Sampling and Analytical Protocols

Sediment Trap Systems

The fluxes of material were measured using two kinds of sediment traps: conventional surface tethered traps ("Clap" Traps) and neutrally buoyant traps (NBSTs). Both trapping systems were deployed with identical sediment trap tubes (diameter 12.7 cm; length 70 cm) that consisted of a polycarbonate tube body, a HDPE tube lid, honeycomb screen (hole size ca. 1 cm diameter), and HDPE tube base. The base was a shallow cone that terminated in a valve with a 0.5 cm diameter orifice. The tube lid was held in place by a length of amber silicone shock cord and the honeycomb screen was fixed at 2.5 cm below the mouth of the tube to accommodate the lid when closed. Each tube lid also had a nylon lanyard that was looped over a withdrawing pin mechanism, contained in a pressure casing located either in the middle of the Clap Trap rosette, or part of the NBST main body. During deployment of the trapping systems, the pin held each tube lid in the open position, against the tension of their shock cords. Just prior to recovery, the pin mechanism was programmed to withdraw into its housing, releasing the lids to their closed position. Thus, the traps were deployed open, but retrieved closed to better preserve sample integrity during recovery. Sediment traps were deployed twice during each site occupation, and the systems remained in the water between 3 to 5 days. For each deployment, the traps were released in as rapid a succession as possible, over the course of about 12 hours. The start dates for the two deployments at each site were about 11 days apart.

Trap Tube Handling, Deployment and Recovery

The assembled trap tubes were cleaned prior to use in three steps: 2 day soak in a 5% detergent (Micro) solution, 1 week soak in 1% HCl and 1 week soak in 1% HNO_3. After each solution, the tubes were thoroughly washed with 18 MΩ cm-1 water, then were double-bagged for transport to the field. At sea, prior to their first use, they were soaked for more than 48 h in 0.2 µm filtered seawater (500m). Just prior to deployment, the tubes were filled with 0.2 µm filtered water from the depth to which they were to be deployed. Then 500 mL of a borate-buffered brine (S > 70; 3 mM borate, pH=8) solution, formed from freeze-concentrating 0.2 µm filtered Sargasso Sea water (400 m), was dispensed into the bottom of the tube by slowly pouring the brine down a acid-washed Teflon tube. The brine was also poisoned with either formalin or Hg at concentrations recommended to retard bacterial activity (37 mM and 180 µM respectively; Lee et al., 1992; Hedges et al., 1993). In most instances, the brine layer was still intact upon recovery of systems as indicated by visual inspection.

During the trap deployments, replicate NBSTs were deployed (3 at 150m, 2 each at 300m and 500m). Each NBST carried on it 5 sediment trap tubes, 4 used for biogeochemical measurements (2 poisoned with formalin and 2 with Hg) and a fifth, preserved with formalin, that was dedicated for biological identification. One Clap Trap array was deployed per target depth and each carried 10 tubes. Five of these were processed identically to those on board the NBSTs, 1 was a covered process blank, 2 were used in trap material aging experiments (see below) and 2 supported the "Gel Traps" prepared by the Univ. of Tasmania group. Surface drift tracks for the CLAP traps and deployment and recovery positions for NBSTs can be found in Buesseler et al. (in press).

Upon recovery of the traps, the tubes were removed from their support/vehicle, and allowed to stand for at least 1 hour so that in-tube material could finish sinking into the brine. Then all but ca. 1 L of fluid was pumped out of top of the tubes, and the remaining liter of fluid/sediment mixture was collected into a 4 L, acid-washed fluorinated HDPE bottle. A small rinse of the tube using depth relevant filtered seawater was also made and collected along with the sample. During the collection, the water/particle mixture was passed through an acid-washed nylon mesh (350 μm pore), in a Teflon filter holder (Savillex) to remove most zooplankton "swimmers." When possible, two tubes of like poison were pooled together. Pooling was not done with the covered process blank or when tubes were deemed to be anomalous (e.g., did not close). When done, pooling simply involved the collection of water/particle mixtures from two tubes in the same 4 L bottle and through the same screen. After sample collection and any pooling, the Teflon filter housing was opened and the screen rinsed with the appropriate filtered seawater and saved for microscopic examination.

Sample Splitting

Once the water/sediment mixtures were collected, they were immediately wet split into 8 equal fractions. This was done by means of a custom splitter device operated within a HEPA-filtering laminar flow bench.

Sample Replication, Processing and Analysis

Typical replication can be summarized as two samples from each device, with 3-4 devices per depth, and 1 or 2 determinations (e.g., for mass) per sample, or a total of 6-16 determinations per depth. Recent statistical analysis of flux modeling has suggested that replicate determinations of flux properties is the best way to help constrain the models of flux in the ocean (Primeau, 2006). The sample splits were processed in different ways to accommodate a variety of determinations. All sample processing took place immediately after splitting in a HEPA air filtered flow bench (Micron-Aire and Ray Products) and observing clean techniques (acid-washed plastic funnels, forceps, Petri dishes and handling with gloved hands, double bagging of samples and processware, etc.).

Determinations

Mass

The mass flux collected in the sediment trap was determined gravimetrically on two of the sample splits, both filtered onto polycarbonate membranes (Nuclepore; 1 μm nominal pore size). Prior to use, the filters were acid-washed by soaking in 1% HCl and 1% HNO_3 for at least one week each, rinsing and drying in a laminar flow bench. The filters were further dried by holding them in a silica gel desiccator for 2 days. Following the drying period, the filters were weighed to the nearest μg on a Mettler AT21 Comparator.

