



Instruments and Methods

A comparison of major and minor elemental fluxes collected in neutrally buoyant and surface-tethered sediment traps

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Abstract

We compare material collected in Neutrally Buoyant Sediment Traps (NBSTs) to material collected in standard Particle Interceptor Traps (PITs) deployed during June and September 2001 at the Bermuda Atlantic Time-series Study site in order to compare sediment traps with various hydrodynamic properties. Current meters located on the PITs array indicated that both experiments were conducted during conditions of relatively low horizontal flow, which are optimal conditions for the unbiased collection of sinking particles by PITs. The NBSTs and PITs both recorded a range of overall flux conditions, as supported by the fluxes of mass, particulate organic carbon, and other elements (S, Mg, Sr, Fe, Mn, Ni, Ti, P, V), which do not significantly differ between the two types of traps. However, the fluxes of Si, Ca, Al, and Ba collected by the PITs are significantly larger than the NBST fluxes of those same elements. Additionally, the fluxes of particulate organic nitrogen (PON) collected by the PITs are significantly smaller than the NBST PON fluxes. How these results compare under conditions of higher flow or differing particle characteristics cannot be assessed from this study.

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1. Introduction

Sediment traps have been extensively used to measure carbon export and to examine other

biogeochemical processes (Eppley and Peterson, 1979; Knauer et al., 1990; Michaels et al., 1994). Rates of remineralization with depth have been studied through sediment traps (Martin et al., 1987) and the resulting relationship has been used in many biogeochemical models (Gnanadesikan, 1999; Christian et al., 2002; Schlitzer, 2002). Sediment traps have also been used to study

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vertical distribution and cycling of trace elements in the upper ocean (Livingston and Anderson, 1983; Martin and Knauer, 1984; Buat-Menard et al., 1989; Buesseler et al., 1990).

Sediment traps offer the advantage of allowing direct collection and examination of sinking particles. However, several known problems with upper ocean sediment traps can make using sediment trap records troublesome (Gardner, 2000). The export fluxes calculated from sediment traps can differ by up to a factor of three to ten from those calculated from ^{234}Th disequilibria (Buesseler, 1991; Buesseler et al., 1994; Murray et al., 1996; Hernes et al., 2001). Trap-derived carbon fluxes have not been able to “close” the C budget at Bermuda Atlantic Time-series Study (BATS) to within a factor of three (Michaels et al., 1994) and active flux of C by zooplankton vertical migration only partially resolves the discrepancy (Steinberg et al., 2000). Additionally, factor of two to five differences in fluxes in upper ocean paired traps have been observed (Gust et al., 1992).

These discrepancies may be the result of several types of biases in upper ocean sediment traps. Hydrodynamic biases resulting from flow across the top of the trap, tilt of the trap, mooring lines, trap geometry, etc. could cause traps to overcollect certain types of particles and undercollect others, leading to particle sorting (Gust et al., 1996). Other potential problems include swimmers—live organisms that swim or are carried into the traps—and solubilization of sinking material within the trap after collection but before analysis (Gardner, 2000).

Neutrally Buoyant Sediment Traps (NBSTs) were developed in order to minimize hydrodynamic biases (Valdes and Price, 2000). When the NBSTs were first deployed in October and June of 1997, the NBST collected fewer swimmers (factor of two to ten), smaller fluxes of ^{234}Th fluxes (factor of three), and comparable mass, particulate organic carbon (POC), and particulate organic nitrogen (PON) fluxes (factor of 1.2) (Buesseler et al., 2000).

In June and September 2001, we deployed Particle Interceptor Traps (PITs) and modified NBSTs, which had improved ballasting capabilities, more sample tubes ($n = 6$), and an improved

closing mechanism. We were particularly interested in whether particle sorting was occurring—were the PITs collecting different particles than the NBSTs and thus though the total mass flux might be comparable, the fluxes of specific elements different? Here we examined particle sorting by comparing the total mass and the elemental fluxes (POC, PON, Si, Ca, Al, Ba, S, Mg, Sr, Fe, Mn, Ni, Ti, P, and V) of material collected in both types of traps. The suite of elements was chosen to include biological components (POC, PON, Si, Ca, Ba), elements with an aeolian source (Al, Fe), elements that are major components of the flux (Si, Ca, Al, Mg, S) and elements that are minor components of the flux (Ti, V, Mn, Sr).

