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The trace metal composition of suspended particles in the oceanic water column near Bermuda

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ABSTRACT

Trace metal partitioning between seawater and particles, both suspended and sinking, must be determined to understand and model oceanic trace metal scavenging processes. In order to improve the oceanic particulate trace metal data base, a new *in-situ* pump was developed and deployed to collect suspended particles from 0–4000 m in the Sargasso Sea near Bermuda. These particles were analyzed for Al, Fe, Mn, Co, Zn, Cu, Ni, Cd and Pb; major particulate carrier phases were estimated from Ca, opaline Si, and P. Cd is the only trace element of this group with a particulate maximum in near-surface waters. The other metals have low particulate concentrations (mol/l) in near-surface waters, and increase with depth into the upper thermocline. Particulate Al and Fe are then uniform with depth below about 1000 m until increasing in the bottom nepheloid layer. The remaining elements (Mn, Co, Zn, Cu, Ni and Pb) decrease from the mid-thermocline values to lower and relatively uniform concentrations in deep waters. The similarities among the vertical profiles for these metals suggest that authigenic Mn oxides influence their uptake from the dissolved pool, although an important or dominant role for other host phases, specifically particulate organic matter, is not ruled out by the data.

Mean intermediate and deep water concentrations are: Al, 3600; Fe, 1200; Mn, 146; Co, 1.5; Zn, 7.4; Cu, 15; Ni, 6.0; Cd, 0.06; and Pb, 2.1 pmol/l. These particulate Al and Mn values agree with previous measurements in this region, but the other elements are lower by a factor of 3 (Fe, Co) to 30 (Zn), suggesting that earlier data were compromised by contamination.

The suspended metal data are used in a simple steady-state two-box flux model to evaluate the role of suspended particles in determining the vertical flux of metals in the Sargasso Sea. The model calculations indicate that removal of suspended particles in the deep (> 500 m) water column contributes less than half of the total deep flux for all of the elements investigated except for Cd. This result implies that uptake of these metals onto particles in the deep central ocean is a minor factor in their oceanic mass balance. If this finding is generally true for oligotrophic ocean environments, whole-ocean residence times for these elements must be governed largely by processes occurring either in near-surface waters or at ocean margins.

1. Introduction

The interaction of dissolved trace metals with particles suspended in seawater has been suggested as the major control on the concentration and distribution of trace metals in the world's oceans [1–4]. While the mechanism of this removal process and its principal locations of influence are difficult to evaluate from available data, it is clear in general that vertical and horizontal variations in dissolved trace metal concentrations result from particle formation, decomposition, and transport superimposed upon physical mixing and advection. A predictive understanding of metal behavior therefore requires a detailed quantitative description of dissolved/particulate interactions and of the movement of particles through the water column. However, even simple metal partitioning data are scarce because few open ocean measurements of trace element concentrations on suspended particles have been made.

Advances in sampling and analysis of trace metals in the past 15 years have provided a fundamental understanding of the distribution of

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TABLE 1

Elemental composition of suspended particles collected near Bermuda [a]

Cruise Date, Station	Depth (m)	Vol. (l)	< 53 μm SM [b] (μg/l)	> 53 μm SM [b,c] (μg/l)	Total SM (μg/l)	Ca (nmol /l)	Si, opal (nmol /l)	P (nmol /l)	Est. C_{org} (nmol /l)	Al (nmol /l)	Fe (nmol /l)	Mn (pmol /l)	Co (pmol /l)	Pb [d] (pmol /l)	Zn (pmol /l)	Cu (pmol /l)	Ni (pmol /l)	Cd (pmol /l)
EN 148	980	607	–	–	7.2	29.4	6.5	0.333	120	3.51	1.48	192.8	1.86	2.55	9.39	15.1	9.2	0.118
9/22–23/86	2000	697	–	–	5.7	17.3	3.0	0.223	113	3.92	1.32	122.1	1.28	1.84	5.37	12.9	7.5	0.027
31°50N, 64°08W	2990	765	–	–	5.1	16.7	4.7	0.224	90	3.32	1.42	132.0	1.16	1.57	4.99	14.2	5.8	0.029
	4000	562	–	–	10.5	21.2	7.1	0.328	39	25.62	7.47	210.0	3.01	1.68	14.80	11.9	14.8	0.044
EN 157	300	241	–	–	18.5	61.2	29.8	1.367	414	1.15	0.24	81.3	0.51	0.94	9.09	8.1	12.2	0.287
3/14–16/87	300 [e]	120	–	–	20.8	48.5	32.9	2.370	561	0.71	0.09	90.8	0.30	0.75	8.92	11.9	15.5	0.297
31°49N, 64°16W	905	710	–	–	6.9	22.2	6.7	0.304	134	3.51	1.20	159.6	1.66	2.23	7.35	13.5	10.2	0.077
						24.4				2.82	1.17	152.8	1.70		6.96	14.2		0.065
	1810	733	–	–	4.9	15.4	6.9	0.371	85	3.11	1.17	103.3	1.09	1.60	4.97	11.1	5.4	0.033
	2715	951	–	–	6.4	19.1	8.4	0.315	124	3.39	1.16	126.4	1.13	1.53	9.06	13.4	6.3	0.055
	3800	548	–	–	11.3	15.8	12.7	0.336	101	23.72	6.35	186.3	2.85	1.39	12.76	16.0	14.2	0.037
WE 9-87	100	415	19.1	6.0	25.1	33.3	22.3	2.487	584	0.96	0.42	7.9	0.65	0.98	4.24	3.4		0.359
9/3–4/87										1.59	0.47	10.0	0.65		7.45	4.0		0.395
32°22N, 64°17W	750	1026	6.5	3.3	9.8	26.2	5.2	0.324	104	3.70	1.35	168.8	1.92	2.17	15.89	23.8		0.101
										2.69	1.04	137.6	1.47		8.64	14.5		0.082
WE 3-88	10	224	26.0	5.8	31.8	70.5	10.3	2.335	746	1.08	0.31	52.2	1.03	0.81	4.46	7.05	4.9	0.188
3/12–13/88												60.4						
32°12N, 64°28W										1.45		65.4						

	100	361	17.0	5.3	22.3	47.4	17.3	2.008 2.075	448	0.93	0.25	47.6 53.7 51.9	1.02	1.22	7.26	7.98	7.2	0.265
	200	760	9.0	1.2	10.2	47.9	4.4	0.618	150	1.03	0.39	193.7	1.68	1.75	8.43	10.79	6.8 9.7	0.129
	494	1053	8.3	1.5	9.8	42.0	5.3	0.425	129	2.52	0.85	224.3	1.79	2.89	11.74 10.97 11.58	21.66	8.3	0.098
	608	1094	6.6	0.7	7.3	32.7	3.5	0.304	93	3.14	0.80	206.3	2.09	2.50	9.04	16.69	8.0	0.092
	861	1182	5.6	0.4	6.0	24.3	3.3	0.239	77	4.01	1.09	131.6	1.76	2.15	7.93	15.97	6.0	0.066
	1013	1026	5.9	0.5	6.3	26.7	5.6	0.254	76	3.60	1.20	139.3	1.61	2.06	6.62	15.24	7.0	0.075
	1483	1529	5.9	1.0	6.9	26.1	5.5	0.278	80	3.56	1.16	162.6	1.60	2.39	8.40	16.75	5.4	0.061
	2000	1342	4.8	0.6	5.3	23.2	5.0	0.208	31	4.97 4.52 5.10	1.36	137.0	1.24	2.33	7.12	18.30	4.6	0.029
OC-197	50	148	41.9	7.4	49.3	146.4	59.3		926	2.16	0.28	16.7	1.01	1.34 [f]	3.11	6.42	5.4	0.388
4/10/88	330	957	8.9	2.5	11.4	43.0	12.4		129	1.82	0.50	241.6	1.83	2.66	12.24	17.17	7.8	0.099
32°07N, 64°23W	1450	1199	4.7	0.9	5.6	20.5	5.2		49	4.05	1.19	130.9	1.27	2.13	7.03	17.91	4.6	0.038

[a] Multiple concentrations listed for one sample are replicate subsamples of a single filter
[b] SM = suspended matter
[c] Upper limit estimate, prefilter mass not corrected for residual seasalt. No prefilter used for EN 148 and EN 157
[d] Mean of three–four replicate subsamples from a single filter [47]
[e] 0.4 μm Nuclepore filter
[f] Contamination suspected in one subsample, not included in mean [47]

many dissolved trace metals in the major ocean basins [5]. More recently, vertical metal fluxes in a limited number of oceanic environments have been quantified by measurements of metals in material collected with sediment traps [6–11]. The reservoir of very slowly sinking fine particles (that comprise the bulk of the suspended matter) is a critical link between dissolved and sinking particulate metals [12,13]. Because of the abundance of these particles and their large available surface area, it has been suggested that they control exchange with the dissolved reservoir. Several studies have described the distribution of suspended mass and of metals that are relatively abundant in suspended particulate matter (e.g. mass [14], Mn [15,16], Al [17,18] and Fe [16,19]), and a few measurements of the trace metal content of particles and plankton in surface waters have also been published [20–23]. Other workers presented average particulate concentrations for a large group of elements in North Atlantic intermediate and deep waters, but did not address horizontal and vertical distributions [24]. Detailed water column suspended particulate profiles are lacking for most trace metals in open ocean regions.

