide information about the source and scavenged fractions, respectively (Landing and Bruland, 1987). The degree of particle reactivity of a trace element or isotope can be assessed by calculating partition coefficients, which describe the equilibrium partitioning between dissolved and particulate phases (Chase et al., 2002). The controls on the scavenging behaviors of many TEIs are not well understood, however, and are thought to be a function of total particle concentration and/or particle phases such as CaCO_3 , opal, particulate organic matter, and lithogenic material (Chase and Anderson, 2004; Chase et al., 2002; Luo and Ku, 2004). All of these metrics of the role of particles in TEI cycling require the physical collection of particles followed by laboratory-based measurements.

Direct measurements of particle fluxes are also important for several reasons. For all particle reactive and/or bioactive TEIs, their association with sinking particles and flux to depth determines their residence time in the surface ocean and recycling within the subsurface waters. These processes also set up the gradient in surface to deep-water concentration profiles. It is therefore imperative that we measure the downward fluxes of carbon, nitrogen, phosphorous, silicon, and the key TEIs in order to quantify the amount of material that is transported to different depth horizons by the ocean's biological pump. These elemental fluxes are necessary to constrain models ranging from mechanistic simulations of particle dynamics to global biogeochemical simulations (Honeyman and Santschi, 1988; Jackson and Burd, 2002, 2014; Schlitzer, 2002, 2004; Yamanaka and Tajika, 1996). In addition to constraints on the quantity of material sinking through the water column, the collection of sinking material can provide insights into the processes and mechanisms that control the flux of particles to depth.

Particle concentrations (C) and fluxes (F) are linked by the sinking rate (w), $F = C * w$ (e.g., Bishop et al., 1987). However, this sinking rate is difficult to determine independently for all particles classes, sizes and chemical compositions, and is known to vary

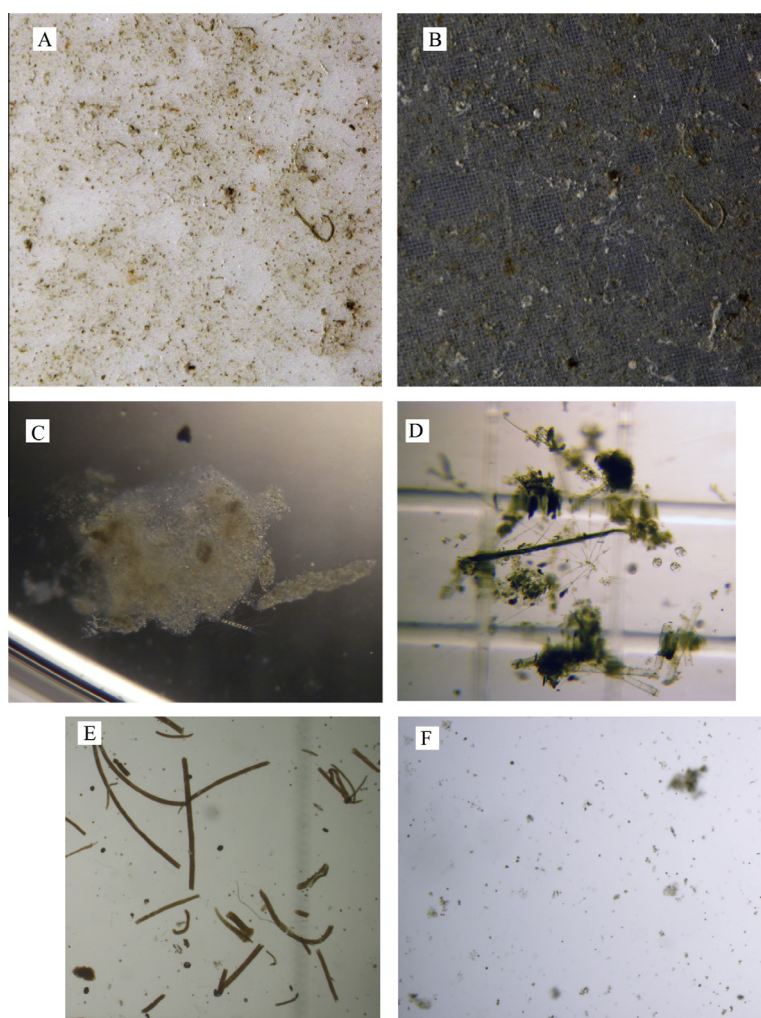


Fig. 1. Images of various particle collections obtained from large volume in situ pumps and polyacrylamide gel sediment traps. Panels A and B show samples from the Multiple Unit Large Volume in-situ Filtration System (MULVFS) on 51- μm mesh filters against white (A) and black (B) backgrounds to highlight the dark and light aggregates, respectively. Samples A and B are from 138 m in the Subantarctic Pacific (from Lam and Bishop, 2007). Panels C and D show examples of large sinking particles collected using the Marine Snow Catcher, (C) a marine snow aggregate from 57 m in the Norwegian Sea (70°N) and (D) a phytodetrital aggregate (whole diatom cells are visible) from 95 m in the South Indian Ocean (55°S). Panels E and F show particle collections from polyacrylamide gel samples of sinking particles from (E) the west Antarctic Peninsula at 50 m and (F) the Sargasso Sea at 150 m.

considerably in space and time as well as vertically in the water column (Bishop et al., 1978; McDonnell and Buesseler, 2010; Stemmann et al., 2004). This general decoupling between concentrations and fluxes demands that both parameters need to be measured concomitantly in order to fully describe the dynamics of particles in the marine environment.

In the following sections we describe the current techniques used to assess both the concentrations and fluxes of particles in the water column and discuss the special considerations that need to be made when designing an experimental plan to measure these parameters. We focus on methods relevant for the study of TEIs and the GEOTRACES program. Sampling methods for collecting suspended particles using in-situ filtration and on-deck filtration from GO-Flo bottles were the subject of intercomparison activities during the U.S. GEOTRACES intercalibration cruises in 2008 and 2009. The results of these studies are reported in the “Sampling and Sample-handling Protocols for GEOTRACES Cruises” (GEOTRACES, 2010) and published in the recent special issue in *Limnology and Oceanography: Methods* (Bishop et al., 2012; Planquette and Sherrell, 2012), and so will only be dealt with briefly here. In contrast, comparison of sampling methods for collecting sinking particles were not part of the GEOTRACES intercalibration activities, and so will be reviewed here more comprehensively. We limit our review to collection methods for particulate matter >0.2 μm and their application in studies of biogeochemical cycling. In doing so, we do not cover methods focused on the collection of very small particles and colloids <0.2 μm or methods that are aimed specifically at the collection of living plankton, despite the important effects these classes of particle have on biogeochemical cycles. Optical and imaging techniques for particles (without collection and retrieval) are covered in Boss et al. (2014).

Measurement of particle concentration

In situ pumps and filtration

In-situ pumping allows the collection of a depth profile of size-fractionated samples of marine particulate matter from the filtration of hundreds to thousands of liters of water in the water column. The large volumes filtered using in-situ pumping allow the collection of sufficient quantities of material for size-fractionation and the distribution of subsamples to multiple investigators for the measurement of many TEIs and other analytes, including low abundance short and long-lived radiogenic isotopes, particulate trace metals, and major particulate components. The collection and measurement of particulate parameters from a large (>53 μm , Fig. 1A–D) and a small size class (e.g., <53 μm) allows for an understanding of basic particle dynamics that would not be possible from total suspended particles alone.

Size-fractionation is an imperfect operational method to separate suspended from sinking particles, since other factors besides particle size, such as particle porosity, excess density and shape, can also be important factors in determining particle sinking speeds. However, size-fractionation by in-situ filtration remains an important tool in the oceanographer’s sampling toolbox as it can provide insights on particle dynamics, particularly when the use of sediment traps is impractical. For example, the analysis of profiles of particulate organic carbon from the sinking and suspended size classes provides a complementary view to that of flux profiles for the transfer of carbon to depth (Lam and Bishop, 2007; Lam et al., 2011). Inverse methods can be used on size-fractionated particle concentrations in combination with multiple thorium isotope distributions to constrain rates of sorption reactions and particle dynamics (Marchal and Lam, 2012; Lam and Marchal, 2015).

