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Pyrophaeophorbide-*a* as a tracer of suspended particulate organic matter from the NE Pacific continental margin

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Abstract

Pyrophaeophorbide-*a*, a degradation product of chlorophyll-*a*, is predominantly formed by grazing processes in sediments as well as in the water column. Water column profiles of pyrophaeophorbide-*a*/suspended particulate organic carbon (SPOC) concentrations, at an abyssal site in the northeast (NE) Pacific (Sta M, 34°50′N, 123°00′W; 4100 m water depth), show low concentrations (0.01–0.1 ng/μg SPOC) at surface and mesopelagic depths, and increasing concentrations with closer proximity to the sea floor (0.05–0.6 ng/μg SPOC). However, in June 1992, the deep maximum of pyrophaeophorbide-*a*/SPOC in the water column of Sta M extended higher into the water column, as much as 1600 m above the bottom (mab) (2500 m water depth); in other seasons they only extended up to 650 mab (3450 m water depth).

Previous studies have demonstrated lateral transport of particulate matter from the continental shelf to the deep ocean off the coast of northern California. Recent work suggests that the benthic boundary layer (BBL) extends to 50 mab, based on sediment trap and transmissometry measurements (Smith, K.L., Kaukmann, R.S., Baldwin, R.J., 1994. Coupling of near-bottom pelagic and benthic processes at abyssal depths. Limnology and Oceanography 39, 1101–1118.), and that lateral transport is significant only during summer, which is consistent with our observations. A partial vertical profile of pyrophaeophorbide-*a*/SPOC from the north central (NC) Pacific provides some evidence that the deep maximum may be absent due to the distance of this site from the continental margin. Thus, the observed deep maximum of pyrophaeophorbide-*a*/SPOC at Sta M is likely due mainly to lateral transport from the continental slope rather than to local vertical resuspension in the BBL exclusively.

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Pyrophaeophorbide-*a* concentrations in SPOC at Sta M were negatively correlated with $\Delta^{14}C$ values of SPOC (SPOC samples from Druffel, E.R.M., Bauer, J.E., Williams, P.M., Griffin, S.A. and Wolgast, D., 1996, Seasonal variability of particulate organic radio-carbon in the northeast Pacific Ocean. Journal of Geophysical Research 101, 20543–20552), further supporting our contention that pyrophaeophorbide-*a* peaks in the deep water column are derived from "older" resuspended sediments that were laterally transported from continental margin sediments. Our molecular biomarker (pyrophaeophorbide-*a*) data are reflective of a specific fraction of SPOC that likely remains in the water column for long periods of time or is derived from resuspended sediments.

1. Introduction

The benthic boundary layer (BBL) is an important zone for the transport, trans-formation, and decomposition of organic carbon between benthic and pelagic systems (Hinga et al., 1979; Smith, 1987; Reimers et al., 1992; Smith, 1992). The thickness of the BBL can vary considerably among different benthopelagic regions of the ocean floor. Temporal and spatial changes in the particle concentrations and thickness of the BBL are influenced by the vertical flux of particulate matter entering this zone, and by resuspension events (Walsh et al., 1988; Smith, 1992; Reimers et al., 1992; Smith et al., 1992; Walsh and Gardner, 1992). The transport of particulate matter from the shelf and slope to the continental rise via lateral advection also may contribute to both the vertical and horizontal extent of the BBL (Jahnke et al., 1990; Reimers et al., 1992; Bianchi et al., 1997). Detection of the BBL is typically achieved using transmissometry measurements; however, it is not possible using this method to establish the relative importance of resuspended versus pelagic particles, nor of organic vs mineral partic-ulates.

Chemical biomarkers that can trace sediment-derived organic sources in the water column may provide a useful tool for documenting resuspension events and lateral transport (Whelan and Farrington, 1992; Bianchi et al., 1997). Plant pigments are commonly used as biomarkers to determine the sources and transformation pathways of organic matter in the water column and sediments (Gieskes and Kraay, 1983; Mantoura and Llewellyn 1983; Welschmeyer and Lorenzen, 1985; Bidigare et al., 1986; Wright and Jeffrey, 1987; Repeta, 1989; Bianchi et al., 1993a, b). Phaeopigments, or chlorophyll degradation products, represent the dominant form of plant pigments in marine sediments (Brown et al., 1981; Baker and Louda, 1983; Furlong and Carpenter, 1988; King and Repeta, 1991; Jeffrey et al., 1997). Phaeophytin-*a*, pyro-phaeophytin-*a*, phaeophorbide-*a*, and pyrophaeophorbide-*a* are quantitatively the most important phaeopigments found in both sediments and the water column (Jeffrey et al., 1997). Pyrophaeopigments are formed by the loss of a carboxymethyl group from the parent chlorophyll (Pennington et al., 1964). Additionally, there are non-polar chlorophyll degradation products, identified as pyrophaeophorbide steryl esters, formed by pre-depositional processes that also may represent a significant

fraction of the sedimentary sink for chlorophyll (Furlong and Carpenter, 1988; Downs, 1989; King and Repeta, 1991).