The dearth of particulate metal data stems in part from the difficulty in obtaining these measurements by conventional sampling techniques. Most previous studies have employed shipboard filtration of discrete water samples (up to tens of liters) brought to the surface, limiting open ocean particulate samples to about 100 μg. With this sample size, filter and handling blanks and the possibility of bottle artifacts [25,26] make accurate metal determinations difficult. Small sample sizes also limit the number of supporting analyses that can be carried out to characterize the major constituents of the sample and provide a geochemical context for interpretation of the metal data. In the present study, we have minimized these limitations by collecting much larger samples using *in-situ* filtration.

The principal goals of this work were (1) to determine accurate full water column profiles of suspended particulate trace metals in an oligotrophic open ocean regime, (2) to investigate factors controlling particulate metal content, and (3) to quantify the role of fine, slowly sinking particles in governing the flux of metals through the deep ocean. These issues are investigated here in the context of new suspended particulate concentration data for Al, Fe, Mn, Co, Zn, Cu, Ni, Cd and Pb at a Sargasso Sea station near Bermuda.

2. Sampling and analysis

Samples were collected from depths of 10 to 4000 m on five occasions at a cluster of stations centered near Station S, ca. 50 km southwest of Bermuda in the Sargasso Sea. Particles were filtered from seawater using the **R**otating **A**utomatic **P**ump for **P**articulate **I**norganics **D**etermination (RAPPID), an *in-situ* pump developed for the project that is described in detail elsewhere [27]. Briefly, this device is a self-contained battery-powered unit that attaches to a standard hydrowire so that it is free to pivot about the central vertical axis. A vane on one end orients the intake (filter holder) upstream in the ambient current, away from particulate contamination from the hydrowire or the metal components of the pump itself. A small computer controls the pre-set pumping period (typically 2–3 hours), and records flow rate and total volume sampled. On the basis of laboratory tests, pressure differential across the filter interface was estimated to be < 1.0 atm during filtration at depth. A single pump was deployed repeatedly to obtain the samples on the earlier two cruises. In the later work, three pumps were deployed simultaneously in a single cast.

Particles were collected using a two-stage filter holder fitted with a 53 μm mesh size polyester prefilter (PeCap, Tetko, Inc., Briarcliffe Manor, N.Y.) and a 1.0 μm pore size Nuclepore polycarbonate primary filter (both 142 mm diameter). Filters were acid-cleaned, rinsed, dried, and preweighed before mounting in a similarly cleaned custom-made filter holder made of acrylic, with silicone rubber O-rings, sintered polyethylene filter support, and Nylon bolts. No prefilter was used for the September, 1986 and March, 1987 samples; the Nuclepore-collected samples represent total suspended matter for these occupations. A 0.4 μm Nuclepore filter was substituted for the standard primary filter on one occasion as a test of the recovery efficiency of the standard 1.0 μm filter. This pore size comparison experi-

ment has been repeated for other locations more recently; results are reported below. For all samples, the volumes filtered ranged from 120 to 1530 l, depending on pumping time and filter clogging rate, yielding 3.1–10.6 mg total dry weight of particulate matter (Table 1).

Within 2 hours of recovery, excess seasalt was rinsed from the samples by dripping 125 ml pH-adjusted distilled deionized water (pH 8.3 by addition of trace element clean NaOH) through each filter under a vacuum of 25–40 mm Hg in a laminar flow clean bench. Rinsing solutions passed through the filter and were collected in a clean bottle placed in an acrylic vacuum chamber under the filter support. Some of the prefilters were placed on Nuclepore filters for rinsing; others were rinsed directly on the sintered polyethylene rinsing support. Weighing the Nuclepore filters revealed that, during rinsing, losses of material from prefilters caused by disaggregation of > 53 μm material or dislodging of < 53 μm particles trapped on the prefilter may approach 50% when prefilter loading is low.

After rinsing, the filters were transferred to acid-cleaned 150 mm polystyrene Petri dishes and dried for several hours in a Class 100 clean bench. The Petri dishes were then closed, sealed within several layers of polyethylene bags, and transported horizontal and upright to the laboratory. The filters were then re-dried in a desiccator and re-weighed to ± 0.1 mg on an analytical balance. Precision of the sample mass, determined from replicate weighings, was ± 2–6% for the < 53 μm fraction, but was estimated to be $\sim$ 10–50% for the > 53 μm fraction due to uncertainties in sample loss during rinsing and the low sample to filter weight ratio for this fraction. For samples using a prefilter, we performed chemical analyses only on the < 53 μm fraction, which accounted for 75–95% of total suspended mass. Some loss of labile species, notably Cd and PO_4 [20], during rinsing is a potential bias in the data. Preliminary analyses of rinsing solutions suggest that Cd loss may be $\sim$ 30%, while Zn loss was generally $<$ 10%.

Subsamples for various analyses were cut from the Nuclepore filters using a polystyrene template and a stainless steel scalpel on an acid-cleaned acrylic cutting board. For metal analysis, subsamples (8% of total) were digested in closed Teflon screw-cap vials for 4 hours at $\sim$ 100°C in a mixture of 0.5 ml concentrated nitric acid and 20 μl hydrofluoric acid. This refluxing solution effected a complete dissolution of the particulate material. After cooling, digest solutions were diluted to 2.5 ml with distilled deionized water and analyzed for Al, Fe, Mn, Co, Zn, Cu, Ni, Cd, Pb and Na by graphite furnace atomic absorption spectrometry (Perkin-Elmer 5000 with continuum or Zeeman background correction) using the method of standard additions. Sodium concentrations, determined using an insensitive absorbance line, were used to estimate residual seasalt as a correction to the mass and particulate calcium determinations. Residual seasalt was typically 0.02–0.20 mg/filter ($\sim$ 0.2–5% of sample weight), but occasionally approached 0.6 mg. Sodium contributed by NaOH in residual rinse water was estimated to be 0.01–0.1% of residual seasalt Na and was therefore ignored in the correction. Calcium was determined using flame atomic absorption (Perkin-Elmer 403) and matrix-matched standards.

Reproducibility of the analyses of replicate subsamples depends on (1) homogeneity of particle distribution across the face of the filter and (2) analytical procedures. In general, these factors contributed about equally, for an overall precision of ± 15% or better. Procedural blanks were determined on unused filters and on process blanks (which were treated in a manner identical to the samples, including submersion to several hundred meters on a non-operating pump). Mean unused filter blanks (nmol/131 cm^2 effective sample area of 142 mm diameter, 1.0 μm Nuclepore filter) were as follows: Ca, not detectable; Al, 20; Fe, 5; Mn, 0.1; Co, 0.04; Zn, 0.4; Cu, 0.3; Ni, 1.6; Cd, 0.001; Pb, 0.03. These values are in good agreement with acid-washed 0.4 μm Nuclepore blanks measured by Wallace et al. [28], and were used for the 0.4 μm sample as well. The sum of digestion reagent and procedural blanks, expressed as nmol/whole filter sample area is as follows: Ca, 40; Al, 20; Fe, 5; Mn, 0.1; Co, 0.04; Zn, 0.1; Cu, 0.3; Ni, 0.1; Cd, not detectable; Pb, 0.02. Total blanks were generally less than 10% of sample signals, and often of the order of 1%; they occasionally exceeded 50% for Zn, Cu and Ni in near-surface samples however. The 0.4 μm filter clogged quickly; hence for this sample blanks exceeded 50% for Zn, Cu, Ni, Co,

Pb and Fe. Within the precision of the data, we could resolve no systematic differences in particulate elemental concentrations between < 53 μm fractions and total particle determinations at depths where both sampling methods were used, verifying the minor chemical contribution of > 53 μm particles.

