

Diagenetic effects on particulate phosphorus samples collected using formalin-poisoned sediment traps

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Abstract

Sediment traps provide vital information on the magnitude and composition of sinking particles. Unfortunately little is known about the integrity of various constituents, particularly phosphorus (P) measured in these samples. We report concentrations of total, inorganic, and organic P in sediment trap particles, supernatants, and rinse water collected from both oxic (275 m) and anoxic waters (455, 930, and 1255 m) in Cariaco Basin, Venezuela. On average 30% of the total P measured in the traps was in the supernatant, with an additional 10% of total P in the rinse water. Greater than 80% of the P in the rinse water and supernatant was in the form of inorganic P, higher than the 50% to 60% of inorganic P found in trap particles. Possible sources of inorganic P to supernatants include swimmer herniation, dissolution of inorganic phases, and solubilization of particulate organic P. The good agreement between particulate organic carbon (C) and organic P suggests that losses of organic C to trap supernatants must also be considered. Although fluxes were underestimated by approximately 30% when supernatant concentrations were not included, temporal and depth trends were maintained. This was confirmed by incubation experiments that suggest that P loss to supernatants occurs rapidly (< 2 weeks), potentially due to particle agitation during transport. While traps may provide insight into the temporal and spatial variability of P within sinking particles, we recommend minimal sample handling and that supernatants be analyzed to determine overall P fluxes.

Introduction

Phosphorus (P) is one of the major nutrients used by all organisms. Owing to its long residence time in the ocean relative to other macronutrients, it is often considered to be a major control on primary production over geologic timescales (millions of years) (Benitez-Nelson 2000; Delaney 1998). Several studies suggest that P may limit production in the modern ocean as well (Karl and Björkman 2002; Wu et al. 2000). Thus, regeneration of dissolved P compounds from particles and the upwelling of these products to the euphotic zone is a critical step in regulating P availability and biological productivity (Benitez-Nelson 2000; Karl and Björkman 2002; Paytan

et al. 2003). Unfortunately, little is known about the particulate P pool with regard to its composition and spatial and temporal variability.

Moored sediment traps provide a qualitative and potentially quantitative tool for estimating fluxes of sinking particulate matter, and hence P, in marine systems. However, studies of total particulate P (TPP) have been hindered by concerns that (1) TPP concentrations are altered significantly during sediment trap deployment (Bodungen et al. 1991; Gardner 1995) and (2) P is preferentially released to the water column relative to other elements such as carbon (C) and nitrogen (N) (Knauer et al. 1979; Minster and Boulahdid 1987). There have been few sediment trap studies that include information on the composition of the trap cup supernatants or the water used to process the sediment trap solids prior to analysis of solid flux constituents. As a result, we have little knowledge of the integrity of sediment trap samples with respect to the exchange between dissolved and particulate phases within sediment trap cups.

In this study, we conducted several experiments regarding the release of P into overlying supernatants and examined the P composition in formalin-poisoned sediment trap cup super-

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nanants from both the oxic and anoxic portions of the water column in Cariaco Basin, Venezuela, as part of the Cariaco oceanographic time series program. This study combines three experiments: (1) analysis of total dissolved P (TDP), dissolved inorganic P (DIP), and dissolved organic P (DOP = TDP – DIP) in sediment trap supernatants collected over the past 7.5 years, (2) analysis of TDP, DIP, and DOP concentrations in sample aliquots collected during sediment trap cup processing, and (3) evaluation of TDP, DIP, and DOP concentrations in supernatant solutions monitored over time in the laboratory. In addition, we compared TDP, DIP, and DOP concentrations in supernatants of poisoned versus nonpoisoned samples and in samples collected under oxic and anoxic conditions. Our results provide insight into sediment trap sample integrity and the mechanisms that affect the distribution and composition of P within sediment trap samples deployed over long periods.

Materials and procedures

Cariaco Basin and sample collection—The Cariaco Basin is anoxic below approximately 275 m and is, therefore, an ideal location for tracking the chemical transformations of marine particulate P across a redox boundary and into anoxic sediments. Four sediment traps are located in the eastern basin at 10°30'N and 64°40'W on a single mooring that is typically deployed for 6-mo intervals. The first trap, trap A, is located near the oxic/anoxic interface at a depth of approximately 275 m. Traps B–D are located at depths of approximately 455, 930, and 1255 m, respectively. The traps are cone-shaped with a 0.5 m² opening that is covered with a baffle top to reduce turbulence. Each trap contains thirteen cups that collect falling particulate matter for two-week intervals and are numbered 1–13, with cup 1 collecting for the two-week interval immediately following deployment, and cup 13 collecting for the 2 weeks immediately prior to recovery. Prior to deployment, each cup is filled with a solution comprised of filtered seawater, salt (~1 g L⁻¹ NaCl added) and formalin (to a concentration of ~3%) that is buffered to pH 8 with sodium borate. This acts as a preservative for the accumulating organic matter and prevents loss of material once collected (Goni et al. 2003; Muller-Karger et al. 2001; Muller-Karger et al. 2000; Taylor et al. 2001; Thunell et al. 2000). We should note that although trap solutions are oxygenated prior to addition to the trap cups, this oxygen is rapidly removed via diffusion and inorganic oxidation reactions in anoxic waters (e.g., <2 d).