The presence of pyrophaeophorbide-*a* may provide a less ambiguous tracer for resuspended particulates in the water column than other phaeopigments (i.e. phaeophorbide and phaeophytin). First, the dominant chlorophyll-*a* decay products formed by senescence and grazing in the water column are the phaeophytins and phaeophorbides, not the pyrophaeophorbides; the typical phaeopigment concentration maximum is located just below the chlorophyll-*a* maximum (Welschmeyer and Lorenzen, 1985; Bidigare et al., 1986). Although pyrophaeopigments are formed by grazing processes in the water column (King and Repeta, 1991), they are predominantly found in surface sediments. Thus, the source for higher concentrations of pyrophaeophorbide-*a* at depth in the water column would likely require an alternative explanation to surface-derived sinking particles. Second, it was recently shown that pyrophaeophorbide-*a* steryl esters are formed in the water column during grazing by zooplankton herbivores (King and Repeta, 1991). Moreover, it appears that the esterification reactions to form sterols do not occur for any of the other phaeopigments. This would suggest that pyrophaeophorbide-*a* has, in addition to photooxidation in the euphotic zone (Soohoo and Kiefer, 1982; Welschmeyer and Lorenzen, 1985), an additional mechanism for its removal from the water column. Thus, there should be less pyrophaeophorbide-*a* derived from surface waters with increasing depth, as shown in the aforementioned studies, making it easier to distinguish between sources of pyrophaeophorbide-*a* formed by pre- or post-depositional reactions in the BBL.

Recent studies at a time series site in the northeast (NE) Pacific (Sta M) have examined the seasonality of $\Delta^{14}C$ profiles of dissolved organic carbon (DOC), suspended (SPOC) and sinking particulate organic carbon (POC$_{sink}$), and dissolved inorganic carbon (DIC) (Druffel et al., 1996; Bauer et al., 1998; Masiello et al., 1997). It was suggested that the lower $\Delta^{14}C$ values of deep suspended and sinking POC during periods of high particulate flux are either due to sorption of 'older' DOC onto the surface of POC or to lateral transport of particles that have been resuspended from slope regions (Druffel et al., 1996, 1998). Other work in this region has also suggested the possible role of lateral transport of resuspended sediment from the continental shelf to the deep ocean (Washburn et al., 1993). We report concentrations of pyrophaeophorbide-*a* in SPOC, collected from the water column and in surface sediment organic carbon (SOC) at Sta M, to examine further the importance of resuspended sources of SPOC from the water column at Sta M. Samples collected during an earlier cruise in 1987 to a station in the north central (NC) Pacific (Druffel et al., 1992) also were analyzed. Collectively these data allow us to compare abyssal sites located both adjacent to and remote from the continental margin. Our primary goal in this study is to demonstrate the potential usefulness of pyrophaeophorbide-*a* as a tracer of resuspended particles in the BBL of the abyssal ocean.

2. Methods and materials

2.1. Sample collection

Water column SPOC was collected at two sites. The first of these sites, Sta M (34°50′N, 123°00′W), is located at the base of the Monterey Deep-Sea Fan, in approximately 4100 m of water (Reimers et al., 1992; Smith et al., 1992). Sta M is characterized by a June–July maximum in upwelling-derived primary production that results in mid-summer pulses of organic matter to the sediment surface (Smith et al., 1992, 1994). Sediment organic carbon (SOC) samples were also collected at Sta M. Samples of SPOC and SOC for pyrophaeophorbide-*a* analysis were collected on Pulse cruises on the R/V New Horizon during 19 February–2 March, 19 June–1 July, and 15–27 October 1992, respectively. The second site, located at 31°00′N, 159°00′W in the NC Pacific, was occupied in July 1987 during the EVE-1 cruise aboard the R/V Melville. This site is generally characterized by oligotrophic surface waters (Williams and Druffel, 1987; Bauer et al., 1992; Druffel et al., 1992), and the water depth is 5750 m.

Suspended POC was collected at both sites using modified *in situ* pumps (Laird et al., 1967; Williams et al., 1980; Druffel et al., 1992). The pumps were deployed at each depth for 2–8 h depending on SPOC concentration. During each deployment, between 600 and 2000 l of seawater were drawn through pre-combusted (550°C), 142 mm diameter quartz-fiber filters (Whatman ultrapure QM-A 0.8 μm pore diameter). The filters were frozen in pre-combusted glass jars with teflon-lined caps at −20°C until analysis. At Sta M, sediment subcores (7.6 cm diameter) were taken from box corers (50 cm × 50 cm × 20 cm deep) deployed on a free-vehicle grab respirometer during February and June 1992 (Smith et al., 1992, 1994). Surface sediments (0–0.5 cm depth interval) of the subcores were sectioned with a clean metal spatula, placed in pre-combusted glass jars, and frozen at −20°C until analysis.

2.2. Pigment analysis

Two replicate filter subsamples (3.0 cm diam.) were subsectioned from each 142 mm diameter filter for pigment analysis using cleaned cork borers. Each replicate was placed into a microfuge tube (1.5 ml) containing 1 ml of 100% acetone and sonicated for 3 min with an ultrasound probe (4 mm diam.). After the sonicated filters were extracted overnight at 5°C, they were centrifuged in a microfuge (13 000 rpm) for 2 min. The supernatant acetone was then filtered through a Gelman polypropylene cartridge filter (25 mm diam., 0.2 μm pore size) to remove any particulates before injection onto the HPLC column.

Reverse-phase high performance liquid chromatography (RP-HPLC) analysis was conducted using a modification of the method recommended by Wright et al. (1991). The system was equipped with a Waters solvent delivery system coupled with dual-channel detection using a Waters 996 photodiode array with absorbance set at 438 nm and a Milton-Roy fluorescence detector with excitation at 440 nm and emission at > 600 nm. The injector was connected via a guard column to

a reverse-phase C_{18} Alltech Adsorbosphere column (5 μm particle size; 250 mm × 4.6 mm i.d.). After injection (200 μl) a gradient program (1 ml/min) was run isocratically with mobile phase A (80 : 20 methanol: 0.5 M ammonium acetate, aq.; pH 7.2 v/v) which then ramped to 100% mobile phase B after 4 min (90 : 10 acetonitrile:HPLC grade water v/v) and then changed to 20% B and 80% mobile phase C (100% ethyl acetate) after 14 min. This was followed by a return to 100% B in 3 min., with a final ramping to 100% A after 3 min. Replicate analytical error for plant pigment analyses ranged between 4 and 6% using 3 replicates. A high purity standard of chlorophyll-*a* was obtained from Sigma Co. A pyrophaeophorbide-*a* standard was provided by D. Repeta of Woods Hole Oceanographic Institution.