The partitioning and systematics of particulate barium in the suspended and sinking size classes provide a qualitative view of the depth of particle aggregation and disaggregation processes (Bishop and Wood, 2008; Bishop, 1988). Lam et al. (2006) discovered micron sized particulate iron oxides of continental margin origin in large aggregate particles far off shore in the subarctic north Pacific, supporting the conceptual view that the origin of large particles is from the aggregation of small, suspended particles. While further investigation is needed, the suitability of size-fractionated large particles as a proxy for sinking particles is qualitatively supported by one study of organic biomarkers: Abramson et al. (2010) found that the biomarker composition of large particles collected by in-situ filtration was often more similar to that of sinking particles collected by sediment traps rather than that of small particles collected by in-situ filtration. The size-fractionated behavior in particulates illuminates the sources and sinks of other TEIs (Lam and Marchal, 2015; Jeandel et al., 2014).

In-situ filtration systems currently in use include the ship-powered Multiple Unit Large Volume in-situ Filtration System (MULVFS, Fig. 2B), the battery-powered McLane Research Laboratories Large Volume Water Transfer System (WTS-LV, known as “McLane pumps”, Fig. 2C), and the Challenger Oceanic Stand Alone Pump System (SAPS). A depth profile of trace-metal clean size fractionated particles is collected by attaching individual in-situ pumps in sequence onto a non-metallic line, and programming them to pump at target depths for 2–4 h. The depth of pumps is determined by the wire out, and monitored throughout the pumping time using a pressure sensor such as a self-recording CTD at the end of the line and/or a submersible pressure data logger attached to individual pumps such as those made by RBR. Typically, up to 12 pumps are attached to a line at once. On the U.S. GEOTRACES North Atlantic Zonal Transect cruise (USGT NAZT), a 16-depth profile of size-fractionated particles was collected over two casts, deploying 8 pumps in the upper 1000 m, and 8 pumps in the lower 1000–5000 m depth range.

Collection of particles for trace metal studies has also been accomplished with in situ submersible impeller pumps that transfer particle-laden water from the water column up to the shipboard laboratory for filtration and sample processing (Savoie et al., 2008; Trull and Armand 2001). This approach enables hundreds of liters of seawater to be passed through a series of Teflon or nylon screens as well as large diameter quartz filters in the laboratory and avoids some of the design challenges of in situ filter holders and ambient fluid motion (see Section ‘Filter holders for in-situ filtration’). However as with some of the towed vehicle pumping systems, these approaches expose fragile particles to turbulent fluid environments as they pass through the pumps and hoses en route to sample processing apparatus in the shipboard laboratory (see Section ‘Underway and towed sampling systems’).

Filter types used for in-situ filtration

A description of the filter types used for in situ filtration is detailed in Table 1. The large particle size fraction is typically collected onto a precision woven mesh prefilter. For the USGT NAZT, a 51 μm polyester mesh prefilter with high percentage open area (33%) (Sefar Petex 07-51/33) was used (Lam et al., 2014; Ohnemus and Lam, 2014) to be as consistent as possible with the large archive of 53 μm data that exists in the literature (Bishop et al., 1977; Lam et al., 2011). Fig. 1A and B shows an example of the types of large particles that are collected on such filters.

No single micron or sub-micron filter type can accommodate the needs of all desired measurements. Glass and quartz fiber filters (such as Whatman GF/F and QMA, respectively) have excellent flow characteristics, even particle distribution, and are suitable for measurement of particulate organic matter by combustion (Abramson et al., 2010; Bishop et al., 1999). Because glass and

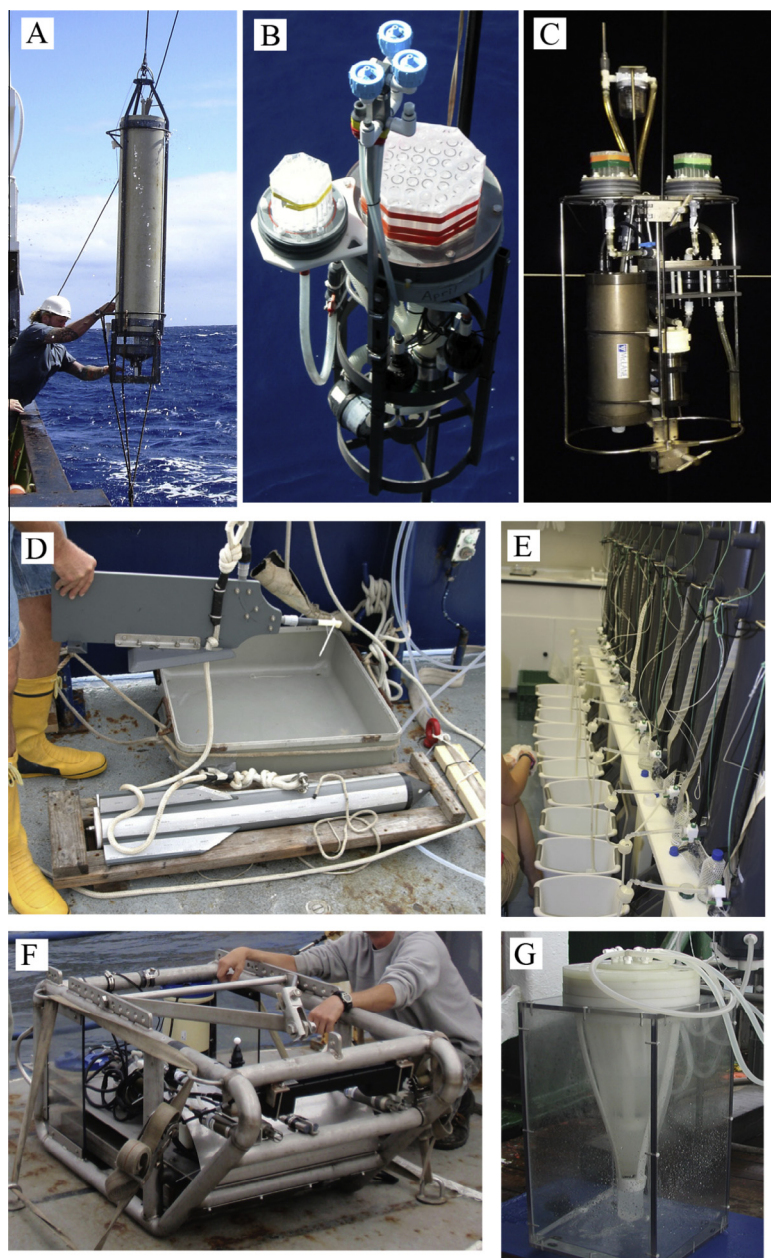


Fig. 2. Oceanographic sampling devices for the collection of suspended particulate matter. (A) The marine snow catcher, (B) MULVFS pump and filtration unit, (C) McLane in situ pump, (D) a towed trace metal clean surface sampler/fish system, (E) Go-Flo bottles, (F) the “SuperSucker” pumping towed vehicle, (G) trace metal clean gravity size-fractionated filtration apparatus.

quartz fiber filters are depth filters, increasing the depth of filtration by stacking more than one filter together increases the efficiency of particle retention. Indeed, a pair of QMA filters, each with nominal pore size of 1 μm , collected similar POC and chlorophyll compared to a single GF/F, with a nominal pore size of 0.7 μm (Bishop et al., 1999). Quartz fiber filters are also suitable for measurement of short-lived radionuclide by counting methods (Buesseler et al., 1998) and measurement of TEIs by weak (Bishop and Wood, 2008) and strong (Bowie et al., 2010) acid leaches. Glass and quartz fiber filters are, however, not suitable for measurement of TEIs that require total digestion using strong acids that include hydrofluoric acid, as the digested quartz filter material contributes a high blank value. Instead, plastic filters are best for the measurement of TEIs by strong acid digestion, but typically have poorer flow and particle distribution characteristics compared to quartz fiber filters, making it more challenging to collect

enough material and to representatively subsample a filter for distribution to multiple investigators. During the GEOTRACES intercalibration cruises, several plastic submicron filter types and pore sizes were tested (Table 1; Bishop et al., 2012). Paired 0.8 μm polyethersulfone (e.g., Pall Supor) filters were selected as the best choice, as the two 0.8 μm Supor filters together collected a particle population similar to a single 0.45 μm Supor filter, as judged by particulate P, Cd, Mn, and Ba concentrations, but with much better flow and particle distribution characteristics (Bishop et al., 2012). Similarly, a single 0.8 μm Supor filter collected a particle population similar to paired QMA filters.

