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Organic geochemistry of particulate matter in the eastern tropical North Pacific Ocean: Implications for particle dynamics

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ABSTRACT

Samples of marine particulate matter were collected in sediment traps and by *in-situ* filtration to depths of 1500 m during VERTEX II and III cruises in the eastern tropical North Pacific. Wax esters, triacylglycerols, fatty acids, sterols and steroidal ketones were analyzed in these samples to compare the compositions of organic matter associated with large sinking particulate aggregates sampled by sediment traps and with fine suspended material obtained by *in-situ* filtration. Distributions of specific compounds indicated that the organic chemical composition of large sinking particles and small suspended particles both in the euphotic zone and at mid-depth result from very distinct particle pools, not only in terms of particle size but also in their sources and transport mechanisms. Suspended particles in the epipelagic zone contain a mix of organic compounds derived from both phytoplankton and zooplankton sources, whereas sinking particles are dominated by zooplankton-derived compounds. In the mesopelagic zone, large, sinking particles contain organic compounds which are indicative of intensive alteration of organic matter, even though transport from the euphotic zone may have been rapid. On the other hand, it is the suspended particle pool which contains a remarkable abundance of labile organic compounds which can be attributed to undegraded phytoplankton cells rapidly delivered from surface waters. These organic geochemical results lead to a modified model of particle dynamics in which there are two distinct large, sinking particle pools which are differentially sampled by the two sampling techniques.

1. Introduction

Particulate matter plays a major role in the biogeochemical cycling of carbon in the ocean, and as such the production, transfer, and decomposition of particulate organic matter in seawater are of importance to biological and geological oceanographers and to marine chemists interested in the cycling of elements in the ocean. Particles in the water column exist in a continuum of sizes (McCave, 1984), but two classes are frequently recognized. Fine suspended material having a negligible settling velocity

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and long residence time constitutes most of the standing stock of particulate matter in the ocean. Sinking particles consisting of fecal pellets and marine snow aggregates are quantitatively rare, but their high settling rates lead to short turnover times; these particles are responsible for most of the vertical transport of material, including labile organic matter (reviewed by Lee and Wakeham, 1988), from the upper ocean to the sea floor. The two particle classes may be distinguished operationally by the sampling method used to collect them, suspended material being collected mainly by filtration and sinking material collected by sediment traps.

The amount and chemical composition of organic matter in suspended and sinking particles results from a balance between biological processes of production and decomposition and physical processes of aggregation, disaggregation, and transport. The organic geochemistry of large, rapidly sinking particulate material collected by sediment trap experiments has been extensively studied (see reviews by Fowler and Knauer, 1986 and Lee and Wakeham, 1988). There is still a question, however, as to whether suspended particles, having long residence times, contain more highly degraded organic matter than rapidly sinking particles (Tanoue and Handa, 1980) or whether the suspended particles may in fact contain relatively undegraded and labile material (Lee *et al.*, 1983; Wakeham *et al.*, 1985).

Interactions between suspended fine particles and sinking macroaggregates are not well known. We have been investigating the geochemistry of specific organic compounds associated with suspended and sinking particles as tracers for elucidating the processes which affect particulate organic matter in the oceanic water column. Our observations suggest that there are substantial differences in the organic chemical composition of suspended vs. sinking particles which are due to source, transport and decomposition processes. In support of this hypothesis, we report here data for lipids (fatty acids, wax esters, triacylglycerols, steroidal alcohols, and steroidal ketones) associated with particulate matter collected during experiments in the eastern tropical North Pacific as part of the VERTEX (Vertical Transport and Exchange) program. Our purpose is twofold: (1) to demonstrate the utility of organic geochemistry in studying sources, transport, and transformation processes of particulate matter and (2) to apply organic geochemical information in characterizing particle dynamics.

The lipid composition of particulate matter can be used to evaluate organic matter source and alterations since many compounds ("biomarkers") are specific as to their source, whether phytoplankton, zooplankton, bacterial, or terrestrial. Lipids represent a small part of the biogenic organic matter of particles but are essential biochemicals in living organisms. Fatty acids are usually present as esters which are involved in energy storage and mobilization (long-chain alkyl esters or wax esters and triacylglycerols) and membrane structure (phospholipids). Triacylglycerols (triglycerides) are biosynthesized and stored by all phytoplankton and many species of zooplankton. Wax esters, on the other hand, are metabolically more stable than triacylglycerols and are biosynthesized by certain zooplankton and fish species inhabiting oceanic regions

Table 1. Deployment data for WHISPs and PITs during VERTEX II, III.

WHISPs				PITs		
Depth (m)	Date	Filtering time (h)	Volume filtered (l)	Depth		
			VERTEX II			
5	11/14/81	5	1734	50	Deployed	10/28/81
200	11/12	10	1912	100	Recovered	11/18/81
1000	11/14	14	2576	470		
				950	Deployment period—	
				1500	21 days	
			VERTEX III			
5	11/28/82	7	1053	100	Deployed	11/10/82
60	11/27	6	340	450	Recovered	11/29/82
140	11/22	9.5	3224	(950	lost)	
450	11/26	10	1727	1500	Deployment period—	
950	11/26	10	1024		19 days	
1500	11/23	10	4082			

characterized by sporadic periods of food availability. Steroidal alcohols (sterols) serve as membrane lipids and as regulators of metabolic processes in all plants and animals. Small amounts of steroidal ketones are also biosynthesized by organisms, but these compounds arise primarily as intermediate products in microbial decomposition of precursor sterols.

2. Methods

Suspended and sinking particles were collected during VERTEX II and III cruises to the oxygen minimum zone of the eastern tropical North Pacific approximately 400 km off Manzanillo, Mexico (15–18N, 107–109W) in October-November, 1981 and November, 1982. Small, suspended particles were collected at night using WHISPs (Woods Hole *In-Situ* Pumps), which are hydrographic-wire mounted, stream-powered large-volume filtering systems. Typically, 300 to 4000 l of seawater were pumped through ashed glass fiber filters (293 mm, type A/E, nominal pore size 1 μm) during 5-14 hr deployments (Table 1). During these collections, no *in-situ* particle size fractionations were made as we have done on more recent cruises. Following recovery, the filters were frozen and returned to the shore-based laboratory.

Free-floating Soutar-type particle interceptor traps (hereafter referred to as PITs; 0.25 m^2 collecting area with 1-cm grid at the cone opening; Martin *et al.*, 1983) were used to collect rapidly sinking, large particles over depth intervals similar to those of the WHISP samples (Table 1). The cones were Teflon-coated stainless steel and the collection cups were electropolished stainless steel. Mercuric chloride was used to

inhibit decomposition of material in the traps; as a result it was impractical to remove "swimmers" so that fluxes and compositions in the upper ocean traps (50 and 100 m) should be viewed with caution (e.g. Knauer *et al.*, 1984a). Deployment periods were 21 days in 1981 and 19 days in 1982.

Particle samples were returned to the laboratory for lipid analysis. WHISP filters were Soxhlet-extracted with toluene:methanol (1:1). PIT samples were decanted and the sediment lyophilized and extracted with methylene chloride. (The different extraction procedures resulted from a need to split the PIT extractable-lipids for analysis of trace levels of chlorinated hydrocarbons which required special care to minimize contamination. We do not believe that the two extraction procedures compromised the results and interpretations discussed below.) Lipid extracts were fractionated by adsorption chromatography on silica gel (7 g Merck silica gel 60, 5% deactivated with water, column size 20 cm × 1 cm diameter) into constituent classes on the bias of their polarity. Hydrocarbons were eluted with hexane, wax esters with 50% toluene in hexane, triacylglycerols and nuclear-unsaturated steroid ketones (stanones) with 10% ethyl acetate in hexane, nuclear-saturated steroid ketones (stenones) with 15% ethyl acetate in hexane, and sterols with 20% ethyl acetate in hexane. Each class was analyzed by capillary gas chromatography and combined gas chromatography-mass spectrometry as described elsewhere (Wakeham and Canuel, 1986).

3. Results and discussion

a. Nature of the study site. The study area was comprehensively surveyed hydrographically during the VERTEX II and III cruises (Broenkow and Krenz, 1982; Broenkow *et al.*, 1983a). Vertical temperature, salinity, and dissolved oxygen distributions (Fig. 1) are typical of conditions both years. The base of the mixed layer was about 40 m, with the euphotic zone extending to about 100 m. This site is in an area of convergence of surface waters from the California Current, the Gulf of California, and the Equatorial Countercurrent, resulting in the formation of the Equatorial Current (Wyrtki, 1967).

Mean primary production rates, integrated over a 100-m euphotic layer, were 860 and 470 mg C m^{-2} day^{-1} in 1981 and 1982, respectively (Knauer *et al.*, 1984b). Evaluation of carbon fluxes associated with sinking fecal pellets obtained by closely spaced sediment traps and net-zooplankton distributions in the euphotic zone (Small *et al.*, 1988) and by $^{234}Th/^{238}U$ disequilibrium data (Coale and Bruland, 1987) showed that the euphotic zone can be thought of conceptually as separated into two layers (e.g. Small *et al.*, 1988). A well-mixed upper oligotrophic layer (0–40 m) characterized by low new production values (e.g. ~ 5% of total primary productivity) was underlain by a subsurface eutrophic layer extending to the base of the euphotic zone (40–100 m) with higher new production values (~20% of total productivity). The primary pigment (fluorescence) maximum was at about 60 m (Fig. 1).