Upon recovery, trap cups are sealed and refrigerated for approximately 1 to 3 weeks prior to processing. All trap samples are processed according to the methods described by the Joint Global Ocean Flux Study (<http://www.pangaea.de/Projects/JGOFS/Methods/index.html>) (Knauer and Asper 1989). These methods have been standardized across various programs, although slight variations in methodology may occur. Briefly, the supernatant from each cup is discarded, along with

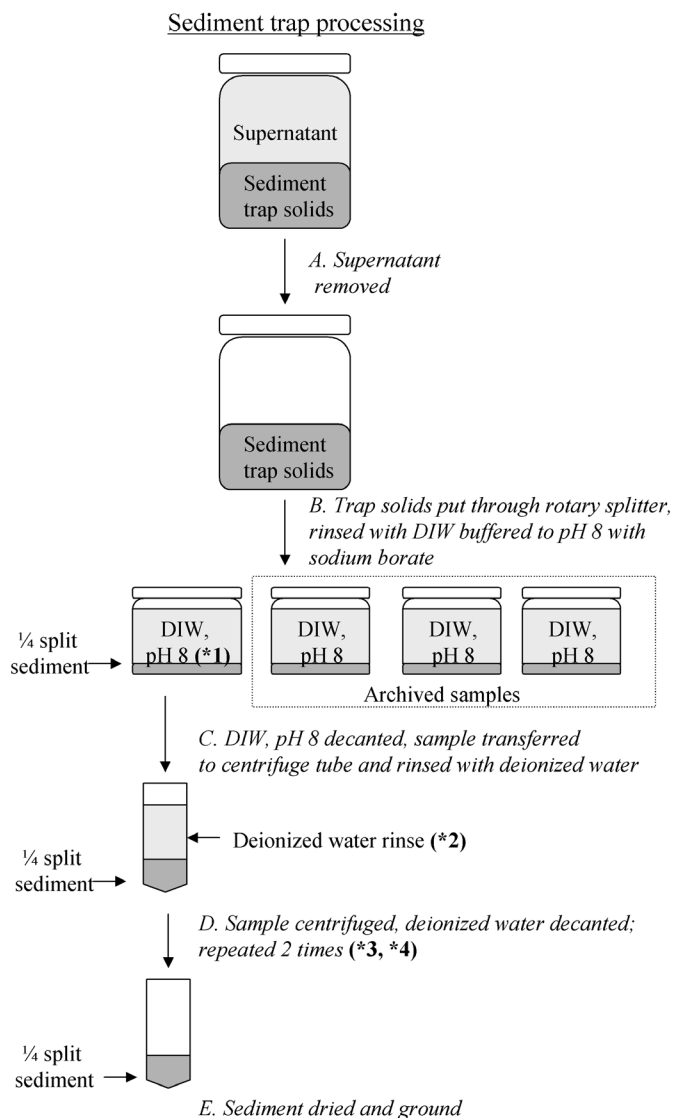


Fig. 1. Diagram of the sediment trap cup sample processing. Asterisks (1*, 2*, 3*, 4*) show where an aliquot of rinse water was taken for P analysis.

all obvious swimming organisms that are not considered part of the particle flux. During the sample processing for some of the cruises, aliquots of the trap cup supernatants were saved and frozen (Fig. 1). Sediment trap solids are split into quarters using a precision rotary splitter. The quarter sample used for geochemical analyses is rinsed a total of three times with deionized water, freeze-dried, and ground (Goni et al. 2003; Muller-Karger et al. 2001; Muller-Karger et al. 2000; Taylor et al. 2001; Thunell et al. 2000). Rinsing with deionized water, while not optimal, is the best mechanism for removing excess salt from trap samples

Experimental design—Experiment 1: To examine the magnitude and composition of possible P transfer from the solid phase to the supernatant, our first experiment was to analyze sediment trap supernatant solutions for TDP, DIP, and hence,

DOP. These supernatants ($n = 298$ samples) were collected from traps deployed between November 1995 and October 2003 and stored frozen or refrigerated until analysis. Immediately prior to analysis, samples were brought to room temperature, shaken gently, and centrifuged for 10 min to remove any residual sediment. Supernatant samples were available primarily for the two upper sediment trap depths, $n = 125$ for 275 m, $n = 111$ for 455 m; fewer supernatant samples were available from the two deeper traps, $n = 29$ for 930 m, and $n = 33$ for 1255 m. Supernatant P results were then compared to the amount of TPP, particulate inorganic P (PIP), and particulate organic P (POP = TPP - PIP) measured in each corresponding sediment trap solid phase. Note, however, that supernatants were not saved from every cruise. Furthermore, supernatants have been stored over a range of time periods, some for as long as several years. As a result, it is possible that P scavenging onto the walls of the container and/or abiotic repartitioning among P phases may have occurred during storage. We argue that these effects are most likely minimal. For example, Monaghan and Ruttenberg (1999) demonstrated that less than 3.5% of a wide number of model organic P compounds stored unacidified and frozen hydrolyzed over an 80-d period. They further demonstrated no loss of DIP or TDP over that time frame (Monaghan and Ruttenberg 1999).

Experiment 2: To examine the possible additional transfer of sediment trap solid phase P to the dissolved phase during the processing of sediment trap solids, aliquots of rinse water were taken during the splitting and rinsing process of trap samples collected during three deployment periods (Cruise 13: June 2002 to October 2002; Cruise 14: November 2002 to May 2003; Cruise 15: May 2003 to November 2003) (Fig. 1). Rinse water samples were stored frozen until analysis for DIP and TDP. At this point, samples were defrosted, gently shaken, and centrifuged for 10 min to remove any residual sediment. The P measured in all of the rinse steps was summed and compared to the amount of P in the sediment trap solids.