Because of the requirement for collection of particles on both plastic filters for the measurement of many TEIs and quartz filters for the measurement of organic matter, a dual in situ pump (e.g., a modified McLane pump (GEOTRACES, 2010)) or multiple flow path (e.g., MULVFS) in-situ pump is the most efficient way to do this.

Table 1
Filter types used for particle collection by in-situ filtration.

Filter type	Example brands	Nominal pore size	Notes
<i>Mesh prefilters</i>			
Nylon mesh	Nitex®	Various (e.g., 1–1000 µm)	Absorbs moisture so less suitable for gravimetric analysis; 53 µm or 70 µm most common
Polyester mesh	Sefar Petex®	Various (e.g., 1–5000 µm)	Suitable for gravimetric analysis; 51 µm most common
<i>(Sub)micron filters for particulate organic matter</i>			
Glass microfiber	Whatman GF/A–GF/F; Sterlitech GF75	Various (e.g., 0.3–2.7 µm for 142 mm)	Whatman™ GF/F most common (0.7 µm pore size)
Quartz microfiber	Whatman QMA	1.0 µm	Lower blanks for leachable trace metals and low level beta counting than GF/F, but only one nominal pore size available
<i>(Sub)micron filters for particulate trace elements</i>			
Polyethersulfone (depth filter)	Pall Supor; Sterlitech PES	Various (e.g., 0.1–0.8 µm for 142 mm)	Depth filter; good flow characteristics; excellent handling; difficult to digest
Mixed cellulose esters (depth filter)	Millipore MF	Various (e.g., 0.1–8 µm for 142 mm)	Depth filter; good flow characteristics; fair handling (brittle when dried); easier to digest than PES; higher particle retention than PES for same nominal pore size
Polycarbonate (track-etch filter)	Poretics PCTE; Whatman Nuclepore	Various (e.g., 0.05–5 µm for 142 mm)	Poor flow characteristics; poor particle distribution; low seawater retention (suitable for gravimetric analysis)

Filter holders for in-situ filtration

The design of the filter holder is important for the in situ collection of size-fractionated particles. Many commercially available (e.g., standard McLane) and “home made” single-baffle 142 mm filter holders were evaluated during the two US GEOTRACES intercalibration cruises. Results demonstrated the loss of up to 90% of the large particle fraction, particularly biogenic or bio-associated elements such as P, Sr, Ba, and Cd (Bishop et al., 2012). Similar losses have been confirmed for biogenic Si (Bishop, unpublished). Bishop et al. (2012) also demonstrated that flow rate (filtration velocity through filters) can lead to a bias in the preservation of large aggregates; however they noted that the bias is not specific to a particular particle size class. The large particle loss bias can be minimized through the use of filter holders that have multiple baffle systems similar to the MULVFS system (Bishop and Wood, 2008) or the newly designed 142 mm “mini-MULVFS” filter holder (Bishop et al., 2012); both styles ensure even particle distribution and minimize the loss of large particles, and thus are strongly recommended. Although fragmentation of fragile aggregates remains a possibility, the effects are manageable at a filtration face velocity below 1 cm/s.

Sample preservation

Bishop and Wood (2008) discovered that post sample collection preservation methodology had a huge impact on the preservation of organics. Samples stored slightly wet had lost 50–70% of the POC and PN prior to analysis months later. Oven drying of samples at 60 °C for at least 24 h is effective at preventing such a bias.

For more details on in-situ pump protocols for GEOTRACES, please see the in-situ pumping protocols chapter in the “Sampling and Sample-handling Protocols for GEOTRACES Cruises” (GEOTRACES, 2010), and findings from the in-situ pump activities of the U.S. GEOTRACES Intercalibration cruises (Bishop et al., 2012).

Bottle collection

For analyses that do not require large volumes, particle collection from ship-board filtration of GO-Flo bottles (Fig. 2E) provides better spatial and temporal resolution. GO-Flo filtration methods were tested on the U.S. GEOTRACES Intercalibration cruises and compared to particle collection by in-situ filtration. The following is a summary of the findings and recommendations that are detailed in Planquette and Sherrell (2012). Particles are generally filtered “on-line”, where the GO-Flo headspace is pressurized with 0.2 µm-filtered air, and the water is filtered through membrane

filters in filter holders (25 mm or 47 mm) that are connected directly to the GO-Flo stopcocks (Fig. 2E). Alternatively, particles may be filtered “off-line”, in which a fixed volume of water (e.g., 4 L) is sampled immediately from the GO-Flo into a sampling bottle, which is then filtered quantitatively. There was general agreement with no systematic difference between particulate TEIs collected by GO-Flo filtration and by in-situ filtration, allowing the possibility of combined sampling strategies for a single cruise. However, the smaller sample volumes and possibility of particle loss by settling in the GO-Flo bottle prior to filtration require that certain precautions be taken for successful particulate sampling from GO-Flo filtration. The selection of a filter with low blanks is critical to the ability to measure dilute particulate TEI concentrations from small volumes. For this reason, Supor 0.45 µm polysulfone filters are recommended, together with extensive and careful characterization of process filter blanks, in which pre-filtered clean seawater is filtered.

The effects of particle settling in the GO-Flo bottle prior to filtration can be minimized by gentle mixing of the sampling bottle prior to filtration, and limiting filtration time to 1–2 h (Planquette and Sherrell, 2012). Filtration of the entire bottle volume, if possible, can also ensure that all particles are collected, provided that particles that settle below the level of the sampling drain valve during filtration are also collected. If particles are pressure-filtered, this can be done by attaching a piece (~25 cm) of acid-cleaned Teflon tubing to the inside of the drain valve with a beveled end that fits against the opposite side bottom of the bottle (Cutter and Bruland, 2012). We focus here on trace metal-clean particle collection from GO-Flo bottles, although the same principles to minimize artifacts from particle settling apply to particle collection from Niskin bottles.

Previously reported discrepancies between Niskin bottle and pump-determined POC (Gardner et al. 2003; Liu et al., 2005; Liu et al., 2009), with bottle POC usually higher than pump POC. One explanation for this discrepancy is large particle loss from washout of the prefilter stage from single-baffled in-situ pump filter holders (Bishop and Wood, 2008; Bishop et al., 2012; Liu et al., 2009). Indeed, when multiple-baffled in-situ pump filter holders were used, there was good agreement between bottle and pump-determined POC (Bishop and Wood, 2008). In addition, bottles have been shown to collect more zooplankton when compared to in situ pumps, whereas larger inlet orifices on in situ pumps can minimize zooplankton retention (Liu et al., 2009).

Dried acid cleaned Petri slides are often used for small volume filter storage prior to analysis. Bishop (unpublished data) has found

that significant fractionation of salt constituents can occur. This is particularly important for the determination of particulate inorganic carbon from salt-corrected Ca in the presence of residual salt. Elimination of this bias is achieved by placement of the filter into the acid cleaned sample bottle where it will be subsequently analyzed.

