

MedFlux: Investigations of Particle Flux in the Twilight Zone

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Abstract

The MedFlux project was devised to determine and model relationships between organic matter and mineral ballasts of sinking particulate matter in the ocean. Specifically we investigated the ballast ratio hypothesis, tested various commonly used sampling and modeling techniques, and developed new technologies that would allow better characterization of particle biogeochemistry. Here we describe the rationale for the project, the biogeochemical provenance of the DYFAMED site, the international support structure, and highlights from the papers published here.

Additional MedFlux papers can be accessed at the MedFlux web site

(<http://msrc.sunysb.edu/MedFlux/>).

Key Words: MedFlux, DYFAMED, ballast ratio hypothesis, organic carbon flux, Mediterranean Sea biogeochemistry

1. Introduction

The following papers describe some of the results from the MedFlux project (2003-2007). This project originated for the purpose of testing some very specific hypotheses about sinking particles in the ocean, and then built on results obtained during the course of the project. 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 (>90%) of the particulate organic carbon (POC) is returned to inorganic form and redistributed in the water column. This redistribution determines the depth profile of dissolved CO₂, which in turn determines the concentration of CO₂ in the surface mixed layer, and hence the rate at which the ocean can absorb CO₂ from the atmosphere. It also controls the depth profile of nutrient regeneration, which controls the time scale of return of remineralized nutrients to the photic zone. The ability to predict quantitatively and mechanistically the depth profile of remineralization is therefore critical to predicting the response of the global carbon cycle to environmental change.

Minerals typically constitute more than half the mass of particles sinking out of the ocean surface (Honjo et al., 1982; Ittekkot and Haake, 1990; Honjo, 1996), and this fraction increases dramatically with depth. Marine plankton contribute biominerals, *e.g.*, opal by diatoms and radiolarians, and CaCO₃ by coccolithophorids 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) through sorption and aggregation processes. Minerals are important for making particulate organic matter (POM) sink faster, and may also protect POM from degradation, allowing it to penetrate deeper into the ocean.

Armstrong et al. (2002) demonstrated that ratios of particulate organic carbon to mineral ballast converge to a nearly constant value (~3-7 wt% POC) at depths >1800 m. The unexpectedly strong quantitative nature of this relationship has since become known as the “ballast ratio hypothesis”, which states that the rain of mineral ballast (opal, carbonate, and dust) to the deep ocean is an excellent predictor of POC flux to the deep ocean. This ratio of organic carbon to ballast is relatively uniform in the deep ocean despite locally highly variable primary productivities and fluxes. A consequence of this hypothesis is the possibility that rains of mineral ballasts at depth will prove superior to surface productivity in predicting POC flux, because POC flux seems tightly constrained by ballast flux, while the relationship of POC flux to productivity is much more variable. This leads to the further hypothesis that the establishment of

a single POC:ballast relationship that varies in predictable ways, will improve carbon cycle predictions derived from General Circulation models, as well as satellite estimates of export productivity (Laws et al. 2000).

Klaas and Archer (2002) developed this idea further in a large-scale analysis of sediment trap data. They demonstrated (1) that different ballast types transported different amounts of POC; silicate was by far the least efficient ballast, transporting ~ 0.025 (weight) units of carbon per unit silicate, while carbonate and dust transported ~ 0.074 units of carbon per unit ballast; (2) that when all three ballast types were included in the same multiple regression analysis, ballast fluxes accounted for 85-90% of the variability in POC fluxes, whereas simple linear regressions on any one of these ballast types accounted for much less ($\sim 60\%$); and (3) that transport efficiencies of different ballast types did not vary significantly with depth below 1000 m, suggesting that the mechanistic basis of these patterns resides largely in the upper 1000 m.

The central goal of MedFlux was to develop a better mechanistic understanding of the ballast ratio hypothesis. In particular, given the many processes that could conceivably cause large deviations from observed ratios, our fundamental goal was to understand why POC:mass ratios seem to be well-constrained, and to use this understanding to create a new mathematical description of decomposition to replace those currently in use (e.g., Martin et al., 1987). This last goal is of utmost significance if, for example, lowered pH of seawater causes carbonate minerals to dissolve preferentially, affecting both ballasting and the average remineralization depth of POC in the ocean.