An $F_{\max}$ was used prior to ANOVA and regression analyses to check for homogeneity of variances of pigment concentrations (Sokal and Rohlf, 1981). A two-way ANOVA was used to test for significant effects of depth and sampling time on pigments. When ANOVA differences were significant, a Scheffe' multiple range test was performed to detect differences among depths at a particular sampling date (Sokal and Rohlf, 1981). A simple *t*-test was used to test for differences between means from two depths or samplings. A Pearson Correlation analysis was used to test for significance between chlorophyll-*a* and pyrophaeophorbide-*a* concentrations, and between $\delta^{13}C$, $\Delta^{14}C$, and pigment values of SPOC.

3. Results and discussion

Chlorophyll-*a* and pyrophaeophorbide-*a* concentrations in SPOC, collected at Sta M in February, June, and October 1992 are listed in Table 1 and shown in Fig. 1. Water-column profiles of chlorophyll-*a* and pyrophaeophorbide-*a* in SPOC showed significant seasonal differences at Sta M (Fig. 1). During all three sampling periods, a deep maximum in pyrophaeophorbide-*a*/SPOC was observed. The maximum appeared at 650 m above bottom (mab) in February and October and at approximately 1600 mab in June.

The highest concentration of chlorophyll-*a*/SPOC, in surface waters (June 1992, 85 m depth), occurred when the highest concentration of pyrophaeophorbide-*a*/SPOC was observed in the deep maximum (June 1992, 2500 m) (Fig. 1A and B). Peak values of pyrophaeophorbide-*a*/SPOC near the bottom were significantly ($P < 0.05$) lower in October (0.2 ng/μg SPOC) than in February or June (0.5–0.6 ng/μg SPOC) at Sta M.

The NC Pacific site had a subsurface chlorophyll-*a*/SPOC and elevated pyrophaeophorbide-*a*/SPOC at 85 m depth in the euphotic zone (Table 1 and Fig. 2). This chlorophyll-*a*/SPOC subsurface maximum at the NC Pacific site occurred at roughly the same depth (between 85 and 100 m) as the pyrophaeophorbide-*a*/SPOC subsurface maxima at Sta M (Fig. 1B).

The prominent near-bottom maxima of pyrophaeophorbide-*a*/SPOC observed throughout the year at Sta M could arise from three potential mechanisms: (1) the vertical flux and accumulation of pyrophaeophorbide-*a* at depth; (2) the vertical resuspension of particles from the sediment surface; and (3) the lateral transport of resuspended shelf/slope particles or deep SPOC. Exploring mechanism 1, we find that

Table 1
Suspended particulate organic carbon (SPOC), chlorophyll-*a* and pyrophaeophorbide-*a* concentrations in the water column for the NE Pacific at Sta M for three dates (February, 1992; June, 1992; and October, 1992) and the NC Pacific (June, 1987) and in surface sediments for Sta M (February, 1992; and October 1992). Concentrations of chlorophyll-*a* and pyrophaeophorbide-*a* are normalized to SPOC (ng/μg SPOC), whereas SPOC concentrations are in μg/l and have been reported elsewhere (Druffel et al., 1996). Concentrations of chlorophyll-*a* and pyrophaeophorbide-*a* in the sediments are in units of mg/g sedimentary organic carbon (SOC). bld = below limits of detection: nd = no data

Depth (m)	SPOC (μg/l)	Chlorophyll-*a* (ng/μg SPOC)	Pyrophaeophorbide (ng/μg SPOC)
Sta M (February 1992)			
25	74.50	3.49 ± 0.40	0.02 ± 0.003
85	12.50	4.60 ± 0.20	0.02 ± 0.002
400	2.80	0.35 ± 0.09	0.06 ± 0.004
700	1.15	0.40 ± 0.10	0.11 ± 0.03
1600	1.74	0.09 ± 0.03	0.02 ± 0.006
2500	1.32	0.11 ± 0.03	0.04 ± 0.02
3450	1.42	0.10 ± 0.01	0.50 ± 0.05
4050	2.08	bld	0.42 ± 0.02
Sta M (June 1992)			
25	38.70	4.03 ± 0.10	0.01 ± 0.001
85	19.60	23.67 ± 1.10	0.06 ± 0.001
450	4.04	0.50 ± 0.25	0.02 ± 0.003
1200	2.38	0.19 ± 0.07	0.03 ± 0.006
1600	3.19	0.06 ± 0.005	0.04 ± 0.005
2500	1.81	0.06 ± 0.006	0.64 ± 0.07
4050	5.63	bld	0.27 ± 0.03
Sta M (October 1992)			
25	78.40	1.56 ± 0.04	0.01 ± 0.004
85	26.20	4.85 ± 0.13	0.02 ± 0.01
450	7.24	0.13 ± 0.008	0.02 ± 0.008
700	5.40	0.09 ± 0.006	0.01 ± 0.004
900	5.48	0.09 ± 0.005	0.01 ± 0.002
1300	5.07	0.07 ± 0.006	0.01 ± 0.004
2500	4.40	0.03 ± 0.004	0.06 ± 0.04
3450	2.50	0.03 ± 0.006	0.19 ± 0.02
4000	4.00	bld	0.13 ± 0.07
NC Pacific (Jun–Jul 1987)			
20	31.20	0.88 ± 0.18	0.04 ± 0.001
85	27.39	4.72 ± 0.16	0.09 ± 0.001
100	15.60	5.49 ± 0.62	bld
450	2.62	0.04 ± 0.04	bld
3000	nd	bld	bld
3400	0.81	bld	0.07 ± 0.02
3600	nd	bld	bld

