



Temporal variability of suspended mass and composition in the Northeast Pacific water column: relationships to sinking flux and lateral advection

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Abstract

Temporal variations in full water column profiles of 1–53 μm suspended mass and bulk composition (calcium carbonate, opal, aluminosilicate and organic matter fractions) were determined by large-volume *in situ* filtration at station M, 220 km west of Point Conception, California (4100 m depth) in the NE Pacific. Occupations during June 1991, October 1991, February 1992, June 1992 and November 1993 demonstrated that suspended mass varied seasonally by a factor of two throughout the mid- and deep-water column, suggesting a dynamic relationship with concurrently measured variations in deep water sinking flux. Suspended mass in the deep water column was highest in the two June occupations and November 1993, and lower during October 1991 and February 1992. Subsurface maxima in suspended Al and opal occurred throughout the upper 1500 m, and are interpreted as lateral advection of shelf and slope derived sediments, occurring mostly in summer and fall. A factor-of-three discrepancy between water column losses of suspended mass between June and October 1991 and integrated near-bottom vertical flux over this period supports the conclusion that sediment traps do not capture important large aggregate flux events which efficiently remove deep suspended matter. Lateral dispersion of advected lithogenous material must occur, but calculations based on the composition and estimated flux of large aggregates suggest that much of the laterally injected mass can be removed vertically on time scales of weeks at this site. As a result, deep suspended particles have a residence time of < 1 year with respect to vertical removal at this site, roughly an order of magnitude shorter than in the oligotrophic deep ocean. The short residence times and seasonally varying inventory have important implications for the role of particle dynamics in “boundary scavenging” of reactive elements in ocean margins. Use of the suspended Al data with a simple mixing model between new surface-derived suspended

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organic matter and old carbon advected at a constant C/AI ratio can account for much of the seasonal and vertical variation in suspended $\Delta^{14}\text{C}$ (Druffel et al., 1998) for the February and June 1992 profiles, lending support to the hypothesis that sedimentary carbon or dissolved organic matter adsorbed to lithogenous mineral particles determines the apparent age of suspended carbon throughout this water column. © 1998 Elsevier Science Ltd. All rights reserved.

1. Introduction

In the open ocean, the relative stability of the deep suspended matter pool makes determination of the controls on its concentration and composition a difficult task. In contrast, the variability of the flux and composition of sinking material is substantial in oligotrophic waters, and has been the focus of several long-term sediment trap programs examining relationships between surface-water productivity and deep-water sinking flux (Deuser 1986; Michaels et al., 1994; Karl et al., 1995). Modeling of radionuclide distributions in the open ocean predicts residence times of 5–10 years for the bulk of the suspended particle population (Bacon and Anderson 1982; Sherrell and Boyle, 1992). This relatively long residence time nevertheless implies a vertical sinking rate that exceeds passive Stokesian settling rates for mean suspended particle sizes, implying active exchange of mass between large fast-sinking aggregates and the small, barely-sinking material that dominates the suspended load (McCave, 1975). The effects of these aggregation/disaggregation interactions on the deep suspended matter pool are difficult to observe because short-term input and removal effects are buffered by the temporal inertia of the small particle population. Previous time-series work near Bermuda has borne this out; little temporal variability in suspended matter mass or composition is observed below 500 m on months-years time scale (Sherrell and Boyle, 1992).

Direct observation could improve understanding of the timing, extent and nature of interactions between sinking and suspended particle populations. To achieve this goal, it is necessary to study more productive oceanic environments with greater vertical flux and substantially shorter suspended matter residence time than is typical in oligotrophic waters. We are aware of no previous attempts to relate temporal changes in suspended matter composition throughout a deep water column to corresponding cycles of vertical flux. In the current study, we present detailed vertical profiles for the bulk composition of suspended matter, collected using large-volume *in situ* filtration, from five occupations of a productive station at the 4100 m isobath on the continental rise off Central California (Fig. 1). Four of these constitute a complete annual cycle, with a follow-up occupation in November 1993, allowing some estimate of interannual variability. We present evidence for pronounced seasonal changes in suspended matter mass concentration and bulk composition, and interpret the results in light of concurrent, continuous sediment trap determinations of the flux and composition of sinking material at the base of this water column (Baldwin et al., 1998). We argue below that aggregation/disaggregation of sinking material redistributes both biogenic and lithogenic material throughout the water column, as well as driving bulk removal of suspended material during periods of intense large aggregate flux.

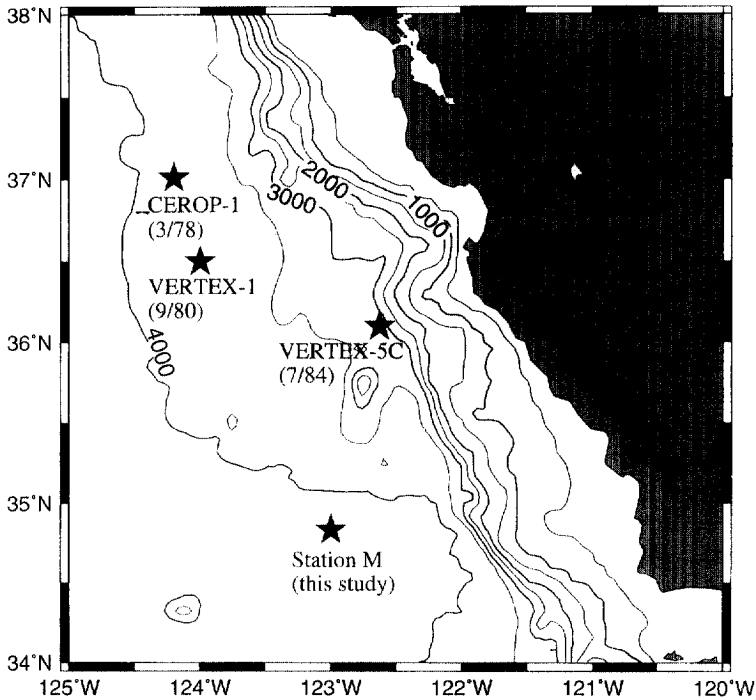


Fig. 1. Map of study area showing bathymetry of slope/shelf region and locations of previously occupied stations for which suspended Al data are available (see text).

The magnitude of interaction between suspended and sinking material has implications for sources of particulate carbon to this region, and for particle dynamics related to mechanisms of “boundary scavenging” of particle-reactive trace constituents in seawater (Shaw et al., 1998). An investigation of the temporal variability of particulate trace metals at this station will be presented elsewhere (R.M. Sherrell and M.P. Field, 1997). A separate study of organic and inorganic suspended phosphorus in these samples will also appear elsewhere (Y. Gao et al., 1997). Here, we confine our discussion to three issues: (1) causes for temporal changes in the bulk constituents of suspended matter; (2) quantitative reconciliation of vertical mass flux with concurrent mass removal from the suspended pool; and (3) an examination of the potential implications of advected lithogenous material for the vertical and temporal variations in radiocarbon ages of suspended organic material.

2. Sampling and analysis

2.1. Sampling station and methods

Sampling of suspended particulate matter was conducted at a Station M, ~ 220 km west of the central California coast in the northeast Pacific (Station M: 34°50'N,

123°00'W; 4100 m depth) during five occupations in late June and late October 1991, late February and late June 1992, and early November 1993 (Fig. 1). Sediment trap samples were collected in deep waters on 10-day intervals throughout this period (Baldwin et al., 1998). This site is influenced by the southward flowing California Current surface waters, which are characterized by well-developed plumes of chlorophyll that develop typically in late Spring following the onset of seasonal upwelling and persist into summer (Michaelsen et al., 1988; Smith et al., 1988). The plumes reflect jets and eddies of upwelling coastal waters that exhibit interannual and spatial variability associated with changes in upwelling strength (Bakun and Nelson, 1991; van Geen and Husby, 1996). The seasonal productivity cycle generates early summer order-of-magnitude peaks in deep-water mass flux at Station M, followed in most years by a secondary flux maximum in the early Fall (Michaelsen et al., 1988; Smith et al., 1994; Baldwin et al., 1998) (Fig. 2).

