

Methods and data processing report for bulk flux determinations from surface-tethered sediment trap (STT) deployments during EXPORTSNP

Instrument name: Surface-tethered sediment trap (STT)

Dr. Meg Estapa
Dept. of Geosciences
Skidmore College
815 N. Broadway
Saratoga Springs NY, 12866
mestapa@skidmore.edu

Document Version 1.2, October 10, 2019

I. Introduction

Surface-tethered sediment traps (STT) are used to directly collect sinking particles at discrete, sub-mixed layer depths. The STT array consists of sets of four sediment trap tubes placed at five depths (nominally 95, 145, 195, 330, and 500 m) and attached to a surface float with a Vectran tether. Each sediment trap tube has a collection area of 0.0113 m². Sediment trap tubes are equipped with custom top cap assemblies with a burn wire controller (built at Woods Hole Oceanographic Institution) that is programmed to close after a specified collection time. The STT array drifts while collecting settling particles until the burn wire mechanism closes the trap tube lids, and then is recovered for sample processing.

Collected particles were analyzed for particulate carbon (PC), particulate inorganic carbon (PIC), particulate nitrogen (PN), particulate phosphorus (P), particulate barium (Ba), biogenic silica (bSi), mass, and ²³⁴Th. Particulate organic carbon (POC) is determined as the difference between PC and PIC. Fluxes are determined by normalizing to the trap collection area and length of deployment. Bulk compositional analysis does not discriminate among sinking particles from different export pathways (single cells, aggregates, zooplankton products), so this method provides an estimate of the sum of all “sinking particle” pathways.

II. Deployment / Sample collection

A. Deployment

A goal of the EXPORTS field campaigns is to characterize export over operationally-defined time periods, termed “epochs”, equivalent to the time necessary for sinking particles to exit the euphotic zone and enter sediment traps in the upper 500 m. The sample collection and analysis procedures described below were repeated during three 8-day epochs.

Prior to deployment, two sediment trap tubes on each STT were filled with filtered surface seawater. 500 mL of formalin-poisoned brine (70 ppt) was then gravity-fed through tubing, forming a layer below the filtered seawater to preserve settling particulate matter for bulk flux analysis. The third tube was prepared with polyacrylamide gel to collect samples for imagery and the fourth tube was prepared with RNA*later* preservative to collect samples for sequencing. STTs sampled for ~5 days until the burn wire mechanism closed the tube lids and then were recovered.

B. Sample preparation

Upon recovery, brine tubes were allowed to settle for at least 1 h in the laboratory. The overlying seawater layer was vacuumed out of the tops of the tubes. The remaining brine layers from the two tubes were drained through a single acid-cleaned, 335- μm nylon mesh screen and combined into a 4-L bottle. The screen was picked clean of zooplankton under a dissecting microscope, and the remaining screen contents were rinsed back into the 4-L bottle with filtered seawater. The combined trap samples were split into eight fractions using a custom rotary splitter.

A, B, and C splits (QMA filters): Three of the eight wet splits (termed A, B, and C) were filtered onto pre-combusted QMA quartz microfiber filters (Whatman) and dried at $45 \pm 5^\circ\text{C}$ using a laboratory oven. QMA filters were mounted and immediately counted for low-level β emission onboard the ship. Second counts were obtained for a subset of samples while still onboard the ship. Filters were stored dry at room temperature until analysis on shore for additional ^{234}Th counts and final background β emission. After β counting was complete, samples were unmounted and PC, PIC, and PN were determined. Some QMA filters were also analyzed for Pb/Po at the Autonomous University of Barcelona and for Ba and P via ICP-MS at WHOI.

D, E, and F splits (polycarbonate filters): Three wet splits (termed D, E, and F) were filtered onto pre-weighed, 25-mm diameter, 0.2- μm pore size polycarbonate membrane filters (Nuclepore) and rinsed with pH 8.5 borate-buffered Milli-Q water. Filters were dried as described above and stored at room temperature until analysis on shore for mass and bSi.

G and H splits: The remaining two $\frac{1}{8}$ wet splits (termed G and H) were shared with collaborators.