Surface sediments (0–0.5 cm depth)

Date	Chlorophyll-*a* (ng/μg SOC)	Pyrophaeophorbide (ng/μg SOC)
February 1992	26.14	2.62
October 1992	25.00	0.86

Chlorophyll-*a* (ng/μg SPOC)

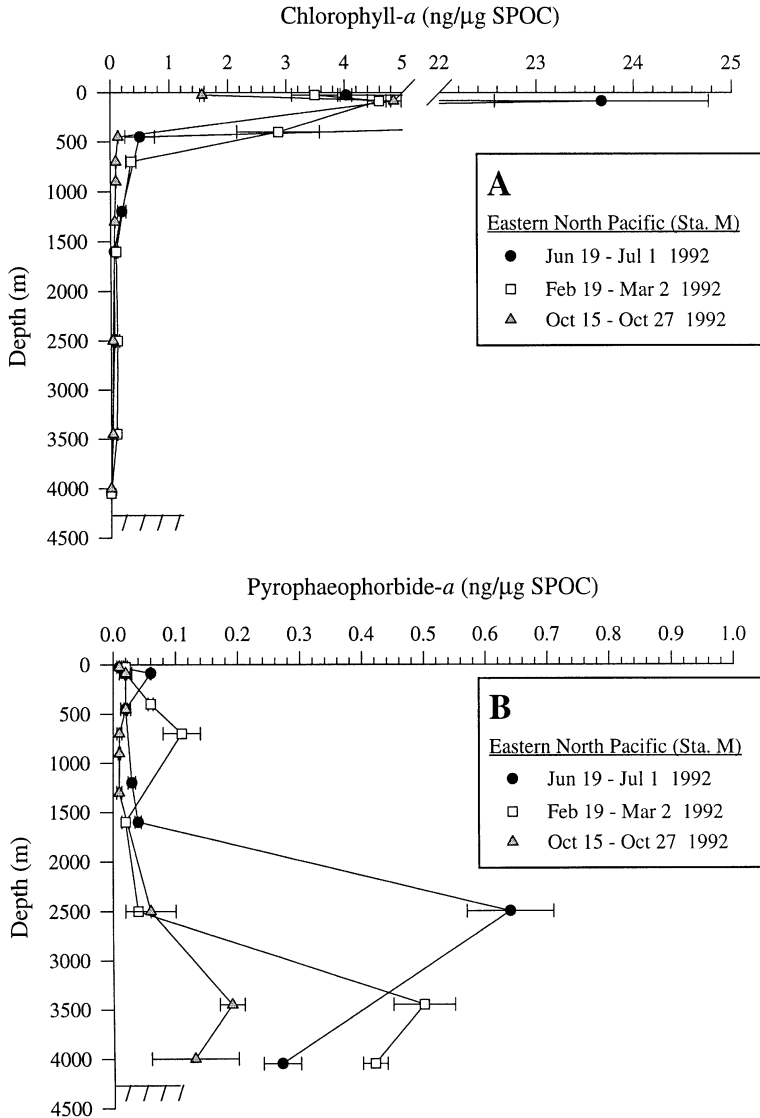

Pyrophaeophorbide-*a* (ng/μg SPOC)

Fig. 1. Chlorophyll-*a* and pyrophaeophorbide-*a* concentration profiles (ng/μg SPOC) of suspended particulate organic matter collected at Sta M in the NE Pacific abyssal site (4100 m) during February 19–March 2, 1992, June 19–July, 1992, and October 15–October 27, 1992. Horizontal bars represent standard error (SE) of duplicate samples. The dashed horizontal bar indicates the sediment water interface.

there are very low concentrations of pyrophaeophorbide-*a* usually between 500–2000 m, followed by an abrupt increase at depth. If the primary source of pyrophaeophorbide-*a* was derived from heterotrophic breakdown of chlorophyll-*a* in surface-derived POC, we would expect a gradual increase in concentration with
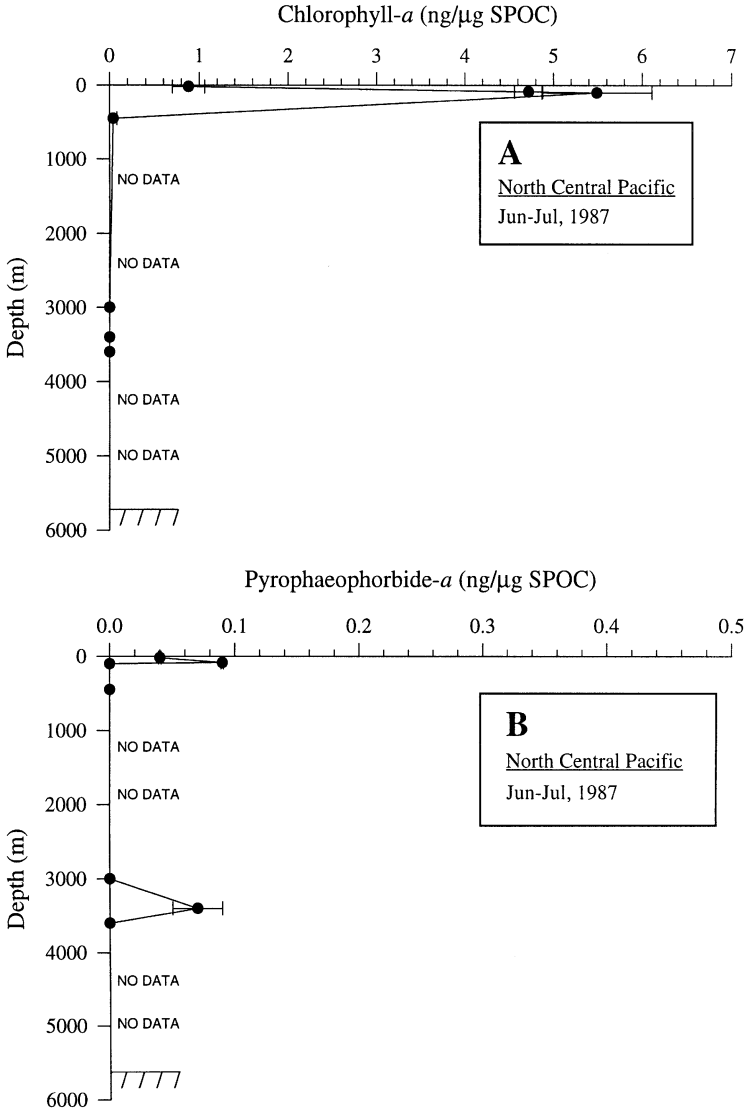
Fig. 2. Chlorophyll-*a* and pyrophaeophorbide-*a* concentration profiles (ng/μg SPOC) of suspended partic-ulate organic matter collected at the NC Pacific abyssal site during June–July, 1992. Horizontal bars represent standard error (SE). The dashed horizontal bar indicates the sediment water interface.