Separate subsamples (2.4% of total) were subjected to wet oxidation in perchloric and nitric acid and analyzed for P spectrophotometrically in a modification of the procedure of Strickland and Parsons [29]. Other subsamples (2.4% of total) were leached in 0.7*M* Na_2CO_3 at 90°C for 4 hours to selectively dissolve amorphous silica, leaving ordered silicates largely undissolved [30]. Leachates were neutralized and analyzed for silicate by a microadaptation of the standard seawater technique [29]. Organic carbon content could

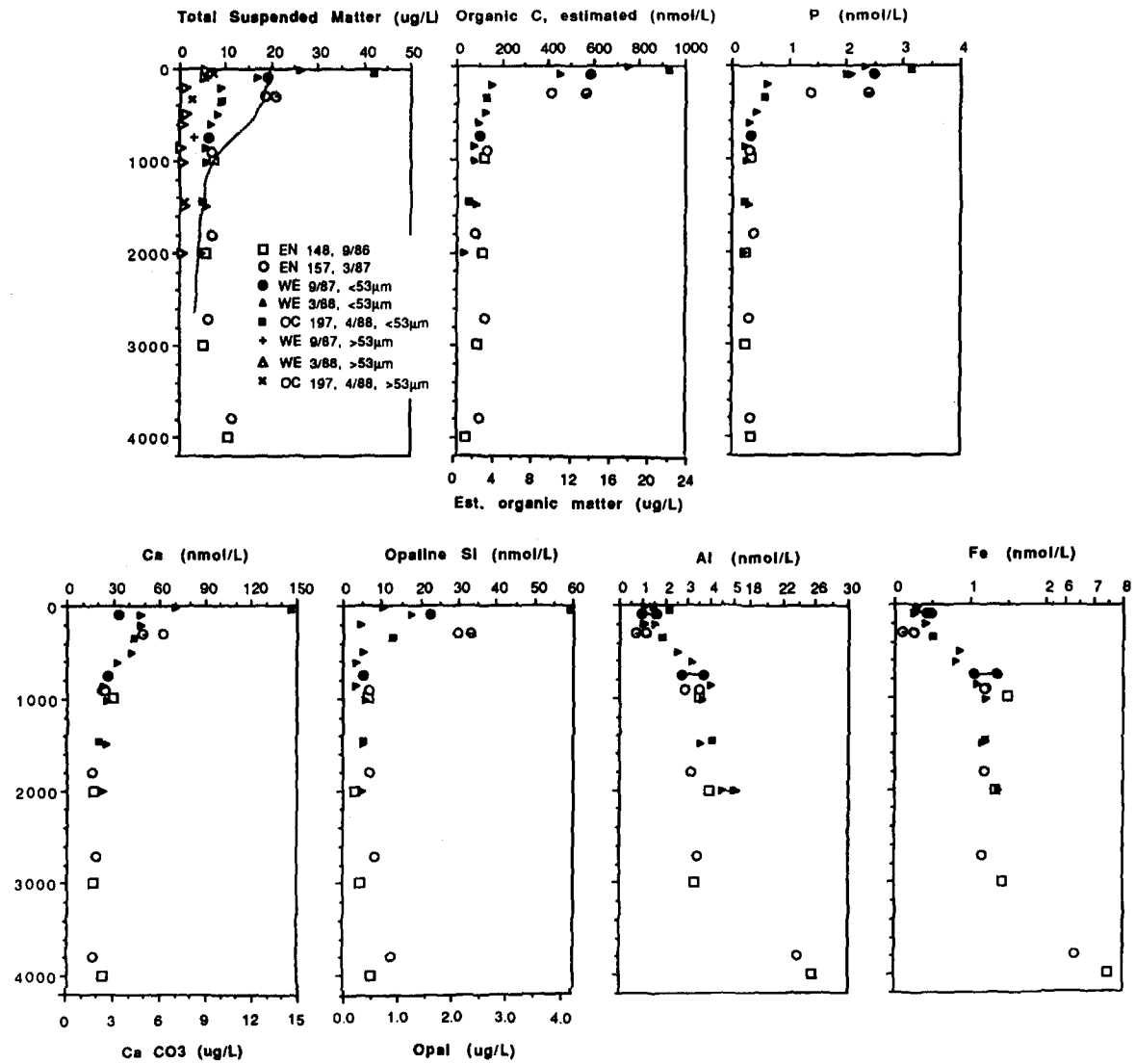

Fig. 1. Profiles of suspended particulate mass and major constituent elements near Bermuda. Depths in meters. Dotted line on suspended mass plot is *in-situ* temperature profile from March 7, 1987, one week before EN 157 occupation [33]. Mass concentrations of organic matter, $CaCO_3$ and opal calculated as described in text. Note change of scale on Al and Fe concentration axes. Symbols connected by a line represent analyses of replicate subsamples of a single filter. Circle with line indicates replicate sample collected using 0.4 μm filter.

not be determined directly, but was estimated by difference between total dry weight and summed inorganic components, assuming carbon equals 50% of the mass difference (see below).

Temporal variability observed between station occupations was generally small; to the extent that real variability may be present in the data, it was insufficiently sampled for meaningful analysis. Therefore, the separate station occupations will be considered as a single composite profile.

3. Suspended particle composition

3.1. Suspended mass

The composite suspended mass profile (Fig. 1) is similar in shape to mass distributions observed in other open ocean sites, but the particulate concentrations are somewhat lower than previously measured in intermediate and deep water. Relatively high values (19–42 μg/l) are seen in the near-surface layer of highest biological productivity (0–100 m); particle mass concentrations decrease rapidly through the thermocline to low and nearly constant values of ~ 6 μg/l (6.3 ± 1.1, 1σ, $n = 13$) in the intermediate and deep water column (500–3000 m). This value is lower and less variable than previous reports of suspended mass in the Sargasso Sea, although the mass profile in the upper water column is in excellent agreement with the profiles obtained by Bishop and Fleisher [15] in the northwest Sargasso Sea and by Bishop and Edmond [31] at two northwest Atlantic stations. Based on filtration of 4–30 l Niskin bottle samples through 0.4 or 0.6 μm Nuclepore filters, particle mass concentrations for the same depth interval were reported as 13 ± 9 μg/l at GEOSECS Station 120 (33°15'N, 56°34'W) and 5.5–14.4 μg/l (9.0 ± 2.2 μg/l, 1σ, $n = 13$) [8] at Parflux Station S (31°31'N, 55°03'W).

It might be thought that filter pore size differences among these studies would result in different particle concentrations. On the contrary, we found that mass concentrations obtained on 0.4 μm versus 1.0 μm Nuclepore filters in consecutive pump samples at 300 m showed only $13 \pm 8\%$ more mass retained on the smaller pore size filter. Preliminary results from repeated comparisons at two other depths in the Northeast Atlantic confirm this result, showing no significant differences in total mass retained using 0.4 μm vs. 1.0 μm filters (Table 2). Although these comparisons do not constitute a rigorous examination of the mass contribution of < 1.0 μm particles, the results do suggest that undersampling of the smallest particles is unlikely to be a major source of uncertainty. In particular, it should be remembered that filter media do not function as sieves —laboratory experiments on natural particles show that filters retain particles which are significantly smaller than their pore size [32]. It is worth noting that all filtration studies in natural waters necessarily collect an operationally defined fraction of the suspended matter.