One mechanism that may give rise to constrained POC:ballast ratios is protection. Minerals may physically protect from degradation the OM with which they are associated (Hedges and Oades, 1997; Nelson et al., 1999). This protection is most clearly exemplified by the organic template upon which biominerals are formed (Lowenstam and Weiner, 1989; Knicker et al., 1996). These organic templates (usually rich in glycoprotein) are inaccessible to bacterial hydrolytic enzymes (King, 1974; Robbins and Brew, 1990). In addition to being protected within biominerals, OM more loosely associated with mineral surfaces can also be physically protected. This phenomenon is established for both soils and marine sediments, although specific mechanisms involved are as yet unclear (Mayer, 1994; Hedges and Keil, 1995). Hedges et al. (2001) showed that decreases in POC 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 hypothesized that a substantial fraction of POM raining through marine water columns is protected by association with mineral grains. Thus, the types and amounts of mineral ballast introduced to the surface ocean may be critical, though largely overlooked, determinants and predictors of the ocean's ability to take up and store carbon.

A second mechanism might be termed the “glue hypothesis”, which states that sinking particles must have a minimum POC:ballast ratio to stick together during their transit through the water column. “Excess” POC above this amount is remineralized during descent through the water column, forcing observed POC:ballast ratios into a narrow band with increasing depth. Circumstantial evidence for this hypothesis is found in the POC:ballast ratios from Klaas and Archer (2002): if, as Hill (1998) has hypothesized, sinking particles tend to converge to similar sinking speeds, then particles ballasted by less-dense minerals should have lower excess densities, and so require less organic glue to maintain their integrities. Since opal is less dense than carbonate or dust (due to variable but substantial levels of hydration in opal), it should require less organic glue; this prediction is in agreement with observed patterns of POC:ballast ratios across ballast types (Klaas and Archer 2002).

A third hypothesis is that differences in the ballasting capacity of different minerals reflect potentially specific chemical interactions of POC with different ballasts, rather than the simpler possible explanations involving protection or glue. The data of Hedges et al. (2001), which show that bulk composition of organic matter tends not to change with depth, provides at least some evidence against this hypothesis, which would also be the most difficult to develop quantitatively to the point where it could be incorporated into models of the global carbon cycle.

The prospect of being able to understand and parameterize spatial variability of fluxes in carbon through its association with ballast minerals, and of being able to predict fluxes mechanistically, has encouraged us to undertake a series of technological, methodological, and modeling challenges. The fundamental relationship is very simple: the flux of carbon $F_C(z)$ at any depth, z , is given by the product of its concentration, $C(z)$, and its average sinking velocity, $\bar{w}(z)$, at that depth: $F_C(z) = C(z) \times \bar{w}(z)$. A predictive theory of fluxes must therefore address both concentrations and average sinking velocities.

We have developed devices and protocols that enable us to measure the fundamental components of this flux equation. In particular, using a specially modified sediment trap, we can measure fluxes of carbon and other chemical constituents in sinking velocity classes. Since these

traps gather sufficient material for chemical analysis, we can then characterize each sinking velocity class by its chemical composition. Such measurements afford the basis for a revealing analysis of transport dynamics.

The field of ocean biogeochemistry is especially rich intellectually due to its inherently interdisciplinary nature, and this richness is necessary to make further progress in understanding the ocean's role in the global carbon cycle. However, methodological and technical issues continue to impede our progress. In MedFlux, we made a concerted effort to address some of these issues in an interdisciplinary fashion. For example, rather than asking whether sediment traps or thorium deficits measure carbon flux more precisely, we asked "What are the differences between sediment-trap-based vs. thorium-based measurements, and how can we use these differences to develop a more complete picture of carbon fluxes?" Such an approach can only be undertaken by a coordinated team effort in which different investigators contribute their expertise in a spirit of cooperation.

Below we describe the site that was chosen, some of the major findings of the project, and the collaboration and funding that allowed MedFlux to occur. In addition to the 15 papers presented in this volume, 12 additional papers describing MedFlux results have been published previously. They are available on the MedFlux web site (<http://msrc.sunysb.edu/MedFlux/>). MedFlux data obtained also appear there, as well as on the OCB data site (<http://ocb.whoi.edu/jg/dir/OCB/MedFlux/>).

2. Site

We chose to locate MedFlux at the French Joint Global Ocean Flux Studies DYFAMED time-series site specifically for three reasons. First, its proximity to the coast allows rapid transit between deep oceanic waters and the land-based facilities of the International Atomic Energy Agency's Marine Environment Laboratory in Monaco for processing samples for short-lived radionuclides and labile organic compounds. Second, the location experiences large seasonal variability in hydrography and biological community production and composition. And third, by continuously sampling for over a decade, the DYFAMED program has build up a formidable database with which to place our results in a broader biogeochemical context. A special issue of Deep-Sea Research focused on the first decade of DYFAMED results (Marty, 2002 and

references therein), and core data since 1991 are available via the web at <http://www.obs-vlfr.fr/sodyf/>.