C. Sample analysis

A splits (QMA filters): ^{234}Th analysis was conducted onboard the ship (see section 3.B). On shore, filters were gravimetrically subdivided with one half of each filter reserved for Pb/Po analysis at the Autonomous University of Barcelona. The remaining half filter was again divided in half. One $\frac{1}{4}$ section was analyzed for PC and PN after high-temperature combustion on a

Thermo Electron FlashEA 1112 C/N analyzer at the WHOI Nutrient Analytical Facility. The remaining $\frac{1}{4}$ section was analyzed for PIC via coulometry after acidifying with 2 ml of 1N phosphoric acid (Table 1).

B and C splits (QMA filters): ^{234}Th analysis was conducted onboard the ship (see section 3.B). Final background counts to measure non- ^{234}Th related β emissions were obtained at WHOI after six ^{234}Th half-lives had elapsed. At this point, QMA filters were unmounted, re-dried, and gravimetrically subdivided. For each trap, either split B or split C was chosen for Ba and P analysis based on the distribution of large particles on the filter surface in an effort to ensure that filter subsections are representative of the bulk sample. For splits on which Ba and P analysis was performed, filters were divided into three equal sections. Splits that did not receive Ba and P analysis were divided into two equal sections (Table 2).

Filter subsections for Ba and P analysis were leached with 0.6 M hydrochloric acid at 60°C for ~16 hours (Bishop and Wood, 2008; Bishop et al., 2012). Leachates were diluted with 2% nitric acid, doped to an indium concentration of ~1 ng/mL, and analyzed for multi-element concentrations using a Thermo Scientific iCAP quadrupole inductively-coupled plasma mass spectrometer (ICP-MS) situated at the WHOI Plasma Facility. Quantification of Ba and P was achieved via comparison of sample ion beam intensities to those of reference solutions with known concentrations. Samples containing sufficient material for Ba-isotopic analysis were aliquoted, spiked with a ^{135}Ba - ^{136}Ba double spike, and Ba purified from the sample matrix using two passes of ion-exchange chromatography. Analyses were performed using a ThermoFisher Neptune multi-collector ICP-MS, also situated at the WHOI Plasma Facility.

One section per filter ($\frac{1}{3}$ if Ba and P analysis was performed, $\frac{1}{2}$ if Ba and P analysis was not performed) was analyzed for PC and PN after high-temperature combustion on a Thermo Electron FlashEA 1112 C/N analyzer at the WHOI Nutrient Analytical Facility. The remaining filter section was analyzed for PIC via coulometry after acidifying with 2 ml of 1N phosphoric acid.

D, E, and F splits (polycarbonate filters): At Skidmore College, polycarbonate filters were re-dried and weighed daily on a microbalance until a constant mass (± 0.005 mg) was obtained on consecutive days. Filter tare weights were subtracted and net mass accumulation was calculated. To determine bSi content, filters were extracted in 0.2 N NaOH for 2 hours at 95°C and then neutralized with 1 N HCl. Subsamples were taken for immediate analysis for dissolved silicate following standard spectrophotometric methods (Strickland and Parsons, 1972).

D. Analytical and process blanks

Blank values for unused filters were obtained for PC, PIC, PN (Table 2), and bSi (Table 3). Filter blanks were obtained for each batch of bSi analyses and subtracted from those samples

analyzed in the same batch (Table 4). Filter blanks were below the detection limit for PC and PN.

Prior to each STT deployment, sets of sediment trap tubes were prepared as if for deployment, but were instead held in the shipboard laboratory for the duration of the deployment. For all epochs, two sediment trap tubes were filled with filtered surface seawater and 500 mL of formalin-poisoned brine (70 ppt) was gravity-fed through tubing to form a layer below the filtered seawater. For Epochs 2 and 3, two additional sediment trap tubes were prepared with 500 mL of formalin-poisoned brine (70 ppt) and no overlying filtered seawater to control for possible elevated blanks from the filtered seawater (which was likely to have rapidly mixed out of deployed traps during sample collection). The tubes were then processed and analyzed in parallel with the deployed tubes to provide a process blank determination (Table 5).

III. Data processing

A. PC and PN fluxes

Filter blanks were below the detection limit for PC and PN. Raw PC and PN contents of the filter sections were normalized by the fraction of the filter analyzed (Table 1). The mean PC and PN contents of the process blanks without overlying seawater from Epochs 2 and 3, normalized to one whole filter, were subtracted (Table 5). Blank-corrected values were normalized by the collection area, deployment length, and number of wet splits to yield flux. Uncertainties are propagated from the filter section weighing uncertainty and the standard deviation of the replicate process blank values.

