PROJECT SUMMARY

Sinking particulate matter is the major vehicle for exporting carbon from the sea surface to the ocean interior. During its transit towards the sea floor, most particulate organic carbon (POC) is returned to inorganic form and redistributed in the water column. This redistribution determines the surface concentration of dissolved CO_2, and hence the rate at which the ocean can absorb CO_2 from the atmosphere. The ability to predict quantitatively the depth profile of remineralization is therefore critical to predicting the response of the global carbon cycle to environmental change.

We hypothesize that minerals produced by organisms, or introduced into the surface ocean by winds, critically influence carbon export to the deep ocean and sediments. Minerals typically constitute more than half the mass of sinking particles, and are important for making less dense organic matter sink. Minerals may also protect organic matter from degradation, allowing it to penetrate deeper into the ocean. We recently demonstrated (a) that ratios of particulate organic carbon to mineral ballast converge to a nearly constant value (~6 wt% OC) at depths >1800 m, and (b) that decreases in flux of over two orders of magnitude are attended by minimal changes in bulk organic composition. Because these patterns are the hallmark of physical protection, we hypothesize that a substantial fraction of particulate organic matter raining through marine water columns is protectively associated with mineral grains. Thus, the types and amounts of mineral ballast introduced to the surface ocean may be critical, although largely overlooked, determinants of the ocean's ability to take up and store bioactive elements

We propose here a multi-tracer approach to explicitly consider different ballast types, along with the associated organic matter and radioisotopes. **Hypothesis 1** is that ballast minerals physically protect a fraction of their associated total organic matter, which persists to predominate over the unprotected fraction in the lower (>1000 m) part of the water column. Understanding the mechanistic basis of such processes will require an understanding of organic-mineral interaction at the compound-specific level. **Hypothesis 2** is that the ratio of organic carbon to ballast is key to predicting variability in the export fluxes and sinking velocities of organic carbon as estimated using radiotracers.

Our overall goal is to develop a seamless description of carbon fluxes and associated mineral ballast fluxes throughout the water column. To achieve this goal, we propose to measure simultaneously a suite of properties that are thought to be indicative of fluxes. We will synthesize these measurements from the top of the water column to the sediments using a variety of modeling and statistical techniques. Our strategy is to unite the power of several disciplines: (i) organic geochemistry for characterizing organic matter in protected and unprotected forms and determining its degradation state; (ii) radiochemistry for assessing processes and time-scales involved in particle dynamics and transport; (iii) zooplankton ecology for assessing radioisotope partitioning and organic biomarker alteration; and (iv) microbiology for its role in organic matter decomposition, and (v) modeling and statistical analyses to provide a process-based model of flux out of the euphotic zone to the sea floor.

1. RESULTS FROM PRIOR NSF SUPPORT

The ideas presented in this proposal result directly from research conducted during the course of the NSF-funded grants on organic geochemistry, radioisotopes, and modeling cited below.

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"Organic geochemical studies in the Southern Ocean" 6/96-7/99, Lee ($254,535; OPP/OCE 95-30891); Hedges ($293,001; OPP/OCE 95-9531763), Wakeham ($252,458; OPP/OCE 95-31759)

During the U.S.JGOFS study, we determined compositions and fluxes of particulate organic matter (POM) raining through the water column. Our goal was to use individual organic compounds as source and diagenetic indicators to reconcile water column production and sinking POM fluxes with corresponding sediment delivery, accumulation, and preservation. Our research assessed sources of organic compounds; their relative reactivities; their accumulation in sediments; the fraction of POM that can be characterized at the molecular level; and how that fraction changes with depth. We investigated POM at sequential stages of transport and diagenesis from the surface ocean to underlying sediments. In the equatorial Pacific, comparisons of amino acids, sugars, and lipids indicate that molecular-level characterization accounts for less total POM with depth: 80% in floating traps, ~25% in deep traps, and ~20% in surface sediments. Highest absolute changes occurred in the upper 100-1000 m. In the Arabian Sea we evaluated effects of monsoon-driven pulses of primary production and the resultant O_2-minimum zone on POM flux and biochemical composition. Strongly bimodal fluxes were observed during monsoon periods, and relative proportions of uncharacterized material increased with depth. In the Southern Ocean we addressed how seasonally-pulsed primary production is transmitted by POM through the water column into the sediments. Our initial data corroborate previous results. We interpret the increase in relative abundance of uncharacterized material as the result of more labile molecules degrading or being incorporated into macromolecular material. During this research we came to appreciate that mineral ballast might play a vital role in both transport and physical protection of POM, and might influence the composition of material reaching the sediment. These ideas are presented in recent papers and are the basis of this proposal. Three undergraduates, 5 graduate students, and 1 postdoc were supported by this research. Papers below resulted from the above grant are marked in the Bibliography with *.

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"Thorium isotopes as indicators of export flux and particle dynamics in the Southern Ocean: Joint Global Ocean Flux Study", 5/96-7/00 ($281,236; OPP 96-12761)

The use of thorium isotopes (principally ^{234}Th and ^{228}Th) as tracers of portions of the carbon cycle has involved a collaborative effort of Cochran with M. Bacon and K. Buesseler at Woods Hole Oceanographic Institution. The objectives have been twofold: 1) to use export flux of ^{234}Th (half-life = 24.1 days) from the euphotic zone as an indicator of sinking flux of particulate organic carbon (POC), and 2) to use ^{234}Th and ^{228}Th (half-life = 1.9 years) to derive rates of aggregation and disaggregation between small and large particle reservoirs. Data have been collected from the North Atlantic, equatorial Pacific, and Southern Ocean. Our experiences using Th isotopes as tracers for carbon cycling in the oceans provide the basis for the present proposal. In particular, flux estimates of POC made from water column profiles of ^{234}Th require measurement of POC/Th ratios on sinking particles. In prior work we have used large particles (either >53 or >70 μm) filtered by in situ pumping as well as sediment trap material. In research proposed here we will measure POC/Th ratios on particles in multiple size classes sinking at different rates to refine estimates of POC flux determined by the ^{234}Th method. Three graduate students and one postdoc were supported by this research. Papers resulting from the above grants appear in the Bibliography marked by †.

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"Observation-based models of ecosystem processes controlling oceanic distributions of nutrients and carbon" 6/97-6/00, Sarmiento, PI; Armstrong, co-PI ($460,000; OCE-9712204)

The purpose of this grant was to develop the infrastructure for a next-generation carbon cycle model. The fundamental premise we followed is that the structure of the next-generation model must be

determined from below; that is, (i) the model of deep-water remineralization must be of central importance, since it determines the partitioning of carbon between oceanic reservoirs, and (ii) the requirements for the photic zone model must be determined by the remineralization model, not the reverse. We found that the types and quantities of mineral ballasts are crucial for predicting remineralization. Predicting abundances of phytoplankton size classes and taxa responsible for different biogenic ballast types (opal; carbonate) then becomes a central requirement for ecosystem modeling. In this regard, we developed the structure needed to capture systematically both size and taxonomic diversity, while also conforming to well-established results concerning algal size spectra. In addition, a mechanism-based iron model was used within each size and taxonomic category to represent the transition between "normal" and High Nutrient Low Chlorophyll conditions. Papers resulting from this work appear in the Bibliography marked by ‡.

2. INTRODUCTION

Sinking particles are the major vehicle for transporting organic carbon from the sea surface to the ocean interior and sediments. Most of the particulate organic carbon (POC) exported from the surface ocean is remineralized (returned to inorganic form) in the first thousand meters of its descent; the remainder survives to the deep ocean and sediments, where its carbon can be sequestered for millennia. Currently, model descriptions of this process assume that a constant fraction of the organic carbon exported from the photic zone is remineralized at a given depth (Martin et al. 1987). This description implies that there should be a tight quantitative relationship between export production and the amount of carbon reaching the sediments. Recently, Armstrong and Jahnke (2001) showed evidence for a major spatial disconnect between surface production and benthic oxygen demand, an indicator of the amount of POC reaching the sediments. As their prime example, they showed that production in the North Atlantic exhibits a steep north-south gradient, whereas benthic oxygen demand shows no north-south gradient, but instead a gradient from high values along coasts to lower values in the central basin. This disconnect is doubly disconcerting because it is large: ratios of production to benthic oxygen demand can vary by two orders of magnitude. Clearly, a better quantitative, mechanistic understanding of this critical link in the oceanic carbon system is essential to our ability to predict the ocean's role in the global carbon system (Sarmiento and Armstrong 1997).

One of the greatest challenges in describing and predicting global cycles of C and other bioactive elements has been to understand and predict rates of degradation and remineralization of organic matter in soils, sediments, and the ocean. Remineralization rates for organic detritus have been particularly difficult to establish due to the myriad molecular structures that comprise organic matter, the contrasting microenvironments in which they occur, and the diversity of biological agents of degradation. To describe this complexity, remineralization of bulk organic matter has been modeled as the sum of multiple individual components that break down at different rates. Recent research on organic detritus in soils and sediments suggests that resistance to degradation of slow-reacting components is due primarily to physical protection by association with mineral grains, rather than intrinsic chemical stability of individual compounds. In the ocean, we recently demonstrated (a) that ratios of particulate organic carbon to mineral ballast converge asymptoticaly to a nearly constant value (~6 wt% POC) at depths >1800 m (Armstrong et al. 2001), and (b) that decreases in flux of over two orders of magnitude are attended by minimal changes in bulk organic composition (Hedges et al. 2001). Because these patterns are the hallmark of physical protection, and because biominerals typically represent at least half of the

mass of sinking marine particles, we hypothesize that a substantial fraction of particulate organic matter raining through marine water columns is protectively associated with mineral grains. Thus, the types and amounts of mineral ballast introduced to the surface ocean may be critical, although largely overlooked, determinants of the ocean's ability to take up and store bioactive elements.

In the ocean water column, depth profiles of sinking particle flux and dissolved nutrient and O_2 concentrations indicate that remineralization profiles of POC vary substantially with location and biological community structure. Nevertheless, all profiles are characterized by rapid attenuation of POC flux in the mesopelagic zone between the base of the euphotic zone (~100 m) and roughly 1000 m, below which <10% of the export flux remains (Fig. 1). The pronounced increase of slope with depth demonstrates that length scales of remineralization increase with depth. Explanations commonly offered for this behavior include the existence of different reactivity classes of organic matter (Berner 1980) that attenuate sequentially with depth or time, and/or more extensive heterotrophic processing of organic matter in the biologically more active upper water column.

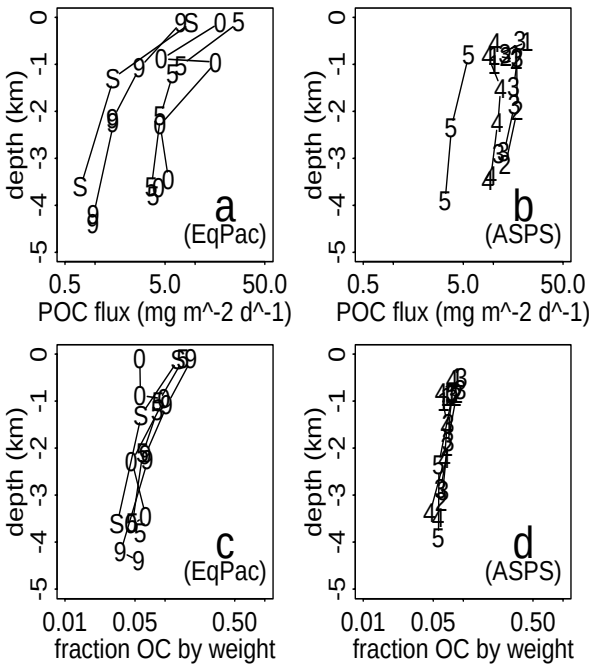

Fig. 1. Fluxes of particulate organic carbon normalized to mass flux are much less variable than are plots of POC flux alone (Fig. 1 from Armstrong et al. 2001). Scales of all abscissas span two orders of magnitude, facilitating visual comparison of slopes and variability across sites. Note particularly the tight clustering of profiles in c relative to a, and in d relative to b.