depth, as opposed to the abrupt deep maxima shown in Fig. 1B. Water column concentrations of chlorophyll-*a* typically show a rapid decrease below the chloro-phyll-*a* maximum with phaeopigments (usually phaeophytins and phaeophorbides) reaching a concentration maximum just below the chlorophyll-*a* maximum (Vernet and Lorenzen, 1987; Downs, 1989). Moreover, the dominant phaeopigments found in

the water column below the photic zone are phaeophytins and phaeophorbides, and the total concentrations of these compounds decrease with increasing water depth (Vernet and Lorenzen, 1987; Furlong and Carpenter, 1988). Thus, the increase in pyrophaeophorbide-*a* at depth, which was first detected thousands of meters below the chlorophyll-*a* maximum, suggests these higher concentrations are not likely to be derived from the usual transformation pathway of chlorophyll-*a* into its decay products – via grazing and senescence as particles sink through the upper kilometer of overlying water (Welschmeyer and Lorenzen, 1985; Bidigare et al., 1986).

Considering mechanism 2, it has been shown that post-depositional formation of pyrophaeophorbide-*a* can be more important than pre-depositional processes based on high concentrations of pyrophaeophorbide-*a* in sediments (Furlong and Carpenter, 1988; Sun et al., 1991). It is very likely that chlorophyll-*a* in sedimented phytodetritus could be converted to pyrophaeophorbide-*a* by macrobenthic as well as microbenthic grazing processes (Bianchi et al., 1988; Sun et al., 1991). We found significantly higher concentrations of pyrophaeophorbide-*a* normalized to sedimentary organic carbon (SOC) in abyssal sediments than in the water column at Sta M in February and October 1992, indicating that abyssal sediments in general are a source of pyrophaeophorbide-*a* (Table 1 and Fig. 3). However, it seems unlikely that pyrophaeophorbide-*a*, if derived from abyssal sediments at Sta M, was vertically resuspended to 2500 m depth, since Smith et al. (1992) have shown (using transmissometry) that the BBL extends to only 100–200 mab at this site. The mean current speed at 50 mab was 2.7 cm s^{-1}, while the average speed needed to resuspend phytodetritus in the abyssal eastern North Atlantic was reported as 7 cm s^{-1} (Lampitt, 1985; Smith et al., 1994; Beaulieu and Baldwin, 1998; Smith et al., 1998). Moreover, there was only a very minor subsurface peak at mesopelagic depths (3300 m) at the NC Pacific site, which may suggest that no significant input from lateral transport at that distance from the NE Pacific margin. However, the limited number of available samples at this station precludes any definitive conclusions (Fig. 2).

We believe that shelf/slope sediment resuspension coupled with lateral transport (mechanism 3) is a more likely cause of the observed near bottom peak in pyrophaeophorbide-*a*/SPOC at Sta M. Horizontal eddy diffusive transport of resuspended sediments from the continental margin is one possible mechanism responsible for the near bottom maxima of pyrophaeophorbide-*a* in SPOC. Although Sta M is located 200 km off the California coast, it has been shown that eddy diffusion coefficients increase with time and distance from the coast due to entrainment from large-scale boundary currents and eddies (Okubo, 1971; Lerman, 1979). In addition, the transport of particulate organic matter from the continental shelf and slope to the rise via the nepheloid layer has been postulated to account for the disparity between benthic carbon demand and the estimated vertical supply (Jahnke et al., 1990; Reimers et al., 1992).