2. Methods

2.1. Sample collection

Both a PIT array and one or two NBSTs were deployed from the R.V. *Weatherbird II* on two separate occasions in the Sargasso Sea at the BATS site ($31^{\circ}40'\text{N}$, $64^{\circ}10'\text{W}$). The PIT array was of the standard cylindrical MultiPIT design (Knauer et al., 1979) that is commonly used in many sediment trap studies including the US JGOFS time-series studies at BATS and in Hawaii. The NBST and PIT had identical collection tubes (0.0039 m^2 collection area). Each PIT had eight collection tubes mounted on the body, with baffles in each tube. Each NBST had six collection tubes with baffles in each tube. Material from two tubes from the NBST was analyzed for mass and major elements and material from two other tubes from the NBST was analyzed for POC and PON.

In June 2001, one NBST was programmed to drift at 150 m. In September 2001, one NBST drifted at 150 m and another drifted at 300 m. Details of NBST deployment procedures are described elsewhere (Valdes and Price, 2000). On both cruises, within 1 km from the NBST deployment site, PITs were deployed at 150, 200, and 300 m according to standard BATS protocols (Knapp et al., 1997). In June, the PIT and NBST were at a relative distance of 5.5 km at recovery.

In September, the PIT and the 150 m NBST were at a relative distance of 13.3 km and the PIT and the 300 m NBST were at a relative distance of 15.3 km at recovery. The traps were in the water for approximately 3 days before being recovered. In September, the NBSTs came to the surface uncapped, which could have caused loss of material. However, no visual indication of brine loss was evident and the NBSTs actually collected more POC and PON than the PITs suggesting that minimal loss occurred.

Horizontal flows were measured on the PIT array at a depth of 170 m using an Anderra RCM style current meter. Data were stored at 2 min intervals. Mean current speeds were 4 cm s^{-1} with excursions up to 11 cm s^{-1} in June 2001 and 8 cm s^{-1} with excursions up to 15 cm s^{-1} in September 2001. The horizontal flow across the NBST will be on the order of the rms vertical shear over the 1.2 m length of the instrument. The flow should be weaker than 0.2 cm s^{-1} , which is less than 5% of the flow across the PIT (Valdes and Price, 2000).

In June, the mixed layer depth based on a 0.3°C change in temperature was 16 m, with a mean temperature of 24°C . In September, the mixed layer depth based on a 0.3°C change in temperature was 40 m, with a mean temperature of 28°C . Profiles of nitrate, phosphate, silicate, and primary productivity (measured through bottle experiments according to standard BATS protocols) were similar in June and September (BATS data reports). Additional hydrodynamic data from the June cruise (BATS cruise #153) and the September cruise (BATS cruise #156) are available at <http://www.bbsr.edu/cintoo/bats/bats.html>.

2.2. Elemental flux analysis

Samples from the NBSTs and PITs were analyzed for a suite of elements (Si, Ca, Al, Ba, S, Mg, Sr, Fe, Mn, Ni, Ti, P, and V). In all cases, one tube provided the material for one sample. Swimmers were hand-picked out of the sample under a microscope, according to standard BATS protocols (Knap et al., 1997). The samples were then mailed to WHOI where the samples were filtered by vacuum filtration onto pre-weighed acid-cleaned 25 mm, $0.4 \mu\text{m}$ Nuclepore membrane

filters. Though the collected material was rinsed three times with Milli-Q water in order to remove contributions from seawater, we did not ascertain that all traces of seawater were removed. After drying in a 60°C oven for 24 h or until a constant weight was reached, the filters were reweighed and then digested for 15 minutes in 2.5 mL of ultrapure nitric acid, 2.5 mL of Milli-Q water, and $100 \mu\text{L}$ of ultrapure hydrofluoric acid in Teflon bombs in a 120°C microwave (Manganini et al., 2002). The digested particle solutions were analyzed by standard curve with a commercially available sector field ICP mass spectrometer (Element1, Thermo Finnigan MAT GmbH, Bremen, Germany). Blank filters prepared alongside the filtering and analysis (but not exposed to the sediment trap deployment or picking procedures) had element concentrations below 10% of that of the concentrations of the September samples. Material from two tubes different from those used for major element analysis were hand-picked for swimmers and then used for POC and PON analysis, according to standard BATS protocols (Knap et al., 1997).