Here we suggest that association of organic carbon with particulate "ballast" minerals (carbonate, silicate, and dust) plays a key, and perhaps dominant, role in lengthening the remineralization scale with depth. Recent results (Armstrong et al. 2001) suggest that deep-water fluxes of organic carbon are directly proportional to total fluxes of ballast minerals at these depths, and that variability in this ratio (6±1%) may be quite small (Figs. 1c, d). In contrast, absolute carbon fluxes are much more variable (Fig. 1 a,b). This observation suggests that we must understand the quantitative relationship between POC and ballast minerals if we are to be able to predict how much organic carbon will reach the sea floor and how much will be remineralized in the water column. While our present model (Armstrong et al. 2001) makes good predictions for deep-water fluxes, and fits flux data from the equatorial Pacific much better than does the

empirically-based curve of Martin et al. (1987), it cannot accurately predict length scales of remineralization near the sea surface. This is a critical shortcoming, since most remineralization occurs in the top several hundred meters of the water column. We believe that understanding the relationship between organic carbon and ballast minerals will be key to improving our ability to predict POC fluxes in this region of the water column, as it appears to be in the deep ocean.

Minerals typically constitute more than half the mass of particles sinking from the ocean surface (Honjo 1980, Honjo et al. 1982, Ittekkot and Haake 1990, Honjo 1996). Marine plankton contribute biominerals (e.g., opal by diatoms and radiolarians, and $CaCO_3$ by coccoliths and foraminifera). Detrital minerals (largely quartz and aluminosilicates) introduced from land by rivers and wind also can become associated with marine plankton (or their remains) in fecal pellets, marine snow and other aggregates. Densities of opal, carbonates and aluminosilicates are around 2.5, whereas values of 0.8-1.2 are typical of most organic materials in their natural hydrated forms. The corresponding excess densities ($\rho_{particle} - \rho_{seawater}$) of inorganic and organic particles over that of seawater ($\rho \approx 1.03$) are therefore ≈ 1.5 and 0.1, respectively. Given that the settling rate of a spherical particle is directly proportional to its excess density (Stokes' Law), pure mineral can be expected to sink at least 10 times faster than a particle of pure organic matter having the same size and shape.

Although “mineral ballasting” sometimes has been taken into account in studies of the sinking rates of individual shell-forming organisms (Ittekkot and Haake 1990; Honjo 1996), as well as fecal pellets and other aggregates, mineral content is rarely included explicitly in current concepts or numerical models of regeneration and sinking of particulate material exported from the euphotic zone. For example, diatoms are traditionally considered strong contributors to POC export because they are "large" and subject to less total "biological processing" during export and sinking, whereas the major impact of diatoms on export may be that they provide ballast to sinking particles.

Along with simple ballasting, minerals have the potential to physically protect from degradation the organic matter with which they are associated (Hedges and Oades 1997, Nelson et al. 1999). This “protection” effect is most clearly exemplified by organic matter constituting the template upon which biominerals are formed (Lowenstam and Weiner 1989, Knicker et al. 1996). Once incorporated within the biomineral matrix, these organic templates (usually rich in glycoprotein) are inaccessible to bacterial degradation and can be expected to persist as long as the surrounding mineral remains intact (King 1974, Robbins and Brew 1990). However, concentrations of organic matter within opal and calcium carbonates in sediments are typically small (<1 wt% OC), which limits quantitatively the possible contribution of matrix organic matter to carbon fluxes to the deep water column and marine sediments. In addition to being protected within biominerals, organic matter also can be physically protected outside mineral grains. This phenomenon is now well established for both soils and marine sediments, although specific mechanisms involved are as yet unclear (Mayer 1994, Hedges and Keil 1995).

We hypothesize that variations in sinking velocity and physical protection will determine depth distributions of remineralization in the upper water column where most organic matter recycling occurs, and that explicit consideration of mineral ballasts - qualitatively, quantitatively, and dynamically - is needed to improve our understanding of (and capability to predict) carbon fluxes

in the sea. Indeed, variability in ballast minerals may ultimately determine variability in deep-ocean POC fluxes more than does primary production.

In pursuing this goal, we will work towards the mesopelagic zone from both ends of the water column: down from the mixed layer and up from the deep sea. First, we will extend our investigation of asymptotic POC:mineral ballast ratios in the deep ocean by investigating quantitatively and mechanistically the association of POC at the molecular level with different types of ballast, and will extend these investigations upwards into the mesopelagic zone. Second, we will investigate the extent to which POC:ballast relations determine variability in shallow-water fluxes estimated using natural radionuclides (^{234}Th and ^{210}Po). Integral to this investigation will be investigations of sinking velocities of particles and aggregates, and how these relate to quantities that are measured in thorium-based studies, including analysis of organic and mineral compositions of particles with different densities and different sinking velocities. Finally, we will combine information gained from investigations of organic, inorganic and radiochemistry, and zooplankton and microbial ecology with that of sinking velocities measured in the field to extend this knowledge into the mesopelagic zone.

3. PRINCIPAL HYPOTHESES

We propose direct tests of two principal hypotheses. Underlying these hypotheses is the goal of producing a process-based model description of export and remineralization that extends through the entire water column. We believe that a better understanding of mineral-organic associations and protection will enable construction of a predictive theory of carbon flux in all parts of the water column. We will determine the quantitative importance of various mechanisms that could couple delivery of mineral material and organic carbon to depth, particularly those that influence organic matter remineralization in the water column. We believe that a comprehensive, multidisciplinary approach studying all parts of the water column simultaneously is the most efficient – and probably the only – way to achieve a seamless, top-to-bottom description.

Hypothesis 1: Ballast minerals physically protect a fraction of their associated total organic matter, which persists to predominate over the unprotected fraction in the lower (>1000 m) part of the water column. The association of organic compounds with ballast minerals may be different in the mesopelagic than in the lower water column.

The hypothesis that minerals protect organic matter from degradation has yet to be demonstrated for water column particles, and remains mechanistically undefined even for marine sedimentary materials. In addition, the observation that ratios of POC to mineral mass in particles sinking through the lower water column asymptotically approach ~0.06 has plausible explanations in addition to protection. One of these is that marine POC includes a fraction that is not actually protected, but occurs in relatively constant proportion to minerals and degrades independently at a comparable rate. Alternatively, marine aggregates may require roughly 5-10 wt% of organic "binder" to maintain the physical integrity needed to sink through the water column. Even if physical protection can be demonstrated for sinking POC, the goal of quantitative prediction will require determining protection capabilities of different minerals, plus confirmation that masses of protected organic matter and minerals are lost at a constant ratio during mineral dissolution. For interpretive and modeling purposes it would be useful to determine the extent to which matrix- and externally-protected organic materials persist in the deep ocean and whether compositional

characteristics of either fraction can be identified for different mineral types. If so, and if these two sub-fractions degrade at different rates, then it might be possible to estimate how extensively different mineral types and associated biochemicals have been recycled in the water column and the subsequent impact on the vertical fluxes of carbon and other bioactive elements.

Understanding the mechanistic basis of such processes will require an understanding of organic-mineral interaction at the compound-specific level. The application of statistical approaches (see below) will allow us to characterize degradation state to a new level. Our previous organic geochemical analyses of fast-sinking POM in the equatorial Pacific (EqPac) and the Arabian Sea have shown exponential losses of planktonic compounds and increased contributions of POM by bacterial and zooplankton heterotrophs throughout the water column and surface sediments, and preservation of selected remains of bacteria, phytoplankton, and vascular plants deeper in the sediments (Hernes et al. 1996; Wakeham et al. 1997b; Lee et al. 2000; Wakeham et al. 2000; Wakeham et al. 2001). Diagnostic lipid, amino acid, carbohydrate and pigment biomarkers fell into groups according to their origin and diagenetic behavior: (1) compounds derived from phytoplankton that are subject to intense heterotrophic alteration dominate surface water POM; (2) resistant phytoplankton compounds or biochemicals that are produced at depth by heterotrophs are most abundant in the mid- and deep-water column; (3) compounds that are produced by early diagenesis are enriched in surface sediments; and (4) refractory compounds resistant to microbial degradation are selectively preserved in deeper sediments (see Table 1). Other compounds useful in this regard include: muramic acid and D-amino acids characteristic of peptidoglycan (Salton 1960; Rogers 1983) and hydroxy fatty acids of lipopolysaccharides (Mayer et al. 1989) all specifically identify the presence of bacterial cell wall material. These and similar compounds will be used as indicators of source and diagenesis in this project.

Table 1. Representative molecular source and degradation indicators

PLANT SOURCE	HETEROTROPH SOURCE	DEGRADATION INDICATOR	MINERAL-PROTECTED ORGANICS
chlorophylls	D-amino acids - bacteria	Phaeopigments ↑	acidic amino acids – $CaCO_3$
carotenoids	muramic acid - bacteria	β-alanine ↑	hydroxy amino acids - opal
24-methylene-cholesterol	branched fatty acids - bacteria	unsaturated lipids ↓	xylose - opal
alkenones	glucosamine - chitin	Glucose/fucose ↓	long-chain n-alkanes - dust
dinosterol	cholesterol - animals	total biochemicals ↓	coccolith lipids – $CaCO_3$

Principal component analysis (PCA) offers a tool for further exploring sources and processing of POM. PCA is a multivariate ordination technique which reduces the number of variables in a data set by constructing "latent variables", or axes through which maximum variability in the data set is explained (Digby and Kempton 1987, Meglen 1992, ten Braak 1994). PCA transforms the data in a large data matrix into smaller matrices that are linear combinations of the original data set. Complex organic geochemical data sets have been analyzed using PCA (e.g., Reemtsma and Ittekkott 1992, Hayakawa 1996, Dauwe and Middleburg 1998, 1999; Wakeham et al 2001). Sheridan et al. (in prep) used PCA to evaluate diagenesis in our EqPac POM

samples. Site scores from the first axis of the amino acid composition PCA (Fig. 2) provides an index of organic matter degradation state for EqPac particles and sediments, after the approach developed by Dauwe and Middleburg (1998, 1999). The decrease in site score with more degraded particles demonstrates the diagenetic continuum from surface waters to sediments, but also suggests that midwater suspended particles were more labile than sinking particles at comparable depths, raising new questions about POM aggregation/disaggregation dynamics. Applying this approach to the full suite of diagenetic markers available to us will allow a quantum leap forward in our ability to characterize organic matter source and diagenetic state.

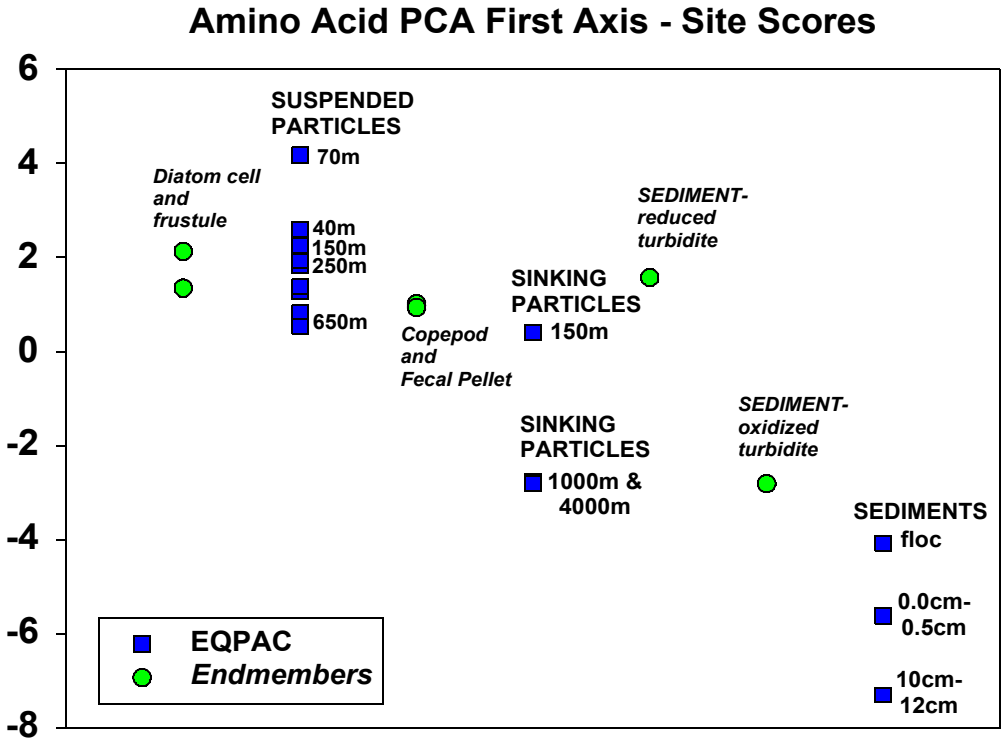

Fig. 2 First axis site scores from PCA of EqPac suspended particles, sinking particles, and sediments. PCA was conducted on amino acid molar ratios of material collected at equatorial (5ºN-5ºS) and higher latitudes (>5ºN, 5ºS). The first axis explained 50% of the variance in amino acid composition. Particle and sediment data is from Sheridan et al. (in prep) and Lee et al. (2000). Diatom, copepod, copepod fecal pellet, and turbidite sediment (end-member) data are from Cowie and Hedges (1996) and Cowie et al. (1995).