Suspended matter samples were collected using self-contained battery-powered large-volume *in situ* pumps (Rotating Automatic Pump for Particulate Inorganic Determination RAPPID; Sherrell, 1991), with procedures very similar to those employed in previous investigations of the Sargasso Sea (Sherrell and Boyle, 1992; Sherrell et al., 1992). In this study, samples were obtained from 17–20 depths per occupation, covering most of the water column. *In situ* filtration allowed collection of ~ 10 mg from 200 to 1500 l of seawater with pumping times of 1–3 h. Full-depth profiles were built up over a period of several days by multiple deployments of three pumps per hydrowire cast. Depths were determined by reversing thermometers attached to Niskin bottles, which were mounted 10 m above each pump and tripped

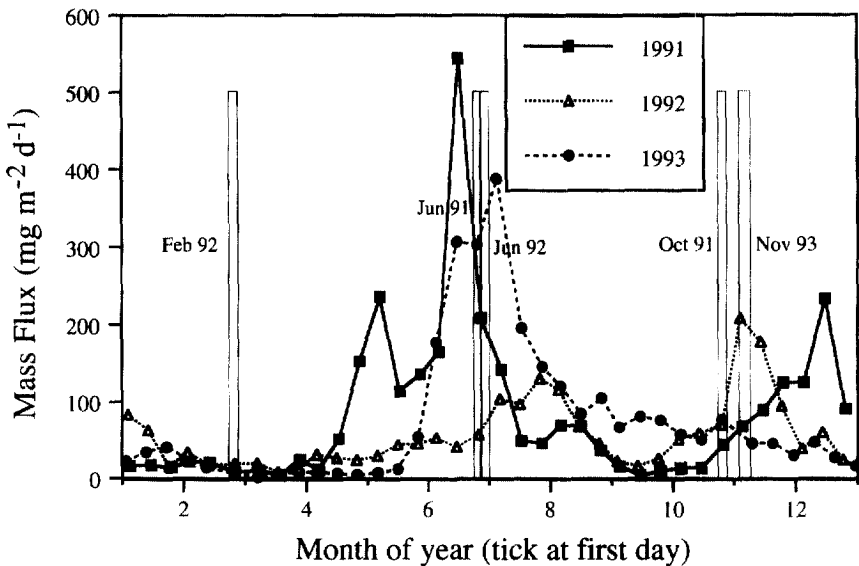


Fig. 2. Sinking flux at 600 mab (Smith et al., 1997) for 1991–1993, with dates of suspended matter collections shown as labeled vertical boxes.

near the end of each pumping period. During each cruise, at least one procedural “dipped” blank sample was generated by deploying a non-operative pump at a depth of 500 m for 15 min to 2 h.

Particle collection was size-fractionated using a two-tiered filter holder loaded with a 53 μm mesh size square weave polyester prefilter (PeCap[®], Tetko, Inc.) followed by a 1.0 μm pore-size polycarbonate primary filter (Poretics, Inc.), both 142 mm in diameter. The present study focuses on fine particulate matter that dominates the suspended mass but has negligible sinking speed, and we present results for the nominal 1–53 μm size fraction. After each sampling cast, primary filters were dropwise rinsed in their original holders with 65 ml deionized, distilled water (ddH₂O; adjusted to pH 8.3 with distilled NH₄OH) to remove sea salt, allowing more accurate particle mass determinations. Samples were dried for several hours in acid-cleaned polystyrene Petri dishes in a laminar flow clean bench before being sealed in plastic bags and transported to the laboratory for mass determinations and chemical analyses. All filter handling in the field and in the lab was carried out in a Class 100 laminar-flow clean bench.

2.2. Mass determination and chemical analyses

Methods for determination of mass and major bulk constituents were similar to those established in earlier work (Sherrell, 1991; Sherrell and Boyle, 1992). We briefly summarize these as follows with a detailed description of procedures that were modifications of previous work. Mass determinations were precise to $\pm 2\text{--}4\%$, including the residual seasalt correction, which was usually $< 2\%$. Filter subsamples (2 pieces, $\sim 15\%$ of sample area) were digested for 4 h at $\sim 120^\circ\text{C}$ in Teflon screw cap vials containing 0.8 ml of concentrated quartz distilled HNO₃ and 40 μl of Teflon sub-boiling distilled HF. Cooled digests were diluted immediately to 4 ml with ddH₂O, and further diluted as necessary for determination of Ca, Al and other trace metals (to be reported elsewhere). Ca was analyzed by flame atomic absorption, with analytical precision of $\sim \pm 1\%$. Al was determined by graphite furnace atomic absorption with a precision of $\sim \pm 3\%$ using the method of standard additions throughout.

Separate subsample pairs (2.3% of sample area) were cut for analysis of biogenic silica. These were digested in 1.5 ml of 1% Na₂CO₃ at 90°C for 2 h, and centrifuged immediately to separate insoluble particles. Supernatant was then removed, diluted 2-fold in 18 M-ohm deionized water, and analyzed by directly coupled plasma – atomic emission spectrophotometry for Si and Al against matrix-matched standards. Al values were used to correct for dissolution of Si from ordered silicates, assuming a Si/Al ratio of 3.2 (molar) for terrigenous particles (Taylor, 1964). This correction was $\leq 10\%$ for 80% of the samples; nepheloid layer samples with high fractions of lithogenic silica required larger corrections and have attendant uncertainties. We found this method produced comparable results ($\pm 10\%$) to the time-series digestion method of DeMaster (1981), with far less effort and decreased sample requirements. Subsampling replicates generally agreed to better than $\pm 5\%$.

In general, subsampling reproducibility is the principal determinant of measurement precision for this sample set. For constituents that can be analyzed very precisely, the subsampling-dominated overall precision was $\pm 3\%$ on average, based on replicate subsampling. Occasional samples for which uniform particle distribution was visually disrupted during pump recovery showed subsampling precision of $\sim \pm 10\%$. Procedural blanks for all determinations were less than 2% of sample signals, with the exception the very low Al concentrations in the upper 100 m, where procedural blanks approached 50% for a few samples.

Mass fractions of the major constituents were determined by estimating the mass-per-mole analyte for the corresponding solid phases. We assumed that particulate Ca represents biogenic CaCO_3 exclusively, a reasonable assumption for most of the water column. In near-surface waters, Ca associated with organic matter may contribute a few percent to the total (Bishop et al., 1977). Opal mass was estimated assuming a molecular weight of 70 g/mol Si, which includes a water content of 14% (Mortlock and Froelich, 1989). Alumino-silicate mass was estimated assuming an Al content equal to the crustal average of 8.3% (wt/wt; Taylor, 1964). Since particulate carbon could not be analyzed on polycarbonate filters, organic matter mass was estimated indirectly by subtracting the summed inorganic bulk constituent masses from the total particulate dry mass. We then estimated particulate organic carbon (POC) assuming a constant carbon content of 50% (wt/wt) for suspended organic matter.

Suspended organic carbon distributions are the least well-constrained of this data set because the use of polycarbonate filters forced an indirect calculation of carbon concentrations. Suspended carbon determinations are therefore subject to the propagated errors in the determination of Ca, Al, and opal, to the assumptions used to convert these molar quantities to the masses of their corresponding bulk constituents, and to the assumption of a constant 50% (wt/wt) fraction of carbon in suspended organic matter. On this basis, we estimate a precision of $\pm 25\%$ for non-nepheloid layer samples. Accuracy may be somewhat worse if assumed values are inappropriate.

3. Results and interpretation

Results for all analyses of particulate material are summarized in Table 1. In the following, we describe results for each of the major bulk components, with brief interpretational comments which set the context for the discussion to follow.

3.1. *Suspended mass*

The mass concentration of fine particles (nominal 1–53 μm), which we refer to hereafter as “suspended” to distinguish them from operationally distinct “sinking” particles, shows substantial temporal variability at all depths between station occupations (Fig. 3). All profiles show greatly elevated suspended mass in the upper 250 m, but mass profiles in deeper waters varied temporally in magnitude and in detailed

Table 1
Suspended matter (1–53 µm) mass and bulk composition for Station M occupations.

Depth (m)	Volume filtered (l)	Mass (µg/l)	Al (n mol/l)	Ca (n mol/l)	Opal (µg/l)	Est. POC (µg/l)
June 1991						
50	178	50.1	0.0	20.6	15.54	16.25
100	579	15.7	0.4	41.5	4.19	3.63
151	338	42.2	19.5	48.1	15.42	7.79
207	321	43.3	22.9	61.3	17.91	5.84
303	661	16.6	1.9	40.7	3.98	3.98
400	530	16.9	8.4	33.2	4.22	3.34
504	457	17.7	11.1	37.8	4.13	3.11
603	490	14.4	13.7	28.5	3.26	1.90
703	707	15.4	4.3	19.5	2.91	4.56
853	701	16.5	13.6	38.6	3.12	2.54
1006	770	15.9	13.2	33.8	3.14	2.55
1241	543	15.2	15.7	36.4	2.91	1.76
1468	767	13.5	14.4	27.6	3.02	1.51
1747	733	13.5			2.91	
2024	515	14.1	9.5		2.26	
2993	866	8.8	12.1	20.3	1.35	0.76
3521	320	14.7	20.3	14.9	2.88	1.85
October 1991						
20	83	104.8	4.9	163.9	1.36	42.73
50	247	51.8	2.5	141.6	2.24	17.31
118	146	49.5	6.9	98.4	5.55	15.91
145	409	13.1	8.7	24.5	2.11	2.85
216	658	10.7	3.4	24.0	1.33	2.91
320	739	7.2	7.7	9.6	0.97	1.40
330	620	7.1	5.3	9.3	0.95	1.73
412	452	5.9	9.8	9.0	0.96	0.41
461	785	7.5	5.9	10.8	1.31	1.57
583	601	14.4	9.9	12.7	2.25	3.84
704	804	10.3	4.8		1.47	
946	812	16.1	21.5	27.5	2.52	1.91
1164	692	14.2	21.9	19.7	2.15	1.46
1430	885	8.4	5.5	23.3	1.05	1.63
2000	766	8.5	6.4	23.0	0.95	1.56
3400	903	7.2	6.0	19.3	0.78	1.27
February 1992						
25	170	52.9	0.6	97.0	5.70	18.66
85	446	20.1	0.7	52.7	2.49	6.05
150	565	19.9	6.0	55.4	2.28	5.08
187	760	13.5	0.9	42.1	0.94	4.04
295	785	8.6	1.1	29.0	0.46	2.45
389	980	7.7	1.3	24.1	0.47	2.22
477	1111	7.7	2.9	19.1	0.57	2.15
588	1372	5.6	1.6	18.9	0.33	1.41
694	923	7.3	4.8	15.7	0.54	1.82
801	816	7.2	5.1	18.9	0.52	1.57