Nonparametric statistics were used to determine if differences observed in fluxes measured in the NBSTs and the PITs were significant; the small number of samples precluded the use of statistics based on normal or known distributions (such as the *t*-test). The Kolmogorov–Smirnov test (Hollander and Wolfe, 1999), a two-tailed distribution-free test for general differences in two populations, was used to determine if the difference between the fluxes for any given element measured in the NBSTs vs. the fluxes of that element measured in the PITs was significant. Due to the small sample size and discrete nature of the data, a significance level of $\alpha = 0.1$ (90% confidence level) was chosen to detect possible important differences in the data. In order to have the maximum number of samples (and thus the most reasonable statistics), we compared the entire NBST data set for a given element in a given month (for example, NBST September calcium fluxes at 150 and 300 m) to the entire PIT data set for that element in that month (PIT September calcium fluxes at 150, 200, and 300 m). We could not compare the NBST data to the PIT data at each specific depth due to the small sample size.

3. Results

The mass flux was significantly larger ($P = 0.002$; Kolmogorov–Smirnov test) in September than in June but did not differ significantly when determined by NBSTs or by PITs (Fig. 1a). Fluxes of Si, Ca, Al, and Ba were significantly larger ($P = 0.06$ corresponding to a 94% confidence level) when determined by the PITs than by the NBSTs in September and were significantly larger ($P < 0.02$) in September than in June (Fig. 1 and Table 1). The Si fluxes as determined by the NBSTs and the PITs were on the same order as the Si fluxes measured by Brzezinski and Nelson (1995) in the Sargasso Sea in August 1991–August 1992 (average Si flux of $55 \mu\text{mol m}^{-2} \text{day}^{-1}$). The Al fluxes we measured were on the same order as estimated annual Al aeolian fluxes in the Sargasso Sea (Jickells, 1999). Fluxes of P, Ti, V, Fe, Mn, Sr, and Ni were all significantly smaller ($P \leq 0.03$) in June than in September and were comparable when determined by the NBSTs and by the PITs (Table 1). Fluxes of S and Mg showed no significant differences in June or September or between NBSTs or PITs (Fig. 1 and Table 1).

In June, one fish was found in each of the two NBST tubes designated for POC and PON analysis. Since picking probably did not remove all the scales of the fish, we do not have accurate data for POC or PON fluxes determined in June by the NBST.¹ In September, fluxes of PON were significantly larger ($P = 0.03$) when determined by the NBSTs than by the PITs (Table 1). The average PON flux in the September NBST 150 and 300 m tubes was $0.25 \text{ mmol m}^{-2} \text{day}^{-1}$ whereas the average PON flux in the PIT 150 and 300 m tubes was $0.15 \text{ mmol m}^{-2} \text{day}^{-1}$. The average of the September POC fluxes determined from the NBSTs ($2.0 \text{ mmol m}^{-2} \text{day}^{-1}$) was not significantly different from the average of POC fluxes determined by the PITs ($1.8 \text{ mmol m}^{-2} \text{day}^{-1}$).

Microscopic inspection of the material collected in NBST and PITs revealed differences in number and type of swimmers collected. For example, in

September, the NBST at 300 m collected a large number of amphipods and their eggs. Amphipods are known to associate with marine snow particles (Steinberg et al., 1994), so the collection of these animals suggests that the NBST may be more efficient at collecting certain types of marine snow. Additionally, copper-rich blue particles were found to be present only in material collected in the NBST (Stanley et al., 2002).

4. Discussion

The assumption behind any sediment trap study is that the quantity and quality of material collected over a given period is an accurate representation of the in situ sinking particle flux in the ocean. Differences in flux and composition of material collected by two traps of differing designs suggest that this assumption may not always be valid (Gust et al., 1992; Buesseler et al., 2000). In the upper ocean, the NBST should remove an expected hydrodynamic bias related to the collection of slowly settling particles in a strong horizontal flow. In this study both trap types indicated that we sampled a range of flux conditions with low flux in June and moderate flux in September. Despite these gross similarities between the material collected in the two trap types, our results indicate significant differences for specific components of the flux. To interpret these differences, we first address the tube-to-tube variability common to this type of sampling.