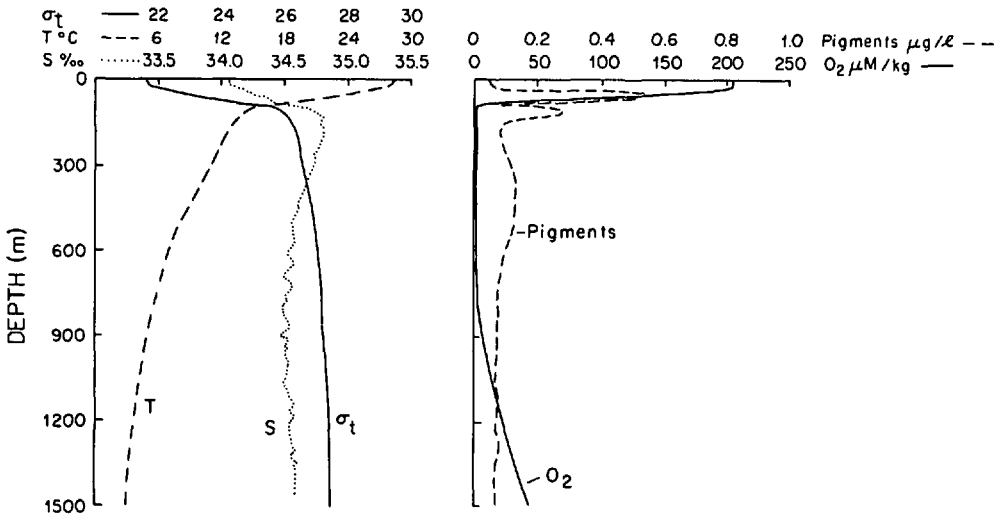

Figure 1. Hydrography at the VERTEX II and III sites. From Broenkow and Krenz (1982) and Broenkow *et al.* (1983a).

The most notable characteristic of this region is the oxygen minimum zone extending from 100 to 800 m (Fig. 1). Minimum dissolved oxygen concentrations of about 1 μM kg^{-1} or less were found between 110 and about 250 m, below which a linear concentration increase was observed. Hydrogen sulfide has not been found in these waters, but iodine-reducing compounds up to 2 μ-equiv. l^{-1} had been detected previously in this area (Cline and Richards, 1972). A secondary nitrite maximum at about 400 m was above the depth of the maximum nitrate deficit at 500 m (Cline and Richards, 1972; Coale and Bruland, 1987), indicating bacterial denitrification in this depth range. A secondary pigment maximum was coincident with the depth of the oxygen minimum, and a broad tertiary maximum was centered near 400 m (Broenkow *et al.*, 1983b).

b. Vertical distribution of organic compounds in particles. Fluxes and concentrations of particulate organic carbon (POC) and lipids in sinking and suspended particles are shown in Figure 2. Strong vertical gradients in flux for all components are consistent with the euphotic zone as the primary site of production of sinking particles and associated organic compounds, coupled with substantial decomposition of organic matter as particles sink out of the euphotic zone and into the interior of the ocean (e.g. Knauer *et al.*, 1979; Honjo, 1980; Karl and Knauer, 1984a, b; Lee and Cronin, 1984; Wakeham *et al.*, 1984b). Except for wax esters, concentrations of suspended organic compounds were highest at 60 m, the depth of the chlorophyll maximum, and decreased sharply with depth. Wax ester concentrations showed a marked increase

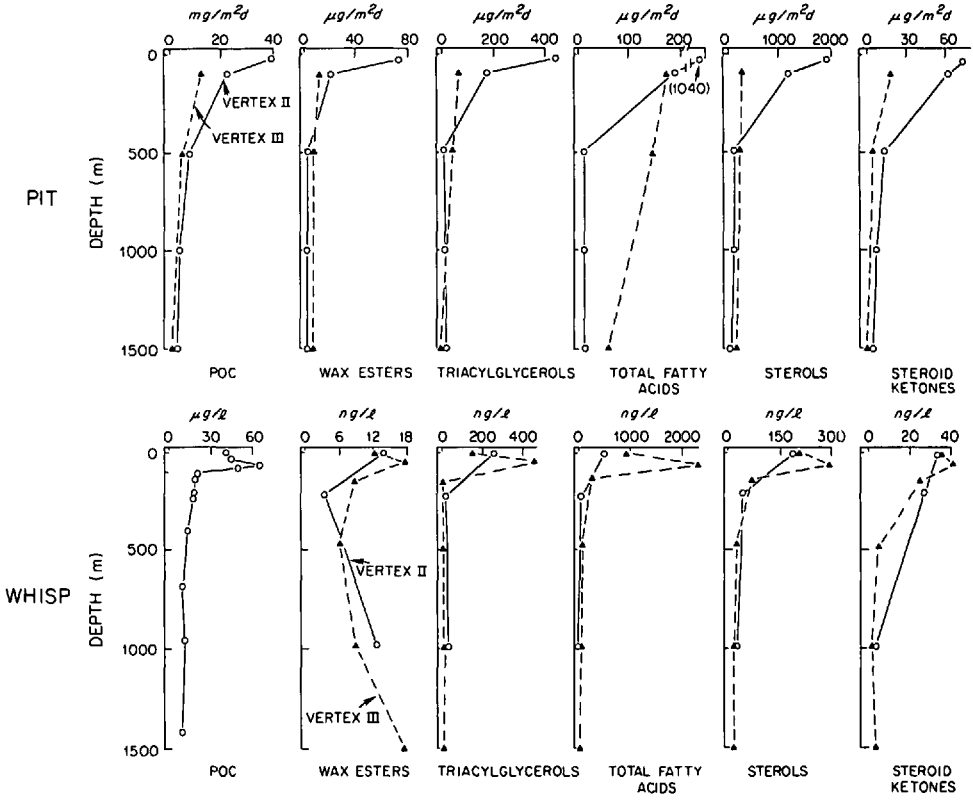

Figure 2. PIT flux and WHISP concentration profiles for organic components during VERTEX II and III.

below the oxygen minimum. Vertical distributions of organic materials were generally similar during the two sampling periods; differences in vertical flux in the upper 500 m probably reflect the almost 2-fold variation in primary production, and hence also particle production, between the two years.

The relative contribution of each lipid class to total particulate organic carbon varied according to particle size class and depth (Table 2). Weight ratios of lipid classes to POC generally decreased with increasing depth for VERTEX II, suggesting preferential degradation of lipid over total organic carbon; VERTEX III appears to be unusual in that lipid/POC ratios increase with increasing depth. The loss of labile organic matter at a faster rate than organic carbon is a generally observed feature in sediment trap experiments (Wakeham *et al.*, 1984b; Lee and Cronin, 1984) and implies a preferential increase in a nonsolvent extractable and possibly more refractory carbon pool, such as "bound" lipids, "humic substances" and nonextractable "kerogen". Characterization of the organic composition of these refractory forms of organic matter remains a major analytical hurdle for marine organic chemists but is crucial for

Table 2. Weight ratios (mg/g) of lipid classes to particulate organic carbon (POC) in VERTEX II and III PIT and WHISP samples. WE—wax ester; TG—triacylglycerol; FA—fatty acid; ST—sterol; SK—steroid ketone.

Depth (m)	WE/POC	TG/POC	FA/POC	ST/POC	SK/POC
		VERTEX II PIT			
50	1.8	11.3	26.0	39.5	1.9
100	1.1	8.9	9.5	24.5	3.0
470	0.28	1.7	2.6	13.6	2.2
950	0.08	0.85	3.3	31.5	1.4
1470	0.22	0.70	4.8	10.3	3.0
		VERTEX II WHISP			
5	0.33	6.2	13.1	3.6	0.92
200	0.22	1.3	4.4	1.2	1.5
1000	1.2	1.4	6.4	1.4	0.66
		VERTEX III PIT			
100	1.4	7.0	17.0	19.0	0.67
450	0.83	0.2	27.8	48.0	1.20
1500	1.7	1.7	26.2	38.0	1.5
		VERTEX III WHISP			
5	0.29	3.5	21.2	4.5	0.60
60	0.27	7.2	37.5	4.1	0.50
140	0.45	0.17	22.2	3.0	1.71
450	0.55	0.28	9.1	1.0	0.55
950	0.73	3.2	8.2	1.1	0.25
1500	1.4	1.3	5.9	1.3	0.36

understanding the biogeochemical cycling of particulate matter in the ocean. Sterols were the least influenced by depth and were the most abundant lipid class in sinking particles; fatty acids were the most abundant lipid class in suspended particles. Triacylglycerols were of roughly equal abundances relative to POC in both particle size classes. Wax esters were similar in distribution, though generally less abundant than triacylglycerols in both large and small particles. However, suspended particles below the O_2 minimum were preferentially enriched in wax esters, in agreement with the increased absolute concentrations of small-particle wax esters seen in the depth profiles. Steroid ketones tend to be enriched in the O_2 minimum zone independent of particle size.