Table 1 (Continued)

Depth (m)	Volume filtered (l)	Mass ($\mu\text{g/l}$)	Al (nmol/l)	Ca (nmol/l)	Opal ($\mu\text{g/l}$)	Est. POC ($\mu\text{g/l}$)
955	670	5.3	5.4	24.5	0.72	0.21
1167 ^a	891	9.3			0.85	
1216	400	7.6	4.9	20.0	0.65	1.69
1480	832	8.5	6.5	20.6	0.77	1.76
1692	1259	8.6	7.3	21.7	0.67	1.68
2015	580	7.1	5.6	23.7	0.51	1.18
2758	1333	6.1	6.1	15.2	0.43	1.07
3500	1259	6.7	9.5	13.2	0.58	0.87
3557	721	6.8	8.7	12.1	0.60	1.10
June 1992						
25	168	58.8	0.3	160.3	0.83	20.94
85	343	25.9	0.0	49.9	1.41	9.72
150	386	17.1	0.2	45.8	2.74	4.85
200	592	12.0	1.2	37.0	0.75	3.57
299	703	10.6	0.2	43.9	0.67	2.75
399	846	12.9	0.9	39.8	1.31	3.68
477	592	13.4	12.1	23.4	1.50	2.80
563	407	17.8	4.6	36.8	1.66	5.51
703	689	19.2	14.0	33.3	1.57	4.86
847	708				1.93	
932	796	12.6	14.6	18.6	1.27	2.35
1169	1113				1.23	
1431	991	15.4	25.0	23.8	1.89	1.52
1875	1240	10.4	12.6	22.0	0.98	1.56
2880	488	11.3	18.6	24.7	1.17	0.78
3480	796	8.8	13.2	13.9	0.78	1.15
4030	826	21.4	49.6	15.2	1.75	1.01
November 1993						
50	210	36.4	0.1	57.2	1.02	14.83
80	354	23.4	0.2	62.3	1.47	7.84
110	559	17.6	1.0	44.9	1.60	5.60
150	561	15.2	2.4	44.6	1.39	4.28
200	527	12.9	2.5	28.5		4.59
297	862	7.4	1.5	15.6	0.61	2.36
398	881	9.7	6.8	18.0	1.00	2.35
444	972	6.3	1.7	16.5	0.68	1.69
598	744	13.9	18.8	19.7	1.79	2.02
724	1023	6.1	2.8	16.3	0.63	1.47
886	1080	7.7	4.0	17.9	0.75	1.93
1186	1085	7.1	6.5	28.7	0.85	0.64
1329	1016	11.9	13.0	19.5	1.66	2.05
1971	953	12.3	12.3	21.4	1.47	2.34
3087	873	9.4	12.2	12.7	1.02	1.58
3490	1046	8.7	13.6	6.7	0.95	1.35
3990	700	18.4	32.6	6.7	1.77	2.65
4040	579	26.0	54.2	16.8	2.57	2.04

^a Filter broke on recovery.

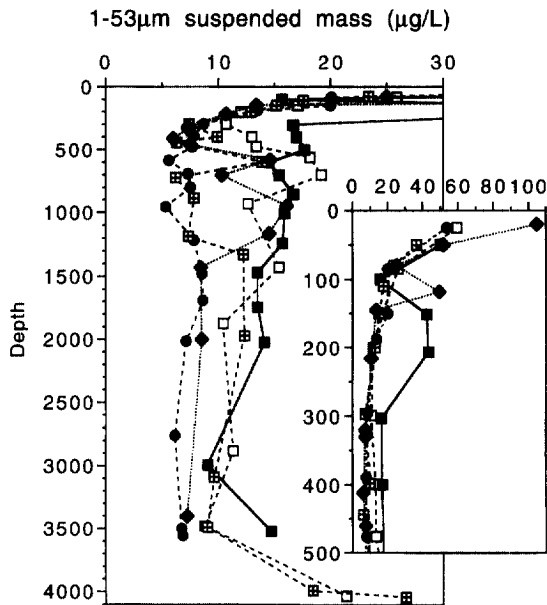


Fig. 3. Suspended mass at Station M for the nominal 1–53 μm size fraction for June 1991 (—■—), October 1991 (---◆---), February 1992 (---●---), June 1992 (---□---), and November 1993 (---◻---).

structure. The upper 250 m was not sampled with great vertical resolution, but all profiles appeared rather similar, except that October 1991 showed the highest mass at the shallowest depth (25 m) compared to June 1991 and February 1992 (Fig. 3, inset). In the mid- to deep-water column (500–3500 m), suspended mass was similarly high in June of 1991 and 1992, generally lower in October 1991, and lowest in February 1992. The November 1993 occupation shows intermediate behavior, with low concentrations at 500–1200 m depth, and higher “June-like” concentrations at 1300–3500 m. Suspended mass differences between seasonal occupations exceed a factor of 2 for the 500–3500 m interval, with an overall range of ~ 6 –19 $\mu\text{g}/\text{kg}$.

Dry weight for the $> 53 \mu\text{m}$ size fraction was estimated by assuming that the salt correction for dipped blanks (non-operating pump deployment) could be applied to all 53 μm filters. Because these filters were not rinsed, and contained relatively little particulate material, these estimates have large uncertainties compared to suspended mass determinations for the 1–53 μm fraction and must be considered provisional. Overall, the results show increased $> 53 \mu\text{m}$ mass concentrations throughout the water column during the June occupations relative to all other occupations. The $> 53 \mu\text{m}$ fraction contributed ~ 5 –25% of the total mass filtered below 500 m, and accounted for as much as 50% in the upper water column. At the outset, we were concerned that disaggregation of larger aggregates during filtration could contribute significantly to the mass collected at the smaller size fraction, possibly leading to

apparent rather than real seasonal changes in 1–53 μm suspended mass, but we are now convinced that this operational artifact is negligible, based on the following reasoning. Disaggregation of marine aggregates requires shear forces in excess of those experienced during natural sinking of the aggregates. Our *in situ* filtration is quite gentle; at typical flow rates during pumping (2–7 l/min), flow velocities across the face of the filter are 0.26–0.90 cm/s, equivalent to flows experienced by particles sinking at 225–780 m/day, which is similar to estimates for the natural settling rates of large aggregates. In addition, the pressure gradient across the face of the 53 μm filter is near zero, since the 1 μm filter provides virtually all the flow resistance during pumping. While some disaggregation undoubtedly occurs, and our size fractionations are understood to be operationally defined (as with any filtration separation), a reasonable estimate of 10% disaggregation of the > 53 μm material would add only 0.5–3% to our measured 1–53 μm mass. An equally plausible artifact is the effective reduction of the mesh size of the > 53 μm filter as it is loaded, resulting in underestimation of true 1–53 μm mass. As our prefilters were lightly loaded throughout this study, especially at > 500 m, we expect that this artifact can be neglected.

Substantial vertical structure in suspended mass is evident for all profiles. A prominent subsurface maximum was observed at 150–200 m in June 1991, and additional maxima are evident at 600–1200 m in October 1991, at 600–750 m and 1500 m in June 1992, and at 600 m in November 1993. The estimated precision of our mass determinations and the excellent agreement between paired samples collected simultaneously with two pumps 10 m apart, or collected 4 days and 57 m apart (October 1991, 320 and 330 m; February 1992, 3500 and 3557 m, respectively; Fig. 3) indicates that both the small variations and the major peaks are real features, not artifacts of sampling or mass determination procedures. Resuspended nepheloid layers were not sampled extensively, but were visible as 50–200% near-bottom mass increases relative to overlying mesopelagic concentrations (600 mab in June 1991, 50 mab in June 1992 and 50–100 mab in November 1993; Fig. 3).

3.2. Lithogenic particles

Particulate Al is associated overwhelmingly with refractory aluminosilicates in this region (Orlans and Bruland, 1986). Al exhibited temporal variability exceeding that for suspended mass (Fig. 4). In the upper 100 m, Al values were always extremely low (< 1 nmol/kg), except in October 1991, when Al was somewhat more elevated at 2–5 nmol/kg. The factor of 2–3 subsurface mass maximum at 150–200 m in June 1991 is also characterized by an order-of-magnitude Al peak, indicating an enrichment in lithogenic particles within this feature. At 500–3500 m, the June occupations show the highest Al concentrations, with October 1991, February 1992 and November 1993 (500–1200 m only) showing reductions by a factor of 2–3.