The DYFAMED/MedFlux site is situated in the NW Mediterranean within the central zone of the Ligurian Sea. It is isolated from the Ligurian Current that separates the coastal zone from the open Mediterranean (Béthoux and Prieur, 1983; Sournia et al., 1990; Astraldi et al. 1994). It is thought that there is little advection of riverine particles or resuspended sediments to this site because no major rivers flow into the basin, and the Ligurian current decreases the transport of suspended coastal material (Copin-Montegut, 1988; Durrieu de Madron et al., 1990) and coastal plankton (Stemman et al., 2002). Periodic inputs of atmospheric dust are well-characterized and large (Buat-Ménard et al., 1989, Migon, 1993, Price et al., 1999, Migon et al., 2002), and substantial dust events occurred during our 2003 and 2005 field seasons. The continental shelf in this region is narrow, and the slope is steep (the 1000 m isobath is ~9 km off Nice, water depth 52 km off Nice is 2300 m). There are strong seasonal variations in surface layer temperature and density (Marty et al., 2002). A winter convective mixing period (December-March) lowers sea surface temperature to ~12 °C down to about 200 m depth, after which a gradual increase in thermal stratification and SST to 25 °C occurs by July/August. Our MedFlux sampling from March-June 2003 covered the range of annual temperatures from 12-24 °C.

Biologically, the DYFAMED/MedFlux site 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. Maximum values of primary production of 1.8 g C m⁻² d⁻¹ have been measured by the DYFAMED program during March/April spring blooms, compared to minimum values of 0.1-0.3 g C m⁻² d⁻¹ for August to January, yielding an annual range in primary production of 86-232 g C m⁻² y⁻¹ (average of 77 g C m⁻² y⁻¹; Minas et al., 1988, Lévy et al., 1998, Miquel et al., 2000; Marty and Chiavérini, 2002). Chlorophyll-*a* (Marty et al., 2002) is highest in surface layers during the spring bloom (up to 230 mg m⁻³) and low during the period of oligotrophy (10 mg m⁻³). Chl-*a* inventories derived from satellite imagery over the past decade showed that sampling in 2003 began when Chl-*a* was close to its annual high ~1 g m⁻³ at the end of March, but by June had dropped to near the annual low of ~0.2 g m⁻³. Phytoplankton pigment analyses (Vidussi et al., 2000; Marty et al.,

2002) show that haptophytes are the dominant group of phytoplankton during most of the year, but that diatoms are responsible for the spring bloom, often following a wind event that introduces nutrients into surface waters. The contribution of small-sized phytoplankton, including cyanobacteria, increase at the beginning of summer stratification. Tanaka and Rassoulzadegan (2002) describe a two-layer microbial community in the NW Mediterranean that comprises a microbial food web (phytoplankton-derived DOC as the carbon source for bacteria) in the euphotic zone vs. a microbial loop (POC derived DOC as the bacterial carbon source) in the aphotic zone.

Biogeochemical fluxes have been continuously sampled at DYFAMED for over a decade (Miquel and La Rosa, 1999; Marty, 2002). Effects of horizontal advection on particle flux appear to be low; most currents measured at 200 and 1000 m were 3 m sec^{-1} , although speeds occasionally reached 10 m sec^{-1} (Andersen and Prieur 2000). Downward fluxes of particles have been determined using sediment traps (Miquel et al., 1994; Miquel and La Rosa, 1999; Stemmann et al., 2002) and underwater video profiling (Stemmann et al., 2000, 2002). Sinking particles are a mix of phytodetritus, largely aggregates formed during the spring bloom, and zooplankton fecal pellets, with salp fecal pellets often being more important than those of copepods (Fowler et al., 1991; Marty et al., 1994). Video profiling allowed Stemmann et al. (2002) to estimate that large particles ($>150 \mu\text{m}$) represent 2-30% of sinking POC, with material $>1 \text{ mm}$ in size contributing $>50 \%$ of the flux during the spring bloom period. Pellet carbon fluxes may constitute up to $\sim 65 \%$ of total OC flux (Fowler et al., 1991; Miquel et al., 1994). Bacteria also play an important role in OC flux. High rates of microbial production at depth at the DYFAMED site have been attributed to bacteria carried down on sinking particles (Tholosan et al., 1999 a,b); however Tamburini et al. (2002, 2003) have shown that the importance of bacterial remineralization on particle flux may be significantly underestimated in experiments where in situ hydrostatic pressure is not maintained.