B. PIC flux

The mean PIC content of the filter blank was subtracted from the PIC content of each filter section analyzed (Table 2). The PIC content was normalized by the fraction of the filter analyzed (Table 1). The mean PIC content of the process blanks without overlying seawater, normalized to one whole filter, was subtracted (Table 5). Blank-corrected values were normalized by the collection area, deployment length, and number of wet splits to yield flux. Uncertainties are propagated from the weighing uncertainty, the standard deviation of the filter blank, and the standard deviation of the replicate process blank values.

C. POC flux

POC flux was determined as the difference between PC flux and PIC flux. POC flux uncertainties are propagated from PC flux uncertainty and PIC flux uncertainty.

D. P flux

The mean P content of the process blanks without overlying seawater was subtracted (Table 5). Blank-corrected values were normalized by the fraction of the filter analyzed (Table 1), collection area, deployment length, and number of wet splits to yield flux. Uncertainties are propagated from the weighing uncertainty and the standard deviation of the replicate process blank values.

E. Ba flux

The mean Ba content of the process blanks without overlying seawater was subtracted (Table 5). Blank-corrected values were normalized by the fraction of the filter analyzed (Table 1), collection area, deployment length, and number of wet splits to yield flux. Uncertainties are propagated from the weighing uncertainty and the standard deviation of the replicate process blank values.

F. bSi flux

The bSi content of the filter blank was subtracted from the bSi content of each filter section analyzed (Tables 3 and 4). The mean bSi content of the process blanks with overlying seawater was subtracted (Table 5). Blank-corrected values were normalized by the collection area, deployment length, and number of wet splits to yield flux. Uncertainties are propagated from the standard deviation of the process blank replicates.

G. mass flux

The mean tare weight of the filter was subtracted from the mean post-deployment filter weight. The mean mass of the process blanks without overlying seawater was subtracted (Table 5). Blank-corrected values were normalized by the collection area, deployment length, and number of wet splits to yield flux. Uncertainties are propagated from the standard deviations of the replicate tare weights and replicate post-deployment weights.

H. ²³⁴Th flux

Process blanks are insignificant for ²³⁴Th and were not subtracted (Table 5). For B and C splits, the final background count rate was subtracted from the initial count rate to yield net count rate. Final background counts were not obtained for A splits, so the mean background count rate of B and C splits from Epochs 1 and 2 (0.28 cpm) was subtracted. Net count rate was corrected for decay between time of collection and time of analysis. The result was corrected for detector efficiency to yield decay rate at time of collection. If a second count was performed for a sample, the decay rates from the two counts were averaged. Decay rates were normalized

by the collection area, deployment length, and number of wet splits to yield flux. Uncertainties are propagated from the counting errors associated with the first (and second, if applicable) count and final background count.

I. Swimmer flagging procedure

Most of the sediment trap samples collected during the EXPORTS North Pacific field campaign contained a large number of “swimmers”, which are zooplankton that actively entered into the trap and then died upon entering the preservative brine within. The standard swimmer removal procedure is to pass the trap sample through a Nitex screen (in this case, 335 μm) to separate swimmers (most larger than this size) from passively sinking material. Then, the screen is picked under magnification to manually separate any large, passively sinking material from the retained swimmers. This material is returned to the <335- μm part of the sample prior to further processing.

During this campaign, the unusually high number of swimmers collected, including some smaller than the Nitex mesh size, meant that we could not successfully remove all the swimmer-derived material from the traps. Many of the reported trap fluxes therefore include a contribution from swimmers. Fluxes that are particularly suspect include total carbon, mass, particulate organic carbon (POC), particulate inorganic carbon, nitrogen, and phosphorus. On the other hand, fluxes of thorium-234, biogenic silica (bSi), and the cross-sectional area flux of passively-sinking particles (“area”) to the co-deployed polyacrylamide gel collector on each trap appear unaffected by swimmer contamination.

A Gaussian mixture cluster analysis procedure was used to identify the subset of samples with POC fluxes that are unlikely to be swimmer contaminated, as evidenced by high covariance among the following compositional ratios: bSi:POC, ^{234}Th :POC, area:POC, and mass:POC. Each sample was identified as “swimmer-contaminated” (swimmer flag = 1), probably uncontaminated (swimmer flag = 0), or unknown (swimmer flag = 2). Samples with flag values of 2 either were missing gel data, or had high relative uncertainty in bSi, ^{234}Th , mass, or POC.