Experiment 3: The third experiment was designed to monitor the rate of P release from the solid to liquid (supernatant) phase. Particles collected in the last sediment trap cup of the deployment period (Cup 13) are the least likely to have undergone diagenetic alteration. These samples were recovered from all four depths during cruises 14 (November 2002 to May 2003) and 15 (May 2003 to November 2003) and were brought back to the lab and kept at approximately 7°C to mimic in situ conditions. Triplicate 5-mL aliquots of supernatant were then removed from each cup approximately twice weekly for 6 mo to monitor possible changes in chemistry that the samples would have experienced during the course of a 6-mo deployment. The samples were stored frozen and analyzed for DIP and TDP within 2 mo of the time series aliquot sampling. Final concentrations were adjusted to incorporate the effects of sample volume removal that occurred throughout the course of the experiment.

During cruise 14, the 275 m trap malfunctioned after cup 8; therefore, it was not possible to perform this experiment on samples from the uppermost sediment trap. Furthermore, cruise 14 samples from all four traps did not arrive at the laboratory for analysis until approximately 3 weeks after retrieval, and were not refrigerated during those 3 weeks. During the recovery of samples on cruise 15 (November 2003), aliquots of supernatant for cup 13 A through D were sampled on board ship in order to obtain a more representative initial sample. Aliquots of filtered seawater, formalin, and sodium borate buffer solutions used to fill and poison the cups were also collected to check for P contamination. During the May to November 2003 collection period (cruise 15), the C trap (930 m depth) was not poisoned with the 3.2% buffered formalin. This trap only contained filtered seawater.

Phosphorus analytical methods—The PIP and TPP concentrations were determined using the Aspila method (Aspila et al. 1976). POP was determined by difference (POP = TPP - PIP). A standard reference material NIST 1573a (Tomato Leaves) was run with each sample set to evaluate total P recovery and the reproducibility of the analyses. The TPP concentration of the standard reference material agreed to within $\pm 5\%$ of the certified value. Approximately 20% of the samples were run in duplicate and the relative percent difference of duplicates was less than 5%. It is important to note that the distinction between PIP and POP concentrations is operationally defined, as the Aspila method was originally developed for use on sediment samples. As such, it is possible that our inorganic particulate P fraction may contain labile organic P compounds as well. DIP and TDP concentrations were determined using the methods described by Koroleff (1983) and Monaghan and Ruttenberg (1999), respectively. Supernatant and rinse water TDP and DIP concentrations were always well above detection limits ($\sim 0.2 \mu\text{M}$ P). Replicate analysis agreed to within 5% of each other, and 98% to 100% of the amount of standard spiked into select samples was recovered. DOP was determined by difference (TDP - DIP = DOP). Again, it should be noted that DIP and DOP are operationally defined terms, presumed to be dominated by inorganic and organic P, respectively.

Assessment

Experiment 1—Supernatant DIP, DOP, and TDP concentrations ranged from 5 to 516, 0 to 64, and 5 to 580 μM , respectively. Blank values (7.3 ± 5.3 , 2.7 ± 2.4 , and $10.1 \pm 5.8 \mu\text{M}$ for DIP, DOP, and TDP, respectively) were obtained by taking the average P concentrations in unused trap cup solutions from cruise 15 and several saved cups from past cruises that did not collect particles due to trap malfunctions ($n = 16$ samples). It is assumed that these blank values are applicable to all of the supernatants analyzed in this study. Average blank P concentrations are 1 to 2 orders of magnitude lower than the dissolved P concentrations measured in our samples.

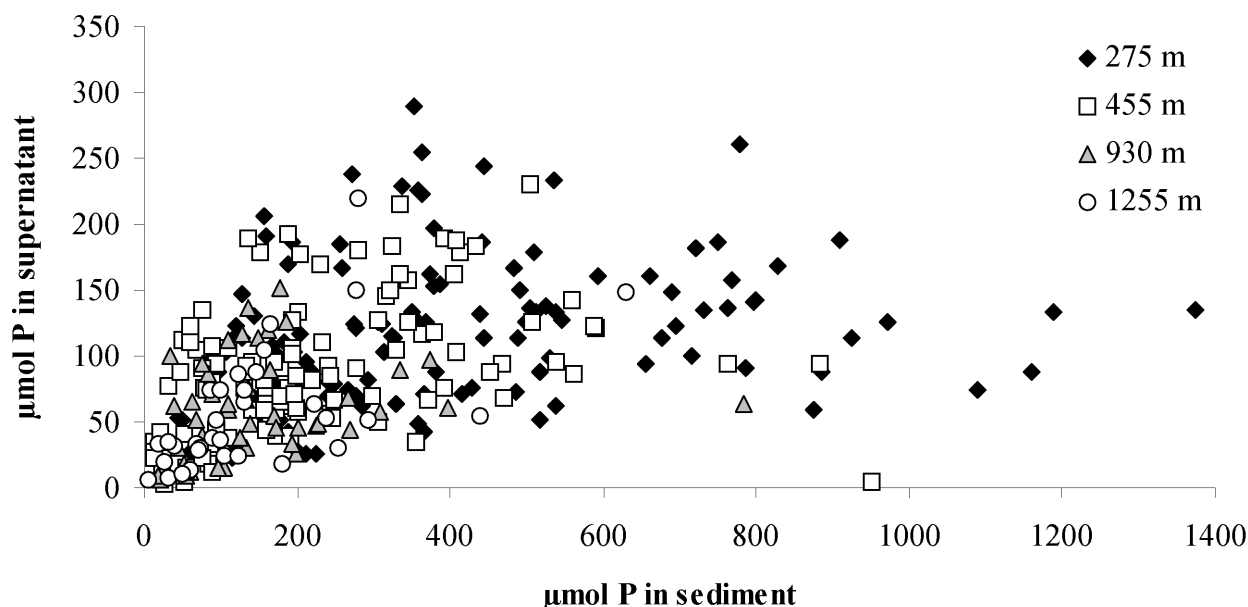


Fig. 2. Amount of P measured in the supernatant versus the amount of P measured in the solid (sediment) phase for samples collected between November 1995 and October 2003 at four different sediment trap depths.