The October 1991 mass maximum at 600–1200 m is reflected roughly in the corresponding suspended Al, suggesting that the mass maximum is due largely to the presence of increased terrigenous particles in this interval. Indeed, subtraction of the

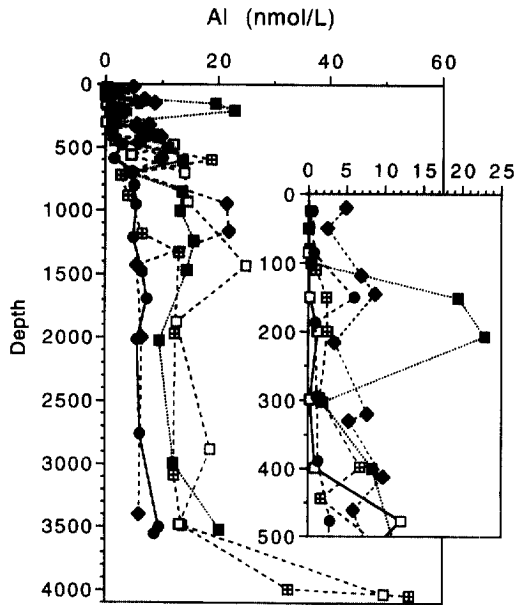


Fig. 4. Suspended Al (1–53 μm) profiles at Station M. Symbols as per Fig. 1.

calculated aluminosilicate fraction removes the mass peak, revealing a nearly monotonic decrease in biogenic mass. The November 1993 profile shows a prominent single-point maximum at 600 m, which is also apparent, but less pronounced, in June and October 1991, and has uniformly high Al concentrations at 1300–3500 m, similar to those observed during June 1991 and 1992. Subtraction of calculated aluminosilicate mass fraction from the November 1993 suspended mass profile eliminates most of the 600 m peak as well as most of the deep water increase, yielding a more vertical profile throughout 500–3500 m ($6.5 \pm 1.5 \mu\text{g/l}$ of biogenic mass). Thus it is clear that many of the most prominent features in the mass profile can be accounted for by vertical variations in the concentration of suspended terrigenous material.

Nepheloid layer samples showed increasing Al enrichments with depth, consistent with the terrigenous mud composition of surface sediments throughout the continental rise and slope in this region (Reimers et al., 1992). Samples collected at 50 mab in June 1992 and November 1993 showed similar particulate Al concentrations of $50 \pm 2 \text{ nmol/kg}$, substantially greater than at 100 mab ($33 \mu\text{g/l}$, June 1992; Fig. 4). Even at 600 mab, small increases in suspended Al were evident in June 1991 and February 1992, relative to overlying deepwaters, suggesting that deep sediment resuspension and/or horizontal advection was occurring at least occasionally at the depth of the upper sediment trap deployed over this period by Smith et al. (Smith et al., 1994; Baldwin et al., 1998).

3.3. Calcium carbonate

Particulate Ca is assumed to be dominated by biogenic calcium carbonate (with a possible additional minor fraction of organic matter-associated Ca in the upper water column; Bishop et al., 1977). The Ca profiles show a great deal of vertical and temporal variability at depths shallower than 1000 m (Fig. 5). In general, June occupations are enriched in Ca in the upper 1000 m relative to other seasons. The shallowest (25–50 m) near-surface Ca concentrations indicate a predominance of calcareous productivity in October 1991 and June 1992, and very little in June 1991. Both Fall profiles have Ca minima near 400 m, suggesting a zone of rapid removal of CaCO_3 detritus from the suspended pool. From 1000 m to near bottom, Ca concentrations are far more uniform with depth and time; all profiles virtually overlay and generally decrease with depth below 2000 m. The deep uniformity gives us confidence that the upper water column vertical structure and variability is real, not a result of measurement imprecision.

The Fall occupations (October 1991 and November 1993) are similar in displaying broad Ca minima at 300–1000 m (Fig. 5). There is no indication from other aspects of bulk composition (e.g. Al) that this is an advected feature from slope water where calcareous production might be lower relative to siliceous. Because large-scale calcium carbonate dissolution is unlikely to occur above the saturation horizon in the water column, the minima likely represent a removal zone for small calcareous particles by aggregation/predation and accelerated sinking processes occurring in the

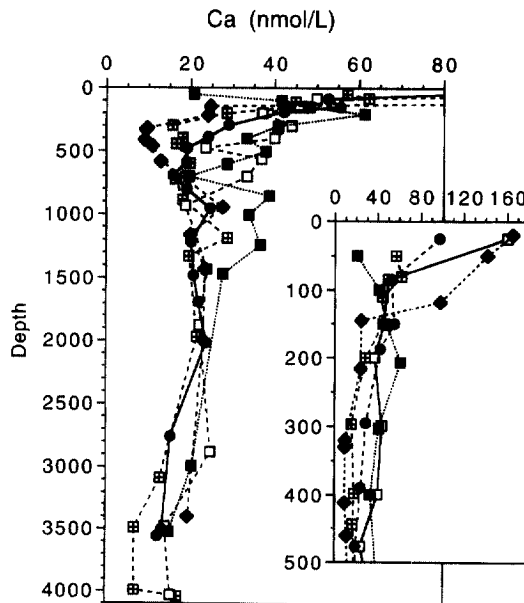


Fig. 5. Suspended Ca (1–53 μm) profiles at Station M. Symbols as per Fig. 1.

upper thermocline. Suspended opal and organic matter show similar minima, supporting the notion that the feature is driven by biological repackaging of small particles into larger, faster sinking particle classes. Interestingly, Al does not show a minimum, suggesting either that terrigenous particles are not subject to the removal processes influencing the biogenic particle profiles at this depth or that they were introduced by lateral advection after the removal of the biogenic material.

3.4. *Opaline silica*

Opal concentrations vary widely between station occupations (Fig. 6). June 1991 is exceptional in showing high opal throughout the water column, suggesting recent, intense delivery of diatom phytodetritus from productive surface waters. Concentrations are highest at 25 m and at a subsurface 150–200 m maximum corresponding to the Al maximum. Four months later most of this opal has been removed or dissolved, although a maximum centered on 1000 m is evident, corresponding again to the October 1991 Al maximum. By February 1992, opal concentrations are very low throughout the water column, with the exception of moderately high concentrations in the upper 100 m. The June 1992 water column was characterized by low concentrations near-surface and only moderate deep water opal concentrations, in sharp contrast to the preceding June. The November 1993 profile is similar to June 1992, but shows enriched opal at 600 m and between 1200 and 3000 m, corresponding to Al

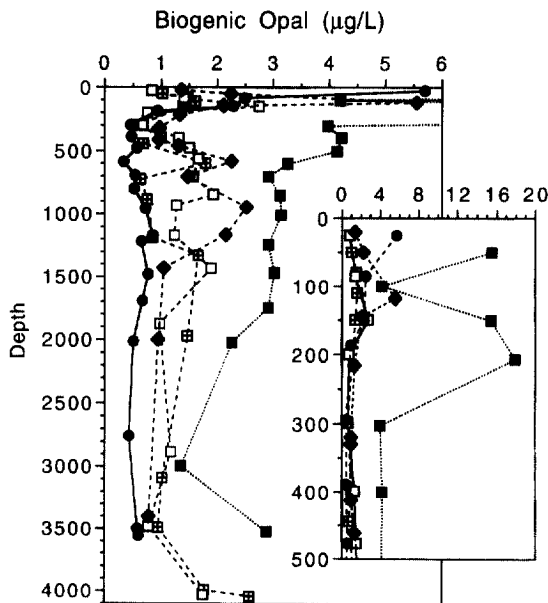


Fig. 6. Suspended biogenic silica (1–53 μm) profiles at Station M. Symbols as per Fig. 1.

enrichments. Overall, the detailed vertical structure of opal and Al profiles shows strong co-variations in space but not in concentration.

3.5. Organic matter

Despite concerns about the precision of the organic matter determination, the profiles are remarkably smooth, and paired samples at 320 m (October 1992) and 3530 m (February 1992) agree to $\sim \pm 10\%$ (Fig. 7). The most obvious feature of the time series is that POC is elevated in the remineralization interval of 400–1200 m during the June occupations, relative to the lower flux periods. The November 1993 profile shows elevated POC of $> 2 \mu\text{g/l}$ in the deep water column below 1500 m.

Interestingly, three of the five occupations show a POC peak at 600–700 m, near the depth of the oxygen minimum (Fig. 7). While these are only defined by one or two data points, the consistency of the feature suggests that it is real. Careful examination of the profiles indicates that these POC maxima are not consistently associated with Al maxima, suggesting that they are not lateral advection features. We speculate that some aspect of organic matter accumulation, migrating zooplankton dynamics, or chemolithotrophic carbon production may concentrate POC at this relatively narrow horizon. Karl and Knauer (1984) came to similar conclusions in attempting to explain a maximum in vertical carbon flux between 700 and 900 m at the nearby VERTEX-1 site (Fig. 1).

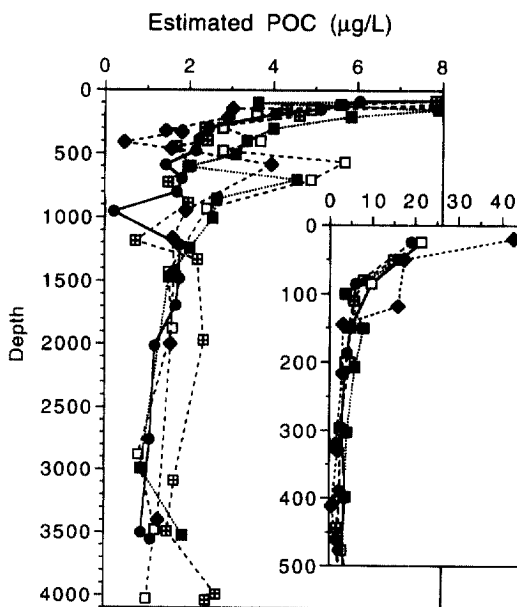


Fig. 7. Estimated suspended POC (1–53 μm) profiles at Station M, determined by mass difference (see text). Symbols as per Fig. 1.