4.1. Consideration of variability between tubes

There was significant variability between the material collected in different collection tubes from the same traps. For example, the mass fluxes often differed by almost a factor of two between two tubes from the same trap (Fig. 1a). The tube-to-tube variability was at least equal to the NBST vs. PIT variability for mass, POC, and PON. There was tube-to-tube variability both for fluxes of all the elements (as reported in Table 1) as well as for the concentrations of the elements on a mass basis. This variability needs to be taken into consideration when differences between the

¹There were no fish scales in the tubes designated for elemental analysis. Thus, fish scales did not contaminate the elemental or mass analyses.

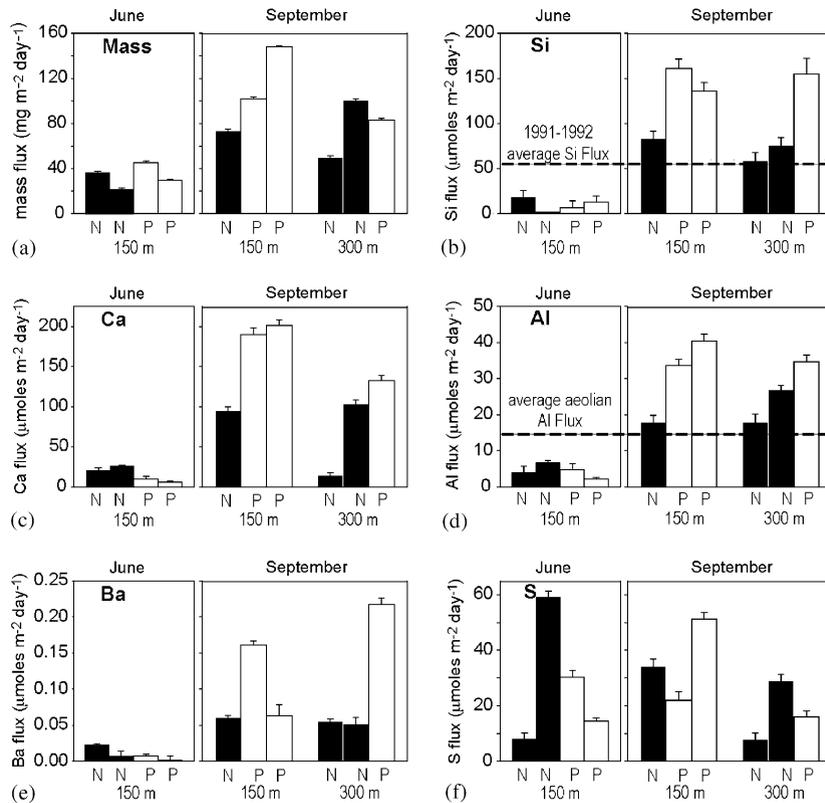


Fig. 1. Fluxes determined from material collected in the NBSTs (black) and the PITs (white) at the depths indicated. Each bar represents the flux from one sampling tube. When two tubes from the same trap and depth were analyzed, the first bar of the pair represents the flux in tube #1 and the second bar represents the flux in tube #2. Error bars on the elemental fluxes reflect the combined analytical error of the ICP-MS and the error due to subtraction of the filter blank. (a) Total mass (dry weight) flux. Error bars reflect the standard deviation of multiple weights of the same sample. (b) Si flux. The average Si flux in the Sargasso Sea between August 1991 and August 1992 (dashed line) is estimated from Fig. 6 of Brzezinski and Nelson (1995). (c) Ca flux. (d) Al flux. The average aeolian Al flux for the Sargasso Sea (dashed line) is from Jickells (1999). (e) Ba flux. (f) S flux.

material collected by the NBSTs and by the PITs are interpreted. Statistical analysis based on the ordering or ranking of the data, such as the Kolmogorov–Smirnov test, allows us to determine whether the differences between the material collected in the NBSTs and the PITs are significant in spite of the tube-to-tube variability.

Variability between tubes is commonly seen in mass, POC, and PON fluxes collected with PITs at BATS during the last decade (BATS data reports at <http://www.bbsr.edu/users/ctd/traplist.html>). The variability is likely a reflection of the small fluxes being collected; a random event that carries just a few more particles into one tube rather than

another can have a significant effect on the calculated flux. Hydrodynamic biases that produce shading of certain tubes could be another cause of variability. However, since we see the variability between tubes in both the NBSTs and the PITs, hydrodynamic biases are probably not the cause. The variability indicates that in order to determine accurate fluxes, one needs larger collection tubes, longer collection periods, or fluxes reported as the average of material collected in many collection tubes. In many studies, multi-element and isotopic analyses are not conducted from the same tube, thus complicating the interpretation of elemental or isotopic comparisons.