Hypothesis 2: The ratio of organic carbon to ballast is key to predicting variability in the export fluxes and sinking velocities of organic carbon as estimated using radiotracers.

The use of ^{234}Th (half-life = 24.1 d) to determine export fluxes of POC from the euphotic zone is based on determining the deficit of ^{234}Th relative to secular equilibrium with its parent ^{238}U in the water column (Buesseler et al. 1992a, 1995, 1998, 2000, Bacon et al. 1996, Murray et al. 1989, 1996, Dunne et al. 1997, Cochran et al. 2000). This deficit is produced by scavenging and

export of ^{234}Th by sinking particles. If such particles are also major carriers of organic C, POC flux may be determined by multiplying ^{234}Th flux by the POC/^{234}Th ratio on sinking particles. Determination of POC/Th on sinking particles is problematic because this value is most frequently estimated from the "large" particle size fraction (>53 or >70 μm) filtered by in-situ pumps. Where comparisons have been made (e.g., Murray et al. 1996, Amiel et al. 2001), ratios so determined often differ from values obtained in trap samples. The underlying presumption in this procedure is that particles caught on large filters are sinking, whereas those that pass the filter are not part of the sinking flux. This assumption may be seriously in error, for 3 reasons.

First, much of the flux of organic C and thorium may be in aggregates composed of a heterogeneous mix of large and small particles. These aggregates can be physically disrupted during filtration; some components of these aggregates will be caught on large filters, while others will pass through. Thus, appropriate C:Th ratios will not just be that of material caught on large filters, but will be a weighted average of material caught on large and small filters. Second, as carbon:ballast ratios may determine sinking velocities of both aggregates and isolated particles, variation in carbon:ballast ratios may produce a variation in size distribution of sinking particles as they are caught on filters. Finally, since Th is a surface-active element, the ratio of C to ballast may directly affect partitioning of Th onto fractions retained on filters of different mesh sizes. For example, studies of ^{234}Th scavenging in the western Mediterranean have shown that dust input (aluminosilicates) to the sea surface radically increases the ratio of ^{234}Th to POC removal, thereby affecting estimates of POC export from the euphotic zone (Lambert et al. 1991). In this respect, the natural radionuclide ^{210}Po (half-life = 138 d) may prove to be a useful counterpart to ^{234}Th in understanding controls on carbon:ballast ratios. Polonium-210 is produced mostly in situ from decay of ^{210}Pb, which itself is added to the surface ocean from the atmosphere and produced in situ from ^{226}Ra decay. Polonium is incorporated into organic matter rather than adsorbed onto particle surfaces, and as such should more closely follow the fate of C in sinking particles (Cherry et al. 1975; Heyraud and Cherry 1979). These considerations suggest that an increased understanding of processes controlling POC/^{234}Th of sinking particles is needed.

Studies conducted under this hypothesis will characterize the size distribution of particulate matter that is retained on filters of varying sizes. These results will be used to characterize the dependence on mineral content of Th partitioning among size fractions. These studies are important in themselves for develop-ing more reliable Th methodologies; they also provide information needed for interpreting studies of the mesopelagic zone. In particular, studies of ^{210}Po and ^{234}Th will be conducted in parallel, with the goal of developing measurement tools capable of extension into the mesopela-gic zone. Zooplankton feeding and microbial decomposition studies will allow us to characterize different partitioning of Th and Po among organic and inorganic components, and will be key to interpreting radioisotope profiles.

4. PROPOSED RESEARCH

4.1 Research Strategy - We propose to develop in a systematic way the compositional and dynamic knowledge of carbon-ballast relationships necessary for constructing the next generation of remineralization models. We believe that a mechanistic approach to predicting remineralization profiles must include both a quantitative characterization of the shape of the remineralization profile between 100 and 1000 m, and knowledge of mechanisms and

consequences of association of organic carbon with mineral material. Our overall goal is to develop a description of carbon fluxes and associated mineral ballast fluxes throughout the water column. To achieve this goal, we propose to measure simultaneously a suite of properties that are thought to be indicative of fluxes. We will then synthesize these measurements seamlessly from the top of the water column to the sediments using a variety of modeling and statistical techniques. Our strategy is to bring together the power of several disciplines: (i) organic geochemistry for characterizing organic matter in protected and unprotected forms and determining its degradation state; (ii) radiochemistry for assessing processes and time-scales involved in particle dynamics and transport; (iii) zooplankton ecology for assessing radioisotope partitioning and organic biomarker alteration; and (iv) microbiology for its role in organic mater decomposition, and (v) statistical analyses to provide a process-based model of flux out of the euphotic zone to the sea floor. Specific mechanistic sub-hypotheses will be addressed later (**4.4**). Here, we illustrate our research approach (Fig. 3).

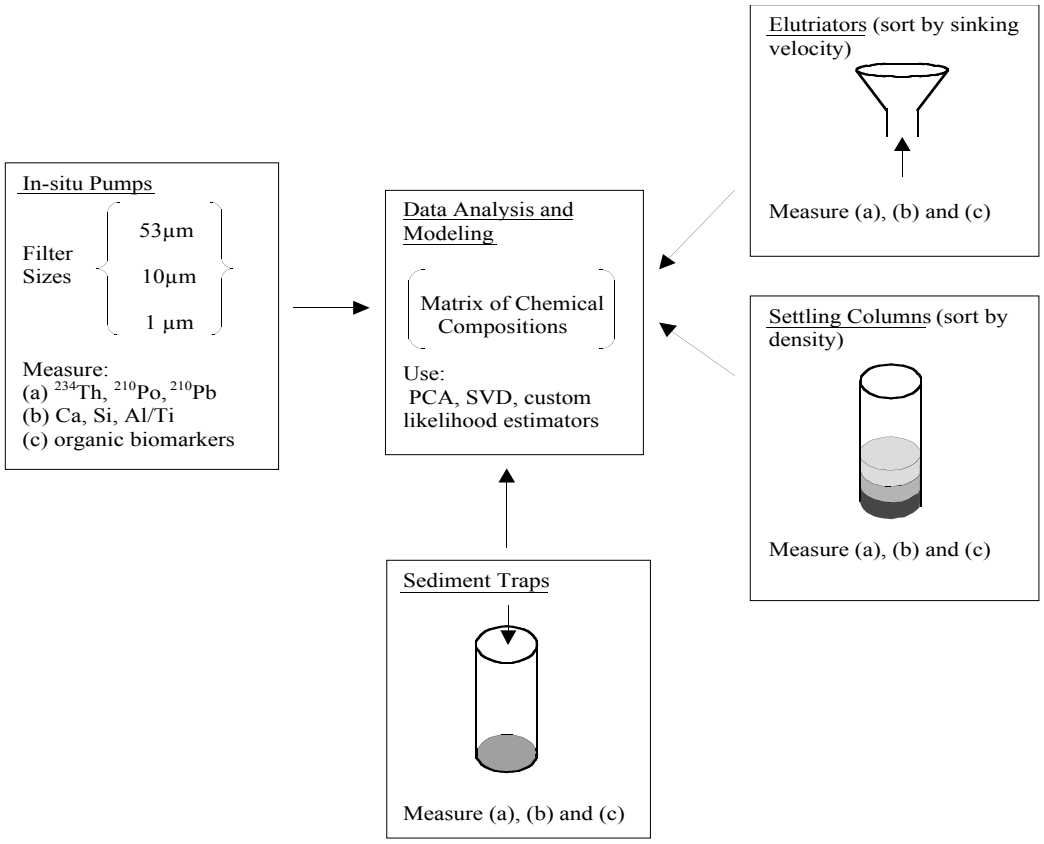

Fig. 3. Overall research strategy. Size fractions of POC collected on filters (1, 10, 53 µm) will be characterized by their radioisotope content (^{234}Th ,^{210}Po and ^{210}Pb), by their ballast minerals (Ca, Si, and Al/Ti), and by their organic biomarkers. Sinking particles, sorted by mass and/or velocity will be characterized in terms of the same tracers. These tracers will be used to construct a transfer matrix whereby sinking fluxes can be mapped statistically onto pump-based (filter) fractions. Information on biological, chemical, and physical mechanisms of quantitative association and protection will determine the form of statistical models used. Conventional traps will provide additional material for mechanistic studies that will be included in these analyses. (Total radionuclide activities will be measured on water samples by small volume techniques.)

We will use in-situ pumps to estimate flux using standard radionuclide techniques, augmented in 4 very important ways. (i) We will use more than two (probably 3) filter sizes, to increase size resolution of the data. (ii) We will use ^{210}Po, as well as ^{234}Th, as tracers. The longer half-life of ^{210}Po (138 d) relative to that of ^{234}Th (24.1 d) will allow us to compare data over two different spatial and temporal scales, to better characterize possible physical effects (advection, mixing, and eddies) on these measurements. Equally, if not more important, the greater half-life of ^{210}Po will allow us to extend our measurements well into the mesopelagic zone. (iii) To identify ballast minerals, we will measure Ca, biogenic Si, and Al (and/or Ti) on all size fractions. (iv) We will measure a suite of organic biomarkers on all size fractions to determine source and degradation state of organic material.

We will analyze the same chemical components as above in samples from IRS (see Methods; Peterson et al. 1993) sediment traps. These traps will give independent estimates of fluxes for use in data analysis, and will also provide material for laboratory investigations of mechanisms by which carbon:ballast ratios are determined. Having fresh trap particles from the same location as pumps is essential for delineating mechanisms to be modeled.

We will conduct chemical analyses of the same suite of radionuclides, mineral ballasts, and organic biomarkers on material collected using devices that separate sinking particles by density and/or by sinking velocity. In the density separation, we will measure particle sizes and use empirical and theoretical relationships to estimate sinking velocity. Sinking velocity of material first gathered from sediment traps will be observed in elutriators. (Elutriation is a particle separation technique that selects based on effective particle sinking rate; see Methods). Although elutriation of particles that we add is a fairly simple process, we will work toward adapting the elutriators to in-situ use so that their results can be more directly compared with those from traps, filters and density separations.

Statistical analysis of data from these four sources will then be used to begin construction of a process-based model of organic carbon flux from the euphotic zone to the sea floor. We will assess how densities, sinking velocities, and fluxes covary with organic biomarker, radionuclide, and ballast concentrations. We will establish functional relationships by using a combination of PCA (principal component analysis) and its more powerful cousin, SVD (singular value decomposition; Bennett 1992, Davis 1986, Wunsch 1996). These are standard linear matrix techniques that should provide a broad picture of how radionuclides, mineral ballast, and organic fractions are related to sinking velocity. Organic biomarkers and ballast types, because of their specificity, will provide key variability in this linking process, as well as insight into the biological mechanisms underlying the statistical results. We will also use custom-derived maximum likelihood estimators (Edwards 1992; Hilborn and Mangel 1997; see also Hurtt and Armstrong 1996, 1999) to increase the power and precision of our analyses when needed.