The VERTEX II and VERTEX III cruises had planned to resample the same oceanic regime, but nature did not cooperate. Oceanic conditions in the two years were different, and these differences appear reflected in differences in particulate organic matter vertical flux, suspended concentrations, and particle compositions. In particular, 1982 (VERTEX III) was an El Niño year. Surface water temperatures were roughly 1°C warmer in 1982 (28–29°C) than 1981 (27–28°C). The oxygen minimum

was shallower and more intense during VERTEX III, where dissolved oxygen concentrations of 1 μmol kg^{-1} were observed at 100–160 m compared with minimum values of 4 μmol kg^{-1} at 130–180 m for VERTEX II. Higher primary carbon production during VERTEX II (i.e. 860 vs. 470 mg C m^{-2} day^{-1}) resulted in higher particle and lipid fluxes that year compared to the second year. The morphology of particles collected in the PITs also varied (K. W. Bruland, M. W. Silver and M. M. Gowing, pers. commun.). During VERTEX II, fecal pellets from the pelagic crabs *Pleuroncodes planipes* dominated the sedimenting material, accounting for up to about 50% of the POC flux at mid-depth. During VERTEX III, however, the crabs were much less abundant, while salps were more abundant than the previous year. Crab and salp fecal pellets were roughly equivalent in their contribution to POC flux, but overall, fecal pellets provided less than 15% of the total carbon flux. The morphology of the WHISPs samples cannot be fully characterized at present, primarily because microscopic examination of the glass fiber filters is not feasible. However, visual examination of filters indicated that few if any zooplankton were collected, and if so they were present in the shallower samples. A few fecal pellets of *P. planipes* were observed on filters collected within the oxygen minimum during VERTEX II.

c. Organic chemical composition of particles. Weight ratios of the lipid classes to POC (Table 2) provide initial evidence of compositional variations of particulate organic matter with respect to particle size class and depth. The specific organic composition of the particles also varies with particle size and depth and yields detailed information about the biogeochemistry of particles. Lipid compositions of sediment trap samples from 100 and 1500 m (PITs) and of *in-situ* filtration samples from 60 and 1500 m (WHISPs) from VERTEX III are shown in Figs. 3–7 to illustrate lipid class distributions in sinking and suspended particles. All samples have been analyzed in similar detail and are consistent with changing compositions as a function of depth and particle size as represented by these four samples. Compound distributions are discussed in terms of geochemical information about particle source and alteration processes which can be inferred from these distributions.

(i.) Wax esters

Wax esters on sinking particles were preferentially depleted with depth relative to POC in the euphotic zone and oxygen minimum (Table 2). Below the oxygen minimum, however, the wax ester:POC ratio increased. Suspended particles in the euphotic zone were wax ester-poor compared to sinking particles. As depth increased, the suspended particle pool became enriched in wax esters.

The molecular composition of wax esters associated with sinking and suspended particles ranged from C_{24} to C_{44}, usually with 32:1 (32 carbon atoms:1 double bond) and 34:1 predominating (Fig. 3), and with variable amounts of longer-chain 36:1, 38:1

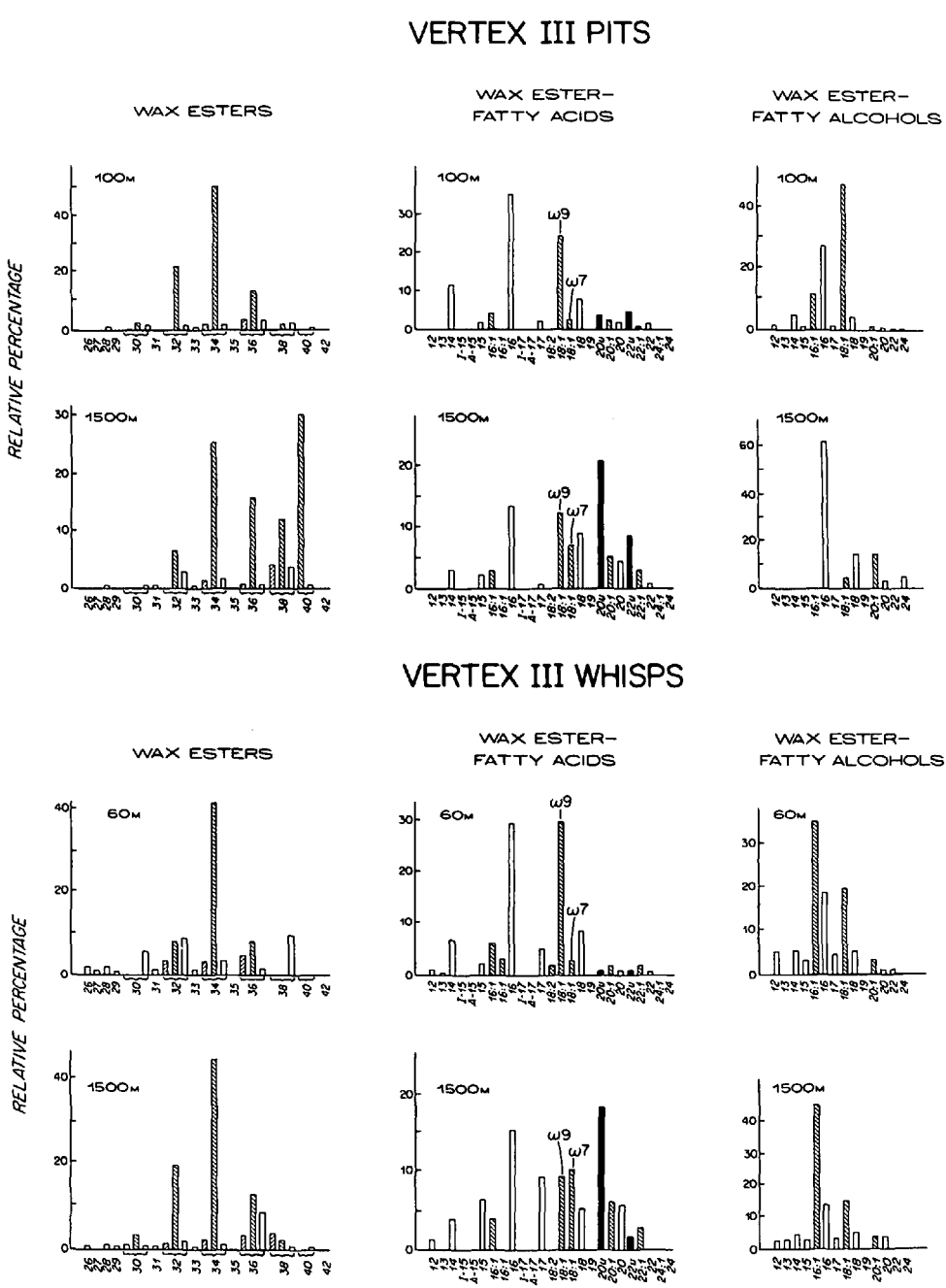

Figure 3. Histograms of relative abundances of wax esters and constituent fatty acids and fatty alcohols for VERTEX III 100 and 1500 m PITs and 60 and 1500 m WHISPs. Open bars indicate saturated compounds (e.g. 32:0 wax ester and 16:0 fatty acid and alcohol), cross-hatched bars are mono- and di-unsaturated components (32:1 wax ester and 16:1 acid and alcohol), and closed bars are summed polyunsaturated components (e.g. 22 u = 22:4 + 22:5 + 22:6). The fatty acid and fatty alcohol distributions were obtained after hydrolysis of the wax ester mixtures and represent fatty acid and alcohol components present in the mixed wax esters.

and 40:1 wax esters. The wax esters, being long-chain esters of fatty acids and fatty alcohols, were composed of acids and alcohols, ranging from C_{12}–C_{22} (Fig. 3). Even though the total wax ester distributions may be similar between samples, for example the 100 m PIT and the 1500 m WHISP, the distribution of constituent fatty acids and alcohols may differ. This results from different combinations of acids and alcohols giving the same wax ester carbon number (e.g. 16:0 acid/16:1 alcohol gives 32:1 wax esters, as do 16:1/16:0 and 14:0/18:1). Thus in the 100 m PIT wax esters, the major fatty acids were 16:0, 18:1ω9 (where ω9 indicates that the double bond is located 9 carbons from the terminal methyl group) and 14:0, and the alcohols were dominated by 18:1 and 16:0, and 16:1. But in the 1500 m WHISP, 16:0 and 20 *u* (*u* = polyunsaturated; i.e. 20:3 + 20:4 + 20:5) were the major fatty acid constituents along with equal amounts of 18:1ω9 and 18:ω7 positional isomers, and 18:1, 16:1, and 16:0 compounds were the major alcohols. The difference in constituent acids and alcohols shows that wax esters are actually quite different.

Particulate wax esters in the marine water column are almost exclusively animal-derived (Sargent, 1976; Sargent *et al.*, 1981; and references therein) and may be associated with live macro- or micro-zooplankton or their carcasses and fecal pellets. The wax ester distributions in VERTEX PIT and WHISP samples are typical for the numerous zooplankton species which have been surveyed (Nevenzel, 1970; Lee *et al.*, 1971a,b; Lee and Hirota, 1973; Volkman *et al.*, 1980d; Wakeham, 1982, 1985; Reinhardt and Van Vleet, 1986). The exact chain-length distribution depends on diet, water temperature, and depth, as do the fatty acid and alcohol combinations. In general, zooplankton wax esters range from C_{24} to C_{44} with C_{30}, C_{32}, and C_{34}, most often unsaturated, as the major homologs. The fatty alcohols are saturated and monosaturated, usually with 16:0 and 18:1 as the usual major components, although in some upper water species 20:1 and 22:1 may be abundant. Fatty acid distributions are usually more complex, but again 16:0, 18:1, 22:1 and 20 *u* and 22 *u* are often dominant. Phytoplankton do not biosynthesize wax esters.

We can therefore postulate two localized zooplankton sources of wax esters associated with particulate matter. One community of zooplankton inhabiting the euphotic zone synthesizes wax esters which were found in particles above the oxygen minimum zone. A second community resides below the oxygen minimum zone producing wax esters associated with particles below the oxygen minimum. Differing epipelagic and mesopelagic zooplankton community structure, as well as the nearly complete absence of zooplankton within the oxygen minimum, were observed in the VERTEX cruises (M. D. Tuel, pers. commun.), and the depth-related changes in particulate wax ester distributions are consistent with analyses of net zooplankton collected throughout the water column during the cruises. The increasing concentrations of wax esters as a function of increasing depth in the water column, especially in the WHISP samples, suggests a depth-related source of small particle-associated wax esters. This source would again be some deep-water population of animals. It is

unlikely, however, that the small particles result exclusively from disaggregation of larger particles because of the significant compositional differences between the two size fractions.