Following the splitting, these filters were rinsed with a small amount of borate buffered 18 MΩ cm-1 water. Upon return to the lab following collection, the samples were again desiccated and

weighed multiple times to a constant weight. During weighing, the filters were handled cleanly so that element analyses could be performed on the same filters. In addition to the covered process tube blanks, unused filters were reweighed as lab blanks.

Carbon and Nitrogen

Total sinking particulate carbon and nitrogen were determined using a high temperature combustion technique on a Thermo Electron FlashEA 1112 C/N analyzer. This analysis was performed on subsamples (determined gravimetrically) of the splits filtered onto Ag membrane filters (Sterlitech; nominal pore size 1.2 μm).

^{234}Th

The activity of ^{234}Th associated with sinking particles was determined on sample splits filtered on Ag filters. Filters were not rinsed following filtering but allowed to dry in the flow bench. The filters were covered with a Mylar/foil layer and counted for total high energy beta activity using a low background, anti-coincidence detector (Risø National Laboratories) at sea and again at 6 months following collection.

Particulate Inorganic Carbon

This analysis was also carried out on rinsed polycarbonate filters, as with mass. Carbonate in the sediment trap samples was determined by coulometric carbon analysis of CO_2 evolved from sample aliquots acidified with phosphoric acid.

Particulate Organic Carbon

The amount of particulate organic carbon was determined by subtracting the particulate inorganic carbon from the total carbon.

Biogenic Silica

Total silica was determined on aliquots of Ag filters using a Lachat QuikChem FIA+ autoanalyzer and standard methods. The filter aliquot was first digested in weak base, and thus the total silica determined in the extract was comprised of only biogenic silica.

Phosphorus and Metal

These elements were determined by Magnetic Sector Inductively Coupled Plasma Mass Spectrometry (ICP-MS), performed on the same splits as for Mass (acid-washed polycarbonate). In brief, aliquots were cut from the whole filter using ceramic scissors and the sample fraction determined gravimetrically. The aliquots were then digested in a hot block (120 °C) for >4 h in small sealed Teflon vials (Savillex). The digestion solution was a 5 mL 4:1 mixture of concentrated trace metal grade HNO_3 and HF. Some samples were also pre-digested with 0.2 mL of concentrated NH_4OH to aid in filter digestion, but results suggested that incomplete digestion of the filter matrix made little difference to the results (Lamborg et al., this volume). Following

cooling of the sample, 0.1 mL of saturated boric acid solution was made to aid in dissolution of CaF_2 (e.g., Collier, 1991). The concentrated samples were held until analysis in acid-washed LDPE vials. Prior to analysis, the concentrated digest was quantitatively diluted to ca. 20x in a 5% 4:1 HNO_3:HF, spiked to ca. 0.5 ppm with ^{115}In. The In-spiked diluent was made in bulk so that all samples analyzed during a single day would be diluted with a solution containing identical In concentrations.

The diluted samples were analyzed on a Thermo Electron Finnigan Element 2, outfitted with an Aridus desolvating nebulizer and ASX-100 autosampler (both CETAC), with sample take up rates at 0.1 mL min^{-1}. ^{114}Cd, ^{115}In, ^{137}Ba and ^{208}Pb were measured in low resolution (Δ=300) with 20 scans while ^{23}Na, ^{25}Mg, ^{27}Al, ^{31}P, ^{44}Ca, ^{45}Sc, ^{47}Ti, ^{51}V, ^{55}Mn, ^{56}Fe, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn and ^{88}Sr were measured in medium resolution (Δ=4000) for 5 scans. No results from Cd, Pb, Ti and Ni are shown as they appeared to be unreliable due to large and/or variable process blanks.

Four different SRMs were processed and analyzed by ICPMS as well (at least two in any given analysis session), including NIST 1573a (Tomato Leaves), NRC HISS-1 and MESS-3 and USGS MAG-1. Results agreed with certified values within 10% in most cases, except for MESS-3, which was not always completely digested by this approach.

Phytoplankton Pigments

Phytoplankton pigments were determined on sediment trap material subsamples stored in liquid nitrogen until analysis, using HPLC methods (Bidigare et al., 1985; Wright et al., 1991).

Process Blanks

As noted, the covered tube on board the Clap Trap array was used as a process blank, and subjected to all the same processing protocols as the samples. The blank "fluxes" are included for comparison to the samples and are calculated by dividing the average blank value for each parameter divided by a nominal deployment time of 4 days. While most samples were well above their respective detection limits, the process blanks often represented non-trivial fractions of the sample. Sodium found in the sediment trap material was assumed to be the result of retention of seawater salt, and was therefore used to correct element fluxes for this artifact. The only elements that were found to require a seawater salt correction were Mg and Ca, with almost all the Mg appearing to be salt derived. The Ca seasalt corrections were generally less than 1%.

Modifications to Original Data

"_f" added to each parameter name to identify parameter as a flux measurement
single column parameter with +/- error term spilt into two columns
parameter error column labelled as "param"_f_err
"n/a" changed to "nd"
"< dl" changed to "bd"
decimal places padded to 1 or 2 places as appropriate for consistency

date, event, ev_code, lon, lat from cruise logs merged with original data

Used common "device" id from these data to determine sample position, date and event code for sed trap data