Techniques used for particle collection from plankton tows, in-situ pumps and sediment traps and for POC flux estimates will be essentially the same as we have previously used (see PI CVs), although our research strategy is quite different. Greater attention will be given to close vertical sampling of sinking particles within the mesopelagic zone. Our major field season will be in 2003; we will conduct lab and preliminary field experiments in 2002. We will obtain vertical profiles of particles by in-situ filtration near the French JGOFS DYFAMED site (see **4.3** below) in March, July, and November, 2003. We will deploy a sediment trap mooring holding arrays of

duplicate traps in March, with recovery in November. Individual arrays will be positioned at 5-6 depths below 200 m, the depth where vertical fluxes are considered equivalent to new or export production (Miquel et al. 1994). Time-series collections will ensure that we can relate specific flux patterns to surface particle production events (e.g., diatom bloom, coccolithophorid bloom, dust input). During cruises we will deploy floating traps (with/without ball valves and with/without biocide) at 100 m for 12-24 h to collect fresh sinking particles for lab experiments. We will also deploy settling columns (see Methods) on free-floating moorings at 100-m water depth. These moorings are to be deployed over 12- to 24-hour periods during all 3 cruises.

Cruises are scheduled to take place during periods that will have different inorganic ballast concentrations. We will participate in regularly-scheduled French cruises out of Monaco to the DYFAMED site for initial deployment (March) and final recovery (November) of sediment traps. We are requesting funding for a third cruise with DYFAMED investigators to service traps and conduct process-oriented field experiments in July since the high flux period usually occurs between April and July. We have requested ship time for a UNOLS vessel in the Mediterranean in 2003 for preliminary experiments, but presently cannot rely on this possibility. Exact timing of experiments will depend on ship scheduling, but the DYFAMED site is regularly visited by ships from France and Monaco. More detailed methods are in **5**.**1** and **5.2**.

4.2. Project Coordination - All participants (see Table 2) will be included in discussions and interpretations of all hypotheses. We have found that our various expertises blend well in general discussions.

Table 2. Investigators, their major area of expertise, and their specific responsibilities.

PI	Expertise	Salary Support	Responsibilities/Measurements
Armstrong	Ecological/biogeo-chemical modelling	This proposal	General modeling & statistical approaches
Bianchi	Microbiology	U. Marseille	Microbial biomass, production, enzymatic activity
Cochran	Radiochemistry	This proposal	Th, Po isotope analyses; pump deployments
Fowler	Zooplankton ecology	MEL	Th analyses; zooplankton collections & feeding experiments; MEL logistics
Hedges	Organic geochemistry	This proposal	Carbohydrate & CHN analyses; trap deployments
Lee	Organic geochemistry	This proposal	Amino acid, pigment & DOC analyses; project co-ordination
Miquel	Zooplankton ecology	MEL	Opal and silicate analyses; trap & pump deployments
Wakeham	Organic geochemistry	This proposal	Lipid biomarker analyses; elutriatior development; PCA analyses

In addition, Giselher Gust and Ellen Druffel have expressed an interest in co-ordinating their research with us at the DYFAMED site (see letters in Appendix). Gust plans to compare collection efficiencies of a new neutrally-buoyant sediment trap with our traps. He plans to independently (from us) measure in-situ fluxes, sinking-particle size and settling-speed spectra, and trap approach velocities at the same site. Druffel will propose separately to make ^{14}C

measurements, particularly on samples separated by density, to refine theories of how older DOC may adsorb to particles at depth.

4.3. Site Justification - The well-studied French JGOFS time-series site (DYFAMED) in the northwestern Mediterranean, 52 km off Nice in the Ligurian Sea (43°20'N; 7°40'E) is characterized by a predictable succession of mineral-secreting and mineral-free phytoplankton that are grazed by a small number of fecal-pellet-forming zooplankton species (Nival et al. 1975, Carroll et al. 1998, Marty et al. 2000). Primary productivity varies seasonally between oligotrophy and mesotrophy with an annual average of 77 gC m^{-2} y^{-1} (Minas et al. 1988, Lévy et al. 1998). Biogeochemical fluxes have been continuously sampled at DYFAMED for over a decade (Lévy et al. 1998). Using undecompressed samples collected at this site, Tholosan et al. (1999) have found high rates of microbial production which they attribute to bacteria carried down on sinking particles. Periodic inputs of atmospheric dust at this site are well-characterized and quantitatively large (Buat-Ménard et al. 1989, Migon 1993, Price et al. 1999). Almost continuous dust forecasts are available at www.nr.mry.navy.mil/aerosol. There is minimal impact from water-borne riverine particles or resuspended sediments at this site as there are no major rivers flowing into the basin. The area is generally free of coastal influence because a hydrological frontal zone separates the coastal zone from the open sea (Astraldi et al. 1994). Effects of horizontal advection on particle flux appear to be negligible at the DYFAMED site (Andersen and Prieur 2000). Other reasons for choosing the DYFAMED site are:

(**1**) particle throughput is sufficiently intense to cause an easily measured deficit of ^{234}Th in the euphotic zone and of ^{210}Po in the underlying water column (Buat-Menard et al. 1988; Masque 1999). Dr. Masque will work with us at least in the first year of the project (see Budget Justification). In addition, Fowler and Miquel will be measuring ^{234}Th profiles (0-300 m) monthly as part of the DYFAMED study.

(**2**) organic compound fluxes are known to be high enough for measurement of appropriate biomarkers throughout the sampling period (Marty et al. 1994; Goutx et al. 2000).

(**3**) periodic but well-characterized dust inputs at this site will allow us to observe the influence of dust on sinking fluxes and on the extent of remineralization of organic matter. For example, the 2001 July dust event in the western Mediterranean was major, see www.nrlmry.navy.mil/aerosol/satellite/seawifs/med/200107/2001072312_med.jpg. This site is one of the few with a dependable dust input of sufficient intensity to allow us to collect particles of different ballast types over time.

(**4**) there is easy access to this deep water site, a potential for rapid response to environmental conditions, and proximity to the superb facilities of the Marine Environment Laboratory (MEL) in Monaco (home of two of our PIs, Fowler and Miquel). This is especially important for the rapid analysis of short-lived radionuclides such as ^{234}Th. The shore-based nature of our combined field and lab experiments require this ability.

(**5**) scientific collaboration and logistical support provided by MEL ***at no cost to this project*** will allow us to accomplish much more than would be otherwise possible (see attached letter from MEL).

(**6**) scientific collaboration with other DYFAMED investigators will add greatly to this project (see letter from Prof. J.C. Marty, head of the DYFAMED program). Prof. Armand Bianchi's group at the University of Marseille has been working on microbiology and organic matter remineralization at the DYFAMED site for many years, and will collaborate with us in both field and lab studies (see attached letter). Christian Tamburini from the Marseille lab

visited Lee in Stony Brook for collaborative studies earlier this year, and Dr. Madelaine Goutx from this lab is interested in working with Wakeham on lipids in degrading particles. Their interests are described in more detail under *Hypothesis 1* below.

(**7**) We considered the two U.S.JGOFS time-series sites for this project, but the dependable and large dust inputs at DYFAMED were a major scientific reason for choosing the Mediterranean JGOFS site over the U.S. sites. Financially, the travel costs among the three sites were similar, but the scientific (zooplankton ecology) and logistical(lab space, ship, PI and technician time) contribution from the MEL group at no cost to this project, and the collaboration with the microbiologists at Marseilles made the decision straightforward.

4.4. Mechanistic Experiments - In addition to the general characterization of pump- and trap-collected particles, a comprehenisve model will require specific information on mechanisms that determine particle compositions and sinking rates. Although it is impossible to fully describe three years of planned research when so much will be determined by results obtained from experiments, below we suggest various approaches we will use initially.

4.4.1. *Hypothesis 1* - We will use the organic geochemical approach described below to determine whether (1) minerals differ in their capability to protect associated organic matter; (2) a fraction of organic matter persists due primarily to intrinsic chemical stability rather than to physical protection, (3) unprotected organic matter is extensively degraded over the mesopelagic zone where POC attenuates rapidly, as indicated by decreasing ratios of organic to mineral components, decreasing concentrations of characteristic components of the unprotected fraction to near-zero values, and increases in diagenetic products within the unprotected fraction.

Despite (as mentioned above in Hypothesis 1) characterizing over 100 major biochemicals in the EqPac and Arabian Sea studies, percentages of molecularly-uncharacterized POC increased progressively down the water column from values near 20% in particles exported from the euphotic zone to near 80% in the underlying sediments. Several hypotheses have been offered for this often-observed decrease in molecularly-resolvable organic substances attending advanced biodegradation. The classic explanation is that labile intermediates released during microbial degradation of biomacromolecules (e.g., lignins, polysaccharides, and proteins) spontaneously recombine to form complex "geopolymers" (Stevenson 1994). Products of such abiotic humification may be too complex structurally to degrade enzymatically or to analyze chemically. Alternatively, organisms may synthesize biomacromolecules that are intrinsically resistant to biodegradation and become selectively preserved in soils and sediments where they resist conventional analysis (Hatcher et al. 1983). Many hydrolysis-resistant biomacromolecules have been identified in terrestrial and marine plants, and in modern and ancient sediments (de Leeuw and Largeau 1993). Finally, refractory organic or inorganic matrices may physically protect intrinsically labile organic substances so that these substrates persist longer than their structure would suggest (Lowenstam and Weiner 1989, Knicker et al. 1996). A key contrast between these protection mechanisms is that humification and selective preservation should be attended by pronounced changes in organic structure, whereas physical protection does not require major compositional changes.

We used solid-state ^{13}C NMR to characterize chemical composition of organic materials in surface plankton and sinking particulate matter from the Pacific Ocean and Arabian Sea (Hedges et al. 2001). ^{13}C NMR measurements indicated minimal changes in bulk organic composition,

even though molecularly-characterized material changed greatly. Protein dominates throughout the water column despite extensive (>98%) biodegradation, and C/N ratios also remain near 6.8 throughout (Hernes et al. 2001). Compositional similarity between phytoplankton biomass and the small remnant of POM reaching the ocean interior indicates that neither extensive humification nor selective preservation of unusual biochemicals is a main control on POC cycling. As organic matter makes up <50% of total mass of all sinking particles, any physical protection likely involves dominant mineral components such as opal, calcium carbonate and detrital aluminosilicates. An important focus of this proposal is to distinguish among various preservation hypotheses.

In this project, we will chemically fractionate organic matter collected at various depths by pumps and traps to estimate profiles of protected and unprotected organic matter. These fractionations will include solvent extraction, peroxide treatments and HF dissolution to measure compounds associated with carbonate and silicate minerals.

We will also conduct degradation and grazing experiments with natural and prepared particles. Relative roles of bacteria and zooplankton as agents of POC remineralization are well studied (Banse 1990), although the relative importance of these two processes is yet to be resolved. We will not address specific roles in remineralization of these two groups of heterotrophs, but will rather investigate their importance in modifying organic-mineral relationships. Effects of zooplankton grazing can be addressed by comparing the organic carbon to ballast ratio (OC/B) and organic compositions of phytoplankton of varying mineral content before and after it passes through the zooplankton gut. Again, dust can be added to various degrees. Most of us, especially MEL PIs, have had previous experience with zooplankton feeding experiments. Bianchi's interest in bacterial remineralization of organic matter will be an important component of this study. His lab's contribution to analytical aspects will be to measure bacterial biomass production, bacterial growth efficiency, and ectoenzymatic lipid ester and biopolymer hydrolysis rates (Goutx et al. 2000; Sempere et al. 2000; Van Wambeke et al. 2001). Microbial decomposition studies of particles from the DYFAMED site have been conducted previously at the Marseille lab (e.g., Sempere et al. 2000), so that our experiments can take advantage of this knowledge. Bianchi's lab would continue their traditional hyperbaric studies at this site at the same time, so that they could take advantage of our flux and remineralization results (e.g., Bianchi and Garcin 1994).