There is a large variation in the amount of total P measured in the trap supernatant relative to the P found in the trap sediment, with similar scatter observed for all four trap depths (Fig. 2). On average, approximately $30\% \pm 15\%$ of the P in the trap was found in the supernatant phase at all depths (Fig. 3A). The composition of supernatant P is quite different from that of the sediment. Approximately $93\% \pm 8\%$ of the P in the supernatants is inorganic P whereas in the sediments, inorganic P comprises only 50% to 60% of the total P (Fig. 3B). This indicates that either all of the P solubilized from the particulate phase is inorganic in nature, and/or that labile organic P compounds are being rapidly converted to inorganic P during particle alteration. Regardless, supernatants contain a significant amount of inorganic P and, therefore, should be included in studies of particulate P flux (Table 1).

Experiment 2—TDP, DIP, and DOP concentrations were measured in the rinse water used to process trap samples collected from cruises 13 to 15 (June 2002 to November 2003). The amount of P measured in the trap sediment, supernatant, and rinse solutions is shown in Fig. 4. The amount of P in the rinse waters is small relative to the P in the sediment. Rinse water P is on average $10\% \pm 9\%$ of the total P in the trap (Table 2). P in the rinse water is again dominated by the inorganic P pool ($82\% \pm 20\%$ DIP), and there are no trends with depth.

Comparison of P fluxes with and without supernatants and rinse water P suggests that on average, rinse waters contribute less than 10% of P to the total P flux. The low concentrations of P measured in the rinses also suggest that although deionized water may potentially lyse biological

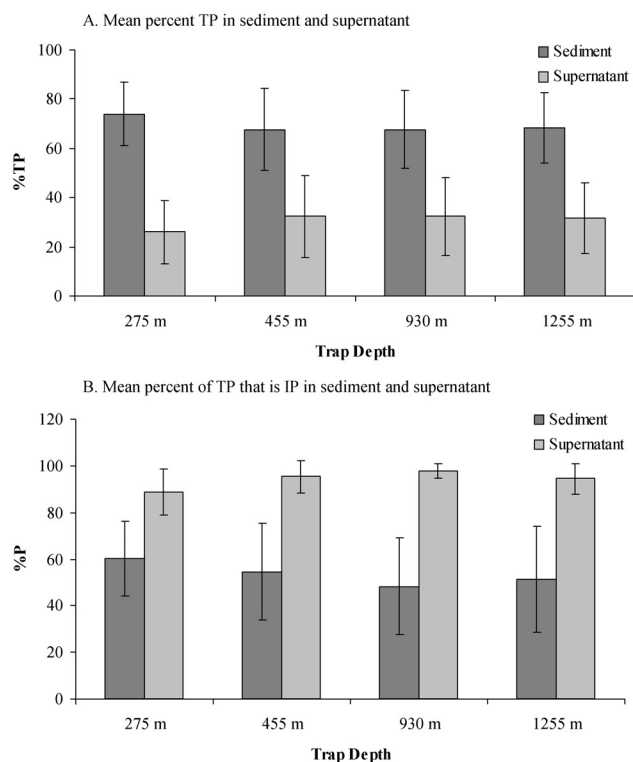


Fig. 3. (A) The mean (± 1 standard deviation) percentage of the total phosphorus in the sediment trap cup that is in the sediment phase (dark gray bars) and the supernatant phase (light gray bars) collected between November 1995 and October 2003 at four different sediment trap depths. (B) The mean percentage (± 1 standard deviation) of phosphorus that is inorganic in the sediment and supernatant of samples.

Table 1. Mean fluxes (± 1 standard deviation) of IP, OP, and TP based on sediment alone, including supernatant P, and including supernatant and rinse water P from cruises 13, 14, and 15 (28 Jun 2002 to 5 Nov 2003) for all four sediment trap depths*

Depth	P Flux ($\mu\text{mol m}^{-2} \text{d}^{-1}$)		
	Sediment P	Sediment + Supernatant P	Sediment + Supernatant + Rinse water P
275 m			
TP	79 \pm 39	96 \pm 43	103 \pm 45
IP	43 \pm 30	58 \pm 34	63 \pm 35
OP	36 \pm 21	38 \pm 21	40 \pm 20
455 m			
TP	27 \pm 22	40 \pm 27	44 \pm 28
IP	14 \pm 16	27 \pm 20	31 \pm 21
OP	12 \pm 12	13 \pm 12	14 \pm 12
930 m			
TP	27 \pm 15	36 \pm 15	40 \pm 15
IP	11 \pm 5	20 \pm 7	24 \pm 9
OP	16 \pm 11	16 \pm 11	16 \pm 11
1255 m			
TP	28 \pm 23	37 \pm 27	40 \pm 28
IP	14 \pm 19	23 \pm 23	25 \pm 25
OP	14 \pm 13	14 \pm 13	15 \pm 13

*IP and OP fluxes only include either the DIP or DOP measured in the supernatant and rinse water, respectively.

components and release P within trap material, it is a relatively minor issue in this study. Nonetheless, it is important to at least monitor rinses for dissolved constituents during sediment trap processing.