IV. Additional information

Cautionary notes

Following Epoch 1, a 10-m length of Vectran tether was replaced with a 25-m length due to a suspect termination. Trap depths for Epochs 2 and 3 are 10 m deeper than their Epoch 1 depths.

Failure of the burn wire mechanism resulted in some sediment trap tubes remaining open until recovery. Tubes at 145, 195, and 330 m were affected during Epoch 1. Tubes at 340 m were affected during Epoch 3.

Related datasets

Additional datasets were generated from these STT deployments (Table 6).

References

Bishop, J.K.B., Wood, T.J. (2008) Particulate matter chemistry and dynamics in the twilight zone at VERTIGO ALOHA and K2 sites. *Deep-Sea Res. I*, 55, 1684-1706.

Bishop, J.K.B., Lam, P.J., Wood, T.J. (2012) Getting good particles: accurate sampling of particles by large volume in-situ filtration. *Limnol. Oceanogr. Methods*, 10, 681–710.

Strickland, J.D.H., Parsons, T.R. (1972) A Practical Hand Book of Seawater Analysis. Fisheries Research Board of Canada Bulletin 157, 2nd Edition, 310 p.

Platform	Depth (m)	Split	Epoch 1				Epoch 2				Epoch 3			
			PC/PN	PIC	Pb/Po	Ba/P	PC/PN	PIC	Pb/Po	Ba/P	PC/PN	PIC	Pb/Po	Ba/P
STT1	95/105	A	0.22	0.25	0.53		0.28	0.25	0.47		0.25	0.28	0.47	
		B	0.47	0.53			0.34	0.35		0.31	0.50	0.50		
		C	0.35	0.33		0.31	0.50	0.50			0.34	0.33		0.34
STT2	145/155	A	0.28	0.25	0.47		0.27	0.26	0.48		0.26	0.26	0.48	
		B	0.49	0.51			0.33	0.35		0.32	0.52	0.48		
		C	0.33	0.34		0.34	0.52	0.48			0.35	0.35		0.30
STT3	195/205	A	0.26	0.31	0.44		0.29	0.25	0.46		0.24	0.25	0.51	
		B	0.52	0.48			0.33	0.31		0.36	0.50	0.50		
		C	0.32	0.35		0.33	0.50	0.50			0.35	0.32		0.33
STT4	330/340	A	0.27	0.28	0.44		0.25	0.28	0.47		0.27	0.28	0.45	
		B	0.50	0.50			0.41	0.30		0.29	0.34	0.39		0.28
		C	0.33	0.32		0.34	0.48	0.52			0.52	0.48		
STT5	500/510	A	0.24	0.26	0.50		0.23	0.28	0.49		0.24	0.24	0.52	
		B	0.49	0.51			0.48	0.52			0.32	0.33		0.35
		C	0.34	0.32		0.34	0.34	0.34		0.32	0.49	0.51		
blank brine only	na	A					0.26	0.25	0.49		0.31	0.23	0.46	
		B					0.33	0.33		0.34	0.35	0.34		0.31
		C					0.51	0.49			0.49	0.51		
blank brine + filtered sw	na	A	0.25	0.24	0.51		0.25	0.25	0.50		0.29	0.23	0.48	
		B	0.55	0.45			0.31	0.34		0.35	0.33	0.36		0.31
		C	0.34	0.36		0.30	0.51	0.49			0.49	0.51		

Table 1. Fraction of the QMA filter used for each analyte.

Replicate	QMA split A		QMA splits B,C	
	C (μg)	fraction	C (μg)	fraction
1	2.65	0.25	2.78	0.50
2	2.83	0.25	2.71	0.50
3	2.75	0.25	2.69	0.50
4	3.01	0.25	2.87	0.50
5	2.82	0.25	2.89	0.50
6	2.85	0.25	-	-
mean	2.82		2.79	
s.d.	0.12		0.09	

Table 2. PIC content of unused pre-combusted QMA filters.

