

# Controls on Organic Carbon Export and Twilight Zone Remineralization

## An Overview from the EUROCEANS Workshop

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Today, the key role played by the ocean in Earth's carbon cycle is widely accepted. The important interface to consider is not the one between ocean and atmosphere, across which the CO<sub>2</sub> concentration gradient is small, but rather the seasonal and permanent thermoclines at ~20–300-m depth. Though both physical and biological pumps act to increase the amount of carbon stored in the deep sea, this workshop focused on the biological pump. More than 90% of the organic carbon annually exported from surface waters (~10 GTC/yr, as compiled in Boyd and Trull, 2007) is respired back to CO<sub>2</sub> in mesopelagic waters (the region below the euphotic zone extending to about 1000 m, also known as the “twilight zone”). This respiration limits the penetration of carbon to the deeper ocean and sediments, and thus limits the extent of carbon sequestration from the atmosphere. The mechanisms controlling both

the magnitude of carbon export and its fate in the twilight zone are not yet well enough understood to assess the impact of ongoing climate and ocean circulation changes on this carbon sequestration.

To identify gaps in knowledge and opportunities for progress, and to outline future research programs that will advance our ability to assess the biological pump's probable response to climate change, the workshop brought together specialists in many processes controlling organic carbon export from the upper mixed layer and its fate in the twilight zone. The workshop addressed the following topics: (1) mechanisms controlling production, export, and subsequent penetration of sinking organic matter into the ocean interior (such as micro- and macronutrient availability, physics, trophic structure and interactions, and the role of lithogenic and authigenic mineral ballasts as well as their spatial and temporal variability); (2) flux and

fate of sinking particles (assessing export flux from sediment traps, inferences from radionuclide and nutrient budgets, suspended particle population dynamics, and other methods); (3) organic carbon mineralization at depth (including prokaryote and zooplankton respiration measurements, controls on mineralization length scales, and links with surface water processes); and (4) modeling the biological carbon pump (empirical versus deterministic and stochastic models). In examining these topics, considerable emphasis was given to regional and temporal variations. Below, we summarize the major conclusions of the workshop, with special emphasis on the challenges for the future.

A supply of macro- and micronutrients from the deep ocean and the atmosphere is essential for supporting new production, which represents the potentially exportable fraction of primary production. Differences in modes of

nutrient supply (e.g., upwelling intensity, margin and shelf sources, dust input) contribute to setting different broad biogeographical provinces identified in the global ocean. However, a supply of new nutrients can be subject to strong variability at the mesoscale. Indeed, satellite remote sensing has clearly highlighted large mesoscale variability of primary production associated with the waxing and waning of eddies and filaments.

*Thus, it is clearly a challenge to connect the flux of sinking particles to surface water processes. In addition, the recognition that significant phase lags can exist between production and export further decouples surface and deep processes. For these reasons, twilight zone studies should focus on sites for which detailed background information about seasonality and long-term trends exists. Other sites that should be selected for study are those experiencing pulsed micronutrient supply, such as areas where dust events occur. Occupying such sites over a sufficiently long period would permit a better understanding of the impact of Fe supply on productivity, export production, deep-water-column particle flux, and regeneration length scales for macro and micronutrients.*

Knowledge about plankton community composition (e.g., relative contribution of test-producing versus naked plankton cells) and the trophic relationships (importance of grazing and by whom) is also required. Although a recent model study by Gehlen et al. (2006) suggests the importance of aggregation-coagulation in initiating export fluxes, the exact nature of the mechanisms controlling particle size—how the reservoir of small, nonsinking particles links to the one of sinking,

vertical-flux-sustaining particles—is still not adequately understood. Processes of aggregation-coagulation include the physical encounter of particles; scavenging of small particles and cells (including prokaryotes) by phytoplankton exudates such as transparent exopolymeric particles (TEPs; Passow, 2002); and grazing, repackaging, and fecal pellet production by zooplankton. In addition, particle composition and, particularly, the loading of aggregates with ballast particles

and type of ballasting minerals ( $\text{CaCO}_3$ ,  $\text{SiO}_2$ , lithogenic material) are major factors correlated with export (Klaas and Archer, 2002; Ploug et al., 2008). These ballast minerals exhibit different types of associations with organic matter (coccolithophorid cells shed their  $\text{CaCO}_3$  liths to the outside, while diatom shells occlude organic matter within the cell) and also differ in density, though the latter effect is thought to be of lesser importance.

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*For a better understanding of these processes, the impact of nutrient stress, mineral delivery, turbulence, and particle size distributions needs to be assessed. The usefulness of large data sets of particle size spectra throughout the water column was recognized, but converting these spectra into fluxes remains challenging, with more study required of the appropriate (fractal) dimensions, porosities, and mineral contents to convert size spectra into mass spectra, and improved methodologies are needed for separating sinking from swimming particles (Stemmann et al., 2004a,b). Translating size spectra observations into transport rates ideally would be based on in situ measurements of sinking rate, density, composition, and flux, which is still an experimental challenge that should be addressed.*

After being formed, sinking particles entering the mesopelagic waters degrade. Degradation is mainly due to local heterotrophic activity (namely, zooplankton feeding on sinking material) and prokaryotic activity, and it eventually results in solubilization of particulate organic carbon (POC) via production of dissolved organic carbon (DOC) and respiratory CO<sub>2</sub>. The large discrepancy between bacterial demand for organic carbon and POC supply from sinking particles was recognized. Bias may be induced during incubation experiments because the measuring of O<sub>2</sub> consumption and DOC utilization requires long-term incubations during which the original prokaryotic community and structure might change. Also, decompression during incubations affects the outcome, stressing the need to assess prokaryotic activities at in situ pressure. Furthermore, it is important to recognize that the twilight zone is not

solely a region where degradation takes place. Indeed, the importance of ammonia-oxidizing Crenarchaea in the oceanic carbon cycle is now well recognized; Crenarchaea fix carbon dioxide in the dark via chemoautotrophy with ammonia as an energy source, and synthesis of organic carbon through this process could amount to up to 20% of export production (Herndl et al., 2005).