Large volume capture

Large volume capture devices are a form of bottle collection that offer the opportunity to collect marine snow aggregates and either measure their sinking rates and composition via observations within the system or once the material has settled within the device. In this manner, individual aggregates can be observed as they sink and can be recovered without having collided into other sinking particles as happens in sediment traps. At least two such systems have been developed. These include the Sea Core Sampler (Kjørboe, 2007) and the Marine Snow Catcher (Lampitt et al., 1993; Riley et al., 2012). In recent years the Marine Snow Catcher has been deployed in a variety of locations to examine the major modes of particle sedimentation and to estimate total flux. These regions include the PAP site in 2009, the open water and ice covered regions of the Arctic in 2010 and 2012, the subtropical Atlantic in 2011 and the South Atlantic Ocean in 2011, and the South Indian Ocean in 2012.

The Marine Snow Catcher (Fig. 2A) is a large volume (100 L) water bottle, 1.5 m tall, composed of two parts, an upper section (93 L) that is detachable from the lower section (7 L). Two large terminal openings allow water to enter the device as it is lowered through the water column from the vessel's winch system. A weighted messenger is sent along the wire to capture a parcel of water at the desired depth. Once recovered, the water and the particles contained in it can be subjected to a variety of analyses or further experimentation. Particle concentration measurements can be made by filtration. Individual particles can also be identified, imaged, or further analyzed.

After recovery aboard the ship, a 2 h settling experiment allows particles to separate into three operationally defined sinking classes: suspended, slowly sinking, and fast sinking (Riley et al., 2012). The fast sinking particles are those collected from the bottom of the base chamber, while the measurement of the difference in particle concentrations between the top and base sections of the Marine Snow Catcher enable the quantification of the concentration of slowly sinking particles. Any aggregates that settle onto the base of the instrument over the settling period can be picked from the base unit (once the upper section is drained and detached) and their sinking speeds and individual particle properties measured. With current analytical capabilities, the measurement of POC content in individual marine snow aggregates is difficult due to their small nature and low concentrations relative to instrumental detection limits. Therefore empirical relationships of marine snow aggregate POC and PON contents following Alldredge (1998) can be used to calculate the POC and PON concentrations of the fast-sinking particle pool. These relationships are based on measurements of several individual marine snow aggregates collected in the coastal region of California. As such, further work is necessary to better constrain the relationships between marine snow aggregates and their particle contents. Once estimates of the particle concentrations and their sinking velocities are obtained, bulk fluxes can be calculated for fast and slowly sinking particles if the concentration of the phase of interest is known.

Limitations of the technology lie with the efficiency of collection of the marine snow aggregates. This is determined by how well an individual can see the particles to isolate and pick them out of the base chamber. Furthermore, in scenarios where large numbers of particles may be sinking, isolation of individual

particles may prove difficult. Therefore further development of the technology is required. Use of polyacrylamide gels (Lundsgaard, 1995) in the base of the chamber (Section 'Collection of intact sinking particles for imaging and other analyses') may be a useful technique to isolate individual particles for enumeration and measurement for flux calculations.

Plankton nets

The first reports of the trace metal composition of plankton were from samples sampled by plankton nets towed or suspended from a research vessel (Martin and Knauer, 1973). Despite precautions to minimize contamination, the authors still reported removing metal particles from plankton samples using a magnet, and manually removing paint chips from samples. Later trace metal clean net towing efforts employed inflated rubber rafts to move upstream of the main research vessel, and removing and stowing the motor before any of the non-contaminating towing equipment was set up (Collier and Edmond, 1984). Nets were lowered and raised repeatedly using a PVC-hand winch until enough sample had been collected, "or until the operators had 'expired'" (Collier and Edmond, 1984). More recent trace metal-clean plankton net sampling efforts have opted to use Teflon-coated GO-Flo bottles to bring large volumes (120 L) of water on board, and using a patented trace metal clean gravity filtration device consisting of a series of acid-washed Nitex nets in sequence enclosed within a polycarbonate container to gently collect size-fractionated phytoplankton (Ho et al., 2007; Wen et al., 2005; Fig. 2G).

Underway and towed sampling systems

To improve the spatial and temporal resolution of marine particle collection from research vessels, there have been several successful efforts to sample from underway and towed systems. In these applications, clean and relatively undisturbed water and particles can be pumped through tubing up to the ship for collection, processing, and analysis. These systems overcome some of the particulate, zooplankton, and trace metal contamination issues posed by the use of conventional hull-mounted seawater flow through systems (Buesseler et al., 1998). Underway and towed sampling approaches also minimize the amount of ship time dedicated to sampling.

The "Kiel Pumping System" allows for trace-metal clean particles to be collected by means of a large volume continuous-flow centrifuge connected to an underway pumping system. All components of the underway pumping system are made of HDPE and Teflon that can be cleaned and transferred between vessels, and the high speed continuous-flow centrifuge is made of chemically resistant and non-contaminating materials (Schüßler and Kremling, 1993). This system was used to determine the spatial variability of particulate trace elements in the North Atlantic (Kuss and Kremling, 1999a,b).

Several different versions of towed sampling devices have been deployed. The simplest type consists of a subsurface vehicle (fish) such as a bathythermograph to which an intake tube is attached and oriented into the oncoming water (Boyle et al., 1982; Vink et al., 2000; Bruland et al., 2005, Fig. 2D). This tube then leads up along the tow line to the ship where a peristaltic pump supplies the sample water to the shipboard collection apparatus. With a long boom extending from the edge of the ship, the vehicle can be towed outside the wake of the ship to avoid sample contamination. A configuration such as this one allows for underway sampling from near-surface waters. Other versions include submersible pumps to transfer particulate matter from the water column through hoses up to various filtration or sample processing setups onboard the ship. The continuous underway fish egg collec-

tor system (CUFES) is one such example that can be used to identify and map the spatial distributions of different particle types such as fish eggs (Checkley et al., 1997).

In an effort to obtain particulate samples from a vertical section in the water column while an oceanographic research vessel is underway, larger and heavier vehicles mounted with depressor plates or wings have been used. Submersible pumps fit to piloted undulating vehicles such as the SeaSoar are capable of pumping seawater samples up to the ship through a long hose embedded in the tow cable (Hales and Takahashi, 2002). While transiting at 6–7 knots, this system can obtain transects from the surface down to a few hundred meters. Similar sampling can be accomplished using an unpowered vehicle with depressor plates (Fig. 2F) while varying the length of wire, however this approach requires significantly slower sampling speeds (Hales et al., 2005).

As water and particles are pumped onto the ship from a towed vehicle, they can be filtered manually or with semi-automated filtration systems. These samples can then be used to calibrate relationships between in situ optical properties (measured by sensors mounted to the towed vehicle) and particle concentration or composition (Hales et al., 2006; Holser et al., 2011).

The collection of marine particles from towed vehicles does involve subjecting fragile marine particles to aggressive intake, pumping, and transfer through long and small diameter tube. As such, while this method has proven useful for mapping out the distributions of particles and bulk concentrations, this method may not be well suited for assessing the size distributions or physical nature of delicate individual particles.

Sorting flow cytometry

Flow cytometry is a technique that has been widely adopted in the study of marine microbes (Marie et al., 1997; Olson and Frankel, 1983; Olson and Sosik, 2007; Yentsch et al., 1983). Although the focus of these efforts has been primarily on the community structure of marine plankton and even their associated biogeochemical rate processes (Lomas et al., 2011), flow cytometers have revealed that the large majority of particles are detrital particles rather than live cells (Minor et al., 1999; Olson and Sosik, 2007). In this sense, sorting flow cytometers represent a promising tool that can be used to enumerate, image, and characterize the chemical composition of various subpopulations of particles in the water column (Minor et al., 1998). To our knowledge this technique has not yet been extended to trace elemental analyses, something that would certainly improve our understanding and models of how particles and microbes affect the cycling of trace elements in the oceans. This technology can be operated remotely, making it well suited for integration with the next generation of ocean observatories. Methodological obstacles in the use of flow cytometers in the study of marine particles remain, however. These include limitations on the size ranges of particles that can be effectively sampled by microfluidic system, the need to pre-concentrate particles so that sufficient quantities of particles can be analyzed, and the potential for particle disruption during sampling and processing. Nevertheless, flow cytometry has the potential to greatly expand our understanding about the nature and dynamics of particulate matter in the oceans through the combination of information about particle physical characteristics, chemical composition, and biogeochemical rate processes.