We will address how microorganisms affect the fate and composition of particulate matter (and POC/B ratios) by conducting incubation experiments to evaluate effects of degradation on POC, total N, Si, IC, Al, Th, Po and organic tracers over time. Several types of particles with different POC/B ratios will be used: 1) natural particles collected by unvalved sediment traps at different depths; 2) aggregates of phytoplankton with differing mass ratios of mineral ballast and organic content prepared in a rotating drum (Shanks and Edmondson 1989); 3) field-collected fecal pellets, and 4) fecal pellets obtained from zooplankton maintained in the lab and fed different food sources containing varying mixes of mineral ballast and organic content. For example, in 2) and 4) we will use a silica-rich diatom, *Thalassiosira pseudonana,* two strains of the coccolithophorid, *Emiliana huxleyi*, one with and one without the $CaCO_3$ test, and the dinoflagellate *Heterocapsa triquetra* or related mineral-free species. Aggregates and fecal pellets will be isolated from shallow, short-term sediment traps. Macrozooplankton (copepods and euphausiids) will be netted over traps and their freshly excreted pellets collected (La Rosa

1976). Differing amounts of Saharan dust collected from rain gauges in Monaco will also be added. All pellet types used in these experiments will be analyzed for POC, IC, N, Al, Si and selected organic biomarkers. Variously-sized screens will allow us to separate particles of approximately similar size for some experiments. Fecal aggregates make up an important (5-50%) fraction of total POC flux out of the euphotic zone at the DYFAMED site, although intact fecal pellets are less significant (Miquel et al. 1994, Carroll et al. 1998). Because of the relatively small variety of dietary particles (diatoms, coccolithophorids, cyanobacteria and continental dust) and herbivorous zooplankton species at this location (Fowler and Knauer 1986, Marty et al. 1994), variety and composition of generated fecal pellets should also be manageably small and should exhibit a correspondingly restricted range of dietary sources (depending on selectivity of herbivore feeding), digestive processing, and size, shape and density due to biological packaging.

The four types of particles described above will be incubated under conditions simulating upper waters and the mesopelagic zone of the NW Mediterranean. Particles will be placed in rotating drums or in an elutriator to keep material in suspension and maintain shear-driven solute exchange. Bacterial degradation will be assessed using parallel controls treated with buffered formalin or a specific bacteriocide. Over time, ranging from hours to weeks, samples of pellets and aggregate particles will be removed for analysis. We have shown the feasibility of this approach earlier at MEL; a significant advantage of doing these studies in Monaco is the proximity of the lab to open sea conditions of the DYFAMED site which permits returning and processing live plankton and particulate samples within only a few hours of collection. This is an important feature for ensuring fresh, non-degraded material with minimal physical disruption for this series of experiments. Collaboration with the microbiology group at the University of Marseille will be an invaluable asset to the planning and execution of these experiments.

Fecal pellets obtained from feeding experiments will be subjected to three degradation regimes: (i) pellets will be allowed to degrade intact; (ii) pellets will be disaggregated and allowed to degrade; (iii) pellets will be fed to coprophagic feeders and new fecal pellets collected (e.g, Prahl et al. 1984, Neal et al. 1986, Harvey et al. 1987, Bradshaw et al. 1990). POC, TN, mineral and selected biomarkers will be measured in initial diets and during degradation. These experiments will demonstrate how particle morphology and packaging and zooplankton metabolism affect mineral-organic associations. Throughout all these grazing and degradation experiments, we will determine diagenetic biomarker indicators, especially bacterial indicators (e.g., peptidoglycan-derived D/L-amino acid ratios, muramic acid and lipopolysaccharide-derived hydroxy-acids (Salton 1960, Rogers 1983, Mayer et al. 1989).

In the above experiments, we will determine whether organic matter is protected from degradation by physical association with ballast minerals by comparing degradation (loss of POC and changes in key diagnostic organic geochemical indicators (Wakeham et al. 1997b; Dauwe et al. 1999; Sheridan et al. in prep) of *E. huxleyi* with and without a $CaCO_3$ test, and by comparing degradation of POM in samples which differ only by the amount of dust added. We can also determine whether different mineral types have contrasting protection capacities by measuring changes in total POC and POC/B ratios with time, and use an adaptation of the Armstrong et al. (2001) model with time replacing depth. This will give the loss of total C (measured) and unprotected C (modeled) with time. Extrapolating these values forward to infinite time will allow calculation of a ratio of unprotected to protected carbon that indicates protection

capability. If the type of mineral ballast in sediment traps changes with time, a parallel analysis of field data will be possible. Comparisons of diagenetic biomarkers in sediment trap and in-situ filtration samples with those from POM in laboratory incubations may provide insight into the relative importance of bacteria vs. zooplankton in degradation at the DYFAMED site.

Zooplankton grazing and coprophagy both package and break up particles, thereby influencing settling velocities, degradation rates and carbon release (Lampitt et al. 1990, Dilling and Alldredge 2000). We will investigate whether the association of organic matter with ballast simply allows it to sink fast enough that the organic fraction has less time to degrade. Once organic matter-mineral aggregates break up, organic matter may be more susceptible to degradation than as an aggregate. Laboratory feeding experiments (Bradshaw and Eglinton 1993, Cowie and Hedges 1996) have documented aspects of organic matter alteration during grazing and coprophagy. Effects on POC/mineral relationships by zooplankton processing of particles has not been studied. To examine physical disruption and subsequent carbon loss from sinking particles, large, locally-abundant euphausiids *Meganyctiphanes norvegica* (see Fowler and Knauer 1986) will be exposed to different types of aggregates (natural and laboratory-produced) in large (1 - 2 L) volumes of sea water, and disaggregated particulate matter will be periodically removed over time (hours to days) and analyzed for carbon, ballast, and biomarkers. DOC will also be measured. Control groups of the same aggregates will be maintained under similar conditions without euphausiids and likewise analyzed to assess physical effects of swimming on carbon degradation.

We also propose to use a settling column (see Fig. 3) to determine how the composition of organic and radiochemistry of particles changes with density. Sinking particles will be stabilized in a density gradient in an in-situ free-floating settling column. The settling column will be constructed so that discrete particles or aggregates may be withdrawn for chemical analysis. Particles characterized by different densities can then be isolated and their elemental, radiochemical, organic geochemical and mineral compositions determined.

4.4.2. ***Hypothesis 2*** **-** We will determine whether (1) sinking speed of particles is related to ballast mineral content; (2) particles with different sinking velocities filter into appropriate size classes; and (3) POC/Th ratios vary in different particle velocity classes.

(1) We will use elutriation to separate particles by effective sinking rate; sinking rate is a major variable in natural particle recycling (Diercks and Asper 1997, Hill 1998). Particle separators will be adapted from commercially available conical elutriators. Ambient seawater will be pumped through the bottom to provide a flow to counterbalance particle sinking. The conical form changes velocity of flow with depth in the cone and provides a mechanism of separating particles according to their sinking rate rather than density or size alone. Particles can be collected on the basis of settling velocity for subsequent chemical analysis. Elutriation should be a particularly useful separation mechanism because it is gentle and applicable to low sample concentrations. In addition, elutriation can be carried out at steady state for a wide variety (sinking rates of 5-500 m/d) of particles in the field or lab, providing a means for assessing biodegradation and disaggregation/aggregation under realistic hydrodynamic and environmental conditions. A laboratory-scale elutriator system will be purchased and adapted for shipboard or shore-based laboratory use and for gentle separation of particulate material collected in sediment traps. During this project, we will work toward the development of an in-situ elutriator.

We recognize that the particles used in our elutriation and other studies will not include large aggregates that may be an important component of the flux (Alldredge et al. 1990, Hill 1998, Burd et al. 2000), as they will likely be disrupted during collection. However, our sinking rate studies will be applicable to times and places where aggregates are relatively unimportant.

(2) As discussed above in Hypothesis 2, we believe that processes affecting the ratio of POC to ballast in sinking particles will also affect POC/Th; we will explore this link in the proposed research. What to use as a measure of Th concentration in sinking particles is currently under debate. Assuming that particles retained by filters larger than a certain size (53 or 70 μm) are those responsible for the sinking flux may produce significant systematic bias in estimating POC/Th in sinking material. Burd et al. (2001) have pointed out that POC/Th ratios are known to decrease systematically with filter size, so that POC/Th estimated using contents of the largest filter alone are likely to be biased low. A related problem is that increased B/POC ratios are likely to increase sinking velocities for particles of a given size; thus, the size spectrum of sinking particles likely will be shifted to smaller sizes when ballasting is higher. Under such conditions POC/Th ratios in the sinking flux should also reflect ratios in smaller particles. To address these problems, we will use an additional filter size, intermediate between 1 and 53 μm, and compare POC/Th ratios in filterable particles with those collected by elutriator or settling chamber, as well as sediment trap. We will assess temporal variations in natural ballast type, POC/Th ratios, POC/B, and organic composition in particles collected by the different approaches.

In addition, we will measure another potentially useful radionuclide pair ^{210}Po-^{210}Pb. As mentioned above, ^{210}Po (half-life = 138 d) is incorporated into organic matter rather than simply adsorbed onto particle surfaces (Cherry et al. 1975, Heyraud and Cherry 1979) and shows surpluses and deficits relative to its parent ^{210}Pb in the mesopelagic zone (e.g., Cochran et al. 1983, Ritchie and Shimmield 1991, Nozaki et al. 1998). There is evidence that remineralization of sinking organic matter releases ^{210}Po to solution in this zone (e.g., Cochran et al. 1983, Ritchie and Shimmield 1991). Coupling ^{234}Th and ^{210}Po should produce a set of tracers that permits us to examine the fates of both organic carbon and ballast as particles sink. As the POC/B ratio changes in sinking material, so should the Po/Th ratio. Indeed ^{210}Po should be a more sensitive tracer of remineralization and flux of POC through the mesopelagic zone than is ^{234}Th and also be relatively free of lateral transport effects on its profile.

A set of lab experiments will focus on the uptake of Th and Po on biogenic particles produced through zooplankton grazing activities. Such information will help establish variation in POC/Th and POC/Po ratios in particles that are processed through zooplankton. Various combinations of phytoplankton cells and mineral ballast mixtures (see above) will be labeled with ^{234}Th and ^{210}Po. Copepods and euphausiids will graze labeled particles under controlled conditions, and resultant fecal pellets isolated and tracer activity counted. Following radioanalysis, pellets will be returned to clean seawater held at constant temperature, and retention of ^{234}Th and ^{210}Po periodically measured over several days. In conjunction with degradation and remineralization experiments (see below), radiolabelled pellets will be analyzed for POC to establish POC/Th ratios over time. It is hypothesized that retention of ^{234}Th and ^{210}Po will be a function of POC/B ratio and degradation rate of the organic fraction of the pellets, and that ratios for the two isotopes will be different. In preliminary experiments (Cochran et al.,

unpubl. results), it was shown that direct ^{234}Th measurements on very small biogenic particles are possible over relatively short time periods.

(3) We will measure ^{234}Th, ^{210}Po, ^{210}Pb, organic compounds, POC, IC, Si and Al on particles collected in different ways. DYFAMED investigators measure surface chlorophyll and diatom and flagellate biomarkers, CTD and nutrient depth profiles on at least a monthly basis. If dust events occur within the time-frame of our sampling, variations in Th distribution will help evaluate effects of dust on POC/Th ratios. Freshness of POM will be evaluated using organic biomarkers (see Table 1). Abundances of IC, Si, and Al will be used to evaluate whether temporal or depth-related shifts in ballast type are related to observed variations in ballast source (e.g., changes in phytoplankton community or pulsed inputs of dust) or to selective dissolution of ballast. Such shifts would allow us to determine whether minerals differ in ballast effect.

5. ANALYTICAL METHODS

5.1. Collection techniques - Sediments and sediment trap material will be split into multiple fractions and stored frozen until analysis. Filters of suspended particles will be subsampled and stored frozen until analysis.