Experiment 3—TDP, DIP, and DOP concentrations were measured over a period of approximately 6 mo in trap cup 13 from cruises 14 and 15. Cruise 15 samples exhibited a 20% increase in the amount of P in the supernatant relative to that in the sediment between the time the trap was closed and the time of the first sampling in the laboratory (13 d) (Fig. 5). Shipboard samples were not taken during cruise 14 and trap cups did not arrive in our laboratory until 26 d after recovery. As such, it is unknown if there was a similar P release. After the initial increase in the percentage of TP present in the supernatant, there was little change observed in any of the samples except for cruise 14 in the 455 m trap (cup B), which had a slight, but significant trend of increasing supernatant TP with time, 0.07% TP d⁻¹ (linear regression $r^2 = 0.81$, $P = 2.8 \times 10^{-5}$). Greater than 90% of all the P measured in the supernatants was inorganic, consistent with the supernatant data from Experiment 1, and remained fairly constant over the course of the experiment.

Our results suggest that most of the P released to the supernatant occurs rapidly after collection, possibly during the transport of the sediment trap samples from the ship to the

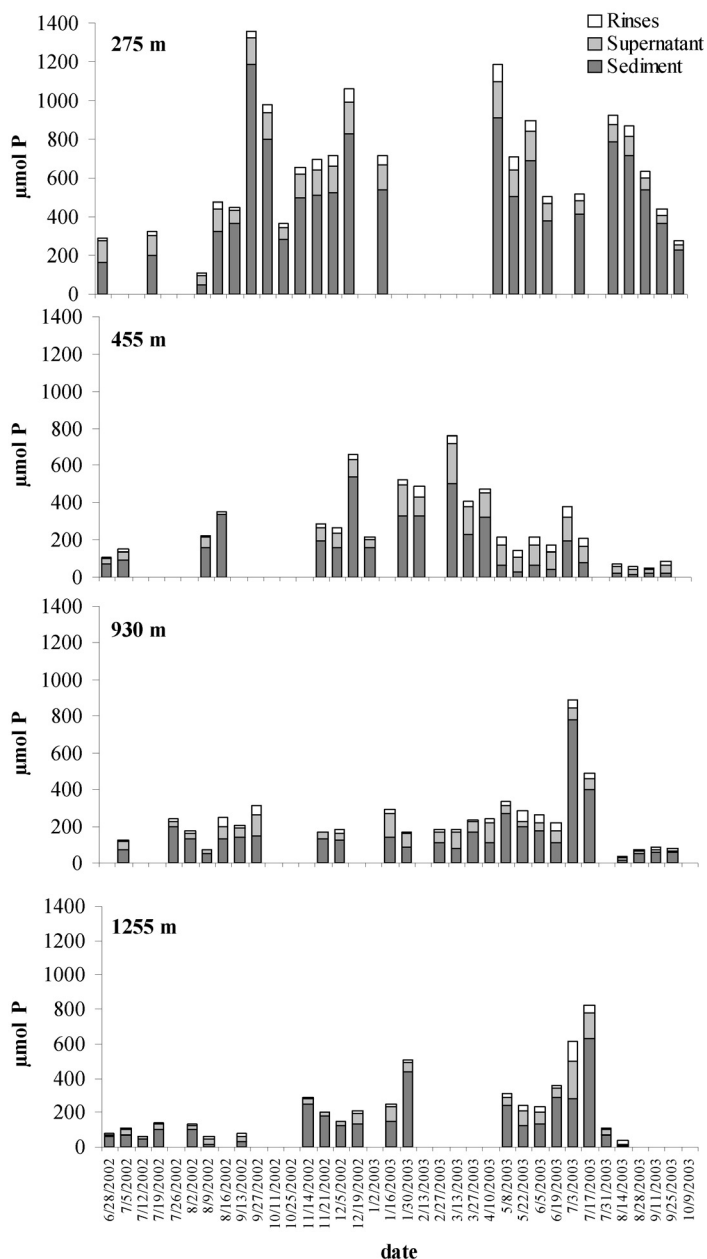


Fig. 4. The amount of P in the sediment (dark gray bars), supernatant (light gray bars), and rinses (white bars) in select sediment trap samples collected during cruises 13, 14, and 15 (28 Jun 2002 to 5 Nov 2003) at all four sediment trap depths.

laboratory. Furthermore, there is no difference in the composition of P released over time between the oxic and anoxic samples. Thus, temporal trends in particulate P between sediment trap samples most likely reflects real differences in sinking particle flux rather than time-dependent postdepositional reprocessing. During cruise 15, the C trap (930 m) was not poisoned with formalin along with the others (Fig. 5). Although the number of samples tested was small and trap to trap variability high, there were no obvious differences between the

Table 2. Mean percentages (± 1 standard deviation) of TP that are present in the sediment, supernatant, and rinses of samples collected from cruises 13, 14, and 15 (28 Jun 2002 to 5 Nov 2003) for all four sediment trap depths

Depth of trap	% of TP in sediment	% of TP in supernatant	% of TP in rinses
275 m	75 \pm 10	18 \pm 9	7 \pm 2
455 m	53 \pm 22	34 \pm 14	13 \pm 9
930 m	65 \pm 13	24 \pm 12	11 \pm 7
1255 m	65 \pm 20	24 \pm 12	10 \pm 14

unpoisoned C trap samples and the other samples from the poisoned traps with regard to the magnitude or timing of P release to either the supernatant or rinse water. These results suggest that the rate of P released to the supernatant is independent of oxygen concentration and, at least under anoxic conditions, is dominated by abiotic (i.e., temperature and agitation) rather than biotic processes.

Discussion

Prior to deployment, sediment trap sample cups are typically filled with filtered, poisoned hypersaline seawater (seawater + poison + additional NaCl) (Gardner 1995; Knauer and Asper 1989; Lee et al. 1992) to hinder microbial degradation and zooplankton grazing in trap cups, while minimizing chemical and physical disturbance of the sediment trap samples. Formalin is one of the most commonly used preservatives due to its high efficiency as a biocide and its relative ease in handling (versus mercuric chloride and sodium azide) (Lee et al. 1992). Unfortunately, it has been found that while formalin hardens tissues, it also introduces dissolved organic carbon (DOC) to supernatants, binds proteins within samples, interferes with stable isotope measurements, encourages increased numbers of swimming organisms to enter traps, and requires careful buffering due to its pH sensitivity (Gardner 1995; Lee et al. 1992; Noji et al. 1999).