SCUBA collection of particles

Large particles greater than about 500 μm are visible to the human eye and can therefore be collected directly by SCUBA divers (Alldredge, 1991). Using syringes or trace-metal clean tubing, individual particles can be collected in situ with minimal quantities of

ambient seawater. As individual particles do not contain enough material for analysis, combining numerous syringe-collected particles into a single sample makes it possible to obtain enough material to conduct chemical analyses such as carbon, nitrogen, and content of those particles (Alldredge, 1998). Alternatively, particles can be hand-collected in larger jars allowing for in situ manipulation or incubation of particulate matter. Other critical properties such as sinking velocity can also be observed directly by divers, and the subsequent collection of these individual particles has enabled very important studies of the linkages between sinking velocity and particle composition (Alldredge and Gotschalk, 1988). Although these approaches are labor intensive and restricted to the upper ~ 50 m of the ocean, these collection methods have yielded information and relationships that form much of the basis of our understanding of individual particle properties. There is still much that needs to be learned about the composition of individual particles, and as such new studies that combine these direct collection methods with modern chemical or biological analyses may lead to new discoveries and understanding.

Measurement of particle fluxes

Flux collection platforms

Sediment traps have arguably taught us more about the sources, magnitude and vertical attenuation of sinking particle fluxes in the ocean than any other tool. These instruments are designed to directly intercept and collect sinking particles during their transit to depth. This collection is typically accomplished with a collection tube or sampling cup (with or without a funnel above to increase collection area). In this manner, sediment traps have the ability to contribute significantly to the GEOTRACES mission of identifying the processes and quantifying the fluxes of TEIs in the ocean.

The earliest ocean sediment traps were developed the 1970s, and generally anchored to the ocean bottom at a fixed depth, or several depths above the seafloor. Moored traps are most often deployed in the deep sea and with the capability to collect a time series of flux samples by rotating a fresh collection cup in place with daily to weekly sampling resolution over a 6–12 month deployment (Berger, 1971; Honjo, 1976). Drifting traps that are tethered below a surface drifter are more commonly deployed in the upper 1000 and are configured with single (or replicate) cylindrical collection tubes of which the most common design is called a Particle Interceptor Trap (Knauer et al., 1979).

More recently, Lagrangian and neutrally buoyant trap designs eliminate the tether completely (Buesseler et al., 2000; Lampitt et al., 2008; Sherman et al., 2011; Valdes and Price, 2000, Fig. 3D and E). Such traps have the advantage of being free from the influence of surface currents/wind stress and can instead move with local currents at the depth of deployment, thus minimizing the hydrodynamic interferences that can bias collection efficiencies when using traditional, tethered traps (Buesseler et al., 2007). One such trap design, which can be used to depths of ~ 1000 m, is PELAGRA (Particle Export measurement using a LAGRangian trap, Fig. 3E). It consists of four sample funnels arranged around an APEX float, widely used as part of the international ARGO project. The float can be programmed to target either a predetermined pressure or density surface, which requires an initial CTD profile from the deployment area, and the trap's position is then maintained by slight changes to the volume of the float's oil bladder. Each of the four funnels leads to a separate detachable sample pot that can be programmed to open and close separately or in unison, giving the flexibility of collecting replicate samples or a short time-series. An attached Idronaut CTD data logger provides a record of in situ conditions throughout the deployment. At the end of the sampling period, after

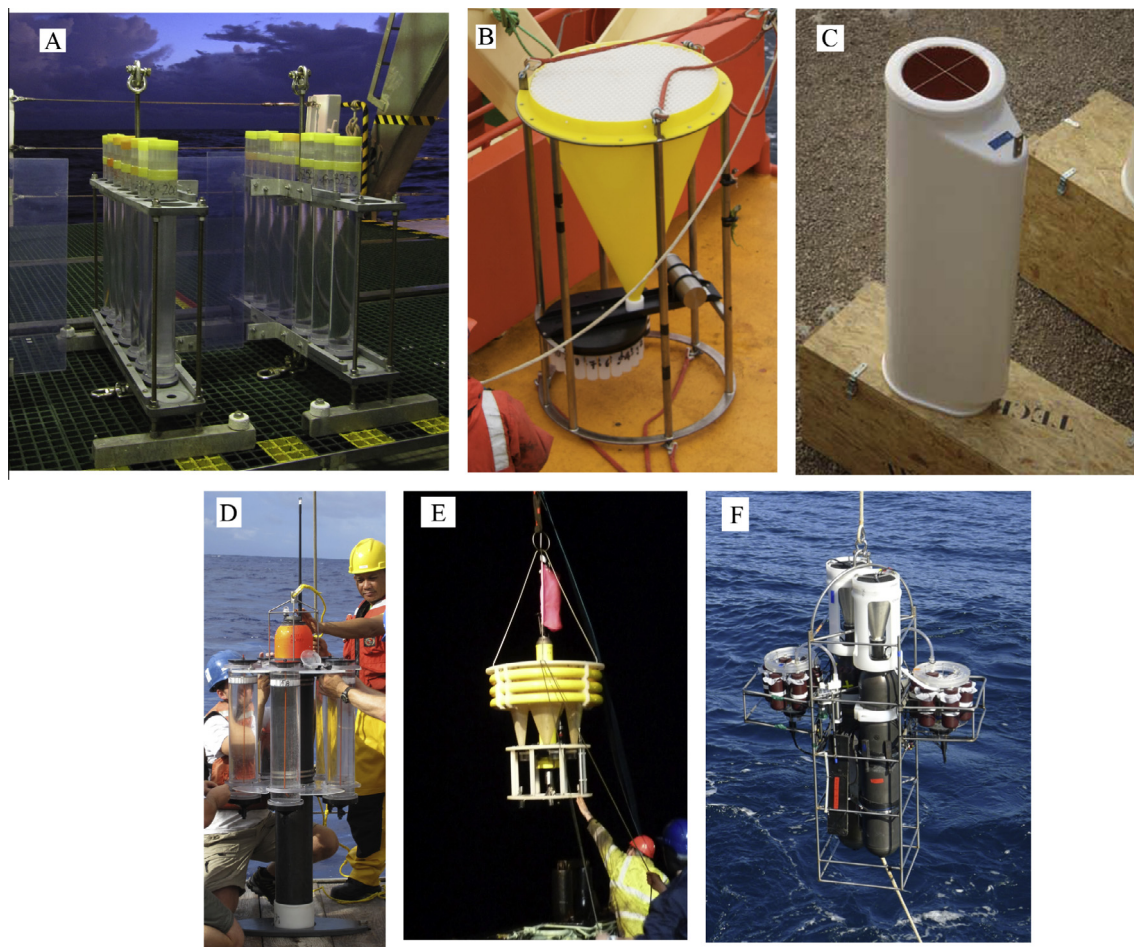


Fig. 3. Various devices for the collection of sinking particles. (A) PITS traps used in the Bermuda Atlantic Time-series Study, (B) the conical McLane time-series sediment trap, (C) the time-series cylindroconical sediment trap manufactured by Technicap, (D) an NBST with its cylindrical collection tubes, (E) the PELAGRA trap, and (F) the sample collecting optical sedimentation recorder (OSR).

the sample pots have closed, a small weight is jettisoned from the bottom of the trap and the float's oil bladder inflates fully, providing the extra buoyancy for the trap to surface. Both PELAGRA and Neutrally Buoyant Sediment Traps (NBST, Valdes and Price, 2000) have been used successfully to collect samples for trace metal analyses. While these types of collection devices behave in a more Lagrangian manner than bottom moored and surface tethered traps, they are still subject to vertical excursions and rocking that may result from the dynamic buoyancy control and the vehicles' compressibility differences with seawater that can be an issue with the passing of internal waves.