TABLE 2

Comparison of suspended mass determined using 0.4 versus 1.0 μm Nuclepore filters

Cruise	Depth (m)	Volume (l)	Filter	Suspended mass (μg/l)		
				< 53 μm	> 53 μm	Total
EN-157 [1]	300	241	1.0			18.5 ± 1.5
	300	120	0.4			20.8 ± 1.6
AII-123 [2]	500 [3]	1342	1.0	9.8 ± 0.2	1.1 ± 0.1	10.9 ± 0.3
	510 [3]	781	0.4	9.3 ± 0.3	1.8 ± 0.3	11.1 ± 0.6
	1929 [4]	1579	1.0	3.9 ± 0.1	0.4 ± 0.1	4.3 ± 0.2
	1925 [4]	830	0.4	4.1 ± 0.2	0.3 ± 0.2	4.4 ± 0.4

[1] Sequential deployments 2 hours apart, no prefilter used

[2] Northeast Atlantic, October, 1989 (24°00'N, 37°30'W), preliminary results uncorrected for residual seasalt

[3] Simultaneous deployment

[4] Sequential deployments 12 hours apart

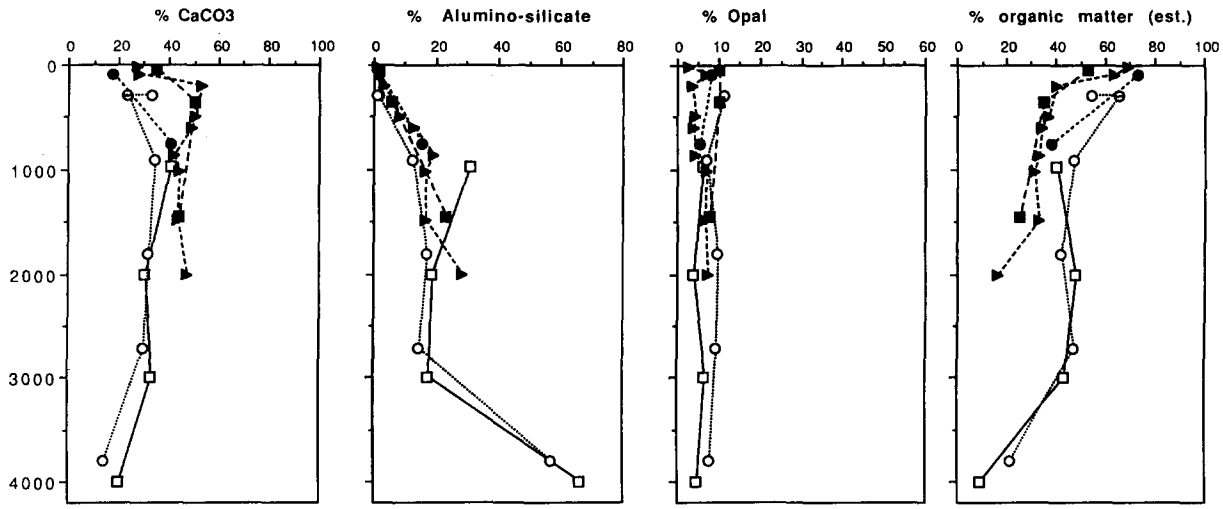

Fig. 2. Bulk composition of suspended particles near Bermuda. Symbols as in Fig. 1. Percentages calculated as described in text.

The discrepancies between our pumping results and the earlier shipboard filtration studies may be due to natural oceanographic variability or to uncertainties introduced by weight correction schemes with filter loadings 2–10 times lower than in this study. Less scatter in the *in-situ* pumping data indicates that these results are more precise, and may be more accurate than earlier bottle-collected data.

One data point which falls off the trend in the mass profile is the 300 m sample in March, 1987. Suspended mass for this sample was about twice the values at bracketing depths in March and April, 1988. Hydrographic data indicates an unusually deep convective mixed layer in early spring 1987 [33], which probably mixed surface-produced particles into the upper thermocline. This conclusion is supported by the anomalous chemical composition of this sample.

3.2. *Biogenic components: $CaCO_3$, opaline silica, organic matter and phosphorus*

Major biogenic particulate components were analyzed in order to examine trace metal distributions in relation to variations in bulk composition. Biogenic material accounted for the bulk of the suspended material, except in the benthic nepheloid layer (> 3000 m).

The vertical distributions of suspended particulate Ca and opal resemble the total mass profile (Fig. 1). Concentrations are highest, but variable, in near-surface waters. Below the euphotic zone (0–100 m), Ca concentrations decrease with constant slope through the thermocline, decrease more gradually from 1000 to 2000 m, and are approximately constant in deep water (20 ± 5 nmol/l). These upper thermocline values are consistent with previous measurements in the northwest Sargasso Sea [15] and the eastern equatorial Atlantic [19], and mid- and deep water Ca concentrations closely match those observed in the eastern Sargasso Sea (GEOSECS Sta. 29 [34]) and the Panama Basin [35].

Calcium carbonate accounts for > 90% of particulate Ca through most of the water column. The remainder is associated with refractory lithogenic material (estimated from suspended Al and an average shale Ca/Al ratio of 0.19 mol/mol [36]), and there may be a small contribution from ion exchanged or non-skeletal cellular Ca [19].

Opaline silica is relatively high and variable in surface waters, but decreases to low and constant values within the upper thermocline (Fig. 1). Below 500 m, opaline Si concentrations are 2–10 times lower than open ocean values in the Panama Basin [35] or the mid-waters of the Antarctic circumpolar current [37]. Because dissolution of a

portion of refractory ordered silicates can bias an opal determination at low levels to high values, rigorous dissolution techniques (concentrated NaOH, Na_2CO_3 fusion) were avoided, and the relatively mild leaching treatment of Eggimann et al. [30] was employed. Honjo et al. [38], using a similar dissolution procedure, found a comparable opal content (~ 5%) for sinking particles over the Sohm Abyssal Plain (31°33'N, 55°55'W).

Particulate organic carbon (estimated by difference) and particulate phosphorus (measured) decrease by about an order of magnitude from relatively high values in surface waters (POC = 750 nmol/l, PP = 2.3 nmol/l) to very low concentrations (POC = 100 nmol/l, PP = 0.3 nmol/l) in thermocline and deep waters (Fig. 1). Values throughout the subsurface water column are lower than those that have been observed in the equatorial and tropical eastern North Atlantic [19,39], but the estimated POC profile almost exactly matches a directly determined profile (0–725 m) in the northwest Sargasso Sea [15]. It should be noted that some P loss may have occurred during rinsing, especially in the upper water column [20], possibly leading to a systematic bias toward low PP in this data set.

3.3. *Lithogenic components: Al and Fe*

The profile variations of particulate aluminum and iron are parallel throughout the water column, suggesting that both elements are contained largely in the same phases (Fig. 1). Aluminum concentrations increase nearly linearly from ~ 1 nmol/l in the upper 200 m to 3.5 nmol/l at 1000–3000 m. Iron concentrations increase from 0.25 to 1.2 nmol/l in the same depth range. Both elements are greatly elevated in near-bottom samples, where sediments enriched in detrital phases are resuspended to at least several hundred meters above the bottom [40]. Much stronger nepheloid layers have been reported for other northwest Atlantic stations, where suspended mass and aluminum concentrations can exceed the values observed here by more than order of magnitude [41].

Aluminum concentrations below 1000 m are similar to previously reported values for North Atlantic intermediate and deep values [24,34]. Low surface concentrations and the monotonic increase through the thermocline have not been previously described. The surface concentrations are several times lower than published mean particulate Al concentrations for North Atlantic surface waters [17,22,24] and are approximately equal to the lowest values observed by Krishnaswami and Sarin [21] (Table 3).