(ii) Triacylglycerols

The sources of particulate triacylglycerols are considerably more diverse than for wax esters. Triacylglycerols are the major or the only known energy reserve lipid in phytoplankton, in most fish, and in zooplankton species which do not biosynthesize major amounts of wax ester. It is not surprising, therefore that triacylglycerol fluxes into the PITs and concentrations in the WHISP samples are greater (Fig. 2 and Table 2) and a dominantly epipelagic source is suggested.

Nevertheless, like wax esters, the triacylglycerol composition of particles varies not only as a function of depth (Fig. 4) but also as a function of particle size. Triacylglycerols in all PIT and WHISP samples ranged from C_{42} to C_{54}, usually with C_{46}, C_{48}, and C_{50} as the most abundant homologs. The fatty acid constituents of the triacylglycerols (Fig. 4) are perhaps more useful in showing compositional differences and elucidating sources than whole triacylglycerols; again similar distributions of intact triaclyglycerols often are composed of very different fatty acids. The major fatty acids of phytoplankton-derived triacylglycerols tend to be 14:0, 16:0, and 16:1ω7 (Lee *et al.*, 1971a,b; Wakeham, 1985), with major variations depending on genus and species. Triacylglycerols of zooplankton typically contain mainly 16:0, 18:1ω9, 18:0 and varying amounts of monounsaturated and polyunsaturated C_{20} and C_{22} fatty acids (Lee *et al.*, 1971a, b; Sargent and Falk-Petersen, 1981; Wakeham, 1985; Reinhardt and Van Vleet, 1986). The PIT triacylglycerols would therefore appear to be dominated by compounds of zooplankton origin. However, the depth-related change in composition cannot be due only to decomposition of the triacylglycerols as the particles sink. Degradation of these lipids should preferentially remove the more labile unsaturated compounds, such as 16:1, 18:1, and 20 *u* fatty acids, leaving the particles enriched in the more stable saturated components (i.e. 16:0 and 18:0). In fact, the deeper PIT particles contain proportionally more unsaturated fatty acid than did the shallower trap samples.

On the basis of the relative fatty acid composition, it would appear that the triacylglycerols in the shallower WHISP samples are primarily phytoplanktonic in origin, while zooplankton-derived triacylglycerols are more abundant in the PITs. This is based on the relatively high amounts of 14:0 (phytoplankton-derived) and low levels of 18:1 and 18:0 (zooplankton-derived) components in the WHISPs. The deeper WHISP samples, on the other hand, contain a different pattern of intact triacylglycerols (an envelope of even-carbon number homologs peaking at C_{50} vs. a bimodal distribution peaking at C_{44} and C_{50} for the 60 m WHISP) with triacylglycerol-fatty acids indicative of zooplankton (e.g. 18:1ω9).

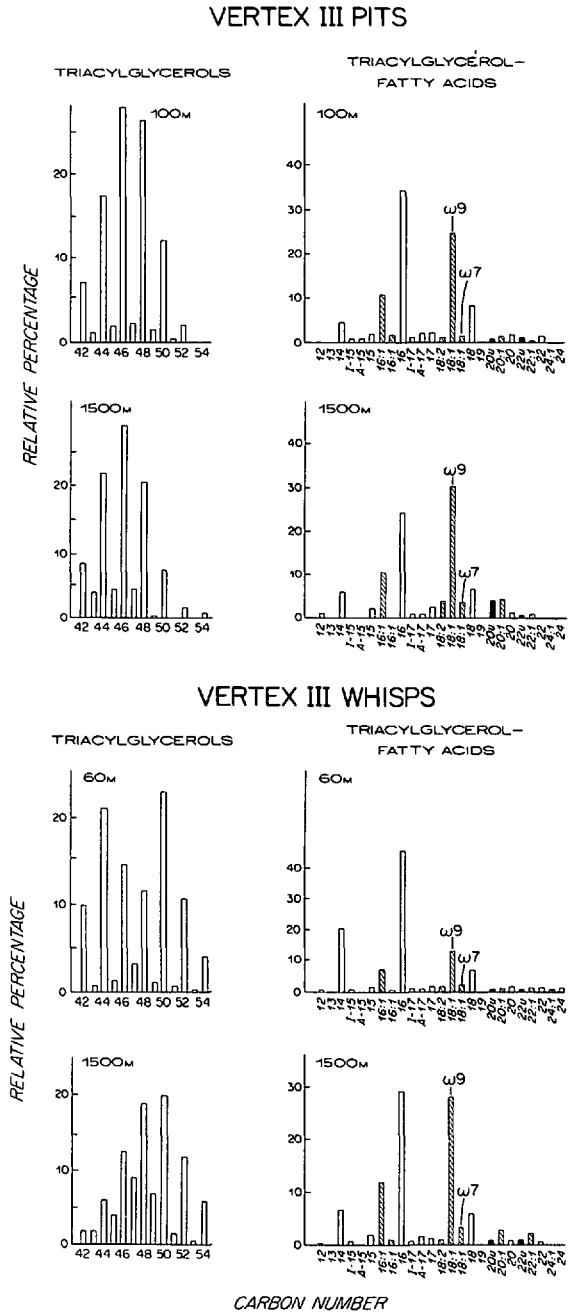

Figure 4. Histograms of relative abundances of triacylglycerols and constituent fatty acids for VERTEX III 100 and 1500 m PITs and 60 and 1500 m WHISPs. Fatty acid distributions were obtained after hydrolysis of the triacylglycerol mixtures. Open bars are saturated components, hatched bars are mono- and di-unsaturated compounds, and closed bars are polyunsaturated components. I- and A-designations (i.e. I-15, A-15, I-17 and A-17) indicate branched (iso- and anteiso) components. Typical phytoplankton fatty acids include 14:0, 16:1ω9, zooplankton indicator acids are 18:0, 18:1ω9, 20 *u* and 22 *u*, and bacterial markers include i- and a-15 and 18:1ω7. Most organisms contain large amounts of 16:0, so it is generally nonspecific.

(iii) Total fatty acids

Total fatty acids as described here include acids which were esterified in wax esters, triacylglycerols, polar and complex membrane lipids (e.g. phospholipids), mono- and diacylglycerols arising from *in-situ* hydrolysis of polar lipids, and free fatty acids derived from *in-situ* hydrolysis of triacylglycerols and any of the above esters. Contributions from wax esters and triacylglycerols to the total fatty acid pool may be estimated by assuming that about 50% of a wax ester and about 95% of a triacylglycerol are comprised of fatty acids. Using these values and the data in Table 2, some 40–45% of the fatty acids in the epipelagic particles and some 10–20% in the mesopelagic particles are contributed by wax esters and triacylglycerols. The remaining fatty acid should come from polar lipid, mono- and diacylglycerols, and free fatty acids. Thus the relative contribution of wax esters and triacylglycerols to the total fatty acid pool tends to decrease with increasing depth in the water column. Since the overall biomass also decreased with depth, it is unlikely that the relative contribution from polar membrane lipids increases significantly. Rather, the difference is probably made up of mono- and diacylglycerols and free fatty acids, which as *in-situ* hydrolysis products of wax esters, triacylglycerols, and phospholipids may be thought of as decomposition products. In addition to this qualitative change within the fatty acid pool itself, the overall abundance of fatty acids, relative to POC, decreases with depth as the labile fatty acids themselves are preferentially consumed.

Particulate fatty acids from VERTEX III are shown in Figure 5. Molecular distributions of fatty acids are indicative of mixed phytoplankton and zooplankton sources (Morris, 1971, 1973; Sargent, 1976; Volkman *et al.*, 1980b, 1981b). Although fatty acid distributions are not unambiguous source indicators (i.e. many sources biosynthesize the same compounds), relative abundances of compounds may suggest inputs from phytoplankton vs. zooplankton. Thus, typical zooplankton fatty acids (16:0, 18:1ω9, 18:0, 20 *u*, and 22*u*) are mixed with a phytoplankton component (16:0, 16:1ω9, and 14:0). Fatty acids in the deep-water PITs reflect primarily a deep-water zooplankton source, while the deep-water WHISPs retain a mixed phytoplankton-zooplankton signature. The extent of a bacterial contribution to the total fatty acid distribution is uncertain. Fatty acids usually attributed to bacterial sources, for example iso- and anteiso-C_{15} and C_{17} and 18:1ω7 (cis-vaccenic acid) (Perry *et al.*, 1979; Volkman *et al.*, 1980e; Volkman *et al.*, 1981a), are present, though not particularly abundant in any samples, and most likely indicated de novo synthesis by bacteria colonizing the particles. Membrane (polar lipid) fatty acids of several marine bacteria are enriched in some unsaturated components, for example 14:1, 16:1, 18:1, and in some cases 20:5, probably in response to increased hydrostatic pressure and decreased temperature (Jones and Prahl, 1985; DeLong and Yayanos, 1985; Wirsen *et al.*, 1987). However, since the analysis procedure used did not distinguish between neutral lipid wax ester- and triacylglycerol-derived fatty acids and polar lipid membrane-derived fatty acids, it is likely that bacterial components are masked by the overwhelming contribution from phytoplankton- and zooplankton-derived fatty acids.