Various sediment trap geometries have been utilized, and there are several commercially available collectors. Many of the original moored sediment trap designs have a conical collection funnel in order to facilitate large collection areas while at the same time concentrating particulate material into an automated carousel of sample bottles (Honjo and Doherty, 1988, Fig. 3B). PELAGRA is another example of a conical collection funnel design (Fig. 3E). In contrast, many of the surface drifting sediment traps (Fig. 3A) and the NBST (Fig. 3D) have cylindrical geometries (e.g., Knauer et al., 1979) with tall aspect ratios designed to minimize hydrodynamic collection biases associated with flow across the trap opening (see below). Hybrid cylindroconical geometries (Fig. 3C) such as those found in the commercially available traps from Technicap (France) have also emerged to combine the benefits of the two styles (Heussner et al., 1990) and have been used in both moored and surface-drifting configurations, as well as trace metal clean applications (Bowie

et al., 2010). In addition to the hard sided collectors, net traps have also been employed to enable the collection of large quantities (grams) of sinking material needed for specialized analyses or degradation experiments (Peterson et al., 2005).

Despite the utility of ocean sediment traps, the global patterns and magnitudes of sinking particle fluxes and their role in redistributing elements throughout the ocean remain poorly understood. While sediment traps are typically viewed as being incompatible with conventional large-scale surveys such as cross-basin sections, much could be learned about the cycling of nutrients and TEIs by deploying these types of instruments on such expeditions. Upper ocean traps tethered below a surface drifter can be deployed upon arrival at a station and left to collect material on short deployments while other core operations such as CTD and in situ pump casts are conducted. Deployment and recovery operations can each be completed within about 1 h, representing only a modest demand on ship operation time. For these reasons, the use of sediment traps may therefore be amenable to the sampling schedules of GEOTRACES-type surveys. Combined with flux estimation techniques from optical instruments and particle reactive tracers, these types of studies have the potential to transform our understanding of how many elements are cycled throughout the oceans.

Trace metal clean considerations

To examine sinking particulate matter for TEIs, samples have to be collected in a trace metal clean way, which generally has not

Table 2
Types of preservatives and brines that have been used in sediment traps.

Preservative	Advantage	Disadvantage
NaCl-added brine	Easy to make, adequate for short-term deployment	Source of trace element contamination
Frozen-seawater brine	Trace element clean	Made at sea from local seawater
HgCl ₂	Highly effective at relatively low concentration	Can affect organic chemistry qualitatively
Formalin	Facilitates cell and DNA preservation	Can be source of trace element contamination
Azide or Chloroform	No particular advantage over other treatments	May require quite high concentrations to be effective

been the case in previous trapping programs. There are a growing number of examples of this in the literature, however, that provide guidance for ensuring metal-clean samples (Collier and Edmond, 1984; Ho et al., 2011; Ho et al., 2010; Huang and Conte, 2009; Jickells et al., 1984; Kuss and Kremling, 1999a,b; Lamborg et al., 2008a; Lee et al., 2009; ; Martin et al., 1989; Pohl et al., 2004). There are no data to date regarding some contamination-prone metals and isotopes (e.g., Pb isotopes), and so the best protocols for analysis of sediment traps for those species will likely need some refinement.

As with any trace metal sampling program, there are a few relatively simple and common sense precautions that can be undertaken to ensure contamination-free sediment trap samples. The cleanliness protocol we describe below is based on the experiences gained during the VERTIGO program, and includes five considerations: material selection, acid-cleaning, the shipboard preparation/processing environment, in-situ preservation, and processing protocols. These protocols are also fully consistent with high quality samples for “bulk” properties (mass, carbon, nitrogen, biominerals), and therefore could be adopted for all trapping programs.

Material selection

As with bottles, the materials used for sediment trap tubes can be very important. In VERTIGO, acrylic and high-density polyethylene were used as the principal components of the trap and seemed clean enough for determination of the flux of most trace elements. Notable exceptions include Pb and Cd, which proved either too contamination-prone (Pb) or too scarce (Cd) given the size of the available samples. Thus, some refinement of sediment trap design for the broadest applicability to TEI determination is probably worthwhile.

Acid-cleaning

There are a large number of acid-cleaning protocols in use by the chemical oceanography community. Such cleaning is essential for reliable data, and these protocols have a few features in common. The first is a detergent type wash to remove greases/oils from newly constructed sediment trap tubes prior to further cleaning as these phases tend to resist acid treatment and can harbor very high TEI concentrations. The remaining steps differ, but involve some multi-day immersion/exposure to acid solutions, usually decreasing in acid concentration but increasing in acid purity to remove TEIs that are present in plastic materials without adding new contaminants from the acids themselves. Furthermore, and as various TEIs have a range of affinities for the anions in the acids, a variety of acids are often employed as well (e.g., a first wash in HCl, followed by a second in HNO₃). As open-ocean water is also often much lower in TEI concentration than even some laboratory deionized waters, a further soaking in filtered seawater prior to deployment is advisable.

Shipboard environment

A clean environment for the preparation and processing of sediment trap material is also essential for high quality data. This can come in many forms, from whole-lab encapsulation in a “bubble” that is fed with HEPA-filtered air to smaller scale clean spaces represented by bench-top hoods that blow filtered air out, rather than

pull air in. The amount of clean space needed will depend on the exact nature of the sampling system used, but we advise enough space for individual sediment trap tubes to be prepped prior to deployment. This could mean a clean space that lies somewhere between the “whole room bubble” and the HEPA flow bench to include a “bench bubble” in the corner of an otherwise ordinary lab space.

Preservation

The in-situ preservation of collected sinking particles prior to the recovery of the sediment trap system has been scrutinized in detail in recent years (Antia, 2005), and shown to be essential for accurate determination of element fluxes. This is critically important for long-term deployments (moored sediment traps) that are deployed for months, but is no less important for drifting tethered and neutrally buoyant systems as well. Several different types of brines and preservatives have been employed, each with their own advantages and disadvantages (Table 2). However, we found that in some short term deployments, the use of a chemical preservative in addition to the brine solution placed in the bottom of the collection vessel was not necessarily required (Lamborg et al., 2008b), however this observation could be dependent on the nature of the collected material, ambient conditions, and the presence of live zooplankton. In the context of accurate collection of TEIs this is an important observation, because the preservatives sometimes used (e.g., formalin, mercury, azide) may not be able to be suitably purified to keep them from adding contamination. The brine solution, however, can be made quite cleanly with the simplest of these techniques being the freeze-concentration of filtered open ocean seawater.

Clean processing

As in all trace element protocols, the minimization of handling and transfer is a desirable goal, but an additional important consideration is adequate homogenization and representative subsampling. This is because following collection, the particles are transferred to a filter prior to analysis and in general no single filter type is appropriate for all analyses. Furthermore, were sediment traps to be included in a GEOTRACES-type program, equivalent subsamples will need to be generated for distribution among several groups. Thus, a clean way to generate high precision replicate subsamples is necessary. During VERTIGO, we made use of an all-plastic “splitter” suitable for use at sea to generate these subsamples after pooling multiple sampling tubes together (Lamborg et al., 2008b). However, other approaches can also be used, including the deployment of a large number of replicate sediment trap tubes on the same array that can be analyzed individually. Interestingly, tube-to-tube variability is quite similar in magnitude as device-to-device variability, suggesting there is some insurmountable heterogeneity in the particle field (e.g., Waite et al., 2000). The approach of combining and splitting samples is attractive because it allows element and component ratios to be examined for trends without the added variability that would come from using two different tubes for different analyses. With or without splitting, the trap subsamples are then generally filtered onto one of a variety of filter media to allow further analysis. To minimize filter blanks, we recommend these filters be as small as possible (e.g., 25 μm

diameter), and can be cleanly loaded using a plastic funnel (e.g., Pall) outfitted on a vacuum manifold.