4. Discussion

4.1. *Suspended mass variability: temporal relationship to vertical flux variations*

This study represents the first comparison between seasonal/interannual variations in deep ocean flux and variations in water column suspended matter with seasonal resolution. As such, it represents an opportunity to examine empirically the results of interactions between two operationally defined classes of suspended matter: fast-sinking but rare large particles and aggregates assumed to account for the bulk of the trap-intercepted flux, and the slowly sinking 1–53 μm fraction that accounts for most of the suspended mass.

The temporal variability of suspended mass in the 500–3500 m interval generally appears to be positively correlated to vertical mass flux at the time of the suspended matter sampling, with high particle concentrations during the early summer high flux period, and minimum concentrations during the winter low flux period (Fig. 2). This overall correlation suggests that vertical flux and suspended matter inventory are related through aggregation/disaggregation processes. A simple vertical one-dimensional model of such seasonally changing interactions between large fast-sinking particles and slowly-settling suspended mass would predict a very short residence time for the suspended pool: on the order of a year or less, substantially shorter than estimates of ~ 5 –10 years for oligotrophic central gyre locations, estimated by modeling radionuclide distributions (Bacon and Anderson, 1982; Sherrell and Boyle, 1992).

A hypothetical relationship between vertical flux and deep water suspended mass can be developed by examining in detail the timing of the suspended matter profiles relative to the Sta. M high-resolution (10-day interval) flux records at 600 mab for their respective years (Baldwin et al., 1998; Fig. 2). The two June occupations have very similar overall 1–53 μm suspended mass distributions in the 500–3500 m interval, and occur near the Spring/Summer mass flux peaks of their respective years. Interestingly, the June 1991 occupation fell about a week after the maximum trap flux measured for that year, while the June 1992 sampling occurred during a long gradual increase in mass flux, which hit a maximum at a relatively low value approximately one month later. The October 1991 profile was collected after a month-long period of very low flux, at the beginning of an increasing flux gradient that hit a maximum in December, the latest “fall” flux peak of the 6-year time series (Baldwin et al., 1998). The February 1992 profile was collected in the middle of a long late-winter low flux period. The last profile, collected in early November 1993, occurred roughly midway through a 3-month period of moderate and relatively constant flux during a year that had no obvious Fall flux peak.

These observations suggest an overall relationship between deep suspended particle inventory and the magnitude and duration of vertical flux. Although we suspect that a record of deep-water suspended mass that matched the trap record in temporal density would reveal higher frequency variations, and that the relationship is strongly influenced by interannual variability, the data suggest overall that deep suspended mass is high during an extended period of high vertical flux, and low during winter

low-flux periods. We hypothesize a qualitative one-dimensional vertical flux model characterized by the following seasonal cycle for 1991–1992: (1) Early summer: high flux of large surface-derived particles exchange mass with the suspended (1–53 μm) pool through rapid aggregation/disaggregation processes, leading to near total replacement of the suspended pool throughout the water column and a build-up of suspended mass relative to the previous winter; (2) Summer and early Fall: moderate-high vertical flux drives continued sinking/suspended interactions, but the types of large particles falling to depth favor aggregation over disaggregation and lead to net removal of suspended matter from the deep water column; (3) Winter: low flux generates only small net removal of suspended matter present the previous Fall, but the vertical structure evident in Summer-Fall suspended matter profiles is removed. This cycle of sinking/suspended particle interactions may drive changes in average suspended mass by up to a factor of two in four months, implying a suspended particle residence time of one year or less. While the longer record (1992–1995) of suspended POC shows significant interannual variability as well, seasonal changes of similar magnitude were seen for suspended POC between high and low flux periods (Druffel et al., 1998), lending support to the assertion that our 1-year cycle is representative of a regular annual suspended matter variation.

Much of the remainder of this discussion will address the validity of this vertical model using several different lines of evidence. The conceptually opposed model is that suspended mass variations are driven by advection of shelf-slope derived resuspended sediments, which pass into and are dispersed away from the station M region. In this scenario, vertically sinking large particles would interact minimally with the background of suspended particles, suspended mass residence time would be much longer with respect to vertical removal, and chemical scavenging rates associated with removal of the suspended inventory would be far slower. As will become evident, the data support aspects of both models, and suggest that particles advected into the region are rapidly removed to a large extent by summertime massive flux events.

4.2. *A discrepancy between vertical mass flux and suspended mass variations*

A problem arises when the strict one-dimensional vertical model is made quantitative. For periods of net suspended matter removal, the calculated mass loss cannot be accounted for by the observed vertical flux at the base of the water column. For the period June 26, 1991 to October 26, 1991, integrated mass flux at 600 mab is 5.1 g/m^2 (Smith et al., 1994; Baldwin et al., 1998). Over the same period, we estimate an average net loss of 5 $\mu\text{g}/\text{l}$ of suspended matter over the 500–3500 m depth interval (Fig. 3), giving a depth-integrated removal of 15 g/m^2 over the same 122 days. Thus, the trapped flux falls short of accounting for suspended matter loss by nearly a factor of three. Implicit in this assessment is the assumption that all deep mass flux is derived from “repackaging” of > 500 m suspended matter (Sherrell and Boyle, 1992), and that no fraction of sinking matter derived from upper water column productivity takes the “express route” from surface waters to abyssal depths. Abundant evidence indicates that this assumption is unrealistic, including the similarity of deep trap particle $\Delta^{14}\text{C}$ to surface POC $\Delta^{14}\text{C}$ (Druffel et al., 1998), observations of high ^{234}Th contents (Shaw

et al., 1998), and significant chlorophyll *a* concentrations in trap material (Baldwin et al., 1998). We conclude that a significant though variable portion of the vertical mass flux has its source in surface waters rather than aggregation of the deep suspended pool, and the flux discrepancy is therefore probably larger than a factor of three. The uncertainty in suspended matter loss resulting from the limited depth-resolution of the vertical structure is small relative to this several-fold discrepancy.

There are three possible explanations for the disagreement: (1) Much of the suspended matter mass loss may result from dissolution and remineralization rather than vertical transport; (2) traps are grossly inefficient at catching some component of the sinking flux during high flux periods of the year; or (3) suspended matter is lost to lateral dispersion, i.e. isopycnal mixing with lower particle waters or advection of cleaner water into the region between June and October.

The first explanation is unlikely to explain a large portion of the mass loss; opal may dissolve rapidly in the water column, explaining up to 2 $\mu\text{g}/\text{l}$ of the $\sim 5 \mu\text{g}/\text{l}$ removal if dissolution were the only loss mechanism. Suspended POC changes little between these two occupations (Fig. 7), suggesting a small role for organic matter remineralization below 500 m. Calcium carbonate is not expected to dissolve substantially above the lysocline, and indeed shows only small changes in deep water concentrations between occupations (Fig. 5). The largest loss over the period in question is for terrigenous particles, accounting for some 60% of the suspended mass removal. Thus, while dissolution of opal may occur to some degree, the factor of three or more discrepancy with the trap results is unlikely to be resolved by loss of suspended mass to the dissolved phase.

The second possibility, that the traps miss a significant portion of the flux, must be considered carefully because the vertical flux model hypothesized above requires quantitative resolution of the sinking and suspended mass records. Several lines of evidence suggest that a discrepancy of this magnitude may be explained if the traps undercollect intense mass flux events dominated by large detrital aggregates, which derive a substantial portion of their mass by sweeping smaller particles from the deep water column.

Benthic camera records show accumulation of cm-sized aggregates covering much of the sea floor at station M for large fractions of the June-October period, 1994. Moreover, these aggregates often appeared in phase with trap-recorded mass flux peaks, and showed compositional similarities to trap material (Beaulieu and Smith, 1998). It can be assumed that deposition of such aggregates occurs several times during the productive summer-fall season, the product of both diatom productivity and discarded zooplankton feeding webs. Many aggregates on the bottom are sufficiently large and discrete to make their passage through the 1.6 cm^2 grid openings in the trap baffle difficult to envision. Indeed, the baffle of the 600 mab trap appears to have been completely clogged for 110 days from July to October 1994, the period when abundant aggregates were observed blanketing the seafloor (Baldwin et al., 1998). While 1994 was one the higher flux years of the 6-year time series, 1991 appears to have had equal or greater annual flux, although neither trap showed evidence of total clogging. It is reasonable to assume that any productive year will experience large aggregate flux during the summer and/or fall, as was observed by benthic

time-series camera observations during 4 of the 6 years monitored by Lauerman and Kaufman (1998) and that such events can cause partial, if not total occlusion of the trap openings.

Mass fluxes associated with these events are difficult to estimate accurately, but a conservative assessment suggests that a single event could deposit 10–25 g/m², very similar to the total deep water column suspended matter removal between June and October 1991 (Shaw et al., 1998). In addition, aggregates sampled in August and September of 1994 had very consistent Ti contents of ~ 4 mg/g, equivalent to a 70% aluminosilicate mass fraction (calculated from average continental crust Ti concentration; Taylor 1964). This exceeds the Ti content of trap material (0.7–2.5 mg/g; Shaw et al., 1998), and indicates that aggregates remove suspended aluminosilicates, found principally at > 500 m (Fig. 4), more effectively than does trapped material. A 15 g/m² event calculates to an Al flux of 31.5 mmol/m², equivalent to a removal of 9.0 nM particulate Al integrated over a 3500 m water column, very similar to the particulate Al loss between June and October, 1991. While all of these estimates have sizeable uncertainties, it is likely that even one large aggregate flux event could account for the mass loss from the suspended pool, and carry sufficient terrigenous material to account for the disappearance of this important fraction observed over the 4-month period. We speculate that the summer period may in fact comprise several such removal and resupply events, which would be reflected in suspended pool variability if sampled with greater temporal resolution. This implies that the suspended terrigenous inventory could be renewed several times during the summer, a process that can only result from lateral advection from shallower sediment sources (see below).