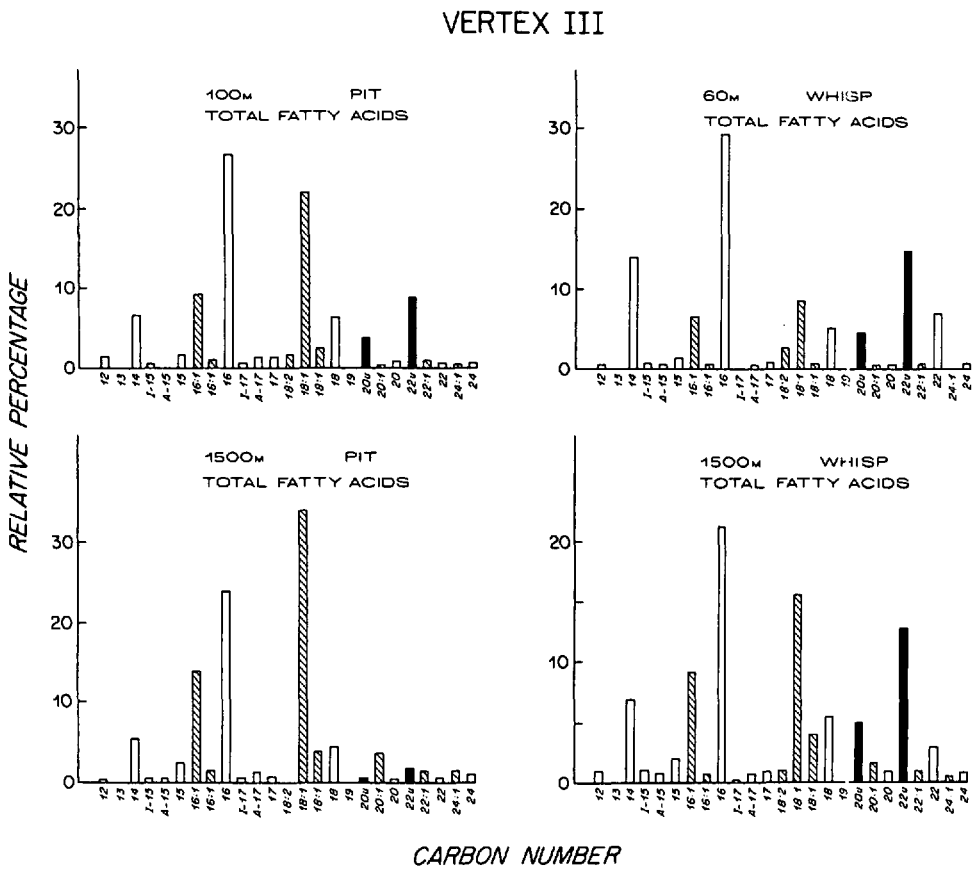

Figure 5. Histograms of relative abundances of total fatty acids for VERTEX III 100 and 1500 m PITs and 60 and 1500 m WHISPs. Bar designations and source indications are as given for Figures 3 and 4.

An unexpected feature of the fatty acid distributions is the abundant polyunsaturated fatty acids (PUFA: 20 *u* and 22 *u*) in the deep-water suspended particles. PUFA (e.g. 20:4, 20:5, 22:5, and 22:6) comprise some 20% of the total fatty acids in the VERTEX III suspended particles in the euphotic zone, and surprisingly, 18% at 1500 m. In contrast, the relative abundance of PUFA in the VERTEX III sinking particles decreased from 12% at 100 m to 2% at 1500 m. Since PUFA are the most readily degraded of all fatty acids associated with marine particulate matter (DeBaar *et al.*, 1983; Prahl *et al.*, 1984; Neal *et al.*, 1986), a long residence time for small, suspended or slowly sinking particles should result in preferential and rapid removal of the most-labile highly unsaturated components. This clearly is not the case.

(iv) Sterols

Sterols (nuclear-unsaturated stenols and nuclear-saturated stanols) were the most abundant lipids in particles collected by the sediment traps (Fig. 2 and Table 2). In

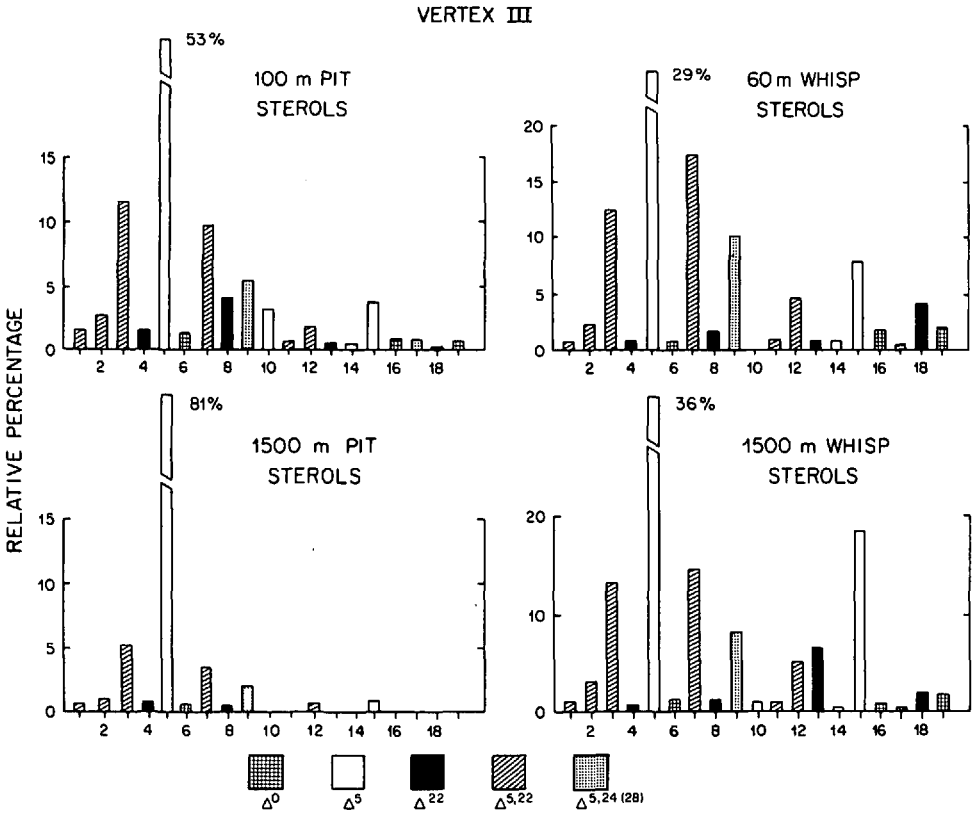

Figure 6. Histograms of relative abundances of sterols for VERTEX III 100 and 1500 m PITs and 60 and 1500 m WHISPs. Bar numbers refer to Table 3 and bar patterns refer to positions of double bonds (e.g. $\Delta^{5,22}$ indicates double bonds in the 5- and 22-positions). Typical phytoplankton markers are brassicasterol (diatoms; bar 7), 24-methylene cholesterol (diatoms; 9) and dinosterol and dinostanol (dinoflagellates; 18 and 19); zooplankton sterols include 22-dehydrocholesterol (3) and cholesterol (5); terrestrial higher plants produce stigmasterol (12) and β-sitosterol (15).

contrast, sterols were much less abundant, relative to POC, in suspended particles sampled by the WHISPs. The inclusion of "swimmers" in the shallower sediment traps probably would not result in the marked abundance of sterols in these traps because sterols are generally less abundant in living organisms than, say, fatty acids. Rather, the sterols predominance most likely results from preferential decomposition of the more labile fatty acids. The major sterol in all particles, both sinking and suspended, is the C_{27} compound cholesterol (cholest-5-en-3β-ol; 5 in Figure 6 and Table 3) which undoubtedly comes from marine invertebrates in which it is the dominant sterol (Nes and McKean, 1977; Goad, 1978; Ballantine and Roberts, 1980). The relative abundance of 22-dehydrocholesterol (cholesta-5,22E-dien-3β-ol; 3) is further evidence of zooplankton-derived material. Phytosterols were also present, but their contribution

Table 3. Identifications of sterols and steroid ketones shown in Figures 6 and 7, respectively.

Bar #	Sterols*	Steroid Ketones**
1	24-norcholesta-5,22E-dien-3β-ol	cholesta-4,22-dien-3-one
2	27-nor-5α-methylcholesta-5, 22E-dien-3β-ol	cholest-22-en-3-one
3	cholesta-5,22E-dien-3β-ol (22-dehydrocholesterol)	cholest-4-en-3-one
4	5α-cholest-22E-en-3β-ol	5β-cholestan-3-one
5	cholest-5-en-3β-ol (cholesterol)	5α-cholestan-3-one
6	5α-cholestan-3β-ol (cholestanol)	24-methylcholesta-4,22-dien-3-one
7	24-methylcholesta-5,22E-dien-3β-ol (brassicasterol)	24-methyl-5α-cholest-22-en-3-one
8	24-methyl-5α-cholest-22E-en-3β-ol	24-methylcholest-4-en-3-one
9	24-methylcholesta-5,24(28)-dien-3β-ol (24-methylene cholesterol)	24-methyl-5α-cholestan-3-one
10	24-methylcholest-5-en-3β-ol (campesterol)	24-ethylcholest-4-en-3-one
11	23,24-dimethylcholesta-5,22E-dien-3β-ol	23,24-dimethyl-5α-cholestan-3-one
12	24-ethylcholesta-5,22E-dien-3β-ol (stigmasterol)	24-ethyl-5β-cholestan-3-one
13	24-ethyl-5α-cholest-22E-en-3β-ol	24-ethyl-5α-cholestan-3-one
14	23,24-dimethylcholest-5-en-3β-ol	23,24-dimethyl-5β-cholestan-3-one
15	24-ethylcholest-5-en-3β-ol (β-sitosterol + clionosterol)	4,23,24-trimethylcholestan-3-one (dinostanone)
16	24-ethyl-5α-cholestan-3β-ol	
17	24-ethylcholesta-5,24(28)-dien-3β-ol	
18	4,23,24-trimethylcholest-22-en-3β-ol (dinosterol)	
19	4,23,24-trimethylcholestan-3β-ol (dinostanol)	

*Refers to Figure 6.
**Refers to Figure 7.

to the total sterol content decreased significantly with increasing PIT depth, and to a lesser extent with increasing WHISP depth. In addition to small amounts of cholesterol and 22-dehydrocholesterol which may also be minor components of some phytoplankton, the major phytosterols in the particles are C_{28} compounds, including brassicasterol (24-methylcholesta-5,22E-dien-3β-ol; 7) and 24-methylene cholesterol (24-methylcholesta-5,24(28)-dien-3β-ol; 9), both being abundant in diatoms (e.g. Ballantine *et al.*, 1979; Boutry *et al.*, 1979; Volkman *et al.*, 1980b, 1981b), as well as other phytoplankton (Goad, 1978). Dinosterol (4,23,24-trimethylcholest-22-en-3β-ol; 18) and dinostanol (4,23,24-trimethylcholestan-3β-ol; 19), generally attributed to dinoflagellates (Alam *et al.*, 1979; Boon *et al.*, 1979) were minor components.