If we use the coefficient of horizontal eddy diffusion reported by Okubo (1971) for a distance of 100 km in the Pacific (1.2×10^8 cm^2 s^{-1}), we estimate that it would take approximately 1 month for resuspended non-sinking particulate material from the margin to diffuse to our abyssal site. It should be noted that these eddy diffusion coefficients were calculated for surface waters, however, they are unlikely to
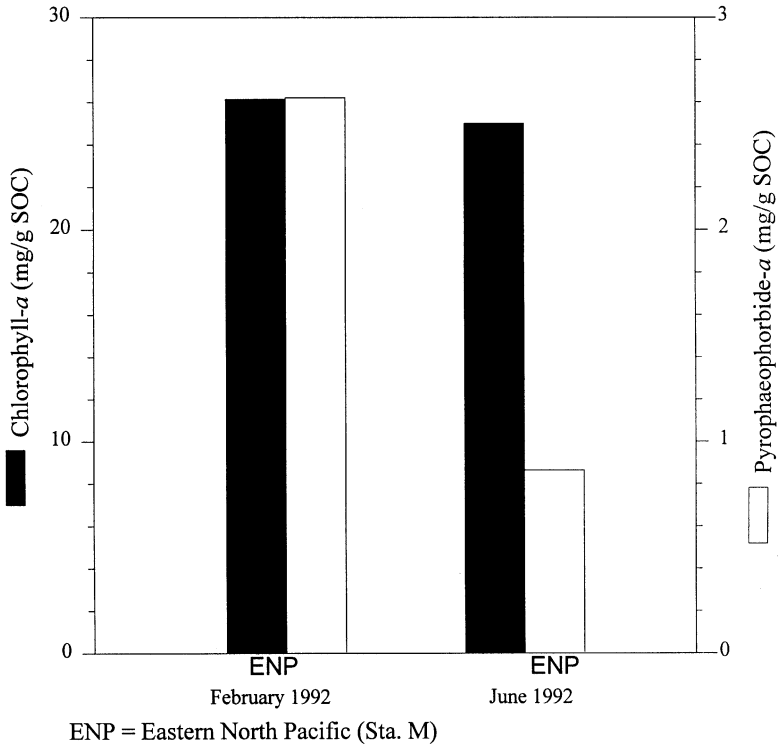
Fig. 3. Chlorophyll-*a* and pyrophaeophorbide-*a* concentrations (ng/g sedimentary organic carbon (SOC)) of surface sediments collected at an NE Pacific site during February 19–March 2, 1992 and October 15–October 27, 1992. No sediment samples were available from the NC Pacific site.

significantly change for deeper waters (Lerman, 1979). This time period is well within the half-life of most phaeopigments (24–51 days, Bianchi and Findlay, 1990). Recent work in the Gulf of Mexico, using loliolide stable pigment decay products that are primarily formed in the sediments (as described by Repeta (1989)), has shown subsurface maxima at 1000–1600 m in slope waters, very similar to the pyrophaeophorbide-*a* profiles at Sta M (Bianchi et al., 1997). When contrasted with the amount of material that would be expected to be locally resuspended based on transmissometry data and current speeds within the BBL for this region of the Gulf, these subsurface maxima were attributed to resuspended sediments from the continental shelf that had been laterally transported to slope waters (Bianchi et al., 1997). Moreover, pyrophaeophorbide-*a*/SPOC maxima always occurred at a water depth above the deepest sampling depth in the water column, suggesting that pyrophaeophorbide-*a*/SPOC concentrations were not likely to be derived from bottom sediments at this site.

Pyrophaeophorbide-*a* concentrations in SPOC found at Sta M are negatively correlated ($R = 0.57$, $p < 0.01$) with $\Delta^{14}C$ values of SPOC from the same samples (SPOC samples from Druffel et al. (1996)) (Fig. 4A). This may further support our
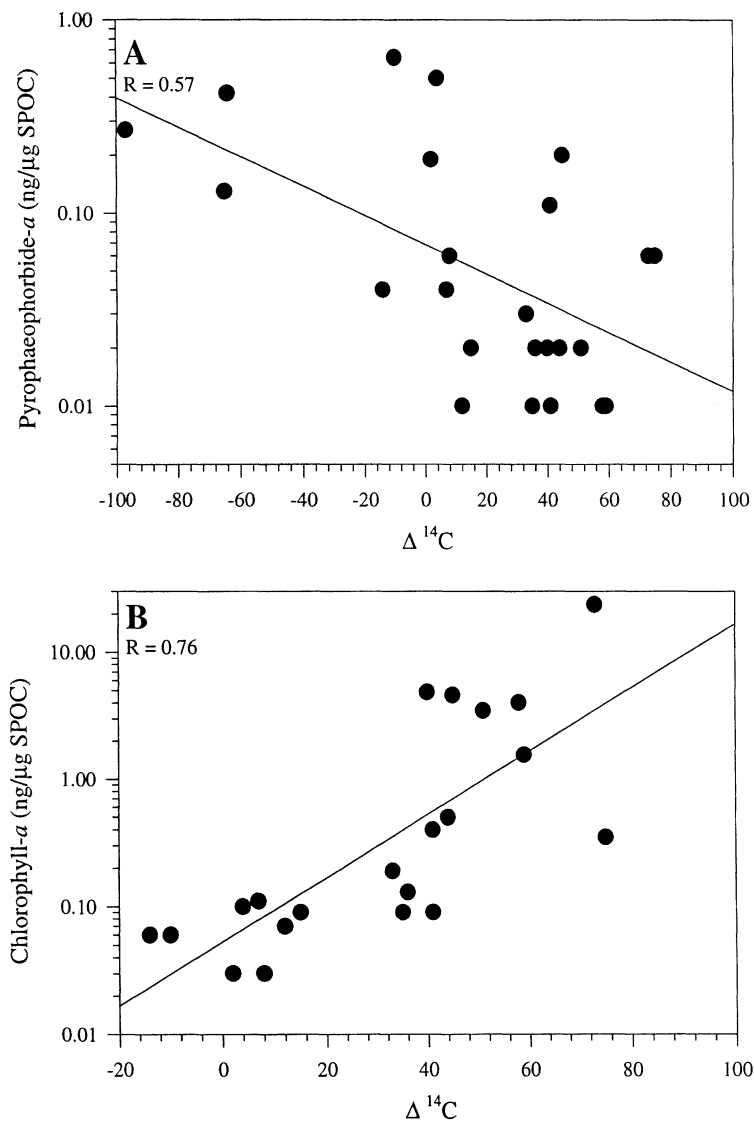
Fig. 4. Pyrophaeophorbide-*a*/SPOC (A) and chlorophyll-*a*/SPOC (B) values vs $\Delta^{14}C$ of SPOC collected at the NE Pacific station (Sta M) for three dates (February, 1992; June 1992; October, 1992). All $\Delta^{14}C$ SPOC data were obtained from Druffel et al., (1996). *R* represents the regression coefficient.