Natural radionuclide budget considerations lend additional support for the assertion that large aggregate events are undersampled by the traps. Measurements of ²³⁰Th in submersible-collected aggregates, trap-collected particles, and underlying surface sediments demonstrate that the sediment accumulation of excess ²³⁰Th exceeds production in the overlying water column by a factor of twenty, and cannot be supported by trapped particle flux or by downslope transport of shallower sediments (Shaw et al., 1998). By contrast, roughly three to four aggregate deposition events could account for the entire annual ²³⁰Th accumulation at this site. The trap flux of ²¹⁰Pb accounts for only 50% of water column production; inclusion of the large aggregate flux would exceed production, as expected for “boundary scavenging” conditions (Lao et al., 1993; Shaw et al., 1998). Collected aggregates have ²³⁴Th/²¹⁰Pb ratios similar to that of trap material, indicating similar water column residence time and countering the suggestion that seafloor aggregates are transported near bottom from shallower sites (Lauerman et al., 1997; Shaw et al., 1998). In sum, radionuclide accumulation at Station M requires a significant source from large aggregates, whose composition reflects efficient sweeping of deep suspended particles from the water column.

Large aggregates also must be disaggregating in the deep water column during some periods to resupply the suspended pool. While temporal variations of estimated POC seen in this study were relatively modest, Druffel et al. (1998) observed rapid and large changes in suspended POC, for example a 3- to 4-fold increase between

February and October of 1992 in depth-integrated suspended POC (500–3500 m). With no strong horizontal gradients of deep suspended POC seen in the region (Druffel et al., 1998) this amount of POC can only have been delivered from surface waters; lateral advection of shelf/slope sediments cannot come close to driving these changes, even assuming unrealistically large resuspended C/Al ratio. A flux equivalent to the entire 1992 annual POC flux caught in the 600 mab trap, if completely disaggregated to deep suspended particles, would generate a change of only $\sim 0.4 \mu\text{g/l}$ over a 3500 m water column, far less than the several $\mu\text{g/l}$ increase in POC observed for the 8-month period in 1992. Thus it seems likely that a POC supply rate of this magnitude could only originate from disaggregating detrital aggregates. Interestingly, this unusual increase of suspended POC through the year occurred in a year with anomalously low summertime flux, a possible result of El Nino-related decreases in upwelling intensity (Baldwin et al., 1998). Rapid resupply of the suspended POC pool during some periods, coupled with rapid net removal during others, as argued above, could drive very short residence times for suspended organic particles, as well as lithogenous particles, at station M.

The organic carbon content of these aggregates is similar to that of sediment trap material $\sim 5\%$ wt./wt.g (Smith et al., 1998). Therefore the vertical flux resolution of the June–October 1991 suspended mass loss discrepancy dictates that untrapped carbon flux exceeds trapped carbon flux by at least a factor of two. Interestingly, inclusion of a non-trapped aggregate flux of this magnitude accounts reasonably well for the factor of 2.5 shortfall found by Reimers et al. (1992) in attempting to reconcile trapped carbon flux with the sum of carbon burial and oxidation in sediments at this site. This suggests that a large flux of horizontal downslope carbon transport, invoked by Reimers et al. (1992) to balance the carbon budget, may play a smaller role than consistent undersampling of the vertical flux.

We conclude that large aggregate flux events, which occur during summer of most years, are not effectively captured in moored traps, and could be responsible for most of the suspended matter removal, including lithogenous particles, during periods of net loss. Resupply of POC and associated biogenic inorganic components may occur through disaggregation of these large flocs, explaining high suspended POC observed in fall of some years (Druffel et al., 1998), but resupply of lithogenous particles to the whole water column is difficult to explain by such a process, since suspended aluminosilicates are generally depleted in near-surface waters, where detrital aggregates likely form. Another source must be invoked to explain the increase in deep lithogenous particle concentration between February and June 1992.

4.3. *Lateral advection of lithogenic particles and opal to station M*

Detailed inspection of the distribution of suspended Al shows subsurface maxima that are difficult to explain with a one-dimensional flux model. The depths of subsurface maxima vary with occupation, but were observed at 150 to 1500 m on every occupation except February 1992. The 150–200 m maximum in June 1991 (Fig. 4) suggests lateral advection of outer shelf material, consistent with previous observations of high concentrations of resuspended shelf-derived particles at similar

depths off the coast of northern California (Washburn et al., 1993). The deeper maxima suggest that material may be advected along isopycnals at several depths well below the shelf-slope break, a point that has not received much attention in the past. Introduction of suspended mass at midwater depths may have important implications for the rate of removal of surface-reactive metals at station M if the advected particles can then be removed vertically by sinking aggregates (Shaw et al., 1998).

An alternative explanation of the mid-depth Al maxima is that they are “snapshots” of vertically propagating populations of lithogenous particles that had been delivered some time previously to the upper water column at Station M. Another possibility is that biological processes at depth decelerate vertical transport and cause local accumulations of surface-derived material (Karl and Knauer, 1984). In the absence of data to address these possibilities, we consider it more likely that the maxima seen at 150 and 600 m in June 1991, October 1991, and November 1993, as well as maxima at 1000 m in October 1991 and 1500 m in June 1992, result from inputs of resuspended shelf/slope sediments which are advected along isopycnals impinging on the slope to the east or north of Station M. That fact that these features are absent in February, when suspended Al is at a seasonal minimum throughout the water column, suggests that either the bottom stress causing resuspension or the advective velocities offshore positively correlated with upwelling intensity. The current meter data for the bottom 600 m at station M show a high degree of variability and offer no real help in identifying advective processes affecting the upper half of the water column (Beaulieu and Baldwin, 1998).

Comparison of our Al profiles with previously published suspended particulate data from this region shows some surprising similarities, suggesting that the depths and perhaps even the seasonal timing of the subsurface maxima may be characteristic of a broad region off the California coast (Fig. 1). Fig. 8a and b compare our June 1991 with refractory particulate Al profiles collected by shipboard filtration of Niskin bottle samples in March 1978 at CEROP-1 (270 km NNW of Sta. M, ~ 4000 m depth; Landing and Bruland, 1987) and in June/July 1984 at VERTEX-5C (145 km NNE of Sta. M, 3100 m depth; Orians and Bruland 1986), and our October 1991 profile with a profile collected in September 1980 at VERTEX-1 (200 km NNW of Sta. M, ~ 4000 m depth; Landing and Bruland, 1987). While the seasons sampled are not identical, and interannual variability certainly exists in any water column record, the profiles show strong similarities both in magnitude and vertical structure. Both CEROP-1 and VERTEX-5c show maxima in the upper 200 m, and CEROP-1 has a broad maximum centered on 1200 m, closely resembling our June 1991 profile (Fig. 8a). VERTEX-5C shows higher Al concentrations below 1500 m, reflecting its closer proximity to slope sediment sources (Fig. 1). As well, VERTEX-1 has a large sub-surface maximum near 1000 m, offset slightly in depth but very similar in magnitude to that seen in October 1991 (Fig. 8b).

Vertical structure of the opal profiles (Fig. 6) shows subsurface maxima that closely match those of Al, suggesting that laterally advected material is relatively opal-rich and is superimposed on a seasonally variable “background” deep water opal inventory that results from local production and vertical flux. The opal/Al ratio is not constant in these features, however. For example, the 150–200 m maximum in June

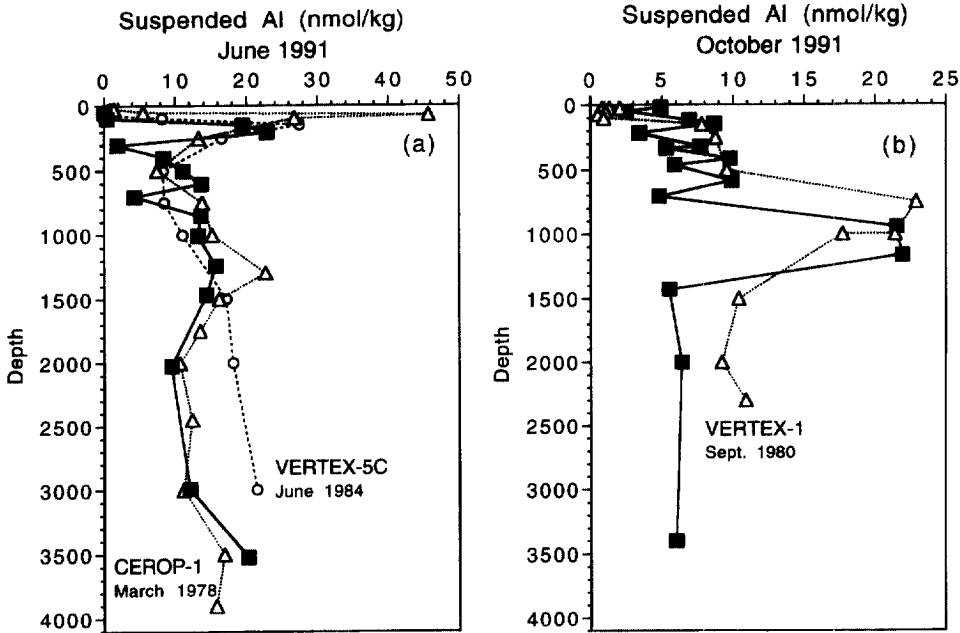


Fig. 8. (a) Suspended Al in June 1991 (closed squares) compared to profiles collected 13 and 7 years previously during early spring and mid-summer at nearby stations CEROP-1 (triangles; Landing and Bruland, 1987) and VERTEX-5C (circles; Orsans and Bruland, 1986). (b) Suspended Al in October 1991 compared to profile collected 11 years earlier during the same season at VERTEX-1 (triangles; Landing and Bruland (1987)).