3. Major findings

Papers in this volume cover many aspects of marine particle science. We investigated basic mechanistic principles, developed new techniques, and learned about how the Mediterranean Sea location influenced particle composition and flux. In the first four papers, the direct association between phytoplankton organic matter and mineral ballast was investigated.

Abramson et al. (2008) used sophisticated spectrometric techniques to show how organic matter is distributed throughout the diatom opal matrix and that the organic matter composition varies with location within the matrix. Based on laboratory experiments, Moriceau et al. (2008) modeled the dissolution of diatom opal as two phases, one a phase of relatively soluble opal that allowed associated organic matter to degrade quickly, and a second phase with much more resistant organic matter and less soluble opal. The two papers by Engel et al. (2008a,b) used calcified and naked forms of the coccolithophorid *Emiliana huxleyi* to show that the calcified organisms aggregated faster, sank faster, and better preserved organic matter.

The remaining papers all contain data obtained from the DYFAMED site. Three papers describe organic and inorganic compositions and fluxes. Lee et al. (2008) present POC and inorganic mineral composition and fluxes of 2003 and 2005 experiments. They found little correlation between ballast mineral composition and settling velocity and concluded that the ratio between mineral-associated organic matter and the mineral ballast itself is formed in the surface waters, so that particles of all sizes reflect this ratio. Ballast is important but perhaps more as a nucleator of aggregates rather than due to its excess density. Using data from the 2003 experiment, Wakeham et al. (2008) investigated organic matter compositions in time-series and settling-velocity sediment traps. Organic matter in faster sinking particles was dominated by fecal pellets and phytoplankton aggregates while slower settling particles were more influenced by bacterial degradation products. Thus the particle field is compositionally heterogeneous over a range of settling velocities, and physical and biological exchange between fast sinking and slow sinking particles as they pass down the water column must be incomplete. Bourquet et al. (2008) used lipid biomarker and lipase activity measurements to demonstrate seasonal and diel variations in the lability of organic matter. Bacterial lipid metabolism slowed from spring to summer while lipase activity per cell increased. This led to incomplete consumption of lipid metabolites and excess DOC in summer. Bacterial community structure was different between day and night in spring and with depth in summer.

The next two papers present estimates of particle settling velocities derived using two novel techniques. The paper by Armstrong et al. (2008) uses data from IRS traps run in Settling Velocity (SV) mode (Peterson, 2005, 2008) to estimate both modal and mean settling velocities during eight deployments of these traps. Modal velocity estimates (that is, estimates of the velocity having the largest mass flux per logarithmic interval along the SV axis) are 353 ± 76

m/d (mean \pm standard deviation), while mean settling velocities, averaged over those SV classes settling at > 50 m/d, are 242 ± 31 m/d. The paper by Xue and Armstrong (2008) uses an advanced “benchmark” approach to estimate settling velocity from Time Series (TS) data. In this approach, Fourier series are fit to data from traps at two (and sometimes 3) different depths; these temporal patterns are compared statistically to estimate the time offsets of the patterns at the two depths, allowing SVs between the traps to be estimated. Their estimated SVs are 220 ± 65 m/d for 3 MedFlux trap pairs and 205 m/d for 15 trap pairs having high-resolution data (data from traps whose cup rotation intervals were ≤ 8.5 d; this estimate includes MedFlux and Arabian Sea Process Study data). The concordance between these estimates and the mean SV estimates from SV-mode traps, but not between these estimates and the modal SVs from SV-mode traps, suggests that the benchmark approach estimates mean, not modal, settling velocities.

Disequilibria between naturally occurring U- and Th-series radionuclides have been used extensively as tracers for POC fluxes in the oceans. MedFlux provided an opportunity to test the underpinnings of these applications, as well as to apply the radionuclides in novel ways to characterize particle dynamics through the Twilight Zone. Cochran et al. (2008) compared fluxes of ^{234}Th measured in time-series sediment traps with those determined from water column deficits of this radionuclide relative to its parent ^{238}U . The distinctly different temporal patterns of the fluxes obtained by the two methods led to the conclusion that the two are influenced by fundamentally different processes (local settling flux of particles and Th in the traps vs advective influences and prior scavenging history in the water column Th profiles). Verdeny et al. (2008) summarize several studies (including that made as part of MedFlux by Stewart et al., 2007) that compare $^{234}\text{Th}/^{238}\text{U}$ and $^{210}\text{Po}/^{210}\text{Pb}$ disequilibria as proxies for POC flux. They note that ^{234}Th traces total mass flux while ^{210}Po traces POC, and the two tracers together provide complementary views of the sinking flux of particles. Szlosek et al. (2008) examine the relationships between POC and ^{234}Th in particles separated according to settling velocity. They find no consistent relationship linking $\text{POC}/^{234}\text{Th}$ and settling velocity, as might be expected from surface area to volume considerations. Instead, compositional differences play the dominant role in determining $\text{POC}/^{234}\text{Th}$. Based on changes in ^{234}Th with depth in slowly and rapidly settling particles, Szlosek et al. (2008) also conclude that there is either additional scavenging of ^{234}Th onto the particles as they settle or significant exchange among particles of different settling velocity.