contention that pyrophaeophorbide-*a* peaks at depth are derived from "older" resuspended sediments that were laterally transported from shelf sediments. It has been suggested previously that $\Delta^{14}C$ values are lower in SPOC collected from deep waters compared to surface waters, in part due to sorption of "old" DOC onto SPOC (Druffel et al., 1996). Chlorophyll-*a*, which is predominantly found in surface waters,
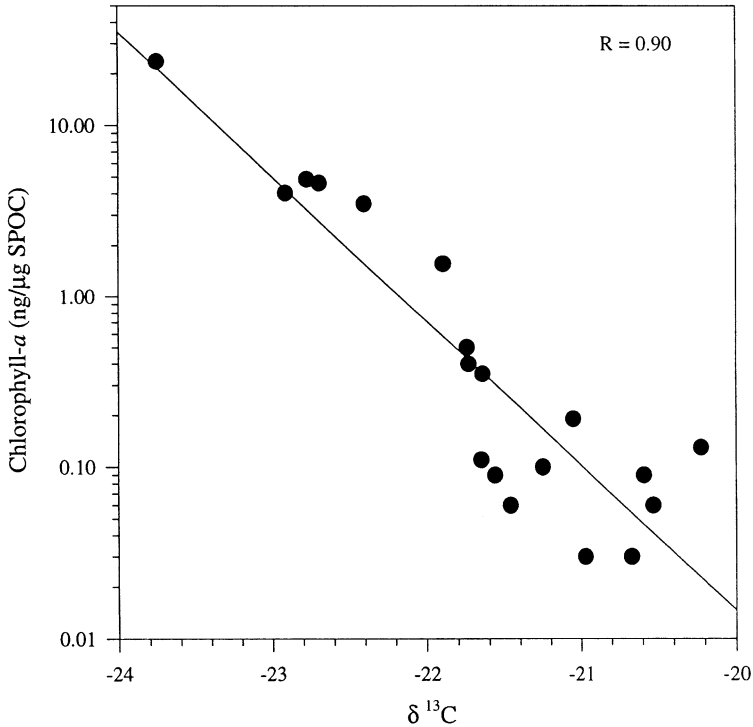
Fig. 5. Chlorophyll-*a*/SPOC values versus δ^{13}C of SPOC collected at the NE Pacific station (Sta M) for three dates (February, 1992; June 1992; October, 1992). All δ^{13}C SPOC data were obtained from Druffel et al., (1996). *R* represents the regression coefficient.

when normalized to SPOC is positively correlated with Δ^{14}C, illustrating the recent origin of this SPOC (Fig. 4B). On the other hand, a robust negative correlation ($R = 0.90$, $p < 0.01$) between chlorophyll-*a*/SPOC values and δ^{13}C of SPOC (Fig. 5), also indicates that recently produced, chlorophyll-rich SPOC is derived from phytoplankton production in surface waters where selective incorporation of the lighter isotope (^{12}C) can occur under high growth and/or low pCO_2 conditions (Druffel et al., 1996; Rau et al., 1986). If SPOC in the pyrophaeophorbide-*a*/SPOC maxima were derived from sinking surface production, Δ^{14}C values of SPOC from the pyrophaeophorbide-*a*/SPOC and chlorophyll-*a*/SPOC maxima should be more similar than observed in this study.