1991 shows a calculated mass ratio of ~ 2.4 for opal to aluminosilicates, while the ~ 1000 m maximum in October 1991 shows a ratio of about 0.3. This suggests that the former is dominated by very freshly deposited biogenous sediment, or even living biomass from the shelf, while the deeper feature is derived from older sediments that have experienced substantial opal dissolution, or have a source in a region of lower diatom productivity. Nevertheless, the strong correlation in Al and opal profile features lends support for the conclusion that significant fractions of both of these components in the station M water column have a source in sediments underlying more productive inshore waters.

This interpretation is consistent with previous findings from the MULTI-TRACERS project (Lyle et al., 1992; Sancetta, 1992), which compared sediment and trapped particles for three sites located "Nearshore" (120 km from the coast), in the "Gyre" (630 km offshore) and "Midway" (270 km offshore) on a transect off the southern Oregon coast. At the "Midway" site, which is probably most comparable to station M (although diatom assemblages more closely resemble the "Gyre" station; Beaulieu and Smith (1998)), trap material and surface sediments showed the presence of *Chaetoseros* spores, benthic diatoms, and a high proportion of lithogenous particles, all interpreted as indicators of lateral transport from the shelf. Lipid analyses of sedimentary organic matter indicated that 20% of the carbon accumulating at the

Midway site was of terrestrial origin (Lyle et al., 1992). While differences in upwelling dynamics, bathymetry, and proximal riverine inputs complicate comparisons between the two regions, the data taken together suggest that advection of shelf/slope sediments can have significant impacts on suspended, sinking and accumulating material at abyssal depths 200–300 km offshore. Our data suggest that this offshore transport may occur both in association with shallow upwelling jets (Michaelson et al., 1988), and as advected sediment plumes as deep as 1500 m, originating from the slope.

The fate of this advected material defines to a large degree the residence time of suspended particles in the deep water at station M, with respect to vertical removal. This is an important question because it bears on whether advected particles can augment chemical scavenging processes in the deep water column, and then contribute to sediment accumulation at station M, or whether they are simply dispersed into cleaner waters offshore and removed over a larger area on much longer time scales. It is clear that sinking material caught in deep traps is removing some of the suspended lithogenic material; the weight fraction of aluminosilicate particles is 12–40 % (Shaw et al., 1998). Based on arguments presented above, however, this trap flux cannot account for removal of lithogenic material over the June to October 1991 period. It is reasonable to assume that lateral dispersion can account for the disappearance of sub-surface Al maxima between station occupations. That is, there is no reason to assume that station M represents a terminus in the extent of lateral advection before vertical aggregation and removal. However, the apparent regional ubiquity of these features over 100's of km along the central California margin (Fig. 1) suggests that they do not represent isolated plumes of limited latitudinal extent and therefore could not be easily advected away from station M by north–south trending currents on the time scale of months (a unidirectional current of 3 cm/s, a speed typically observed but with highly variable direction at 600 mab (Beaulieu and Baldwin, 1998), is equivalent to a scale length of 310 km over 4 months). Thus if dispersion is important for removing advected lithogenic material, it likely occurs only in the offshore direction, where the concentrations of suspended aluminum are lower (Orlans and Bruland, 1986).

While such dispersion may explain months-scale mass losses from the suspended pool, it is not easy to dismiss the role of large aggregates in removing shelf/slope advected materials at station M. The arguments to this effect, presented above, strongly suggest that a large fraction of advected lithogenous material suspended in the water column at station M can be removed on time scales of weeks by these massive flux events. This interpretation is qualitatively consistent with seasonal variations in $^{230}\text{Th}/\text{mass}$ in the deep trap, which is argued to reflect removal from a seasonally variable suspended inventory (Shaw et al., 1998). We conclude that while dispersion must occur, and undoubtedly helps to maintain the gradually decreasing inventory of deep lithogenous particles between the California Margin and the central North Pacific (Orlans and Bruland, 1986), summertime aggregate flux events probably limit severely the horizontal extent of this dispersion by removing a large fraction of the advected material to the margin sediments. Assuming that these aggregates are also formed to a similar extent further inshore, we therefore would expect to observe

strong gradients in deep lithogenous material on a summertime transect offshore from slope waters. This scenario has yet to be proven.

4.4. POC sources to Sta. M: A possible connection between suspended Al and $\Delta^{14}\text{C}$

Resuspended sediment advected to Station M from shallow shelf and slope sites carries a complement of associated carbon. While this organic matter probably does not contribute more than a small fraction of total suspended carbon to the Station M water column, it is worth examining the potential influence of old carbon associated with this advected material on the perplexing vertical distribution and temporal variability of suspended matter ^{14}C content at station M. A correlation between the ^{14}C age of suspended matter and an independent tracer of lateral sediment resuspension would support an interpretation of suspended matter $\Delta^{14}\text{C}$ profiles as mixing products of fresh, surface-derived carbon and older carbon associated with lithogenous resuspended sediments.

Druffel et al. (1996) determined the concentration, $\Delta^{14}\text{C}$, and $\delta^{13}\text{C}$ of POC over four occupations of Station M from February 1992 to July 1993. This time series has now been extended to June 1995 and includes slope and shelf stations to the east (Druffel et al., 1998). They showed that $\Delta^{14}\text{C}$ of POC decreased with depth, with the strongest gradient in the 0–1000 m interval, indicating older carbon at greater depths. As well, suspended POC $\Delta^{14}\text{C}$ at depths below about 2000 m shifted from values of 0–10‰ during low flux periods (February 1992 and October 1992) down to values $20 \pm 5\%$ lower during times of high vertical flux (June 1992 and July 1993) (Druffel et al., 1996). This seasonal decrease in $\Delta^{14}\text{C}$ signature appeared to be independent of the suspended POC concentration; POC concentrations in mid- to deep-waters for the two summer occupations were similar to each other but intermediate between the profiles of October 1992 (high) and February 1992 (low). In addition, $\Delta^{14}\text{C}$ of sinking POC caught in sediment traps at 650 mab showed lower $\Delta^{14}\text{C}$ values of 20–50‰ during high flux periods, compared to higher values similar to surface DIC and POC of 70–100‰ during low flux periods.

These observations led Druffel et al. (1996, 1998) to argue that both the decreasing trend and the seasonal shift in $\Delta^{14}\text{C}$ were caused by depth-dependent adsorption of DOC (with a very low $\Delta^{14}\text{C}$ value of -450% to -550% ; Bauer et al., 1998a, b) onto POC or associated suspended particles. The summertime shift of -20% is somewhat counter-intuitive, since one might expect that enhanced vertical flux would deliver high $\Delta^{14}\text{C}$ surface-derived particles into the mid- and deep-water column, but Druffel et al. (1996) attributed the negative shift to a modest summertime increase in adsorbed DOC, overwhelming any effect of fresh surface-derived POC.

Lateral transport of old sedimentary POC also was examined by Druffel et al., (1996, 1998) as an alternative explanation for the $\Delta^{14}\text{C}$ trends in suspended POC, and was not ruled out. However, they argued that while a resuspension sedimentary source was likely to cause the sharp negative shift at depths > 2500 m, a similar process is unlikely to affect the entire water column. Our suspended Al profiles, which we attribute to a shelf/slope sedimentary source, allow us to test this assumption, at least for the February and July 1992 occupations for which both Al and $\Delta^{14}\text{C}$ data are

available. We are spurred to attempt a quantitative evaluation of this connection by the observation that early summer appears to be a time of both high suspended Al concentration and old suspended POC in the 500–3500 m interval at station M.

The Al-associated old carbon has two potential sources: (1) advected sedimentary material tightly associated with mineral grain surfaces and carried without modification to Sta. M; (2) carbon adsorbed onto clay surfaces from the ambient DOC pool, possibly exchanged for sedimentary carbon after resuspension. To evaluate this hypothesis of a clay/old carbon connection, we adopt a simple mixing model for POC in which we assume that suspended carbon is a simple two-component mixture of surface derived POC (fixed at 60‰; Druffel et al., 1998) and old carbon associated with advected clays by one of these two mechanisms. We assume initially that the advected carbon is unaltered relative to bulk surface sediments at Sta. M and slope sediments to the east, with $\Delta^{14}\text{C} = -250\text{‰}$ (Bauer et al., 1998a, b) and a C/Al mass ratio of 0.5 (4% carbon in sediments that are 95% lithogenous; Reimers et al. (1992)). Then, we interpolate suspended Al values from our depth profiles for every point in the $\Delta^{14}\text{C}$ profiles for February and June of 1992 (Druffel et al., 1996).