Traps. We will use bottom-moored traps with indented-rotating sphere valves to minimize collection of zooplankton "swimmers" and time-series carousels (IRS-C traps; Peterson et al. 1993). The IRSC trap configuration has been successfully used on JGOFS EqPac, Arabian Sea, and Southern Ocean programs to collect material for organic geochemical studies (see Prior Results). Traps will be fitted with 12-position carousel subsamplers capable of collecting individual samples at approximately 3-day intervals. IRSC traps will be treated with mercuric chloride in brine to minimize microbial degradation during the collection period (Lee et al. 1992). Arrays will include an unvalved, formalin-treated cylinder to provide material for microscopic examination of particle morphology and for further experimentation. Floating traps will be deployed on a drogued-surface tether, with and without poison, and with and without an IRS valve.

Suspended particles. Samples will be collected by in-situ pumping using battery-operated pumps that pass large volumes of water (100-1000 L) through a series of filters (Livingston and Cochran 1987, Buesseler et al. 1992b). At present, particles are collected on two 142 mm diameter filters in a series consisting of a 70 μm pore sized Teflon mesh filter followed by a 1 μm pore sized Microquartz filter. For the proposed research we will modify pumps to collect one additional size class of particles intermediate between 1 and 70 um. Low flow rates of 2-4 l min^{-1} will be used to minimize loss of particles caused by high pressure shear.

Elutriator. Particle separators for laboratory use will be adapted from commercially available instruments (e.g., Beckman Coulter or Metalindustrie) used in biomedical and industrial laboratories. In elutriation methods, particles are placed in a vertical tube (or cylinder) in which water (or another fluid) flows slowly upward. Particles fall through the water at speeds that vary with their size and density. If the flow rate of the water is slowly increased in a cylinder, the most slowly sinking particles will be swept upward with the fluid flow and removed from the container. Intermediate particles will remain stationary, and the largest or densest particles will continue to migrate downward. Flow can again be increased to remove the next

most slowly sinking particles. Thus, by careful control of flow, particles can be separated according to sinking velocity. If the elutriator is cone shaped, the vertical flow rate of water will decrease upward (away from the water source) as the crossectional area of the cone increases. Under this circumstance of gradational flow, particles with contrasting sinking rates will separate at different depths in the cone where their sinking speeds match the upward flow rate of fluid.

Settling Column. Particle composition as a function of density will be characterized using an in-situ free-floating sediment column. For microscopic and inorganic analysis, settled particles will be stabilized in agarose, a porous, resilient medium that allows for transport, staining, washing,and subsampling of aggregates with minimal or no destructive forces (Droppo et al. 1996). For organic analysis, particles will also be collected using an inorganic density gradient such as sodium metatungstate.

Water. Small volume water samples (~10 l) will be taken using a rosette to characterize detailed depth distributions of total ^{234}Th, ^{210}Po and ^{210}Pb. These samples will be analyzed as described below.

Sediment. Samples will be collected by box core or multicore with the DYFAMED coring group. Sedimentation rates will be obtained from depth distributions of ^{230}Th in cores. Surface sediment also will be analyzed to assess whether resuspension of bottom sediment has contaminated the near-bottom trap material. Cores will be archived for future projects, but will not be further analyzed for this project.

5.2. Chemical Analyses

Radionuclides. Activities of dissolved and particulate ^{234}Th in pump samples will be determined at MEL promptly after collection. For dissolved ^{234}Th extracted onto manganese cartridges, 63 keV gamma emission will be counted using intrinsic germanium detectors (Buesseler et al. 1992b, Bacon et al. 1996, Cochran et al. 1995). ^{234}Th in particulate fractions will be determined using nondestructive beta counting. Particle fractions will then be analyzed for ^{210}Po and ^{210}Pb using standard radiochemical techniques (Cochran et al. 1983). Cochran worked with the MEL group in Monaco to set up the ^{234}Th method which is now standardized between SUNY and MEL. Measurements of ^{234}Th in pump samples will be complemented by measurements of total ^{234}Th activities in small volume (~2 l) samples (Buesseler et al. 2001). Total ^{210}Po and ^{210}Pb also will be analyzed on small volume (~4 l) water samples by coprecipitation with Co-APDC and subsequent assay by alpha spectrometry (Cochran et al. 1983).

Opal, Al and $CaCO_3$. Al, Ti and Si will be measured by ICP-MS at MEL or SUNY. Opal will be measured after extraction with Na_2CO_3 (Mortlock and Froelich 1989). Inorganic carbonate will be measured by difference between total carbon in untreated and acid-treated samples.

Organic C and specific compounds. Analytical methods for determining various organic compounds are presented in detail in Wakeham et al. (1993). Sample splits for carbohydrate and CHN analyses will be centrifuged, and part of the supernatant saved for salt and residual poison analysis. The centrifugate will be freeze-dried and ground for carbohydrate

and CHN analyses. Wet and dry weights will be determined for each unrinsed samples; corresponding bulk flux and organic concentrations will be salt corrected. Particulate material in all other sample splits will be recovered by filtration (GF/F). Filtrate will be analyzed for both dissolved organic carbon (DOC) and dissolved amino acids.

POC and total nitrogen will be measured by CHN analyzer at UW, SUNY or MEL. DOC in sediment trap waters will be measured with a Shimadzu TOC 5000 analyzer, following the general method of Benner et al. (1992), at UW or SUNY. We will blank correct all measured values. Individual compounds will be analyzed using well developed methods that we have used in the past: individual aldose components by the amperometric method of Kaiser and Benner (2000) at UW; lipids at SkIO by gas chromatography/mass spectrometry (Wakeham et al. 1997a); amino acids at SUNY by fluorescence- high pressure liquid chromatography after acid hydrolysis (Lindroth and Mopper 1979, Lee and Cronin 1982, 1984, Lee et al., 2000); and major chlorins at SUNY by HPLC with fluorescence detection (Mantoura and Llewellyn 1984, Bidigare et al. 1985, Lee et al. 2000). D/L- amino acids were analyzed similarly, except that chiral OPA derivatives were made with N-isobutyryl-L-cysteine and N-isobutytyl-D-cysteine (Brückner et al. 1991).

6. SIGNIFICANCE

The proposed research will provide mechanistic knowledge needed for constructing a model capable of describing and predicting transport of particulate organic matter and associated bioactive elements into the interior ocean. The concept that mineral particles may both "ballast" and "protect" associated organic matter is consistent with theory and recent experimental observations, but is not included in current models. We propose to synthesize experiments, observations and models to attain a view of recycling from the base of the mixed layer to the sediments, focusing on the mesopelagic zone, where the bulk of organic matter recycling occurs and where mechanistic understanding is least. This research bridges organic and inorganic geochemistry, and focuses the experimental triad of mineralogy, radiochemistry and organic geochemistry in unique combination with zooplankton and microbial ecology on the workings of the biological pump. In addition, the proposed research will provide new tools and information about: (a) comparative fates of dietary minerals and specific biochemicals during passage through guts of different types of animals, (b) reaction histories of both the organic and inorganic moieties of sinking particles based on molecular process indicators, and (c) limits to particle size and settling velocity in the sea.

REFERENCES (incuding papers mentioned in Results from Prior Support)

Adler P.M. 1979. A study of disaggregation effects in sedimentation. AIChE J. 25: 487-493.

Adler P.M. and P.M. Mills. 1979. Motion and rupture of a porous sphere in a linear flow field. J. Rheol. 23: 25-37.

Alldredge A.L., T.C. Granata, C.C. Gotschalk and T.D. Dickey. 1990. The physical strength of marine snow and its implications for particle disaggregation in the ocean. Limnol. Oceanogr. 35: 1415-1428.

Amiel D., J.K. Cochran and D.J. Hirschberg. 2001. $^{234}Th/^{238}U$ disequilibrium as an indicator of the export flux of POC in the North Water (NOW) polynya. Deep-Sea Res. II, In revision.

Andersen V. and L. Prieur. 2000. One-month study in the open NW Mediterranean Sea (DYNAPROC experiment, May 1995): overview of the hydrobiogeochemical structures and effects of wind events. Deep-Sea Res. I, 47: 397-422.

Anderson R.F., M.P. Bacon and P.G. Brewer. 1983. Removal of Th-230 and Pa-231 from the open ocean. Earth Planet. Sci. Lett. 6: 7-23.

‡Armstrong R.A. 1999a. A model of iron-ammonium-light co-limitation of nitrate uptake and phytoplankton growth. Limnol. Oceanogr. 44:1436-1446.

‡Armstrong R.A. 1999b. Stable model structures for representing biogeochemical diversity and size spectra in plankton communities. J. Plankton Res. 21:445-464.

‡Armstrong R.A. and R.A. Jahnke. 2001. Decoupling surface production from deep remineralization and benthic deposition: The role of mineral ballasts. U.S.JGOFS News 11: 1-2.

*‡Armstrong R.A., C. Lee, J.I. Hedges, S. Honjo and S. Wakeham. (2001) A new, mechanistic model for organic carbon fluxes in the ocean, based on the quantitative association of POC with ballast minerals. Deep-Sea Res., in press.

Astraldi M., G.P. Gasparini and S. Sparnoccia. 1994. The seasonality and interannual variability in the Ligurian-Provençal basin. In: Seasonal and Interannual Variability of the Western Mediterranean Sea, Coastal and Estuarine Studies Vol. 46, P.E. La Violette, ed., American Geophysical Union, Washington, DC, pp. 93-113.

†Bacon M.P., J.K. Cochran, D. Hirschberg, T.R. Hammar and A.P. Fleer, 1996. Export flux of carbon at the equator during the EqPac time-series cruises estimated from ^{234}Th measurements. Deep-Sea Res. II 43: 1133-1153.

Banse K. 1990. New views on the degradation and disposition of organic particles as collected by sediment traps in the open sea. Deep-Sea Res. 37: 1177-1195.

Benner R., J.D. Pakulski, M. McCarthy, J.I. Hedges and P.G. Hatcher. 1992. Bulk chemical characteristics of dissolved organic matter in the ocean. Science 255: 1561-1564.

Bennett A.F. 1992. Inverse methods in physical oceanography. Cambridge University Press, England.

Berner R.A. 1980. Early Diagenesis, A Theoretical Approach., Princeton University Press, Princeton, N.J. 241 p.

Bianchi A. and J. Garcin. 1994. Bacterial response to hydrostatic pressure in seawater samples collected in mixed-warer and stratified conditions. Mar. Ecol. Progr. Ser. 111: 137-141.

Bidigare R.R., M.C. Kennicutt and J.M. Brooks. 1985. Rapid determination of chlorophylls and their degradation products by high-performance liquid chromatography. Limnol. Oceanogr. 30: 432-435.

*Bidigare R.R., A. Fluegge, K.H. Freeman, K.L. Hansen, J.M. Hayes, D.J. Hollander, J.P. Jasper, L.L. King, E.A. Laws, J. Milder, F.J. Millero, R. Pancost, B.N. Popp, P.A. Steinberg and S.G. Wakeham. 1997. Consistent fractionation of ^{13}C in nature and in the laboratory: growth-rate effects in some haptophyte algae. Glob. Biogeochem. Cycles 11: 279-292.

Bradshaw S.A. and G. Eglinton. 1993. Marine invertebrate feeding and the sedimentary lipid record. In: Organic geochemistry. Principles and application, M.H. Engel and S.A. Macko, eds, Plenum Press, New York, pp. 225-235.

Bradshaw S. A., S. C. M. O'Hara, E. D. S. Corner and G. Eglinton 1990. Changes in lipids during simulated herbivorous feeding by the marine crustacean Neomysis integer. J. Mar. Biol. Assoc. U. K. 70: 225-243.

Brückner H., R. Wittner and H. Godel. Fully automated high-performance liquid chromatographic separation of DL-amino acids derivatized with o-phthaldialdehyde together with N-isobutyryl-cysteine. Application to food samples. Chromatographia 32: 383-388 (1991).