Collection of intact sinking particles for imaging and other analyses

While the bulk sediment trap collections allow for the assessment of a wide range of compositional characteristics, this sampling strategy is not ideal for determining the physical nature of individual particles. As particles are collected in the base of standard sediment traps, they have a propensity to aggregate with other particles, often combining into a nearly homogenous mixture of particulate material. Subsequent filtration onto small diameter filters also degrades the physical structure of individual particles, and as such, many of the characteristics such as size, shape, type, and color are lost as the material becomes amalgamated into a single sample for chemical analysis. Despite this challenge, some of the more robust and distinct particle types such as intact phytoplankton cells and zooplankton fecal pellets can be sorted from bulk sediment trap material for visual identification and enumeration with microscopic techniques (Salter et al., 2007; Wilson et al., 2008).

The use of a viscous polyacrylamide gel in the base of cylindrical sediment traps is one approach that overcomes this limitation by allowing for the collection and imaging of fragile intact particles (Fig. 1E and F). This methodology was first developed and demonstrated by Jannasch et al. (1980), and has since been adopted by numerous others (e.g., Ebersbach and Trull, 2008; Ebersbach et al., 2011; Jackson et al., 2005; Jouandet et al., 2011; Lundsgaard, 1995; McDonnell and Buesseler, 2010; McDonnell and Buesseler, 2012; Waite and Nodder, 2001). As particles come in contact with the polyacrylamide gel at the base of the trap, they become embedded and immobilized in its viscous matrix. The collection duration of the deployment needs to be chosen appropriately in order to minimize particle–particle interaction and overlap in the gel, while still capturing enough particles to allow for the precise enumeration of particles across all size ranges.

A trace metal clean sample collecting surface-tethered optical sedimentation recorder package (Fig. 3F, Bishop 2009) has also been developed to both yield images of sedimented particles at hourly intervals and provide samples for calibration. Particles are imaged at 15 μm resolution under transmitted, transmitted cross polarized, and darkfield illumination. Methodological advances such as this that link the physical attributes of individual particles (via photography) to their elemental composition would enable substantial improvement in our understanding of the cycling of elements throughout the oceans.

The recent interest in polyacrylamide gels and optical sedimentation recording methodology is largely due to its utility in quantifying the flux size distribution. A growing number of studies are recognizing the importance and utility of this information because particle size affects and responds to a myriad of particle processes. Rates of sinking, production, destruction, consumption, repackaging, aggregation, disaggregation, and microbial decomposition all depend on particles size (Stemann and Boss, 2012). By pairing the data from polyacrylamide gels with other compositional or morphological information from in situ optical instruments, pumps, or bulk sediment trap collectors, it is possible to elucidate the relationships between these different parameters.

Other quantitative and qualitative characteristics can be obtained from polyacrylamide gel traps. Particle shape, color and type can provide important information about sources of particles and their role in controlling the function and efficiency of the biological pump. Particle shape and porosity can affect the drag coefficients and excess density of particles, thereby altering their sinking characteristics. By classifying sinking particles into various categories such as amorphous aggregates, phytoplankton cells, or

fecal pellets, the influence of ecosystem structure on the export of particulate matter can be assessed (Ebersbach et al., 2011). Even the shape and color of fecal pellets can be indicators of particle repackaging, degradation, and zooplankton trophic levels (Wilson et al., 2008).

Separation of particulate matter by sinking velocity

Various methods have been developed to functionally separate out particles by their sinking velocities. The indented rotating sphere (IRS) design (Peterson et al., 1993) is a valved sediment trap that arrests sinking particles on top of the IRS. By coupling this design with a skewed funnel and sample carousel that function as an in situ settling column, particles can be partitioned into separate collections based on their respective settling velocities (Peterson et al., 2005). Subsequent imaging and chemical analysis of the different velocity fractions facilitates the investigation of the linkages between velocity, composition, and particle size and morphology (Trull et al., 2008). Collections of sinking particles have also been retrieved and fractionated based on sinking velocity with the use of a laboratory apparatus consisting of series of elutriator tubes that provide vertical countercurrents of varying speeds (Peterson et al., 2005). Similarly, collections of small sinking particles and neutrally buoyant colloids can be separated via the combination of cross flow filtration with split flow thin-cell fractionation (CFF-SPLITT, Gustafsson et al., 2000). While some of these approaches have yet to see widespread adoption in studies of particulate cycling, they do represent innovative methodologies that provide the opportunity to investigate the variability of particle sinking velocities and the mechanisms that control these sinking rates.

Sediment trap collection biases

With the application of sediment traps as quantitative flux tools, several issues became apparent that might bias collection efficiencies. These issues can broadly be broken down by (1) hydrodynamic biases, i.e. any process related to flow in/around a trap and its impact on collecting sinking particles; (2) solubilization, or the loss of material in the collection cup or tube after deployment and prior to collection of the sinking particles, most commonly via filtration; and (3) swimmers, or the active migration of zooplankton and larger biota into a trap and its potential bias to either remove, i.e. consume, sinking particles or add to the flux, most often by dying in the preservatives used to reduce trap solubilization. These three potential biases may vary greatly even for a single trap and experimental set up as a function of depth (currents are higher in shallow waters; zooplankton swimmer abundances are also higher in the upper 100 m), location and season, which leads to large variability in the dominant type of sinking particle and its lability and sinking rate.

Several reviews of these potential trap biases provide more detailed discussion of these issues and how they might be reduced or at least quantified in sediment trapping programs (Buesseler et al., 2007; Gardner, 2000; GOFs, 1989). For hydrodynamic biases, progress has been made in reducing mooring line motions with elastic elements to reduce vertical motion, or to reduce flow over the trap mouth by including sub-surface drogues, or by the deployment of NBSTs, which as a Lagrangian design, should reduce hydrodynamic effects to near zero. Lab experiments to examine hydrodynamic biases under controlled conditions are hard to interpret, with some studies indicating an increase and others a decrease in collection efficiencies with an increase in flow over the trap mouth (Buesseler et al., 2007). Comparisons between traps of different designs show times when standard drifting PITS traps agree with NBSTs, or differ by factors of 20–50% with NBST designs,

and this difference can be element specific (Stanley et al., 2004). A recent three year time-series study at BATS showed only three periods when PITS fluxes were factors of 2–3 higher than the NBST, and in agreement during other months, though the reason for this difference could not be attributed to any physical or obvious change in particle type (Owens et al. 2013). Another issue likely related to particle motion relative to the traps, is when traps are deployed within the mixed layer. Perhaps the most complete example is from BATS, where Steinberg et al. (2001) noted that there were unexplained flux peaks during periods of deep mixing and cautioned that this could be causing a trap bias. Comparison of the particle collection performance of identical imaging optical sedimentation recorders deployed in Lagrangian (Carbon Flux Explorers, Bishop, 2009) and surface tethered modes is underway in coastal California waters where marine snow particles are abundant. Results indicate undersampling of marine snow by surface tethered instruments.

Preservation issues are particularly of concern for organic matter and labile elements such as P. Such biases might be expected to be higher in the upper ocean where particles are more labile, or in longer deployments, such as in annual deployments of deep traps (e.g., Antia, 2005). The goal of adding preservatives and brine is to preserve particle integrity and to stop continued bacterial breakdown of particles once collected. The most common poisons are formalin and Hg, (e.g. Lee et al., 1992), both of which also kill any zooplankton swimmers that enter the collection area, so they can be later removed (see below). Formalin may be marginally more attractive as it aids in cell and DNA preservation and HgCl₂ may promote qualitative changes to trapped organic matter (e.g., Liu et al., 2006). One option is to measure both particles in the trap and changes in the poisoned brine solution for the concentration of a given element, but this is rarely done. Some studies indicate that approximately 30% of the POC flux and 70–90% of particulate organic phosphate flux can be lost to solution from the particles that enter the trap cup, and thus fluxes would be underestimated (Buesseler et al., 2007). However, in an incubation study of freshly collected trap material in the upper 500 m, losses for P were smaller, 10–20% for P and negligible for C and other biominerals (Lamborg et al., 2008b). Indeed, that study also found that a brine layer without additional preservative did as well as those with amendments, further suggesting that short-term deployments are much less vulnerable to in-trap degradation.