Our results clearly demonstrate that a significant amount of P captured in sediment traps is lost to overlying sample cup supernatants (30% \pm 15%) and that this process occurs fairly rapidly. There is considerably less P released during trap processing, e.g., rinsing of the particulate material (10% \pm 9%). There have been few similar studies on the release of P in supernatants. Ruttenberg (pers. comm. unref.) measured P concentrations in sediment trap cup supernatants and rinse water for samples collected from the Bermuda Atlantic Time-series site ($n = 9$, sediment trap depths = 500 and 1500 m, poisoned with mercuric chloride). Her results showed that between 50% to 78% of the total P measured within the traps was in the dissolved phase as DOP, except under suboxic conditions, where it was predominantly released as DIP. In contrast, Bodungen et al. (1991) found that most of the P lost to the supernatants (> 90% of

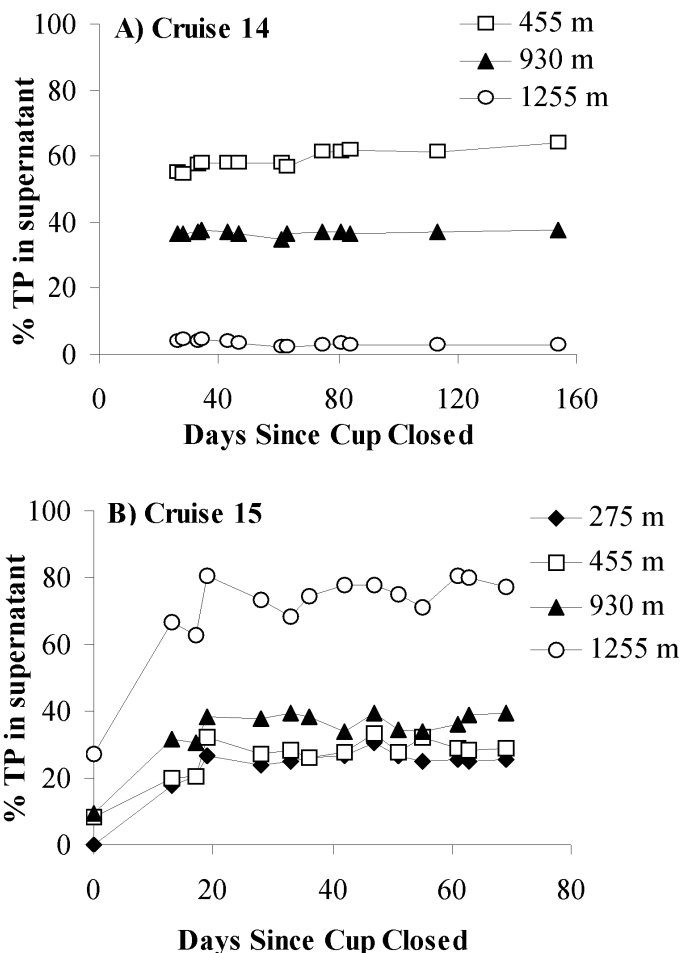


Fig. 5. The percentage of P that was measured in the supernatant of sediment trap cup 13 samples from cruises 14 and 15 over time (%TP in supernatant = amount P in supernatant/(amount P in supernatant + amount P in sediment) \times 100). Time zero samples were not taken for cruise 14 samples. Cruise 15 time zero samples were removed shipboard. The remainder of the monitoring was done in triplicate in a laboratory setting. Error bars are smaller than plotted symbols.

total P measured in the trap) was as DIP in mercuric chloride poisoned sediment trap samples ($n = 6$, sediment trap depths = 500 m) collected from the Greenland Sea.

In this study, nearly all of the P released from the particulate phase occurred as DIP (>90%), regardless of oxic versus anoxic conditions. The magnitude of the supernatant release is, in general, considerably smaller than that found by the studies above. It is possible that at least some of this difference is due to the type of poison used. Unlike formalin, mercuric chloride chemically alters the DNA in mitochondria of certain organisms. Hence, there is the possibility of enhanced release of ATP, and hence P, to the solution (Palmeira and Madeira 1997). However, we should note that Paytan et al. (2003) found no consistent difference in POP concentration or composition between formalin and mercuric chloride poisoned sediment trap samples.

A potential source of supernatant DIP is the release of P from inorganic material within trap particles. The distinction between inorganic and organic P species is important as the bioavailability of P differs between them. Faul et al. (in press) used sequential extraction to determine the various forms of P in sediment traps from a wide range of oceanic environments and depths. They determined that inorganic P comprised approximately 38% of sediment trap material (25% authigenic P + 13% detrital P), a substantial portion of the total particulate P flux. Ranhofer (2005) conducted a similar study in Cariaco Basin and determined that inorganic P comprised, on average, approximately 27% of the total sinking P material (20% oxide associated P, 6% authigenic P, and 1.3% detrital P). An exchangeable P fraction comprised 32% of total P, and is likely a mixture of weakly absorbed inorganic P and labile organic P. The large fraction of particulate matter that is oxide-associated P is of particular interest in this study because this P will be released to the dissolved phase (e.g., in the 455, 930, and 1255 m traps) during dissolution of particulate metal oxides in the anoxic water column of Cariaco Basin (Ho et al. 2004).