This model yields $\Delta^{14}\text{C}$ profiles that do show a modest decrease with depth and reproduce the $\Delta^{14}\text{C}$ difference for deep POC between February and June 1992, but give absolute $\Delta^{14}\text{C}$ values that are 30–50‰ too high. To tune the model we increased the assumed C/Al mass ratio of the advected component to 1.0. This decreased the $\Delta^{14}\text{C}$ values throughout the water column, giving a better fit to the data (Fig. 9). We note that the modeled February midwater $\Delta^{14}\text{C}$ is still slightly high, and June nepheloid layer values are poorly represented. Nevertheless, this simple two-component mixing model reproduces the sense of the vertical and seasonal changes in $\Delta^{14}\text{C}$ without complicated or unrealistic assumptions. The C/Al ratio of 1.0 would require a relatively high carbon sedimentary source, or a fractionation during resuspension and transport that would act to double the C/Al or preferentially transport an older refractory carbon fraction, relative to the bulk properties of likely sedimentary source areas.

If lithogenous material accumulated old carbon by the second route, adsorption of DOC, the C/Al ratio could relax back to 0.5 since DOC is considerably older than bulk surface sediment carbon ($\Delta^{14}\text{C}$ of DOC $\sim -500\text{‰}$; Bauer et al., 1998a, b), and the same model fit would be retained (Fig. 9). Such a mechanism is speculative, but experimental work with shelf/slope sediments suggests that a significant fraction of mineral-associated carbon is exchangeable (Hedges and Keil, 1995), and that a C/Al ratio of 0.5 could be accommodated by a “monolayer” equivalent of surface-bound carbon on clay-sized particles (Keil et al., 1994). Among the uncertainties with this model is whether the carbon exchange kinetics would allow replacement of sedimentary carbon with DOC on the time scale of resuspension and transport offshore.

The most important point of this exercise is the demonstration that the $\Delta^{14}\text{C}$ of POC could be determined by processes independent of those that govern the total suspended POC concentration, since the clay-associated carbon can only account for a small fraction of total POC ($\leq 20\%$ at C/Al = 1.0 wt/wt) and the suspended clay concentration may vary independently of POC. Our evidence for Al distribution at station M controverts the assumption of Druffel et al. (1996, 1998) that advection of

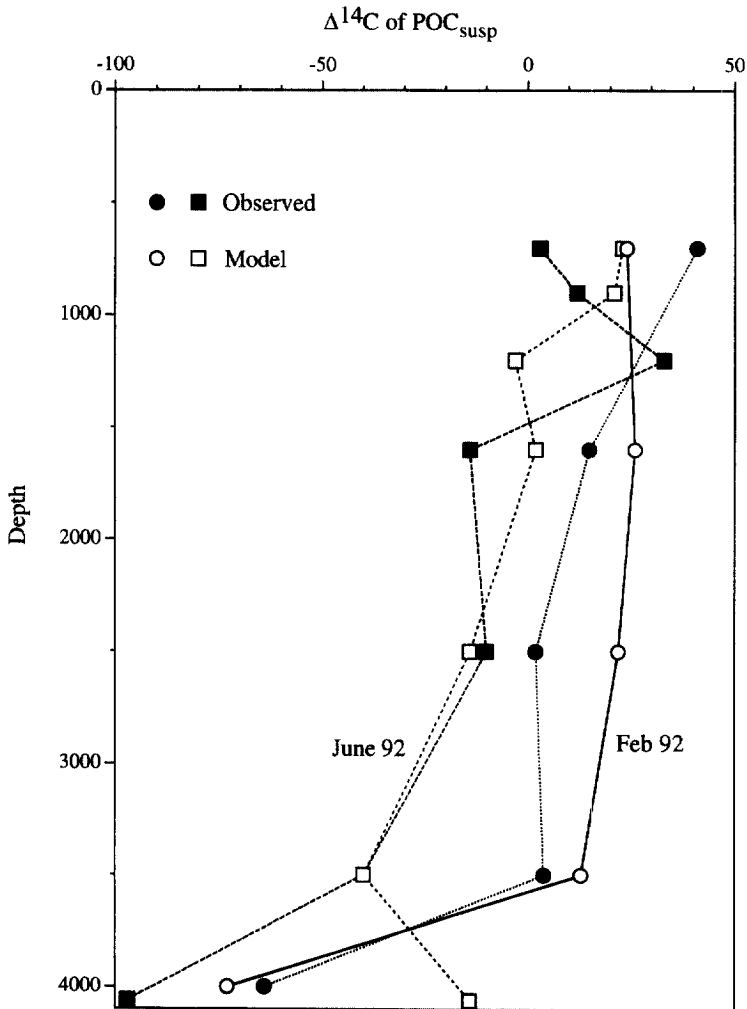


Fig. 9. Vertical $\Delta^{14}\text{C}$ profiles for suspended POC in February and June of 1992 (closed symbols), compared to mixing model results (open symbols). See text for details.

sedimentary carbon is unlikely to affect the whole water column. The recent finding that $\Delta^{14}\text{C}$ of POC shows no discernable gradient between station M and a slope water profile to the east (Druffel et al., 1998) suggests that an advective source may be located to the north (Fig. 1) or may be episodic. Our speculative suggestion that DOC adsorption may indeed be the controlling process, but with lithogenous particles as the host, not suspended POC, has not been considered previously. The advective mixing hypothesis could be further tested relative to the vertical POC-DOC interaction model by determining suspended Al for all existing POC profiles, and examining

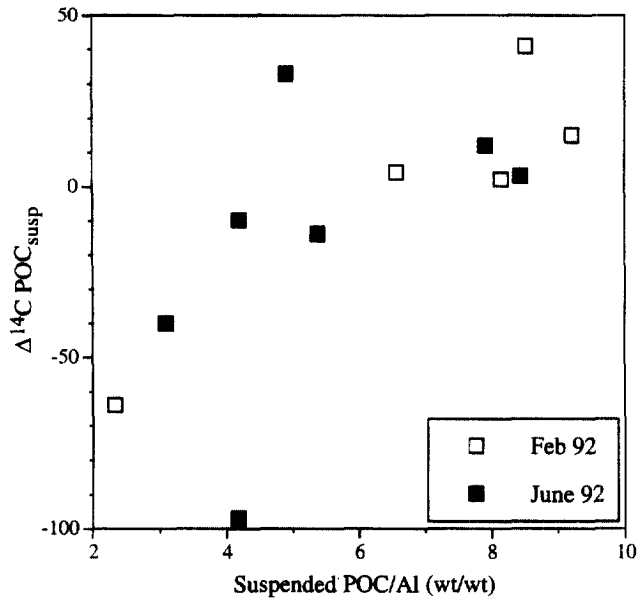


Fig. 10. $\Delta^{14}\text{C}$ of organic matter (Druffel et al., 1996, 1998) vs POC/Al ratio in suspended particles at Station M for February and June 1992 occupations.

the entire time series for a positive relationship between POC/Al and $\Delta^{14}\text{C}$. For the available data, these two parameters are roughly linearly correlated (Fig. 10), bolstering the case for a two-component mixing model.

5. Conclusions

(1) The mass concentration and bulk composition of suspended matter at Station M, ~ 220 km off the California coast (water depth 4100 m) is temporally variable on time scales of months or shorter. Suspended mass varies two-fold throughout the water column over 4-month intervals, and shows a general positive correlation to vertical mass flux cycles over a one-year period.

(2) Changes in the abundance and composition of the suspended particle pool are consistent with supply by both disaggregation of vertically sinking particles, and lateral advection of Al and opal-rich material from shelf/slope sediments. Large aggregates produced during the high-productivity period of summer 1991 are estimated to have removed a large fraction of the whole water column suspended mass, perhaps requiring only one event. Mean particle residence time with respect to vertical removal is therefore estimated to be less than one year, roughly 10% of that of deep suspended matter in oligotrophic regions. Scavenging mechanisms for particle-reactive minor constituents are expected to differ from those operating in areas with steady-state suspended particle populations.

(3) Removal of suspended mass over a 4-month summer–early-fall period (June 1991 to October 1991) exceeds by at least a factor of three the sinking mass caught in a deep sediment trap over the same period. We argue that lateral dispersion contributes to this discrepancy, but that a more important process involves periodic large aggregate sinking events which efficiently remove suspended matter but are systematically undersampled by traps.

(4) Vertical structure in the suspended Al profiles correlates with that of opal, and shows surprising agreement with previously published profiles in the NE Pacific, suggesting that lateral input of resuspended terrigenous material at several depths within the upper 1500 m is a regional phenomenon. These injections of sedimentary material, and their efficient vertical removal, may be important in driving the boundary scavenging of particle-reactive trace elements.

(5) Differences in the $\Delta^{14}\text{C}$ of suspended POC between two station occupations (February and June 1992; Druffel et al. (1998)) correlate with changes in the Al/POC ratio. Model profiles of suspended $\Delta^{14}\text{C}$ for these occupations were generated with a two-component isotopic mixing model in which young surface-derived carbon mixes throughout the water column with a small fraction of old carbon associated with mineral particles at constant C/Al. The model curves reproduce quantitatively most of the features of the observed profiles, suggesting an alternative to previously proposed mechanisms requiring variable DOC uptake onto the POC.

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