Table 1
Elemental and total mass (dry weight) fluxes as determined by NBSTs and PITs at the depths indicated in June and September 2001

Element	June flux ($\mu\text{moles m}^{-2}\text{day}^{-1}$)		September flux ($\mu\text{moles m}^{-2}\text{day}^{-1}$)			
	NBST 150 m	PIT 150 m	NBST 150 m	PIT 150 m	NBST 300 m	PIT 300 m
Si	19, 2	7, 13	83	161, 136	59, 76	155
Ca	21, 26	10, 6	95	190, 201	15, 104	132
Al	4, 7	5, 2	18	34, 40	18, 27	35
Ba	0.02, 0.01	0.01, 0.002	0.061	0.16, 0.063	0.056, 0.052	0.22
PON ^a			0.21, 0.29	0.12, 0.26, 0.16, 0.17	0.23, 0.28	0.12, 0.09, 0.17
P	0.8, 1.1	1.4, 1.3	4.6	5.0, 4.4	3.2, 6.8	3.4
Ti	0.9, 0.3	0.2, 0.1	1	1.2, 1.0	2.2, 7.2	0.9
V	0.06, 0.01	0.01, 0.01	0.05	0.04, 0.04	0.03, 0.05	0.03
Fe	8, 3	3, 1	10	14, 18	12, 10	10
Mn	0.09, 0.05	0.06, 0.01	0.11	0.16, 0.16	0.13, 0.15	0.13
Sr	0.10, 0.21	0.08, 0.05	1.01	0.98, 0.54	0.09, 0.41	0.42
Ni	0.35, 0.07	0.07, 0.01	1.82	0.46, 0.47	0.59, 0.23	0.21
Mass ^b	37, 22	45, 29	74	102, 148	50, 101	83
POC ^a			2.1, 2.2	0.9, 2.2, 1.6, 1.2	1.7, 2.1	1.3, 1.0, 4.2
S	8, 59	30, 14	34	22, 51	8, 29	16
Mg	16, 97	59, 30	26	25, 79	11, 32	24

When more than one tube was analyzed from the same depth, all fluxes determined are listed, with the first flux always corresponding to the first tube (and thus the first bar on the bar graphs in Fig. 1). Horizontal lines divide the elements into four groups: (i) fluxes in PITs in September significantly greater ($P = 0.06$) than fluxes in NBSTs in September; (ii) fluxes in NBSTs significantly greater ($P = 0.03$) than fluxes in PITs (iii) fluxes comparable in NBSTs and in PITs and fluxes significantly greater ($P \leq 0.03$) in September than in June; (iv) fluxes comparable in NBSTs and PITs and in September and in June.

^aPON and POC flux in units of $\mu\text{moles m}^{-2}\text{day}^{-1}$.

^bMass flux in units of $\text{mg m}^{-2}\text{day}^{-1}$ dry weight.

4.2. Elemental fluxes

The total mass flux, POC flux, and the fluxes of many elements (P, Ti, V, Fe, Sr, S, Mg, Mn, Ni) did not differ significantly when determined by the NBSTs or by the PITs (Fig. 1, Table 1). The fact that the NBSTs and the PITs agree in some cases is good news for the trapping community—perhaps hydrodynamic flow is not preventing sediment traps from being good recorders of upper ocean export fluxes of many major carrier phases, at least in these conditions. The currents, as measured on the PITs during these deployments, averaged 4 cm s^{-1} in June and 8 cm s^{-1} in September and were thus considerably less than the limit of 15 cm s^{-1} , below which PITs are expected to give accurate estimates of particle flux (Gardner, 1980; Butman et al., 1986).

Elements that are primarily aeolian in origin (Al, Fe, Ti) and those that are primarily biological in origin (P, Si, Ba) all show higher fluxes in September relative to June, suggesting that the observed seasonal variability cannot be attributed solely to increased dust fluxes during the September cruise or due to an increase in late summer productivity. This seasonal variability in fluxes is not surprising, given that prior PITs data and deep trap data from BATS and other locations show significant seasonal variability in total flux (Karl et al., 1996; Michaels and Knap, 1996; Conte et al., 2001).