The last four papers describe new or improved methods for investigating particles. Tamburini et al. (2008) constructed a novel apparatus that simulates the temperature and pressure effects of sinking. Particles collected from 200 m and placed in this simulator decompose more slowly than particles maintained at atmospheric pressure. Peterson et al. (2008) describe an adaptation of their large-volume NetTrap whereby they attach a settling velocity (SV)-IRSC trap. This allows the collection of a large enough sample to measure settling velocity profiles over a few-day period. They also describe several tests that examined the accuracy of the SV-IRSC traps. Lastly, Liu et al. (2008) show how zooplankton caught in Niskin bottles bias the POC measurement made using these bottles, and highlight the importance of screening samples. They also show how inlet systems on in-situ pumps can influence POC measurements.

Taken as a whole, the MedFlux studies refined the ballast ratio hypothesis, developed methods for taking large particle samples, for separating particles by settling velocity, and for determining pressure effects on particle biogeochemical composition. They also investigated challenging problems with the use of in-situ pumps and Niskin bottles for measuring POC, and sediment traps and Th and Po isotopes for estimating POC export.

4. International collaboration and funding

International collaboration made the MedFlux project both possible and enjoyable. Such collaboration is not easy to fund because different national foundations and agencies have different priorities and different funding cycles. It is of interest to know what scientific research costs, and this information is seldom part of the published record. MedFlux was funded by many sources in the U.S. and Europe:

The Ocean Sciences Section (Chemical Oceanography) of the U.S. National Science Foundation funded salaries of U.S. participants (Armstrong, Cochran, Fowler, Lee, Peterson, and Wakeham), their participation in cruises, preparation and deployment of sediment traps, and some in-situ pumps, organic and radiochemical analyses of trap and some pump samples, and laboratory aggregation experiments (\$2,217,177 over 5 years). NSF also provided ship time for 1-2 week cruises in 2003 (RV Seward Johnson II), 2005 (RV Endeavor), and 2006 (RV Endeavor).

In 2004, NSF INT funded U.S. participants to attend collaborative meetings to discuss results (\$9,000); jointly, the French Centre National de la Recherche Scientifique (CNRS)

funded French participants to attend collaborative meetings to discuss results (9,200 €). In 2006, CNRS supported Wakeham for a fellowship to work in Marseille.

The International Atomic Energy Agency (IAEA) supported Marine Environment Laboratories (MEL) participant salaries (Fowler, Gasser, Miquel), participation in cruises, deployment of in-situ pumps, and analyses of pump samples, and help with the deployment of sediment traps. IAEA is grateful for the support provided to MEL by the Government of the Principality of Monaco. CNRS funded the R/V Tethys II cruises in 2002 (1), 2003 (3), 2005 (2), and 2006 (2), through IAEA request. IAEA served as the staging area for much of the pre-cruise preparation and post-cruise sample handling.

CNRS also funded French investigator salaries (Goutx, Sempere, Tamburini), their participation in cruises, and particle incubation experiments through the PROOF-PECHE, PROOF-SINPAS, and ANR-POTES projects.

Max Kade Foundation, and later Helmholtz Foundation, paid Engel's salary to participate in laboratory aggregation experiments in Stony Brook, and later, at AWI.

The European Union funded salaries of two Marie Curie post-docs (Fabres, Moriceau) to participate in Medflux cruises and research (~375,000 €).

Giselher Gust tested a neutrally buoyant sediment trap and videotaped sinking particles in the IRS traps in 2003 as part of his national research funding from Germany.

Pere Masqué participated in cruises and made radioisotope measurements as part of his national research funding from the Spanish Ministerio de Educación y Ciencia through Special Actions (28,000 €). In the early stages of MedFlux, Masqué also was supported by a Fulbright Fellowship.

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