C_{29} sterols such as campesterol (24-methylcholest-5-en-3β-ol; 10), stigmasterol (24-ethylcholesta-5,22E-dien-3β-ol; 12) and 24-ethylcholest-5-en-3β-ol (15) were present and could be indicative of terrigenous organic matter being incorporated into the particles, since the sampling site was only about 400 km off the coast of Mexico. However, the case for 24-ethylcholest-5-en-3β-ol being a terrigenous biomarker is equivocal since its stereochemistry has not been determined in these samples. The 24(R) epimer (β-sitosterol) is generally assigned a terrigenous origin while the 24(S) epimer (clionosterol) may be marine (e.g. Lee *et al.*, 1980; Volkman, 1986). 24-Ethylcholest-5-en-3β-ol (of undefined stereochemistry) has been reported in seawater particulate matter and sediments in regions where terrestrial influences are minimal and in various species of marine phytoplankton (Matsumoto *et al.*, 1982; Volkman, 1986).

Distributions of sterols changed with sample depth and were also dependent on particle size. The epipelagic PIT material is clearly a mixture of zooplankton and phytoplankton sterols, while the contribution of phytosterols decreases with sediment trap depth so that the 1500 m PIT sample, in which cholesterol (5) was 86% of the total sterols, collected primarily zooplankton-sterols. It should be noted that the absolute flux of cholesterol during VERTEX III decreased by a factor of about 2, from about 100 $\mu g\ m^{-2}\ d^{-1}$ at 100 m to 65 $\mu g\ m^{-2}\ d^{-1}$ at 1500 m, even though its relative abundance increases. Phytosterols were not particularly important in the deeper sinking particles, indicating a decrease in vertical transport of surface-derived sterols by large particles. A mesopelagic source of zooplankton sterols which would contain high abundances of cholesterol is consistent with these data, as was observed at 1000 m depth at the PARFLUX E site in the equatorial North Atlantic (Gagosian *et al.*, 1982).

Sterol distributions in suspended particulate material were much less variable down the water column than in sinking particles. Even at 1500 m, a substantial phytoplankton signature was evident (Fig. 6), although cholesterol always dominated. Other sterols, in particular, stigmasterol (12) and 24-ethylcholesterol (15) associated with suspended particles showed maxima in relative abundance in and below the oxygen minimum zone. For example, 24-ethycholesterol (15) represented 9% of total sterols in the VERTEX III 60 m WHISP vs. 19% at both 450 m and 1500 m. This compound was not as abundant in the sinking particles (<5%), nor did its relative abundance increase in the oxygen minimum. If the primary source of C_{29} sterols is assumed to be terrigenous in nature, then their increased abundances on suspended particles at greater depths are suggestive of lateral advection at mid-depth of terrestrially-derived material, perhaps off the continental shelf. Similar lateral advective transport within the oxygen minimum was also reported at this same location by Martin and Knauer (1984). They found that 70% of the manganese-maximum in the O_2 minimum could be derived from continental shelf sources.

Bacteria are generally thought not to synthesize 4-desmethyl sterols, although microorganisms are actively involved in transformations of sterols produced by

phytoplankton and zooplankton. Nuclear-unsaturated sterols (stanols, e.g. cholestanol, 6 in Fig. 6) are microbial degradation products of nuclear-unsaturated sterols (stenols, e.g. cholesterol); increased stanol-stenol ratios in Recent sediments (Gaskell and Eglinton, 1975) are usually indicative of this transformation. Stanol:stenol ratios in VERTEX sinking particles were 0.04–0.09 throughout the water column and were typical of plankton. Suspended particles, however, had similar ratios in the epipelagic zone, but stanols became relatively more abundant with increasing depth, giving stanol:stenol ratios of up to 0.22 in the middle of the oxygen minimum and decreasing to about 0.13 below the oxygen minimum. Microbial transformation of stenols to stanols appears to occur preferentially on fine particles (further details of steroid geochemistry at VERTEX II/III are discussed in Wakeham, 1987), but these microbial processes will not produce the phytosterols present in the deep-water WHISPs.

(v) Steroidal ketones

Figure 2 shows that steroidal ketones (nuclear-unsaturated stenones and nuclear-saturated stanones) were associated with both sinking and suspended particles throughout the water column. Large-particle steroidal ketone fluxes and small-particle ketone concentrations gradually decreased with depth. However, in contrast to sterols, steroidal ketones were generally enriched relative to POC in the sediment traps compared to the WHISPs (Table 2), and in fact, the relative abundance of the ketones generally increases with trap depth. Cholestenone (cholest-4-en-3-one; 3 in Fig. 7) was usually the major steroidal ketone, making up about 25–30% of the total.

Both stenones and stanones are present in minor abundances (10–15% of sterols) in pelagic marine organisms (Withers *et al.*, 1978; Schmitz, 1978), and a source in the euphotic zone could account for the observed depth trends for steroid ketones at the VERTEX site. It appears unlikely, however, that both stenones and stanones have the same source, since the stenone:stanone ratios vary differently depending on particle size and depth. The stenone:stanone ratio in the PIT samples goes through a minimum in the oxygen minimum zone (e.g. for VERTEX III total stenone:total stanone ratios were 6.7, 2.0 and 6.8 at 100, 470, and 1500 m, respectively), but in the WHISP samples the ratio goes through a maximum in the oxygen minimum zone (0.5, 6.6 and 2.3 at 60, 450, and 1500 m, respectively).

An alternative source for steroidal ketones associated with particles is an *in-situ* biogeochemical transformation of biogenic sterols (steroid ketones are intermediates in the stenol → stanol conversion). Microbial oxidation of sterols to steroid ketones has been demonstrated in several experimental studies (Bjorkhem and Gustafsson, 1971; Eyssen *et al.*, 1973) and inferred in field investigations (Gagosian *et al.*, 1982; Wakeham and Canuel, 1986). Conversion of sterols to steroid ketones in the VERTEX samples is suggested by increased steroid ketone: sterol ratios with increasing depth for both sinking and suspended particles. For VERTEX III, steroidal ketone: sterol ratios

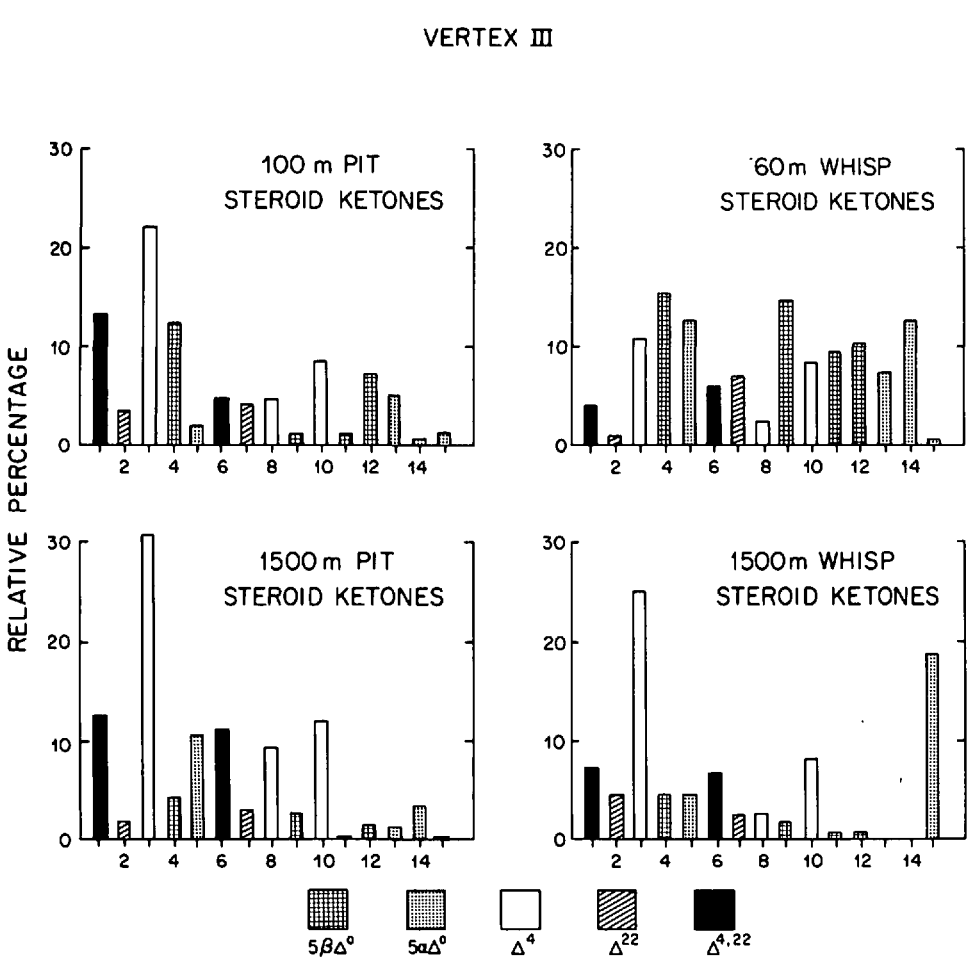

Figure 7. Histograms of relative abundances of steroid ketones for VERTEX III 100 and 1500 m PITs and 60 and 1500 m WHISPs. Bar numbers refer to Table 3; bar patterns refer to double bond configuration and $5\alpha/5\beta$ indicate the stereochemistry at the 5-carbon in stanones.