Another source of DIP to the supernatants may be via direct release from planktonic material and/or solubilization of POP. Within organisms, P is comprised of a wide variety of compounds ranging from polyphosphates (storage) to phospholipids (cell membranes) and adenosine triphosphate (metabolism). It is possible that more reactive components, such as mono- and di-phosphate esters, are released from cells and converted to phosphate within trap cups. This conversion may be enhanced by the presence of enzymes (e.g., phosphatases), which may still be active in poisoned traps. As a result, the extent of P released from organic matter is difficult to determine.

It is important to note that the source of P in the supernatants and rinse water may not be solely from P within sinking particles. Bodungen et al. (1991) suggested that high DIP concentrations within trap supernatants are due to herniation (release of interstitial fluids rich in organic material) of "swimmers," organisms that attempt to feed on the sediment trap material and are poisoned. The extent of this process is difficult to quantify because the manual removal of swimmers is a highly subjective process. Nonetheless, because swimmers were picked out of the samples analyzed here, it is possible that some of the P in the two uppermost trap cups (Trap A, 275 m, and B, 455 m) may be related to swimmer herniation. Swimmer herniation, however, cannot explain the high P supernatant concentrations found at 930 (Trap C) and 1255 m (Trap D).

The lack of knowledge regarding the source of supernatant P is a dilemma for determining the flux of particulate P using moored sediment traps. In our study, if all supernatant P is derived from sediment particles, then TP fluxes increase by approximately 30%. This flux increases by another 10% when rinse water P is also included (Table 1). Inorganic P fluxes are

clearly more affected than organic P fluxes if one assumes that all the supernatant DIP is from the inorganic phase, but again this assumption is tenuous. Therefore, supernatants must be measured along with trap sediments in order to accurately determine P flux.

Although supernatant concentrations must be included for estimates of P flux, relative temporal and depth trends appear to be preserved in the particulate material. All P fluxes decrease at the same rate with depth regardless if supernatant and rinse water P are included ($\pm 10\%$, Table 1). Temporal trends in P flux are also maintained (e.g., no apparent bias due to the length of deployment) (Fig. 4). This maintenance is likely due to the relative consistency of P loss in the supernatant relative to changes in flux (Fig. 2), as well as the rapid release of P observed with time (< 2 weeks) in our sediment trap incubation experiments (Fig. 5). Thus, we argue that sediment traps still provide insight into the processes affecting the flux of particulate P through the water column.

Sediment trap elemental ratios are often used to indicate the nutrient status of an ecosystem. As such, we evaluated the relationship between particulate organic C (POC) and TP, IP, and OP with and without supernatant concentrations included (Fig. 6). There is a strong linear relationship between POC and TP ($R^2 = 0.50$) and OP ($R^2 > 0.62$) with and without supernatant P and rinse water included. In contrast, the relationship between POC and IP is considerably weaker ($R^2 = 0.24$ to 0.25). This is most likely due to differences in P source function (i.e., biogenic versus terrestrial).

The molar ratio of POC to TP and IP does not change significantly with or without supernatant and rinse water P added, approximately 61 to 73 (Fig. 6), substantially lower than the C/P molar ratio of 106 associated with Redfield (Redfield et al. 1963). The molar ratio of POC to OP, however, decreases from 193 with no, or only OP in supernatant and rinse water added, to 142 when the OP flux is corrected for the TDP in the supernatant. Although both ratios are higher than that expected from Redfield, interpretation of the magnitude of possible nutrient limitation by either N or P would be considerably different.

Ultimately, interpretation of molar C/P ratios within traps will depend on the source of the inorganic P within the trap supernatant. If DIP is derived from dissolution of particulate inorganic material or desorption of adsorbed phosphate, then it can be excluded from interpretations of organic elemental ratios in sinking particles. If, however, the DIP is derived from the hydrolysis of organic compounds within sinking biological material, then it must be considered. For example, proteins, which have an average C/N ratio of 2.7 but virtually no P, may comprise as much as 70% of eukaryotic algae. In contrast, nucleic acids have an average C:N:P ratio of 9.5:3.7:1, and may comprise as little as 10% to more than 40% of cellular biomass (Sterner and Elser 2002). Thus, variations in the release of nucleic acids and proteins to trap supernatants will have a relatively small effect on the C/N