One of the reasons we set out to test the effect of reducing horizontal flow to near zero with the NBST was to see if hydrodynamic bias alone could account for the apparent C imbalance at BATS (Michaels et al., 1994). These data indicate under

these conditions, reducing hydrodynamic biases does not increase collection efficiency by the factor of two or more needed to close the C budget at BATS. How these results would compare at velocities above 15 cm s^{-1} or under conditions of differing source particle composition and sinking rates cannot be determined from these data.

Even under these low-flow conditions, fluxes of Si, Ca, Al and Ba as collected by the PITs in September were significantly larger than those collected by the NBSTs. In contrast, the flux of PON collected by the PITs was significantly smaller than the NBST PON flux. The ratios of Si/Al, Ca/Al, and Ba/Al did not differ significantly between material collected in the NBSTs and the PITs and between September and June (Fig. 2). This suggests that the differences seen in Si, Al, Ca, and Ba fluxes between the NBSTs and the PITs may be due to carrier phases with common hydrodynamic characteristics. The Ca/Al ratios

measured in the sediment traps are larger than the mean crustal ratio of 0.34 mole Ca per mole Al, suggesting the particles are not simply aggregated aeolian particles. The Si, Ca, Al and Ba fluxes determined by the NBSTs may differ from the fluxes determined by the PITs in September but not in June because of the slightly higher currents in September or because of differences in the source particle characteristics. Additionally, because fluxes are so low in June, it is analytically difficult to see differences in fluxes between the two trap types.

These data bear on the issue of trap “calibration”. While first-order corrections for over- or under-collection biases using radionuclide activity calibration can be made (Murray et al., 1996; Hernes et al., 2001; Scholten et al., 2001; Yu et al., 2001), the data on particle sorting suggest that different particle types may have different collection biases. For example, slowly settling marine snow particles might be caught less efficiently than rapidly sinking fecal pellets or planktonic tests under conditions of significant horizontal flow over the trap mouth. Which fraction each radionuclide is tracking may be an issue. Particle sorting, therefore, complicates the use of single calibration factors. Nevertheless, radionuclide calibration is still valuable—if traps cannot be shown to quantitatively collect natural radionuclide fluxes without bias, then there is good reason to question the accuracy of other elemental fluxes (Buesseler, 1991).

While we cannot prove from these data that the NBST is more accurate, the assumed removal of a hydrodynamic bias in the NBST implies that these NBST data are more likely to be representative of in situ fluxes. The differences in the fluxes of PON, Ca, Ba, Al and Si in material collected in the NBST vs. PITs suggest that sediment traps of different designs lead to particle sorting which in turn can lead to significant differences in estimates of upper ocean particle flux. Thus particle sorting should be of concern when interpreting prior data and when designing new experiments.

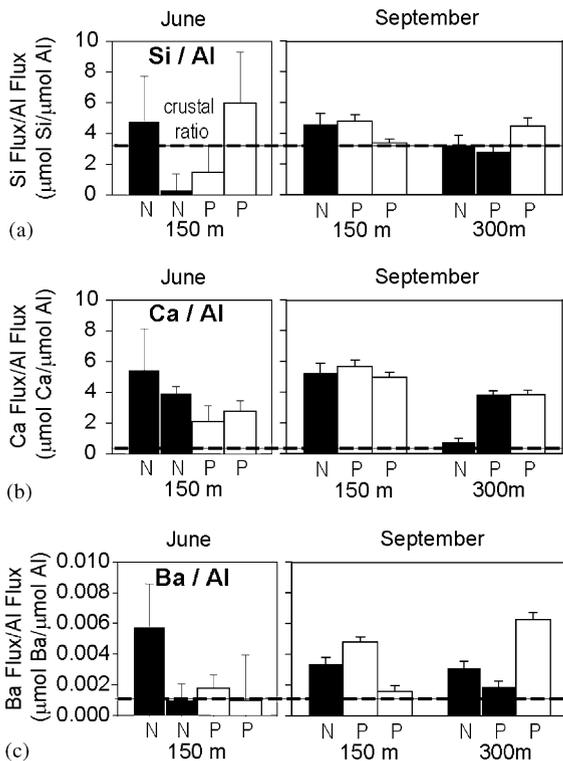


Fig. 2. (a–c) Ratios of Si/Al, Ca/Al, and Ba/Al fluxes presented in the same way as the mass and elemental fluxes. Dashed lines denote the crustal ratios on a $\mu\text{mole}/\mu\text{mole}$ basis.

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