in the traps increased from 0.01 at 100 m to 0.04 at 1500 m, while ratios in the pump samples ranged from 0.15 at 5 and 60 m to 0.6 at 450 m and 0.4 at 1500 m. Note also the marked increase in abundance of dinostanone (4,23,24-trimethylcholestan-3-one) in the 1500 m WHISP relative to the 60 m WHISP in conjunction with a simultaneous decrease in the abundance of its possible precursor dinosterol (4,23,24-trimethylcholest-22-en-3β-ol; Fig. 6). Thus there is evidence of a microbial transformation sequence involving stenol → steroid ketone → stanol → steroidal hydrocarbon (sterenes; Wakeham *et al.*, 1984a; Wakeham, 1987) conversions on suspended particles in the oxygen minimum zone.

d. Processes controlling the organic composition of particulate matter. Vertical profiles of sinking particulate organic carbon flux (e.g. Knauer *et al.*, 1979; Honjo, 1980; Betzer *et al.*, 1984; Karl and Knauer, 1984a) and suspended particulate carbon concentration (reviewed by Simpson, 1982) have been reported for many oceanic regimes. Particulate organic carbon distributions in the oceanic water column indicate a coupling between POC flux, surface water primary production and complex decomposition, ingestion, disaggregation, and solubilization processes during vertical transport from the upper ocean to the sea floor (Knauer *et al.*, 1979; Honjo, 1980; Suess, 1980; Deuser, 1986; Martin *et al.*, 1987). Depth distributions of POC at the VERTEX II/III site fit this pattern.

Vertical profiles of particulate lipids and similarities between lipid compositions of particles in the upper ocean and organisms inhabiting the euphotic zone suggest that the dominant source of particulate lipids is upper ocean production. Most of the lipids are degraded before particles exit the euphotic zone. Our lipid analyses also show considerable differences in organic composition between suspended particles and sinking particles in the epipelagic zone. Suspended particles contain more of a phytoplankton signature and less of a zooplankton signature than sinking particles. The VERTEX results are in agreement with lipid analyses of size-fractionated particulate material in other areas (Wakeham *et al.*, 1985; Gagosian *et al.*, 1983; Repeta and Gagosian, 1984; Saliot *et al.*, 1982).

The organic composition of particulate material at mid-depth will reflect inputs of organic compounds via sinking from the surface and deep-water production and removal of compounds by heterotrophic consumption. Recent evidence suggests that biological production of organic matter and organic compounds does indeed occur in the mesopelagic zone (Karl and Knauer, 1984a,b; Wakeham *et al.*, 1984b). Karl and Knauer (1984a,b) conducted *in-situ* experiments during VERTEX cruises which show isolated regions of microbial productivity at mid-depth in which organic matter production results in small but apparent increased carbon flux into sediment traps. During VERTEX III, the increased microbial production was centered in the oxygen minimum zone between about 300 and 800 m depth. Karl and Knauer proposed that this *in-situ* carbon production is the result of chemolithotrophy supported by the vertical transport of allochthonous energy in the form of reduced end-products of organic matter decomposition. At VERTEX III, they estimated that 90% of the microbial production at 550 m was chemolithotrophic, but this microbial production was only 0.1% of the primary productivity.

Microbes are present on or within particles throughout the water column (Gowing and Silver, 1983) and are important members of the pelagic marine food web (Pomeroy, 1984; Williams, 1981; Azam *et al.*, 1983). Gowing and Silver (1983) and Karl and Knauer (1984a) have concluded from VERTEX data that sinking particles contain a much more active microbial community than suspended particles. Bacterial marker fatty acids are present in the PIT and WHISP particles, and distributions of

steroid ketones reported here and steroid hydrocarbons reported previously (Wakeham *et al.*, 1984a) probably result from microbial alterations of particulate organic matter. Analyses of particulate amino acids by Lee and Cronin (1984) at the VERTEX II/III site also support microbial decomposition of particulate organic matter. For example, an inverse relationship was observed between dissolved oxygen and the relative molar concentration of ornithine, an indicator of decomposing algal material. However, although microbial processes probably play an important role in modifying particulate organic matter which is biosynthesized by other organisms, there was no obvious increase in a microbial signature in the lipids reported here. This is because microbial lipids are not greatly different from phytoplankton and zooplankton lipids and any differences may be masked by phytoplankton and zooplankton lipids present in greater amounts.

Zooplankton and fish alter the organic composition of particles, living and detrital, ingested during feeding. Alterations occur via enzymatic reactions during assimilation or by transformations by gut microflora, the final end product being fecal matter which may have a significantly different composition than the animal's diet (see review by Corner *et al.*, 1986). Organic matter in fecal pellets may continue to be degraded after defecation because of fresh inocula of gut microorganisms from the animals. Volkman *et al.* (1980a), Prahl *et al.* (1984) and Harvey *et al.* (1987) found marked differences between lipids in zooplankton and their phytoplankton diet. Material defecated by the animal contained extensively modified algal lipids as well as compounds endogenous to the zooplankter. For example, zooplankton-derived compounds not present in the algae were found in fecal pellets, while algal sterols and fatty acids were efficiently metabolized by the zooplankton. Other lipids may be more stable against metabolism. Unsaturated C_{37} and C_{38} methyl and ethyl ketones have unique algal sources (Volkman *et al.*, 1980c; Marlowe *et al.*, 1984), and, despite their high degree of unsaturation, appear to be more resistant to degradation than other compounds; thus initial experiments by Volkman *et al.* (1980a) suggest these ketones may be enriched in fecal matter relative to the algal source.

Feeding mechanism can determine which compounds are metabolized and which compounds are preserved. The effect of herbivory and subsequent coprophagy was investigated in the laboratory by Neal *et al.* (1986) who followed changes in lipid composition during a planktonic feeding sequence involving barnacle nauplii feeding on unicellular algae, and adult copepods feeding on barnacle nauplii fecal pellets. Fecal pellets produced during coprophagy and herbivory showed minimal differences in fatty acid composition, while a much wider range of plant sterols were present in fecal pellets of *Calanus* feeding by coprophagy compared with direct herbivory. Modification of organic compounds continues up the food web as shown in a laboratory study of carnivorous feeding of fish on zooplankton (Prahl *et al.*, 1985). During VERTEX III the organic composition of fresh fecal pellets of the pelagic crab *Pleuroncodes planipes* was compared to their presumed dietary zooplankton (Wakeham and Canuel, 1986).

Fatty acids were the most abundant lipid in the zooplankton, but passage of ingested material through the gut of the crab yielded fecal pellets depleted in fatty acids and enriched in sterols. Steroidal hydrocarbons and ketones, absent from the zooplankton, were detected in the crab feces and were ascribed to be tranformation products generated from dietary sterols by enteric flora of the crab. Fecal pellets of *P. planipes* made an important contribution to the vertical flux of inorganic (Coale and Bruland, 1987) and organic materials (Wakeham and Canuel, 1986) during VERTEX II and III.

Preformed organic matter provides heterotrophs with energy, with essential organic compounds which the organism is unable to synthesize, with dietary substrates to be biochemically converted to essential compounds which cannot be synthesized, and with elements which may be used in de-novo synthesis of a new suite of organic compounds. The result is that the organic composition of the consumer and any particulate matter derived from it can be very different from the material initially consumed, with the changes occurring to meet specific metabolic requirements of the consumer. Most phytoplankton are autotrophic and thus synthesize constituent fatty acids de novo. Animals, on the other hand, are unable to synthesize de novo essential polyunsaturated acids (e.g. 18:2, 18:3, 20:4, 20:5, 22:6), and zooplankton must obtain polyunsaturated acids directly from phytoplankton they consume or indirectly via chain elongation and desaturation of dietary fatty acids (Sargent, 1976). In a similar manner, zooplankton are generally incapable of de novo synthesis of sterols needed for membrane structure and regulation of metabolic processes. Herbivorous zooplankton must convert dietary C_{28} and C_{29} phytosterols into C_{27} cholesterol by dealkylation (Goad, 1981); carnivores obtain C_{27} sterols directly from their diet. Copepods often elaborate and store large amounts of wax ester as an energy reserve against periods of food scarcity, even though the diet of herbivorous copepods contains no wax ester. Some deep water and high latitude species of copepods may contain 70–90% of their dry weight in the form of wax esters. The fatty acid composition of wax esters tends to reflect dietary fatty acids whereas the fatty alcohols may be both dietary or may be synthesized de novo by the animal following complete breakdown of dietary fatty acids. Deep-sea bacteria and fish maintain membrane fluidity at elevated hydrostatic pressures and decreased temperature by increasing the proportions of unsaturated fatty acids. Therefore lipid compositions of mesopelagic organisms can be significantly different from the particles they consume and from similar classes of organisms inhabiting surface waters.

e. Particle dynamics inferred from organic geochemical results. Physical models of deep-ocean particle dynamics describe a particle field consisting of many suspended fine particles and a few rapidly sinking aggregates (McCave, 1975). Radioisotopic measurements show that fine material moves through the water column at 1–3 m/d (Krishnaswami *et al.*, 1981; Bacon and Anderson, 1982) while laboratory studies and field observations show that fecal pellets and marine snow may sink at rates of

tens-to-hundreds of m/d (Small *et al.*, 1979; Alldredge, 1979; Shanks and Trent, 1979; Bruland and Silver, 1981; Silver and Alldredge, 1981; Madin, 1982; Asper, 1987). If, for the sake of this discussion, we assume that the two size classes remain distinct, then the organic matter composition in each class should be different, and, more importantly, small suspended particles with long residence times might consist of a highly degraded and refractory residue while large sinking particles might be relatively "fresher" because of the shorter timescale between their production and collection in the sediment traps. Our observations do not support this model. Bacon *et al.* (1985), on the other hand, have described a model in which there is continuous exchange of material between the two size classes. Aggregation, or scavenging of fine material by macroaggregates (McCave, 1984), occurs throughout the water column and must be accompanied by disaggregation. Thus a particle is exchanged several times between a freely suspended particle pool having a minimal settling velocity and a population of rapidly sinking aggregates. This concept would suggest that there be close similarities in chemical composition between small and large particle populations. Our results do not appear to support this model either.