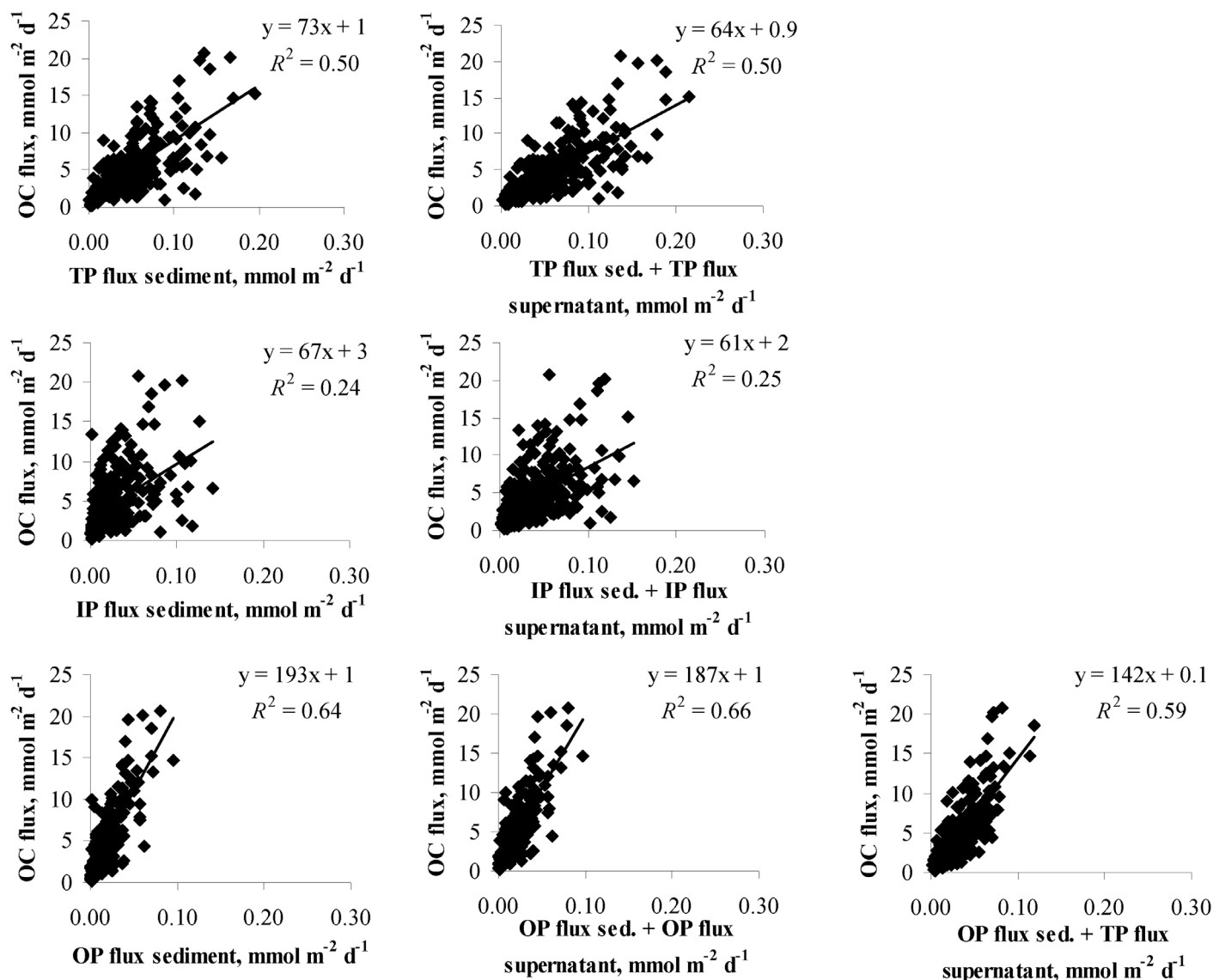


Fig. 6. Organic C fluxes versus TP, OP, and IP fluxes measured across all depths in sediment, and in sediment including supernatant and rinse water. OP fluxes were determined with both supernatant DOP and supernatant TDP included. Regression lines and R^2 values are also given.

ratio of trap material, but a potentially large effect on C/P and N/P ratios of trap particles.

In order to accurately assess C/P ratios of sinking material, all dissolved substances derived from biological material within trap solutions must be included. It should be noted that only supernatant P was added to the P flux for this discussion, no similar correction was completed for organic C. That a good relationship does exist between the measured POP and POC suggests that dissolved C loss from particles must also be considered. DOC concentrations in supernatants of sediment traps poisoned with formalin are complicated by the fact that formaldehyde has a large DOC blank and that it is difficult to differentiate between DOC from swimmer

herniation versus that derived from POC solubilization. In the few studies that have measured DOC within supernatants, C losses of 0.1% to 1% per day have been documented (Budge and Parrish 1998; Gardner 1995; Kortzinger et al. 1994; Noji et al. 1999).

Comments and recommendations

In our study, a considerable portion of TP, approximately 30%, is within the trap supernatants in the dissolved phase. As such, supernatants should be monitored for P whenever possible. The lack of depth or seasonal changes in supernatant P loss suggests that the flux of TP within Cariaco Basin may be adjusted using a constant correction factor. However, we

would argue that this correction may only be applied to TP at this time given the inherent uncertainties regarding the source of DIP and DOP within the trap solutions (e.g., is DIP derived from POP, PIP, or both?). An additional amount of P, approximately 10%, is released during the rinsing process. Although deionized water rinsing is a relatively minor component of the P loss in these samples, use of deionized water to remove salt is still not ideal. Extended contact between deionized water and cell material may result in cell lysis. Thus, deionized rinses may have a much larger impact in shallower sediment traps or immediately following large plankton blooms where intact biological material dominates the particle flux.

The loss of P to supernatants appears to occur rapidly, within 2 weeks of collection. This suggests that there are no time-dependent changes in P concentration or flux related to how long the material sits in the trap solution. The rapid loss of P coupled with the relatively constant percentage loss of P into the supernatant suggests that seasonal- and depth-dependent trends in P fluxes are maintained. Interestingly, much of the P lost to the supernatant occurred between recovery on board ship and transport back to the laboratory (e.g., experiment 3). It is possible that agitation of the trap samples during transport, rather than length of deployment, may play a strong role in the magnitude of particulate P released to the trap solution. As such, we suggest that sediment trap processing occur immediately upon recovery of the sediment trap as it is possible that much of the P lost to the supernatant may be avoided. Further testing of trap samples collected and allowed to sit in situ for time periods greater than 2 weeks should be conducted to confirm this theory.

We recommend further characterization of the chemical composition of P, as well as other flux constituents within sediment trap sample supernatants, in order to better understand the release and exchange process between inorganic and organic P. Toward that end, we suggest that investigations into specific P-containing compounds, beyond just the organic and inorganic distinction, are necessary to understand which P-containing chemical phases are released preferentially to others and on what timescales these processes occur. Finally, we recommend comparing P concentrations in sediment trap supernatants and rinse water using a variety of poisons. This information will clarify the effect of poison type on P release and allow for better comparisons between studies where different poisons are used.

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