   Smith et al. (1994) found higher fluxes of sinking POC in near bottom sediment traps (50 mab) than in traps higher up in the water column (600 mab) during summer; this further suggests that lateral transport and/or vertical resuspension of sinking POC are important factors at this site. However, integrated sinking POC fluxes at 600 and 50 mab over an 852-d period from June 1989 through October 1991 agreed to within 4%, which may suggest that net lateral transport of organic carbon is not important at this site (Smith et al., 1994).
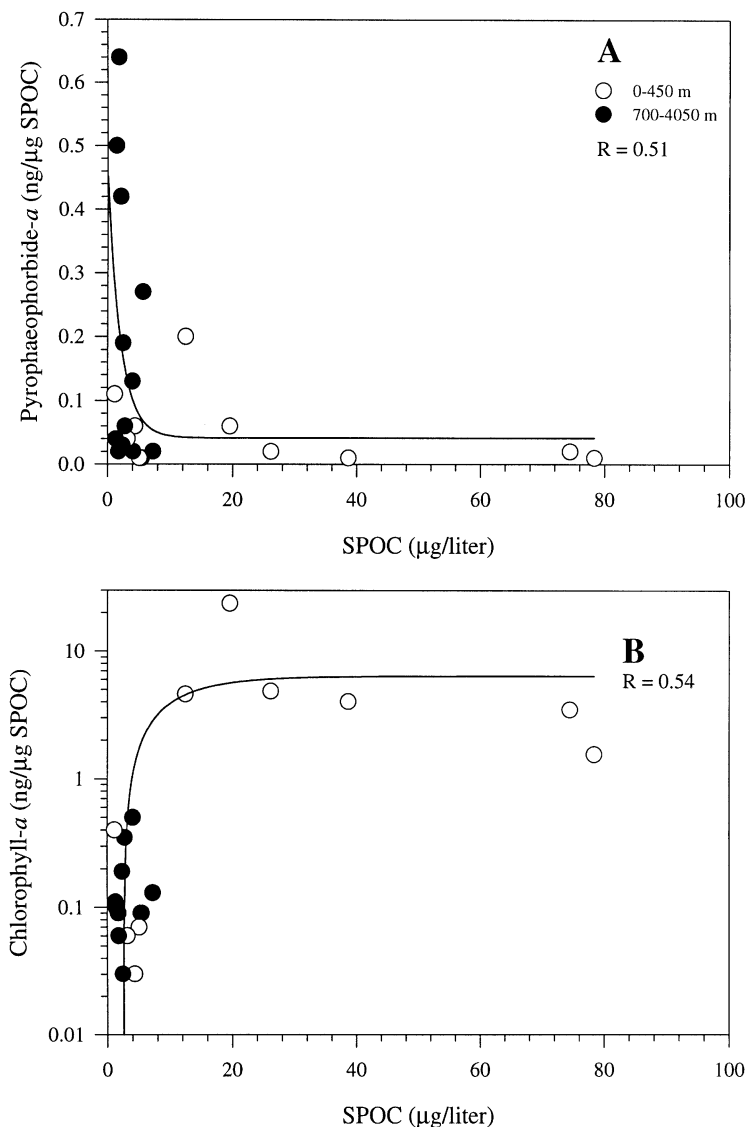
Fig. 6. Pyrophaeophorbide-*a*/SPOC (A) and log chlorophyll-*a*/SPOC (B) values vs SPOC concentrations at the NE Pacific station (Sta M) for three dates (February, 1992; June 1992; October, 1992). All SPOC data were obtained from Druffel et al. (1996). *R* represents the regression coefficient. Exponential curves were fitted to the data using the simple models $f = y_0 + a \exp(-bx)$ and $f = y_0 + a \exp(-bx) + c \exp(-dx)$. Open circles represent samples taken from 0 to 450 m water depth while black circles represent samples taken between 700 and 4100 m.

The molecular biomarker data (pyrophaeophorbide-*a*) for SPOC, the transmissometry, and sediment trap data for POC all agree that there are higher concentrations of both sinking and suspended POC (Smith et al., 1994) and

pyrophaeophorbide-*a* concentrations in near bottom waters in summer months. There are significant differences in the processes that control the overall transport of sinking POC versus SPOC; sinking rates of POC are primarily controlled by Stokes' law, whereas most SPOC is subject to Brownian motion. Thus, it is more likely to have lateral transport of significant quantities of SPOC rather than large particles from shelf sediments to slope waters. Moreover, pyrophaeophorbide-*a* may serve as a biomarker of a chemically specific fraction of SPOC that is not derived from recently sedimented material in the water column, and may not represent a significant fraction by weight of the total SPOC pool. For example, while there appears to be an overall negative correlation ($R = 0.51$, $p < 0.05$) between pyrophaeophorbide-*a*/SPOC and SPOC concentrations and a positive correlation ($R = 0.54$, $p < 0.05$) between chlorophyll-*a*/SPOC and SPOC in surface waters, the data can be divided into two categories based on water depth (Fig. 6). In surface depths (0–450 m) high SPOC co-occurs with high chlorophyll-*a* and low pyrophaeophorbide-*a* concentrations, and at greater depths low SPOC values do not correlate with pigment concentrations (Fig. 6). These patterns may indicate that a large fraction of "older" SPOC in deep waters is devoid of pyrophaeophorbide-*a* due to pigment loss with time and is likely derived from sediments (Fig. 6). Conversely, high chlorophyll-*a*-containing SPOC in surface waters is due to the recent origin of this material compared with "older" chlorophyll-*a*-depleted SPOC derived from resuspended sediments in bottom waters. Nonetheless, these data strongly suggest that there is transport of a fraction of SPOC from continental shelf sediments to the deep NE Pacific over three periods of 1992.

4. Conclusions

Measurable concentrations of pyrophaeophorbide-*a*/SPOC in the deep water column of the NE Pacific extend as high as 1600 mab during June and as high as 650 mab during February and October of 1992. Since previous studies have shown that most local resuspension occurs within 100–200 mab, it is unlikely that vertical resuspension could be responsible for the pyrophaeophorbide-*a*/SPOC maxima in the deep ocean. Pyrophaeophorbide-*a* concentrations in SPOC found at Sta M are negatively correlated with $\Delta^{14}C$ values of SPOC (SPOC samples from Druffel et al. (1996)); this further supports our contention that pyrophaeophorbide-*a* peaks in the deep sea are derived from "older" resuspended sediments that are somehow transported laterally from shelf and/or slope sediments. Furthermore, data from an incomplete vertical profile of pyrophaeophorbide-*a* in the NC Pacific shows a smaller maximum at 3300 m which may be due to the distance of this site from the continental margin. Using a representative horizontal eddy diffusion coefficient for the Pacific, we estimate that it could take as little as 32 days for resuspended, non-sinking particulate-derived material from the upper slope sediments to be transported to this abyssal site. Thus, the observed near bottom maximum of pyrophaeophorbide-*a* in the NE Pacific is likely due, in large part, to lateral transport from the continental shelf/slope. However, pyrophaeophorbide-*a* may only be tracing a chemically specific fraction of SPOC which remains in the water column for extended periods or is simply derived from

resuspended sediments that contribute little to the net flux of organic carbon to the deep ocean. Further work is needed to determine if these sources of SPOC are important contributors to deep ocean carbon fluxes.

Acknowledgements

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