Buat-Menard P., H.V. Nguyen, J.L. Reyss, S. Schmidt, Y. Yokoyama, J. La Rosa, S. Huessner and S.W. Fowler 1988. Temporal changes of Th-234 concentrations and fluxes in the northwestern Mediterranean. In: Radionuclides: A Tool for Oceanography, (J.C. Guary, P. Guegueniat and R.J. Pentreath, eds.) Elsevier, London, UK. pp. 121-130.

Buat-Ménard P., J. Davies, E. Remoudaki, J.C. Miquel, G. Bergametti, C.E. Lambert, U. Ezat, C. Quetel, J. La Rosa and S.W. Fowler. 1989. Non-steady state removal of atmospheric particles from Mediterranean surface waters. Nature 340: 131-134.

Buesseler K.O. 1998. The decoupling of production and particulate export in the surface ocean. Glob. Biogeochem. Cycles 12: 297-310.

Buesseler K.O., J.A. Andrews, M.C. Hartman, R. Belastock and F. Chai. 1995. Regional estimates of the export flux of particulate organic carbon derived from ^{234}Th during the JGOFS EqPac program. Deep-Sea Res. 42: 777-804.

†Buesseler K.O., M.P. Bacon, J.K. Cochran and H.D. Livingston. 1992a. Carbon and nitrogen export during the JGOFS North Atlantic Bloom Experiment estimated from ^{234}Th: ^{238}U disequilibrium. Deep-Sea Res. 39: 1115-1137.

Buesseler K., L. Ball, J. Andrews, C. Benitez-Nelson, R. Belastock, F. Chai, and Y. Chao. 1998. Upper ocean export of particulate organic carbon in the Arabian Sea derived from thorium-234. Deep-Sea Res. II 45: 2461-2487.

†Buesseler K.O., J.K. Cochran, M.P. Bacon, H.D. Livingston, S.A. Casso, D. Hirschberg, M.C. Hartman an A.P. Fleer. 1992b. Determination of thorium isotopes in seawater by non-destructive and radiochemical procedures. Deep-Sea Res. 39: 1103-1114.

†Buesseler K.O., L. Ball, J. Andrews, J.K. Cochran, D. J. Hirschberg, M.P. Bacon, A Fleer and M. Brzezinski. 2000. Upper ocean export of particulate organic carbon and biogenic silica in the Southern Ocean along 170°W. Deep-Sea Res., in press.

Buesseler K.O., C.Benitez-Nelson, M.R. Rutgers van der Loeff, J. Andrews, L. Ball, G. Crossin and M.A. Charette 2001. An intercomparison of small- and large-volume techniques for thorium-234 in seawater. Mar. Chem., 74: 15-28.

Burd A.B., S.B. Moran and G.A. Jackson. 2000. A coupled adsorption--aggregation model of the POC/ ^{234}Th ratio of marine particles. Deep-Sea Res. 47: 103-120.

Carter P.W. and R.M. Mitterer. 1978. Amino acid composition of organic matter associated with carbonate and non-carbonate sediments. Geochim. Cosmochim. Acta 58: 1231-1238.

Carroll M.L., J.C. Miquel and S.W. Fowler. 1998. Seasonal patterns and depth-specific trends of zooplankton fecal pellets fluxes in the Northwest Mediterranean Sea. Deep Sea Res. 45: 1303-1318.

Cherry R.D., S.W. Fowler, T.M. Beasley, and M. Heyraud 1975. Polonium-210: its vertical oceanic transport by zooplankton metabolic activity. Mar. Chem. 3, 105-110.

Cochran J.K., M.P. Bacon, S. Krishnaswami and K.K. Turekian 1983. ^{210}Po and ^{210}Pb distributions in the central and eastern Indian Ocean. Earth Planet. Sci. Lett. 65: 433-452.

Cochran J.K., C. Barnes, D. Achman and D.J. Hirschberg. 1995. Thorium-234/Uranium-238 disequilibrium as an indicator of scavenging rates and particulate organic carbon fluxes in the Northeast Water Polynya, Greenland. J. Geophys. Res. 100: 4399-4410.

†Cochran J.K., K.O. Buesseler, M.P. Bacon and H.D. Livingston. 1993. Thorium isotopes as indicators of particle dynamics in the upper ocean: Results from the JGOFS North Atlantic Bloom Experiment. Deep-Sea Res. 40: 1569-1595.

†Cochran J. K., K.O. Buesseler, M.P. Bacon, H.-W. Wang, D.J. Hirschberg, L. Ball, J. Andrews, G. Crossin and A. Fleer. 2000. Short-lived thorium isotopes (^{234}Th, ^{228}Th) as indicators of POC export and particle cycling in the Ross Sea, Southern Ocean. Deep-Sea Res., 47: 3451-3490.

Cowie G.L. and J.I. Hedges. 1996. Digestion and alteration of the biochemical constituents of a diatom (Thallasiosira weissflogii) ingested by a herbivorous zooplankton (Calanus pacificus). Limnol. Oceanogr. 41: 581-594.

Cowie, G. L., J. I. Hedges, F. G. Prahl and G. J. de Lange. 1995. Elemental and biochemical changes across an oxidation front in a relict turbidite: An oxygen effect. Geochim. Cosmochim. Acta 59: 33-46

Dauwe B. and J.J. Middelburg. 1998. Amino acids and hexosamines as indicators of organic matter degradation state in North Sea sediments. Limnol. Oceanogr. 43: 782-798.

Davis J.C. 1986. Statistics and data analysis in geology. Wiley, New York.

de Leeuw J. W. and C. Largeau. 1993. A review of macromolecular organic compounds that comprise living organisms and their role in kerogen, coal, and petroleum formation. In Organic Geochemistry (eds. Engel, M. and S.A. Macko) p. 23-72. Plenum, New York.

Dierks A.-R. and V.L. Asper. 1997. In situ settling speeds of marine snow aggregates below the mixed layer: Black Sea and Gulf of Mexico. Deep-Sea Res. I 44: 385-398.

Digby P.G.N. and R.A. Kempton. 1987. Multivariate analysis of ecological communities. Chapman and Hall, New York.

Dilling L. and A.L. Alldredge. 2000. Fragmentation of marine snow by swimming macrozooplankton: a new process impacting carbon cycling in the sea. Deep-Sea Res. 47: 1227-1245.

Droppo I.G, D.T. Flannigan, G.G. Leppard, C. Jaskot, and S.N. Liss. 1996. Floc stabilization for multiple microscopic techniques. Appl. Environ. Microbiol. 62: 3508-3515.

Dunne J.P., J.W. Murray, J. Young, L.S. Balistrieri and J. Bishop. 1997. ^{234}Th and particle cycling in the central equatorial Pacific. Deep-Sea Res. II 44: 2049-2083.

Edwards A.W.F. 1992 Likelihood. Johns Hopkins University Press, Baltimore MD, 275 pp.

Fowler S.W. and G.A. Knauer. 1986. Role of large particles in the transport of elements and organic compounds through the oceanic water column. Prog. Oceanogr. 16: 147-194.

Goutx, M., A. Momzikoff, L. Strilby, V. Andersen, J. C. Marty, and I. Vescovali. 2000. High-frequency fluxes of labile compounds in the central Ligurian Sea, northwestern Mediterranean. Deep-Sea. Res. I, 47: 533-556.

Harvey H.R., S.C.M. O'Hara, G. Eglinton and E.D.S. Corner. 1987. Biotransformation and assimilation of dietary lipids by Calanus feeding on a dinoflagellate. Geochim. Cosmochim. Acta 51: 3031-3040.

Hatcher P.G., E.C. Spiker, N.M. Szeverenyi and G.E. Maciel. 1983. Selective preservation and origin of petroleum-forming aquatic kerogen. Nature 305: 498-501.

Hayakawa K., N. Handa, K. Kawanobe and C.S. Wong. 1996. Factors controlling the temporal variation of fatty acids in piculate matter during a phytoplankton bloom in a marine mesocosm. Mar. Chem. 52: 233-244.

* Hedges J.I., J.A. Baldock, Y. Gélinas, C. Lee, M.L. Peterson, and S.G. Wakeham. 2001. Evidence for non-selective preservation of organic matter in sinking marine particles. Nature 409: 801-804.

Hedges J.I. and R.G. Keil. 1995. Sedimentary organic matter preservation: an assessment and speculative synthesis. Mar. Chem. 49: 81-115.

*Hedges J. I., C. Lee, S.G. Wakeham, P.J. Hernes and M.L. Peterson. 1993. Effects of poisons and preservatives on the fluxes and elemental compositions of sediment trap materials. J. Mar. Res. 51: 651-668.

Hedges J. I. and J.M. Oades. 1997. Comparative organic geochemistries of soils and marine sediments. Org. Geochem. 27: 319-361.

*Hernes P. J., J. I. Hedges, M.L. Peterson, S.G. Wakeham and C. Lee (1996) Neutral carbohydrate geochemistry of particulate material in the central equatorial Pacific. Deep-Sea Res. II 43: 1181-1204.

*Hernes P.J., M.L. Peterson, J.W. Murray, S.G. Wakeham, C. Lee and J.I. Hedges (2001) Particulate carbon and nitrogen fluxes and compositions in the central equatorial Pacific. Deep-Sea Res. I, 48: 1999-2023.

Heyraud M. and R.D. Cherry 1979. Polonium-210 and lead-210 in marine foodchains. Mar. Biol. 52: 227-236.

Hilborn R. and M. Mangel 1997 The Ecological Detective: confronting models with data. Princeton University Press, Princeton NJ, 315 pp.

Hill P.S. 1998. Controls on floc size in the sea. Oceanography 11: 13-18.

Honjo S. 1980. Material fluxes and modes of sedimentation in the mesopelagic and bathy-

pelagic zones. J. Mar. Res. 38: 53-97.

Honjo S. 1996. Fluxes of particles to the interior of the open oceans, in Particle Flux in the Ocean, SCOPE Vol. 57, V. Ittekkot, P. Schäfer, S. Honjo, and P. J. Depetris, Eds., John Wiley & Sons, New York, pp. 91-154.

Honjo S., S.J. Manganini and J.J. Cole. 1982. Sedimentation of biogenic matter in the deep ocean. Deep-Sea Res. 29: 608-625.

Hurtt G.C. and R.A. Armstrong. 1996. A pelagic ecosystem model calibrated with BATS data. J. Plankton Res. 21: 445-464.

‡Hurtt G.C. and R.A. Armstrong. 1999. A pelagic ecosystem model calibrated with BATS and OWSI data. Deep-Sea Res. I 46: 27-61.

Ittekkot V. and B. Haake. 1990. The terrestrial link in the removal of organic carbon, in Facets of Modern Biogeochemistry (V. Ittekkot, S. Kempe, W. Michaelis, and A. Spitzy, Eds.) Springer, Berlin, pp. 319-325.

Kaiser, K. and R. Benner. 2000. Determination of amino sugars in environmental samples with high salt content by high-performance anion-exchange chromatography and pulsed amperometric detection. Anal. Chem. 72: 2566-2572.

King K. 1974. Preserved amino acids from silicified protein in fossil radiolaria. Nature 252: 690-692.

Knicker H., A.W. Scaroni and P.G. Hatcher. 1996. ^{13}C and ^{15}N NMR spectroscopic investigation on the formation of fossil algal residues. Org. Geochem. 24: 661-669.

Lambert C.E., S. Fowler, J.C. Miquel, P. Buat-Menard, F. Dulac, H.V. Nguyen, S. Schmidt, J. L. Reyss and J. La Rosa. 1991. ^{234}Th: An ambiguous tracer of biogenic particle export from northwestern Mediterranean surface waters. In: Radionuclides in the Study of Marine Processes (P. J. Kershaw and D. S. Woodhead, eds), Elsevier , New York, pp. 116-128.

Lampitt R.S., T. Noji and B. Von Bodungen. 1990. What happens to zooplankton fecal pellets? Implications for material flux. Mar. Biol. 104: 15-23.

†Langone L., M. Frignani, J.K. Cochran and M. Ravaioli (1997) Scavenging processes and export fluxes close to a retreating seasonal ice margin (Ross Sea, Antarctica). Water Air Soil Poll. 99: 705-715.