Particulate Fe concentrations give molar Fe/Al ratios which cluster within 40% of the average crustal ratio of 0.33 [42] throughout the water column. Surprisingly, other workers have found much higher particulate Fe concentrations for North Atlantic suspended particles above the nepheloid layer (mean NW Atlantic, 3°N–42°N

TABLE 3

Suspended particulate trace metals in Atlantic surface waters. Al and Fe concentrations in nmol/l, all other elements in pmol/l

Element	Sarg. Sea, 0–100 m, 4 sam., [this work],		Subtrop. N. Atl., 2 sam., [21]	Sarg. Sea, 4 sam., [22]	Atl., 4 sam., [24]	Sarg. Sea, 146 sam., [45]
	Mean	Range	Mean	Mean	Mean	Mean
Al	1.2	0.5 – 2.2	2.5	3.0	2.9	6.7
Fe	0.32	0.25– 0.45	2.2	1.1	4.0	
Mn	34	9.0 –59	58	29	64	110
Co	0.93	0.65– 1.0				
Pb	1.1 *	0.8 – 1.3 *		5.4	22	
Zn	5.2	3.1 – 7.3		34	240	
Cu	6.3	3.7 – 8.0	50	40	57	
Ni	5.8	4.9 – 7.2	34	18	31	
Cd	0.30	0.19– 0.39		0.4		

* One replicate subsample of one sample rejected due to suspected contamination [47]
sam. = samples.

and mean NE Atlantic, 15°N–40°N [24,41]), giving Fe/Al ratios of 1.0–1.3 mol/mol, far in excess of mean ratios for major crustal rock types [36]. Because non-aluminosilicate Fe may be an important scavenger of some trace metals, the source of this discrepancy should be identified. A better understanding of the magnitude of the authigenic Fe component is currently under investigation using a larger set of North Atlantic particulate samples.

The estimated bulk composition of suspended particles near Bermuda is presented in Fig. 2. Mass fractions for calcium carbonate, opaline silica, aluminosilicates and organic matter were calculated from elemental concentrations assuming that (1) total Ca minus refractory Ca (estimated

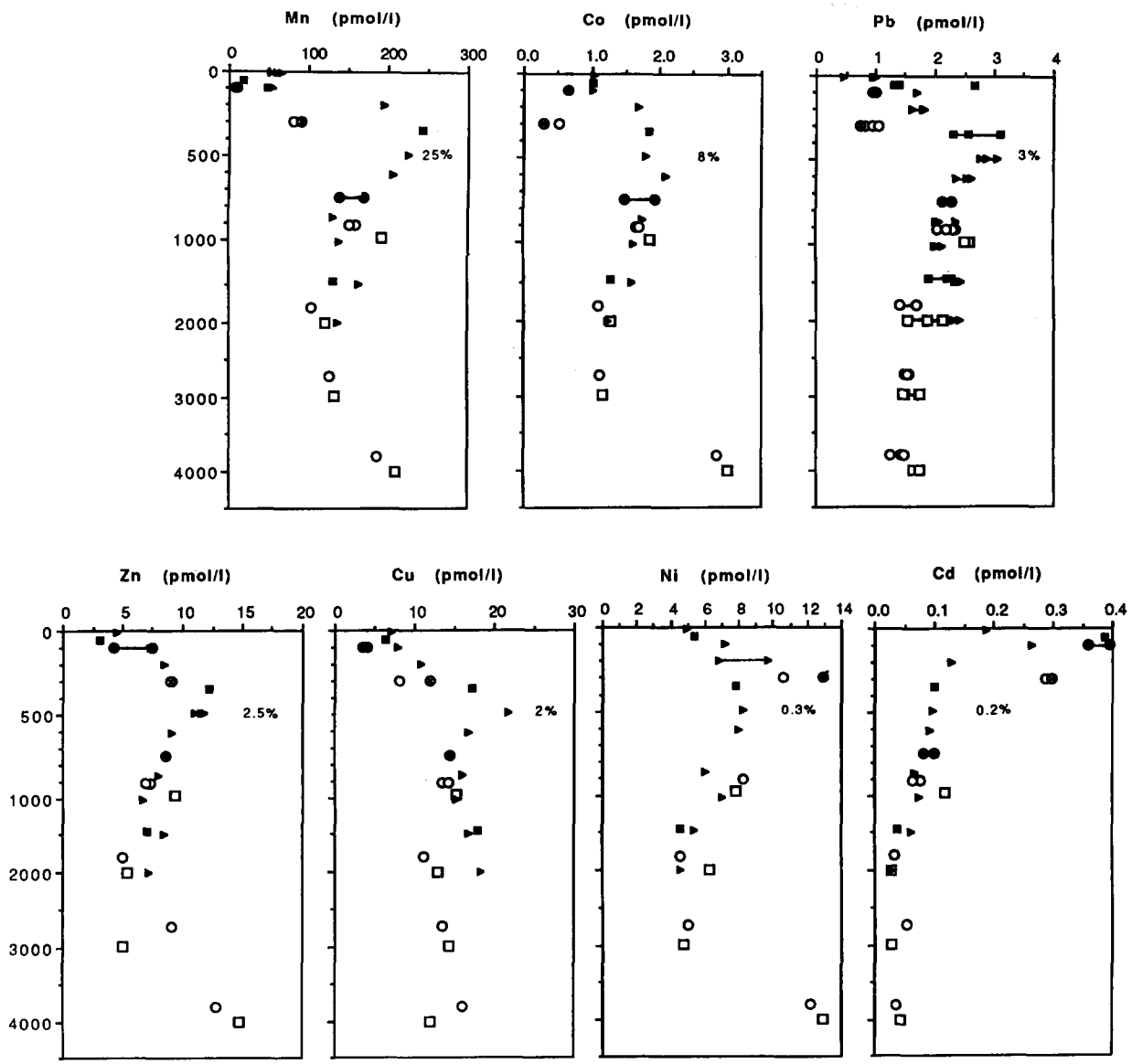

Fig. 3. Particulate trace metal profiles. Symbols as in Fig. 1. Circle with cross indicates sequential replicate sample collected using 0.4 μm filter. Percentages indicated in each plot are approximate fraction of total (dissolved + particulate) metal at 500 m, the region of the particulate metal maximum for all metals except Cd (dissolved data from [46,50,51]). Note change of depth scale at 1000 m.

from mean shale Ca/Al = 0.19 [36]) equals calcium carbonate Ca, (2) opal mass equals 2.5 times opaline Si [43], (3) mass of aluminosilicates equals 10 times Al mass [44], and (4) organic matter is total dry weight minus the sum of these three mineral phases. At this station, calcium carbonate dominates suspended particle mass, accounting for ~ 50% of the total mass, with the exception of surface waters, where organic matter dominates. Organic matter content decreases rapidly as remineralization occurs in the upper water column, in agreement with the upper water column profile of Bishop and Fleisher [15], while lithogenic material increases from less than 1% in surface waters to ~ 20% at 2000–3000 m, jumping to 60% at 4000 m in the nepheloid layer. Opaline silica appears to be a minor fraction of suspended mass throughout the water column. Uncertainties in the above calculation schemes should not shift any of these fractions by more than ±5%, although the propagated uncertainty for organic matter is an exception (±15%).

3.4. Trace metal composition

Particulate trace metal profiles vary smoothly with depth and, except for Cd, have similar profile shapes (Fig. 3). Particulate Mn, Co, Pb, Zn, Cu and Ni are low near the surface, increase to relative maxima at ~ 500 m and, except for Cu, decrease to relatively constant values at 1000–3000 m. Particulate Cu is approximately constant at depths > 500 m. This difference is probably due to deep water scavenging, a phenomenon that was not seen for the other metals. Only particulate Cd differs dramatically from these other metals in vertical distribution; it is greatly enriched in surface waters and decreases monotonically to very low levels at depth, similar to the particulate P distribution (Fig. 1). The profile of particulate Cd/P ratio nearly overlays the dissolved Cd/P profile [50; Sherrell, unpublished data].

Nepheloid layer samples show increases in Mn, Co, Zn and Ni concentrations that are roughly equal to that expected from the contribution of resuspended clays, based on average crustal metal/Al ratios ([42], Table 4). Increases are not observed for Pb and Cd, but are expected to be only ~ 20%. Thus the particle composition at 4000 m is consistent with simple mixing of ambient deep (2000–3000 m) suspended matter with an approximately equal mass of resuspended material of near-crustal composition. Copper appears to be an exception, however. Application of the crustal Cu/Al ratio predicts a 50% increase in total particulate Cu between 3000 m and 4000 m, but no increase is observed. Thus either the refractory mineral Cu/Al ratio in these particles is several times lower than the mean crustal ratio, or Cu is somehow removed from ambient particles within the nepheloid layer. A more complete

TABLE 4

Estimated percent of total particulate metal carried in aluminosilicate mineral lattice

Element	Crustal ratio [a] (mol/mol)	Percent aluminosilicate [b]		
		100 m	3000 m	4000 m (nepheloid)
Al	–	100	100	100
Fe	0.33	~ 100	90	95
Mn	5.7×10^{-3}	80	15	70
Co	1.4×10^{-4}	28	42	100 [c]
Zn	3.5×10^{-4}	7	13	63
Cu	3.1×10^{-4}	10	7	54
Ni	4.2×10^{-4}	5	60	83
Cd	5.9×10^{-7}	1	11	37
Pb	2.0×10^{-5}	2	4	24

[a] [42]

[b] Estimates based on average crustal metal/Al ratios [42], assuming all Al is aluminosilicate

[c] Exceeds mean crustal Co/Al ratio [24]

study of nepheloid layer chemistry is needed to understand this observation.