Resolution of this apparent dilemma requires modification of existing models of particle dynamics such that there be a mechanism by which trap-collected material at mid-depth has been extensively reworked but suspended material can still contain a significant labile component apparently originating in surface waters. Sediment traps will collect sinking particles, including fecal pellets and amorphous fecal matter and marine snow. As discussed above, feces will contain a mixture of residual unmetabolized dietary material, compounds excreted by the animal, and transformation products resulting from action of enteric microbial populations. Thus particles containing fecal matter may appear on average to be highly reworked relative to particulate material produced in surface waters, even though these large particles may have sinking velocities in the range of tens-to-hundreds of meters/d and may reach the mesopelagic zone in a few days or weeks. However, in general fecal pellets do not appear to be contributors of POC to mid-water traps, perhaps typically only 10–20% of the POC flux (Pilskaln, 1985; M. W. Silver and M. M. Gowing, pers. commun.). Large detrital associations of marine snow may provide an additional, and quantitatively more important, mechanism for rapid vertical transport of aggregations of fecal matter and intact and often viable phytoplankton (Alldredge and Cox, 1982; Silver and Alldredge, 1981; Knauer *et al.*, 1982; Platt *et al.*, 1983; Silver *et al.*, 1986). Marine snow represents some 25–40% of the carbon flux at several VERTEX sites and 10% of the POC flux at 1000 m (M. W. Silver and M. M. Gowing, pers. commun.). As they sink, these macroaggregates intercept and accumulate fine, suspended particles, incorporating them into larger packages having sinking velocities faster than the constituent parts. Physical considerations (McCave, 1984) suggest that biologically-mediated aggregation processes will be far more important than physical aggregation in the formation of marine snow, and in fact entire communities of phytoplankton and

bacteria are associated with these macroaggregates (Silver *et al.*, 1986). Although the specific organic composition of marine snow-type particles has yet to be determined, the inclusion of undergraded algal cells might make its organic composition appear fresh and "phytoplanktonic" in appearance.

As to the apparent abundance of relatively undegraded phytoplankton "marker" lipids associated with fine particulate matter collected by *in-situ* filtrations at mid-depth, the total numbers of suspended algal cells in the deep-sea argues for rapid delivery rates (Silver *et al.*, 1986). Phytoplankton cells at depth, the so-called "olive green cells" (Fournier, 1970, 1971; Silver and Bruland, 1981), must have originated in surface waters, and dispite negligible sinking velocities, pico- and ultra-plankton are numerically abundant in deep water (Silver *et al.*, 1986). Photosynthetically-competent algae have been recovered from aphotic depths by Platt *et al.* (1983). Fecal pellets (e.g. Platt *et al.*, 1983; Fowler and Fisher, 1983) and marine snow (Silver *et al.*, 1986) will again be the probable mechanism for rapidly transporting intact algal cells into the mesopelagic zone and thereby sustaining the suspended pool of cells. Massive pulses ("clouds") of algal material reaching the deep-sea, presumably as large particles, have been reported (Honjo *et al.*, 1982; Billett *et al.*, 1983; Smetacek, 1985) and may provide a seasonal control over the introduction of phytoplankton-derived organic matter to the mid-water column. In order to contribute to the suspended particle pool, however, large particles of whatever origin must disaggregate, either due to physical or biological processes. Disintegration of fecal pellets will be highly dependent on the stability of the peritrophic membrane, if present, and the intensity of coprophagy and microbial decomposition. Calculated mass fluxes for marine snow based on sinking velocities ranging from 1 m/d for 4–5 mm aggregates to 36 m/d for 1–2.5 mm are greater than the measured flux determined in sediment traps and indicate that substantial numbers of these aggregates are lost by disaggregation or grazing (Asper, 1987). Organic compound distributions in suspended particles suggest that a major source of suspended organic matter is phytoplankton transported by marine snow rather than the degraded material carried to deep water in fecal pellets.

Several points need further elaboration. Asper (1987) has shown evidence that lateral transport of flocculent, and hence resuspended, material off the continental shelf may contribute to the pool of marine snow in the ocean's interior. This process cannot, however, yield the organic composition we observed for suspended particles, since sedimentary material, even the "surface floc," is relatively degraded compared to particulate material in the water column (Wakeham *et al.*, unpublished results). Moreover, it seems unlikely that a short-term pulse of algal material from a phytoplankton bloom at the surface is responsible for the labile compounds associated with suspended particles. Both VERTEX II and III cruises were late in the year (October-November) at a time when blooms would not be expected. In addition, similar particle size and depth differences have been observed for particles at the oligotrophic VERTEX IV site off Hawaii (sampled in early summer, 1984) (Wakeham *et al.*, unpublished results), leading to the conclusion that our observation may

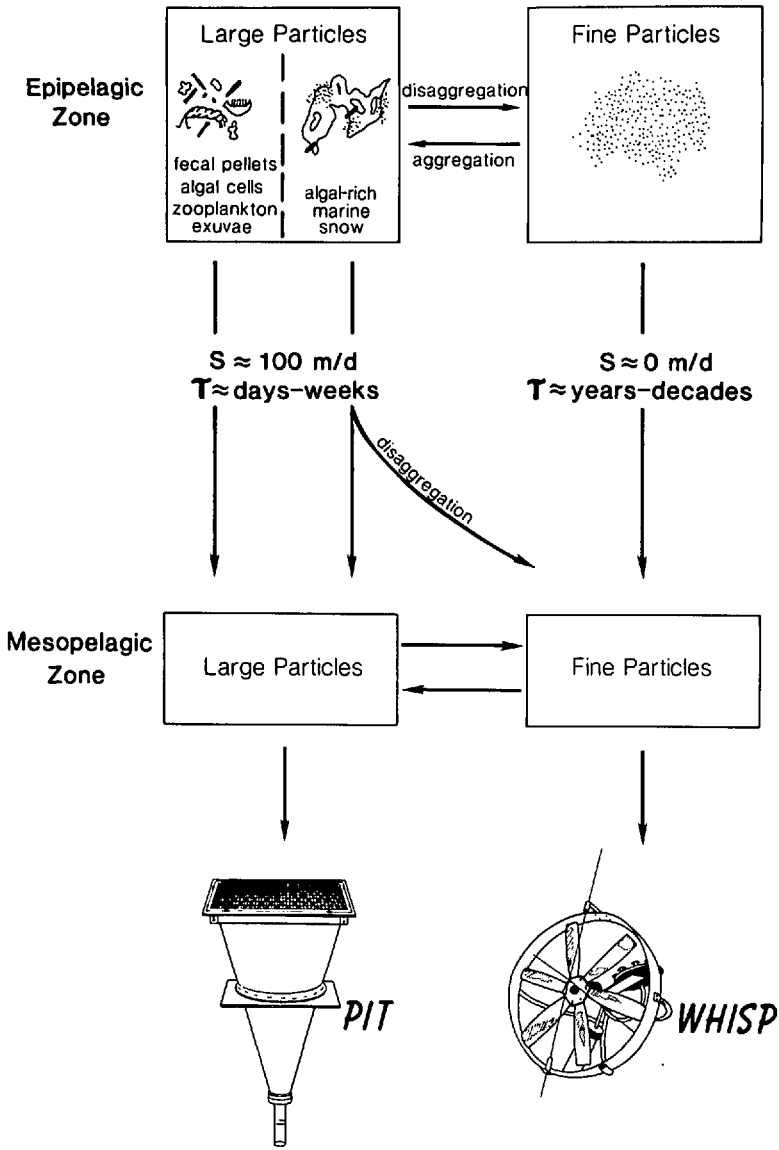

Figure 8. Conceptual model of particle dynamics in the upper 1500 m of the ocean. Particle sinking rates are from Bacon *et al.* (1985).

represent a general oceanic condition rather than an isolated situation. Finally, the differences in organic composition for particulate matter as discussed are valid only on a relative basis. For example, it is impossible to quantify the amounts of "degraded" vs. "undegraded" material in each particle size class. Inclusion of only a few percent of undegraded algal material in the suspended particle pool compared to the sinking

particle pool, say, for the sake of argument, 4% vs. 2%, could result in a doubling of the labile signature of suspended particles, but without having undegraded materials make a major quantitative contribution to POC as a whole.

In summary, it would appear that particulate organic matter collected in sediment traps and by *in-situ* filtration at mid-depth in the ocean represents very distinct particle classes, not only in terms of particle size but also in their organic composition. The behavior and composition of particulate matter in the mesopelagic zone is best described by a model involving a slowly sinking suspended particle pool but with two classes of sinking larger particles (Fig. 8). One large particle pool contains a distribution of organic compounds which are indicative of intensive alteration of organic matter during transport from the euphotic zone to mesopelagic depths. This material is collected in sediment traps. The second large particle pool contains a larger proportion of apparently undegraded algal cells, perhaps bound loosely together in marine snow aggregates, and rapidly carries them from surface waters to depths of 1000–2000 m. Disintegration of these particles at depth will contribute relatively undegraded algal material to the suspended particle pool sampled by *in-situ* filtration.

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