Replicate	Batch 1a	Batch 1b	Batch 1c	Batch 2	Batch 3
1	0.0462	0.0204	0.0306	0.0618	0.0300
2	0.0451	0.0251	0.0327	0.0766	-0.0385
mean	0.0457	0.0228	0.0317	0.0692	-0.0043
s.d.	0.0008	0.0033	0.0015	0.0105	0.0484

Table 3. bSi content (μmol) of unused polycarbonate filters.

Platform	Depth (m)	Split	Epoch 1	Epoch 2	Epoch 3
STT1	95/105	D	1c	2	2
		E	2	1a	3
		F	3	3	1c
STT2	145/155	D	1a	1c	1b
		E	2	2	2
		F	1a	3	3
STT3	195/205	D	1c	1c	2
		E	2	2	3
		F	3	3	1a
STT4	330/340	D	2	1c	1c
		E	3	2	2
		F	1a	3	3
STT5	500/510	D	2	1c	1c
		E	1a	2	2
		F	3	3	3
blank brine only	na	D	-	1c	1c
blank brine only	na	E	-	2	2
blank brine only	na	F	-	3	3
blank brine + filtered sw	na	D	2	1c	1c
blank brine + filtered sw	na	E	3	2	2
blank brine + filtered sw	na	F	1c	3	3

Table 4. Batch number of bSi analysis.

Epoch	Type	QMA filters							Polycarbonate filters		
		Split	C (μmol)	N (μmol)	PIC (μmol)	P (ng)	Ba (ng)	^{234}Th (dpm)	Split	mass (mg)	bSi (μmol)
1	brine + sw	A	10.417	0.514	0.048			0.18	D	0.280	0.044
		B	7.795	0.000	-0.016			0.13	E	0.198	0.003
		C	10.236	3.005	0.070	1056		0.10	F	nd	nd
2	brine + sw	A	4.867	0.000	0.024			0.06	D	0.077	0.042
		B	3.638	2.571	0.022	1015		0.18	E	0.067	-0.019
		C	3.340	0.395	0.004			0.19	F	0.082	0.048
3	brine + sw	A	8.222	0.534	0.051			0.84	D	0.100	0.034
		B	7.862	3.010	0.056	1158		0.22	E	0.163	0.046
		C	6.130	0.000	-0.029			0.41	F	0.261	-0.037
all	brine + sw	mean	6.945	1.114	0.026	1076		0.26	mean	0.153	0.020
		s.d.	2.622	1.334	0.034	74		0.24	s.d.	0.085	0.033
2	brine only	A	3.913	0.000	0.097			-0.10	D	0.064	0.050
		B	3.816	2.463	0.111	707	8.9	0.05	E	0.053	0.107
		C	2.864	0.513	0.039			0.15	F	0.067	0.018
3	brine only	A	1.567	0.000	0.033			-0.02	D	0.108	-0.020
		B	1.397	0.000	0.037	709	7.9	0.13	E	0.057	0.031
		C	0.395	0.000	-0.036			0.16	F	0.041	0.067
2,3	brine only	mean	2.325	0.496	0.047	708	8.4	0.06	mean	0.065	0.042
		s.d.	1.428	0.985	0.053	1	0.7	0.10	s.d.	0.023	0.044

Table 5. Process blank values.

Dataset	PI	Affiliation	Platform	Collector
Particulate ^{210}Po and ^{210}Pb	K. Buesseler	WHOI	NBST, STT	brine
Particulate Ti, trace element, and REE concentrations	P. Lam	UCSC	NBST, STT	brine
Stable isotopes, amino acids	H. Close	RSMAS	NBST, STT	brine
Lipidomic analysis of particles	B. Van Mooy	WHOI	NBST, STT	brine
Optical attenuation flux from gel traps	M. Estapa	Skidmore	NBST, STT	polyacrylamide gel
Images of sinking particles	C. Durkin	Moss Landing	NBST, STT	polyacrylamide gel
Cell and zooplankton number fluxes	C. Durkin	Moss Landing	NBST, STT	polyacrylamide gel
Zooplankton product flux	C. Durkin	Moss Landing	NBST, STT	polyacrylamide gel
DNA sequencing	C. Durkin	Moss Landing	NBST, STT	<i>RNAlater</i>
DNA sequencing	A. Santoro	UCSB	STT	RESPIRE trap (live)

Table 6. Additional datasets generated from STT deployments.