Near-surface particulate metal concentrations varied considerably between our station occupations, but even the highest values we observed for Co, Pb, Zn, Cu and Ni are substantially lower than previously reported surface values. Our Al, Mn and Cd concentrations are in reasonable agreement with earlier studies (Table 3). Decreasing atmospheric input of anthropogenic Pb since earlier studies [47] may explain the factor of 4.5 difference between our Pb results and those determined on 1974 samples by Wallace et al. [22].

Exclusion of the >53 μm fraction from the pump samples may partially account for our low surface values. Zinc and Cd content (mol/g dry weight) of >44 μm plankton, collected in Pacific waters with similar dissolved metal and nutrient concentrations to the Bermuda station, was about an order of magnitude higher than in our <53 μm particles [20]. However, Cu and Ni content was not significantly greater in the plankton. If plankton composition as roughly equivalent to that of our >53 μm particles, then the >53 μm fraction, although contributing $<25\%$ of total mass, could contain a substantial fraction of total particulate Cd and Zn. If so, our upper water column values for these two elements must be considered representative of particles smaller than the nominal 53 μm cut-off. This possibility needs to be tested systematically. Preliminary determinations of rinsing losses, as noted above, may bias our Cd measurements to values that are too low by $\sim 30\%$. For surface particulate Fe, Cu and Ni, discrepancies between this work and previously published values are difficult to reconcile on the basis of large particle exclusion, and instead may be due to contamination artifacts in the earlier studies.

Mean concentrations of Fe, Cu, Zn, Co, Pb and Ni in intermediate and deep waters (500–3000 m) are lower than previously reported North Atlantic values by a factor of 3 (Fe, Co) to 30 (Zn) (Table 5). Moreover, previous workers' data showed no systematic trends in concentration from 300 to 5000 m [24]. Differences from the older measurements are greatest for Zn and Pb, elements known to be especially subject to contamination during sample collection and processing [48,49]. However, results for Al and Mn, which are relatively abundant in suspended matter, are in good agreement, indicating that the differences are not caused by a systematic bias in collection method or analysis. Our comparison of 0.4 versus 1.0 μm filters also showed no large or consistent differences for the metals (Table 1, Fig. 3), suggesting that the use of 1.0 μm filters in this study is unlikely to have generated a significant sampling bias. We believe our metal concentrations are representative of distributions on particles >0.4 μm in a broad region of the Sargasso Sea, and that most of the older trace metal measurements were subject to contamination artifacts.

Thus these results include the first accurate measurements of suspended particulate distributions for several trace metals at an open ocean oligotrophic site. From previous measurements of dissolved and total metals in the Sargasso Sea [46,50,51], we now know that particulate metal fractions are $<5\%$ of total Cu, Ni, Cd, Zn and Pb concentrations, $<10\%$ for Al and Co, $<25\%$ for Mn, and $\sim 50\%$ for Fe (Fig. 3). These new

TABLE 5

Suspended particulate metal concentrations: Intermediate and deep water means compared to previous data. Al and Fe in nmol/l, remainder in pmol/l

	Al	Fe	Mn	Cu	Zn	Co	Cd	Pb	Ni
Sargasso Sea [this study, 500–3000 m]	3.6	1.2	146	15	7.4	1.5	0.06	2.1	6.0
N. Atlantic [24]	4.1	3.6	87	47	230	3.9		42	34
NW Atlantic, 42°N–3°N [41]	5.2	6.3	140						
NW Sargasso, 230–725 m [15]			200						

data allow a realistic assessment of the role of suspended particles in trace metal scavenging processes.

4. *In-situ* scavenging: A possible role for suspended manganese

The most striking aspect of the particulate metal distributions shown in Figure 3 is that profiles for Mn, Co, Pb, Zn, Cu, and Ni all have the similar shapes, despite the differences in global scale geochemical behavior evident from dissolved distributions [5]. Surface concentrations are generally depleted relative to deep concentrations, and all the elements show maxima in the upper thermocline. The similarity implies control by a common phase or process, but examination of vertical variations in the major terrigenous and biogenic components reveals no similar pattern (Fig. 1). The lack of covariance suggests that none of these phases, as simple non-exchanging metal carriers, is important to the total particulate metal distributions. Estimates of the contributions of lattice-bound metals in aluminosilicates corroborate this result (Table 4). Apart from nepheloid layer samples, only the aluminosilicate contribution to Co and Ni (and to Mn in near-surface waters) is estimated to contribute more than 15% of total particulate metals. Trace metals carried in $CaCO_3$ and opal matrices contribute negligibly ($< 1\%$) to the total suspended concentration, with the possible exception of Zn ($< 10\%$) [20]. Therefore, the most likely host phases for the group of metals considered here are either organic matter or minor inorganic phases.

In Bermuda waters, particulate Mn contents are 1–2 orders of magnitude greater than for other metals, presenting substantial sorptive surface if present in the form of a fine-grained authigenic mineral. The similarity in the profile shapes, especially the depth of the upper thermocline maxima, that these metals (except Cd) share with Mn suggests that sorptive uptake of dissolved metals onto recently oxidized Mn solids may be an important control on particulate metal contents. We cannot exclude an important role for particulate organic matter, or some fraction thereof, as a carrier phase for metals [52]. Clearly, however, suspended metals do not show vertical variations simply related to bulk organic carbon (Figs. 1 and 3).

Control of metal scavenging by inorganic surfaces such as Mn oxyhydroxides has been suggested on the basis of laboratory studies [53]. The sorptive behavior of Mn oxides has been demonstrated in the laboratory using pure mineral phases [54] and natural sediments [55], but not, to our knowledge, using particles from the open ocean water column. In the open ocean, Mn may form as oxide coatings on carbonate particles [56], in association with encapsulated bacteria [57], or as a separate finely dispersed hydrous oxide [15]. Thus, understanding of the formation and distribution of particulate Mn in the upper water column may shed light on the distribution of other metals as well.

The shape and magnitude of the Mn profile are consistent with the 0–725 m profile of Bishop and Fleisher [15] adjacent to the Gulf Stream in the northwest Sargasso, and may be generally representative of Sargasso Sea waters at temperate latitudes. The similarity of the profiles suggests that the particulate Mn distribution in the western Sargasso may be influenced by horizontal advection from the Gulf Stream/slope water system, perhaps in association with mesoscale eddies. Thus it is possible that the Mn phases observed near Bermuda have adsorbed or co-precipitated trace metals in distant locales rather than the local water column.

Alternatively, authigenic Mn-oxides may be formed by *in-situ* oxidation of dissolved Mn near the sampling station. The data at hand are insufficient to distinguish between this mechanism and horizontal particle advection. The issue could be clarified by determining Mn oxidation rates in this portion of the water column, and by measuring particulate Mn profiles in a basin-scale array of North Atlantic stations.

The available evidence thus suggests an important, though not necessarily dominant, role for authigenic Mn phases in water column metal scavenging near Bermuda. The major influence of Mn on suspended metal distributions may be limited to depths near the particulate metal maximum, which largely defines the similarity of the profile shapes. Experiments to determine the phase associations of metals in particle samples might be helpful in quantifying the role of Mn as

a principal variable. Knowledge of particulate metal distributions in other open ocean environments with substantially different particulate Mn distributions would shed further light on the importance of authigenic Mn as a host phase for scavenged metals.