Swimmer issues are harder to avoid, at least in the upper 1000 m, where zooplankton are common and often the swimmer “flux” removed from a trap exceeds the net flux (Buesseler et al., 2007), though this is also rarely quantified and reported. Removal of swimmers from traps is also an inexact science, with both picking and screening methods used, and only with careful comparison in one location, depth and time, can they be truly evaluated for which is appropriate to use. Ideally, one would like to reduce swimmers entering traps, such as by having a more complicated trap opening that separates passively sinking material from actively swimming zooplankton (Coale, 1990). Swimmers have been excluded from traps using an indented rotating sphere (IRS) design, whereby material that lands on the sphere within the collection tube is rotated and passive sinking particles are collected below while zooplankton are inhibited from entering the lower chamber (Peterson et al., 1993). As with any device, there are concerns with the IRS about subtle changes to particle characteristics as they settle on the sphere (for minutes to hours) and possible reduction in flux due to feeding on the ball prior to rotation, but overall IRS designs show a large reduction in overall swimmer abundances. Imaging sedimentation recorders (Bishop, 2009) appear to have minor interference of swimmers since sample is removed every several hours.

What is difficult to know is whether or not traps collect a quantitatively and qualitatively accurate flux. Attempts to balance upper ocean C or nutrient budgets have large errors (± 50 –100%) as the changes to stocks are small relative to the measured fluxes. Radioactive isotopes have been used to calibrate traps, and have a reduced uncertainty since their dominant control on the measured abundances is commonly the production and decay rates. In the upper ocean, the most commonly used radionuclide is ²³⁴Th with a 24-day half-life, and in the deep sea, the activity balance and fluxes of ²³⁰Th and ²³¹Pa are compared. When first applied, an early comparison of the ²³⁴Th budgets and ²³⁴Th fluxes suggested that in 1/3 of the studies when both had been measured trap fluxes were 50% higher or lower than predicted with simple 1D ²³⁴Th models (Buesseler, 1991). Since this time, considerable effort has been made to investigate non-steady-state impacts on the ²³⁴Th budget, its variability in space and time, and the impact of physical transport on predicted fluxes (Savoie et al., 2006). This increases the reliability of the calibration but care is needed to separate considerable spatial variability in ²³⁴Th from the seasonal changes to ²³⁴Th due to particle export increases or decreases. In the deep ocean, several compilations of ²³⁰Th/²³¹Pa suggest that traps below about 1000 m collect what is expected within 20–30% of the production rates, but above this depth there is a systematic low bias in the trap fluxes (Scholten et al., 2001; Yu et al., 2001). The exact cause is not known, but it could include a larger hydrodynamic bias at shallower depths as conical traps are a poor design for high current conditions, and/or simply the impact of zooplankton who graze on sinking particles as they enter the common conical trap design, and their abundance decreases dramatically in most basins below 1000 m.

An additional consideration in sediment trap collection biases is the potential for incidental collection of particles during deployment and/or recovery. Many trap designs incorporate a mechanism to seal off the sample tube or cup at the end of the sampling period (Lamborg et al., 2008a,b; McDonnell and Buesseler 2010; Valdes and Price, 2000). Trap designs that include a rotating carousel to collect time-series samples seal off individual samples from the surrounding water by moving each sample cup away from the collection funnel, and typically incorporate an empty position in the carousel to move underneath the collection funnel during deployment and recovery, so that all sample cups are sealed at that time (Heussner et al., 1990; Honjo and Doherty, 1988; Honjo et al., 2008; Martin et al., 2011; Sherman et al., 2011).

Positively buoyant particles

The particle collection techniques described above require a unidirectional interpretation of oceanic particle flux. Some of these collection methods preclude the capture of ascending particles (e.g., upright sediment traps), while others may obscure ascending particle contributions (e.g., pumps), and thus overestimate sinking particle flux. Positively buoyant particles originate at multiple depths in the water column, such as organic material with high lipid content in hydrothermal plumes (Cowen et al., 2001), abyssal biogenic production of lipid-rich organic material following decomposition/consumption of surface-derived material (Simoneit et al., 1986), formation and vertical migration of diatom mats (Villareal et al., 1999) and other buoyant organisms, such as Trichodesmium (Letelier and Karl, 1998; Villareal and Carpenter, 2003) in the upper water column, or material associated with ice particles (Lannuzel et al., 2010). Although the total flux of ascending particulate material can be substantially lower than sinking particulate flux (Simoneit et al., 1986), it can also exceed 50% of the downward particle flux in some regions (Smith et al., 1989), and consideration of ascending particle fluxes can be especially

important when assessing nutrient transport. Diatom mats of the genus *Rhizosolenia* can contribute half of the new nitrogen requirements of the North Pacific Gyre through vertical migration between the nutricline and the surface (Villareal et al., 1993, 1999), while *Trichodesmium* is theorized to undertake similar vertical migrations in the same region to mine deep phosphorus (Letelier and Karl, 1998). Micronutrient transport by frazil ice can also occur following scavenging of micro-organisms and detritus onto ice crystals (Lannuzel et al., 2010). These hotspots of microbial activity thus both transport particulate material through the buoyancy of the frazil ice and facilitate the transfer of micronutrients from the particulate to the dissolved phase by microbial activity, providing a source of new nutrients to surface waters (Lizotte, 2003). Future studies wishing to assess ascending particle flux should couple sinking particle collection with ascending particle collection using inverted sediment traps.

Temporal and spatial scale considerations

Most methods used to directly measure or estimate particle flux integrate the flux over the time period of collection (sediment traps) or over the timescales associated with a tracer's removal rates and inventories (e.g., ^{234}Th , CO_2 and nutrient deficits). Often we combine together multiple sediment trap observations at different levels such as those we have made using the drifting PELAGRA traps (Lampitt et al., 2008; Salter et al., 2007) or the NBST (Buesseler et al., 2007; Steinberg et al., 2008) to estimate the attenuation of flux in the ocean (e.g. Martin et al., 1987). Implicit within this calculation is an assumption that the observed flux attenuation is due to microbial degradation and zooplankton consumption of sinking material, i.e. that the system is operating at steady state with material fluxing through the mesopelagic on much faster timescales than the input of material to the mesopelagic zone changes. However, on occasions systematic increases in flux with depth have been observed (e.g., Martin et al., 2011). These patterns could be due to complex spatial or temporal variability in sinking fluxes, and may not necessarily reflect changes in local remineralization rates. Temporal variability in the magnitude of sinking particle fluxes from the euphotic zone could be one reason for these vertical patterns in flux, especially if a significant proportion of the flux was being carried by slow sinking material. Spatial variability in export fluxes (McDonnell and Buesseler, 2012) coupled with lateral transport of sinking particles throughout the mesopelagic from distant source regions (Siegel et al., 2008) could also produce flux patterns that are not easily interpreted in a one-dimensional vertical space.

Conclusions

As we have illustrated here, methodologies for the collection of sinking and suspended particles have improved and diversified over the past several decades. These methodological advancements reflect the growing scientific interest in the many different roles that particles play in the marine environment. They also present many new opportunities for advancing our understanding of marine particle dynamics and biogeochemistry through the simultaneous deployment of multiple sampling tools. Through the direct intercomparison of various particle collection methodologies, we can learn more about the strengths and biases of each technique and find ways to improve their accuracy, precision, interpretation, and sample throughput. Together with the various advances in other particle related studies (see the other articles in this special issue) there exists the opportunity to greatly elucidate the mechanistic relationships between various particle properties and biogeochemical rates, while also clarifying the biogeochemical and

ecological roles of particles in the cycling of carbon, oxygen, nutrients, and TEIs.

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