La Rosa J. 1976. A simple system for recovering zooplanktonic faecal pellets in quantity. Deep-Sea Res. 23: 995-997.

Lee C. and C. Cronin. 1982. The vertical flux of particulate organic nitrogen in the sea: decomposition of amino acids in the Peru upwelling area and the equatorial Atlantic, J. Mar. Res. 40: 227-251.

Lee C. and C. Cronin. 1984. Particulate amino acids in the sea: Effects of primary productivity and biological decomposition, J. Mar. Res. 42: 1075-1097.

*Lee C., J.I. Hedges, S.G. Wakeham and N. Zhu. 1992. Effectiveness of poisons and preservatives in retarding bacterial activity in sediment trap material. Limnol. Oceanogr. 376: 117-130.

*Lee C., D.W. Murray, R.T. Barber, K.O. Buesseler, J. Dymond, J.I. Hedges, S. Honjo, S.J. Manganini, J. Marra, C. Moser, M.L. Peterson, W.L. Prell and S.G. Wakeham. 1998. Particulate organic carbon fluxes: Compilation of results from the 1995 US JGOFS Arabian Sea Process Study. Deep-Sea Res. II 45: 2489-2501.

*Lee C., S.G. Wakeham and J.I. Hedges. 2000. Composition and flux of particulate amino acids and chloropigments in equatorial Pacific seawater and sediments. Deep-Sea Res. I 47: 1535-1568.

Lévy M., L. Mémery, and J.M. André, 1998. Simulation of primary production and export fluxes in the Northwestern Mediterranean Sea. J. Mar. Res. 56: 197-238.

Lindroth P. and K. Mopper. 1979. High performance liquid chromatographic determination of subpicomole amounts of amino acids by precolumn fluorescence derivitaziation with o-phthdialdehyde. Anal. Chem. 51: 1667-1674.

Livingston H.D., and J.K. Cochran. 1987. Determination of transuranic and thorium isotopes in ocean water: in solution and filterable particles. J. Radioanalyt. Nucl. Chem. 115: 299-308.

Lowenstam H.A. and S. Weiner. 1989. On Biomineralizaiton. Oxford Press, New York. 324 p.

Mantoura R.F.C. and C.A. Llewellyn. 1984. Trace enrichment of marine algal pigments for use with HPLC-diode array spectroscopy. J. High. Res. Gas Chrom. Chrom. Comm. 7: 632- 635.

Martin J.H., G.A. Knauer, D.M. Karl and W.W. Broenkow. 1987. VERTEX: Carbon cycling in the northeast Pacific, Deep-Sea Res. 34: 267-285.

Marty J.C., E. Nicolas, J.C. Miquel and S.W. Fowler. 1994. Particulate fluxes of organic compounds and their relationship to zooplankton fecal pellets in the northwestern Mediterranean Sea. Mar. Chem. 46: 387-405.

Marty J.C., I. Vescovali, J. Chiaverini and A. Stock. 2000. Temporal variability of hydrological conditions and related phytoplankton pigment dynamics in the Mediterranean Sea: a nine year study at the DYFAMED time-series station. 2nd JGOFS Open Science Conference, Bergen (Norway), 13-17 April 2000, 132.

Masque P. 1999. Studies of the behavior of ^{210}Pb and ^{210}Po in the Catalanobalearic Sea (Mediterranean) and their use as radiotracers (translation). PhD. Thesis, Universitat Autonoma de Barcelona.

Mayer H., U. Ramadas Bhat, H. Masoud, J. Radziejewska-Lebracht, C. Wideman and J.H. Krauss. 1989. Bacterial lipopolysaccharides. Pure Appl. Chem. 67: 1271-1282.

Mayer L.M. 1994. Surface area control of organic carbon accumulation in continental shelf sediment. Geochim. Cosmochim. Acta 58: 1271-1284.

Meglen R.R. 1992. Examining large databases: a chemometric approach using principle components analysis. Mar. Chem. 39: 217-237.

Migon C., 1993. Riverine and atmospheric inputs of heavy metals in the Ligurian Sea. Sci. Total Environ. 138: 289-299.

Minas H.J., M. Minas, B. Coste, J. Gostan, P. Nival and M.-C. Bonin. 1988. Production de base et de recyclage: une revue de la problématique en Mediterranée nord-occidentale. Oceanol. Acta 9: 155-162.

Miquel J.C., S.W. Fowler, J. La Rosa and P. Buat-Menard. 1994. Dynamics of the downward flux of particles and carbon in the open NW Mediterranean Sea. Deep-Sea Res. 41: 242-261.

Mortlock R.A. and P.N. Froelich. 1989. A simple method for the rapid determination of biogenic opal in pelagic marine sediments. Deep-Sea Res. 36: 1415-1426.

†Murnane R.J., J.K. Cochran, K.O. Buesseler and M.P. Bacon. 1996. Least-squares estimates of thorium, particle, and nutrient cycling rate constants from the JGOFS North Atlantic Bloom Experiment. Deep-Sea Res. 43: 239-258.

†Murnane R.J., J.K. Cochran and J.L. Sarmiento. 1994. Estimates of particle and thorium cycling rates in the northwest Atlantic Ocean. J. Geophys. Res. 99: 3373-3392.

Murray J.W., J.N. Downs, S. Strom, C.-L. Wei, and H.W. Jannasch. 1989. Nutrient assimilation, export production and ^{234}Th scavenging in the eastern equatorial Pacific. Deep-Sea Res. 36: 1471-1489.

Murray J.W., J. Young, J. Newton, J. Dunne, T. Chapin and B. Paul. 1996. Export flux of particulate organic carbon from the central equatorial pacific determined using a combined drifting trap-^{234}Th approach. Deep-Sea Res. II 43: 1095-1132.

Neal A.C., F.G. Prahl, S.C.M. O'Hara and E.D.S. Corner 1986. Lipid changes during a planktonic feeding sequance involving unicellular algae, Elminius nauplii and adult Calanus. J. Mar. Biol. Assoc. U. K 66: 1-13.

Nelson P.N., J.A. Baldock, J.M. Oades and G.J. Churchman. 1999. Dispersed clay and organic matter in soil: their nature and associations. Aust. J. Soil Res. 37: 289-315.

Nival P., S. Nival and A. Thiriot. 1975. Influences des conditions hivernales sur les productions phyto- et zooplanctoniques en Mediterranee nord-occidentale. V. Biomasse et production zooplanctonique- Relations phyto-zooplancton. Mar. Biol. 31: 249-270.

Nozaki Y., F. Dobashi, Y. Kato and Y. Yamamoto 1998. Distribution of Ra isotopes and the ^{210}Pb and ^{210}Po balance in surface seawaters of the mid Northern Hemisphere. Deep-Sea Res. I 45: 1263-1284.

*Peterson M.L., D.S. Thoreson, J.I. Hedges, C. Lee and S.G. Wakeham. 1993. Field evaluation of a valved sediment trap. Limnol. Oceanogr. 38: 1741-1761.

Prahl F.G., G. Eglinton, E.D.S. Corner, S.C.M. O'Hara and T.E.V. Forsberg. 1984. Changes in plant lipids during passage through the gut of Calanus. J. Mar. Biol. Assoc. U. K. 65: 547-560.

Price N.B., T. Brand, J.M. Pates, S. Mowbray, A. Theocharis, G. Civitarese, S. Miserocchi, S. Heussner and F. Lindsay. 1999. Horizontal distributions of biogenic and lithogenic elements of suspended particulate matter in the Mediterranean Sea. Prog. Oceanogr. 44: 191-218.

Reemtsma T. and V. Ittekkot, 1992. Determination of factors controlling the fatty-acid composition of settling particles in the water column by principal-component analysis and their quantitative assessment by multiple-regression. Org. Geochem.18: 121-129.

Ritchie G. D. and G. B. Shimmield 1991. The use of ^{210}Po/^{210}Pb disequilibria in the study of the fate of marine particulate matter. In: Radionuclides in the Study of Marine Processes, (P.J. Kershaw and D.S. Woodhead, eds.) Elsevier, London, UK, pp. 142-153.

Robbins L.L. and K. Brew. 1990. Proteins from the organic matrix of core-top and fossil planktonic foraminifera. Geochim. Cosmochim. Acta 54: 2285-2292.

Rogers J. J. 1983. In: Aspects of Microbiology. Vol 7, pp. 6-27. Van Nostrand, Wokingham, U.K.

Salton M.R.J. 1960. Microbial Cell Walls. Wiley and Sons, New York. 94 pp.

Sarmiento J. and R.A. Armstrong. 1997. U.S. JGOFS synthesis and modeling project implementation plan. U.S. JGOFS Planning and Coordination Office, Woods Hole Oceanographic Institution, Woods Hole, MA, USA, 73 p.

Sempere R., S.C. Yoro, F. Van Wambeke, and B. Charriere. 2000. Microbial decomposition of large organic particles in the northwestern Mediterranean Sea: an experimental approach. Mar. Ecol. Progr. Ser. 198: 61-72.

Shanks A.L. and E.W. Edmondson. 1989. Laboratory-made artificial marine snow: A biological model of the real thing. Mar. Biol. 101: 463-470.

Sheridan, C.C., Lee, C., Wakeham S.G., and Bishop J.K.B. Suspended particle organic composition and cycling in surface and midwaters of the equatorial Pacific Ocean. In prep.

Stemmann L., M. Picheral and G. Gorsky. 2000. Diel variation in the vertical distribution of particulate matter (>0.15 mm) in the NW Mediterranean Sea investigated with the Underwater Video Profiler. Deep-Sea Res. I 47: 505-531.

Stevenson F.J. 1994. Humus Chemistry. Wiley, New York.

Tholosan O., J. Garcin and A. Bianchi. 1999. Effects of hydrostatic pressure on microbial activity through a 2000 m deep water column in the NW Mediterranean Sea. Mar. Ecol. Progr. Ser. 183: 49-57.

Van Wambecke F., Goutx M., Striby L., Sempere R., and Vidussi F. 2001 Bacterial dynamics during the transition from spring bloom to oligotrophy in the northwestern Mediterranean Sea: relationships with particulate detritus and dissolved organic matter. Mar. Ecol. Progr. Ser. 212: 89-105.

*Wakeham S.G. 1999. Monocarboxylic, dicarboxylic and hydroxy acids released by sequential treatments of suspended particles and sediments of the Black Sea. Org. Geochem. 30: 1059-1074.

*Wakeham S.G., J.I. Hedges, C. Lee and T.K. Pease. 1993. Effect of poisons and preservatives on the composition of organic matter in a sediment trap experiment. J. Mar. Res. 51: 669-696.

*Wakeham S.G., J.I. Hedges, C. Lee, M.L. Peterson and P.J. Hernes. 1997a. Compositions and transport of lipid biomarkers through the water column and surficial sediments of the equatorial Pacific Ocean. Deep-Sea Res. II 44: 2131-2162.

*Wakeham S.G. and C. Lee. 1993. Production, transport, and alteration of particulate organic matter in the marine water column. In: (M.H. Engel and S. A. Macko, Eds) Organic Geochemistry, pp. 145-169. Plenum Press.

*Wakeham S.G., C. Lee, J.I. Hedges, P.J. Hernes and M.L. Peterson. 1997b. Molecular indicators of diagenetic status. Geochim. Cosmochim. Acta 61: 5363-5369.

*Wakeham S.G., C. Lee and J.I. Hedges. 2000. Fluxes of major biochemicals in the equatorial Pacific Ocean. In: Dynamics and Characterization of Marine Organic Matter. (N. Handa, E. Tanoue and T. Hama, eds.), Terra Scientific Publishing Co. (TERRAPUB), Tokyo/ Kluwer Academic Publishers, Dordrecht, pp. 117-140.

*Wakeham S.G., M. L. Peterson, J. I. Hedges and C. Lee. 2001. Biomarkers in the Arabian Sea: spatial and temporal variability in lipid flux driven by the monsoon cycle. Deep-Sea Res. II, In revision.

Wunsch C. 1996. The ocean circulation inverse problem. Cambridge University Press, England.