5. Suspended particles and vertical metal flux through the deep ocean

Fast-sinking particles, produced by biological activity in near-surface waters, interact with slowly sinking suspended particles in the deep ocean, removing smaller particles more rapidly than predicted by passive settling [58]. Although the details of this interaction are not understood, particle scavenging of chemical species can be considered most simply as the sum of two processes: (1) incorporation into particles in surface waters forming large aggregates that sink rapidly to the deep ocean, and (2) association with deep suspended particles that are removed by incorporation into the surface-derived flux. Sediment trap measurements of total fluxes for some trace metals have been made in a few locations [6,8,9,59], but a quantitative estimate of the relative contribution of surface scavenging versus deep removal has not been possible without accurate suspended metal distributions for the same locations. The new suspended particulate metal data, combined with published metal concentrations of sinking material trapped at this site, make possible such an estimate for the Sargasso Sea near Bermuda.

5.1. A simple flux model

The problem can be formulated using a simple one-dimensional steady-state two-box flux model for the Sargasso Sea (Fig. 4). Following the lead of Bacon and Anderson [60] and Nozaki et al. [61], metal scavenging and particle interactions are characterized by dividing the natural spectrum of particulate matter into two size classes [13,61]. Large fast-sinking particles that dominate the flux, but contribute negligibly to the suspended mass, are assumed to be produced by biological activity in the surface box or by aggregation of deep suspended particles. Small suspended particles that make up the bulk of the suspended mass are assumed to sink only by

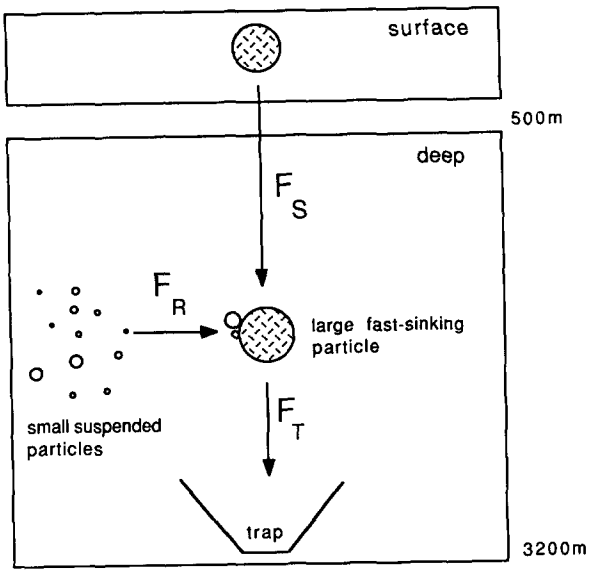

Fig. 4. Steady-state two-box metal flux model. See text for explanation of terms.

association with large particles. The large particle flux thus regulates the removal of suspended particles, but only suspended particles, by virtue of their greater concentration, surface area and residence time, are assumed to exchange metals with the dissolved pool.

The suspended particle pool must be maintained by disaggregation of sinking large particles in a one-dimensional water column, but the source of suspended particles and their associated metals is unimportant to the central conclusion here. Hence the flux arrows in Fig. 4 show only the processes of interest and are not intended to demonstrate all fluxes in the system.

The total metal flux leaving the deep box is equal to the sum of the surface-derived flux and the flux associated with removal of suspended particulate metals, the "repackaging" flux:

$$F_T = F_S + F_R \quad (1)$$

The "repackaging" flux can be calculated from the suspended metal data:

$$F_R = (Me_p{}^*D)/\tau_p \quad (2)$$

where Me_p is the mean deep ocean (500–3000 m) suspended metal concentration per volume seawater, D is the depth of the deep box (2700 m) and τ_p is the estimated suspended particle residence time. Total metal flux (F_T) is taken as

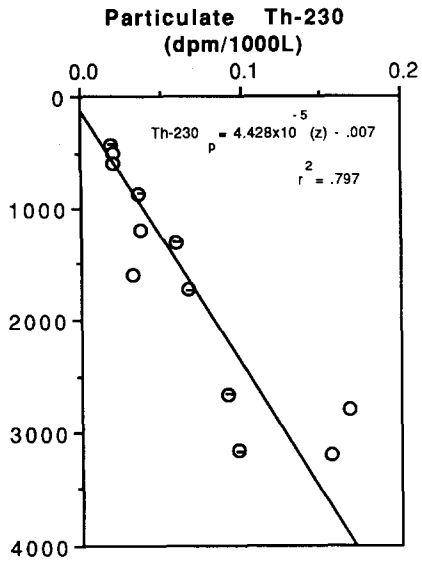

Fig. 5. Distribution of particulate ^{230}Th in the Sargasso Sea [M. Bacon, unpublished data]. Composite of two profiles: OFP, 31°50′N, 64°10′W, March, 1985 (circles) and OC 86–4, 31°36′N, 57°07′W, August, 1980 (circles with lines).

the mean flux determined from eleven 2-month sediment trap deployments during August, 1980 to August, 1982 at 3200 m near Bermuda [6], assuming a trapping efficiency of 100% [12]. Because this was a period of anomalously high mass flux compared to the long-term (1978–1991) mean, we divide the mean measured metal flux by 1.3 [62; Deuser, pers. commun.], assuming that the metal flux is simply proportional to mass flux over time scales of years to decades, and that the 13 yr mean is more representative of flux conditions during the residence time of deep suspended particles sampled in 1987–1988.

In order to estimate τ_p, we exploit measurements of suspended particulate ^{230}Th distributions in this region of the Sargasso Sea [M. Bacon, unpublished data], assuming that Th and the other trace metals are removed by a single population of particles. The ^{230}Th profile increases approximately linearly with depth in the 500–3200 m interval (Fig. 5), as predicted by both reversible and irreversible one-dimensional models of Th scavenging [60]. A more recent time series study of Th fluxes at 3200 m near Bermuda led Bacon et al. [12] to the conclusion that 71 ± 11% of the total water column production of ^{230}Th is removed vertically; the remainder is carried horizontally to other oceanic sinks. The depth dependence of the horizontal loss fraction is unknown. Here we assume it to be independent of depth, and modify the one-dimensional model equation describing vertical particulate ^{230}Th variation [60] to the form:

$$^{230}\mathrm{Th}_p(z) = f_V \frac{P}{S} z + k \qquad (3)$$

where P is the production rate of ^{230}Th per volume of seawater (0.0259 dpm/m^3 yr), f_V is the fraction of total water column production removed vertically (0.71), S is the mean particle sinking speed, z equals the water column depth in the interval 500–3200 m, and k is a constant which sets the boundary condition of $^{230}\mathrm{Th}_p$ at $z = 500$ m. This equation therefore predicts a linear increase in Th_p with depth, with slope inversely proportional to the mean sinking speed. Taking the slope of the linear regression of the $^{230}\mathrm{Th}_p$ profile (Fig. 5) and solving for S yields a mean particle sinking speed of 415 ± 95 m/yr and a mean particle residence time of 6.5 ± 1.5 yrs. Note that this value depends only on the slope of the profile in the interval 500–3200 m, not on the magnitude of $^{230}\mathrm{Th}_p$ at any depth. (The regression was not forced through the origin because we are applying the model only to the 500–3200 m deep box; another functionality may better describe $^{230}\mathrm{Th}_p$ distribution in the upper water column. The uncertainty in S is the propagated error, approximately one standard deviation, calculated from the standard error of the regression slope and the uncertainty in f_V [12].) This estimate of deep water column particle residence time is consistent with the range of estimates based on similar modeling of Th distributions in other ocean basins [13].

Available Th data also provide a check on the validity of the model assumptions and the value of τ_p. Unlike the other trace metals, ^{230}Th has no significant exogenous input to the surface box, and *in-situ* production occurs mostly in the deep box (2700/3200 = 84%). Therefore, we can make the approximation that $F_S = 0$ and predict that $F_R = F_T$. Although the repackaging flux for the other trace metals is assumed to be uniform within the deep box, F_R for ^{230}Th increases with depth as a simple multiple of $^{230}\mathrm{Th}_p$. Calculating the value of $^{230}\mathrm{Th}_p$ at 3200 m and multiplying by

$S = 415$ m/yr yields $F_R(^{230}Th) = 56 \pm 16$ dpm/m^2 yr. This is in excellent agreement with the mean annual flux, $F_T = 60$ dpm/m^2 yr, measured in sediment traps at 3200 m [12]. Thus applying the model to the magnitude of Th_p in the deep box, using a sinking speed derived only from the slope of the Th_p profile, predicts a total flux very close to the trap value. (Note that the presence of the constant k in eq. 3, which admits unknown behavior of Th_p at 0–500 m, prevents this from being a trivial result.)

Having thus calibrated the model using the ^{230}Th distribution, the resultant particle residence time can be applied to calculate F_R for the other trace metals.

5.2. *Flux model results*

The model results indicate that the repackaging flux provides less than half of the total flux in the deep ocean for all the trace metals examined (Table 6). The fraction (F_R/F_T) is remarkably constant (median $\pm$ range $= 0.32 \pm 0.09$) for all metals analyzed except Cd (0.81 ± 0.44) and Zn (0.11 ± 0.04). Thus, in contrast to ^{230}Th, the repackaging and vertical removal of deep suspended particles plays a minor role in governing the total flux of trace metals in the deep ocean; processes occurring in the surface waters of the ocean (< 500 m) contribute about two thirds of the deep flux. The conclusion is valid regardless of the source of deep suspended metals. Even in the extreme hypothesis that all suspended metals are derived from a laterally advected source, that source could not dominate the local vertical flux, and would not be expected to generate large vertical gradients in total flux for these elements.

This conclusion rests on the assumption that published measurements of trapped metals are accurate. Uncertainties in F_R/F_T are otherwise dependent on the calibration of the model using the τ_p estimate and on the standard deviation of the deep suspended metal concentrations about the 500–3200 m mean (taken to include and subsume analytical error). Because the traps were unpoisoned [6], some loss of metals to solution

TABLE 6

Sargasso Sea two-box model flux calculation. Relative standard deviations of each measurement and propagated uncertainties in calculated values are given in parentheses (see text)

Element	Mean deep conc. [a] (Me_p)	"Repackaging" flux [b,c] (F_R)	Total flux [b,d] (F_T)	$\frac{F_R}{F_T}$
Al	3600 (14%)	150 (27%)	650 (10%)	0.23 (29%)
Fe	1210 (14%)	50 (27%)	170 (10%)	0.30 (29%)
Mn	146 (20%)	6.1 (30%	19 (10%)	0.32 (32%)
Ni	6.0 (23%)	0.25 (33%)	0.77 (12%)	0.32 (35%)
Cu	15 (14%)	0.62 (27%)	1.5 (10%)	0.41 (29%)
Zn	7.4 (21%)	0.31 (31%)	2.9 (23%)	0.11 (39%)
Cd	0.06 (48%)	0.002 (53%)	0.003 (10%)	0.81 (54%)
Pb [e]	2.1 (17%)	0.096 (29%)	0.32 (17%)	0.30 (33%)
^{230}Th	0.14 [f] (18%)	56 (29%)	60 (20%)	0.93 (35%)
^{228}Th	0.43 [f] (39%)	179 (45%)	560 (20%)	0.32 (49%)

[a] Mean suspended particulate metal concentration from 500–3200 m, with uncertainty equal to standard deviation about the mean. Concentration units: dpm/m^3 for ^{230}Th and ^{228}Th, pmol/l for other elements

[b] Flux units: dpm/m^2/yr for ^{230}Th and ^{228}Th, nmol/cm^2/yr for other elements

[c] "Repackaging flux" calculated assuming particle residence time $\tau_p = 6.5$ yrs, 2700 m deep box
Uncertainties are propagated from mean deep concentrations and uncertainty in τ_p (see text)

[d] Mean sediment trap flux at 3200 m during 8/1980–8/1982 [6,63], adjusted to mean mass flux during 1978–1991 (see text), except for Th isotope fluxes. These were assumed equal to one year mean from 7/1980 to 7/1981 [12], with estimated uncertainty based on uncertainty in trap efficiency [12] and comparison to mean 1984–1986 fluxes [M. Bacon, unpublished data]

[e] Pb fluxes calculated for ~1981, assuming deep suspended Pb inventory was ~10% greater than measured in this study [47]

[f] Th_p from M. Bacon [unpublished data]. Value for $^{230}Th_p$ calculated at 3200 m from regression in Fig. 5, with estimated uncertainty (see text). $^{228}Th_p$ is mean 600–3200 m concentration at Bermuda, March, 1985 [$n = 4$, M. Bacon, unpublished data]

may have occurred during the 2-month deployments. However, this would tend to strengthen the argument by further reducing F_R/F_T for these metals. Contamination of the trap samples, which would push the result the opposite way, seems unlikely for most of these elements since the metal content (moles/g dry weight) is relatively constant over the eleven deployments, with no apparent spikiness, and strong correlations of metal flux with mass and organic carbon flux are observed [6]. Zinc, cadmium, and perhaps aluminum values of F_T carry more uncertainty because of possible contamination from trap hardware [6]. The value for Cd was actually estimated from P fluxes because of suspected contamination in the direct measurement [63]. These considerations may contribute to the anomalous values of F_R/F_T for Zn and Cd.

It is interesting to note that the metal content (mol/g dry weight) of trapped material is generally within a factor of 2 (lower) of that determined for suspended matter (calculated from Table 1 and [6]). Accepting the model result that large particle composition cannot be greatly altered by interaction with deep suspended particles, and noting that surface particles have much lower (factor of 5–10) metal contents, this compositional similarity implies substantial exchange between the two size classes at < 500 m. A thorough time series comparison of metal contents in 500 m vs. 3200 m trapped material would provide one test of this model result.

The scenario emerging from the model depicts large particles which, having interacted extensively with small particles in the upper water column, sink through the deep ocean exchanging, on average, only a minor portion of their mass and trace metal content with suspended particles. In a non-steady state view, however, the extent of exchange with suspended particles might depend on the seasonally variable large particle flux [12]. If so, the composition of sinking and suspended particles would be more similar during some periods than others. However, the sediment trap measurements indicate that the composition of sinking particles is more constant than the flux: relative standard deviations about the mean metal contents were generally less than 25% for the eleven 2-month deployments, compared to 55% for total mass flux in the same sample set [6]. Thus, large particles enter the deep ocean with relatively invariant trace metal composition over a large range of mass flux, and the fraction of the deep flux derived from the suspended pool is relatively constant, consistent with observations of a strong correlation between ^{230}Th and mass flux [12].

Several factors must influence F_R/F_T for each element: (1) The affinity of each element for incorporation into surface particles, (2) the influence of surface ocean sources relative to deep sources, (3) the depth and extent of remineralization from sinking particles, and (4) scavenging from the dissolved phase in the deep ocean. While it is difficult to estimate from this study the contributions of each process for each element, the general conclusion of the flux calculation is clear: the vertical transport of deep ocean suspended particles and their associated metals is a relatively minor component of total metal removal in the Sargasso Sea. If this result can be extrapolated to other central gyres, removal of suspended particles in the ocean interior is not the dominant sink of metals from the ocean. A growing body of evidence suggests that this control is exerted at ocean boundaries—the surface of the ocean and the continental margins [64,65,66].

6. Summary

With the use of *in-situ* filtration, the first accurate depth profiles of suspended particulate concentrations for several trace elements have been obtained near Bermuda. These data provide some insight regarding potential carrier phases for suspended trace metals. Vertical variations in the particulate concentrations of Zn, Cu, Ni, Co and Pb (but not Cd) suggest influence by the distribution of authigenic Mn. However, while the matrices of clays and major biogenic inorganic phases carry a minor or negligible fraction of particulate trace metals, particulate organic compounds cannot be ruled out as important host phases.

Estimates of the residence time of suspended particles in the deep water column put constraints on the contribution of deep suspended particle removal to the total metal flux measured in sediment traps. A simple flux model demonstrates that half or more of the total deep flux of

Al, Fe, Mn, Ni, Cu, Zn and Pb is derived from the upper water column (< 500 m). Thus, in general, processes occurring in the surface waters of the ocean are more important determinants of metal removal from the open ocean environment than is uptake on small particles in the deep ocean. This implies that whole ocean residence times for trace metals may be more dependent on removal processes near ocean boundaries (surface waters and continental margins) than on dissolved/particulate fractionation in deep waters. These conclusions should be verified by combined suspended particle and sediment trap measurements in other open ocean and ocean margin environments.

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