*Clearly, the relative importance of prokaryotic- versus zooplankton-mediated degradation (these processes can be of the same order of magnitude; see, for example, Steinberg et al., 2008) needs to be better assessed because they impact remineralization length scales differently. Assessing the prokaryotically mediated organic carbon degradation rate at the individual particle level (see, for example, Ploug et al., 2008) and developing methods for accurate, bias-free, in situ oxygen consumption rates would help resolve the discrepancy between organic carbon demand and supply.*

The integrated effect of the different processes involved in export and remineralization varies spatio-temporally, and this might be reflected in variability of sinking flux attenuation, often parameterized by a power law and referred to as the Martin curve attenuation factor, or b-value (Martin et al., 1987; Kwon, 2008). The close dependency of atmospheric CO<sub>2</sub> on the biological carbon pump is highlighted in Figure 1, which shows the modeled impact of variability in nutrient utilization and b-values on atmospheric CO<sub>2</sub> content. Increasing winds due to stratospheric ozone depletion and climate warming, stratification due to climate warming, and ocean acidification due to rising atmospheric CO<sub>2</sub> content are likely to impact the biological pump (Le Quéré

et al., 2007). However, it was recognized that there is a misfit between the surface ocean and the twilight zone regarding the complexity of existing biogeochemical models, with the twilight zone representation being oversimplified at present.

*In order to forecast future changes in the biogeochemical cycling of organic matter, the need for a proper mechanistic understanding of the essential processes at stake was stressed. The identification of the essential processes and their parameterization is vital to improving the predictive capability of state-of-the-art global ocean biogeochemical models (e.g., Buitenhuis et al., 2006; Aumont et al., 2006).*

At the end of the workshop, participants recommended that future research priorities include:

1. Assessing the relative role of prokaryotes and zooplankton in changing the POC attenuation rate, including how these controls vary with depth, season, and locale.
2. Assessing the links among particle stocks, particle properties, sinking velocities, and fluxes.
3. Assessing the biological, chemical, and physical processes that induce aggregation and coagulation (such as abundance and activity of prokaryotes, nutrient stress, mineral delivery, and turbulence) as well as the resulting particle size distributions and fluxes.
4. Resolving key processes at the mesoscale (typical length scale of 100-km, i.e. eddy scale) and sub-mesoscale that have strong nonlinear responses to environmental forcing (e.g., episodic nutrient supply) and their subsequent impacts on particle flux and attenuation.

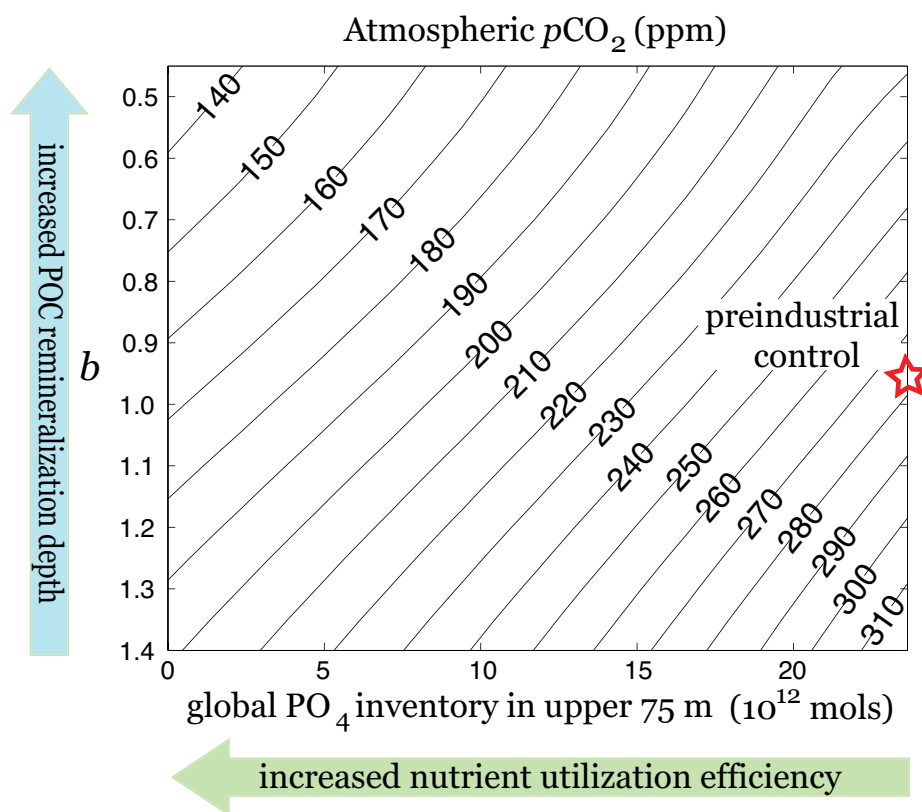


Figure 1. Response of atmospheric  $p\text{CO}_2$  to variations in the efficiency of the ocean's biological pump. The calculation was done using a three-dimensional OCMIP-type ocean carbon model in equilibrium with a well-mixed atmospheric box. Organic carbon production is keyed to phosphate using Redfield stoichiometry, and the downward POC flux,  $J$ , follows a Martin-type power law,  $J(z) = J_0(Z/Z_0)^b$ , where  $J_0$  is the POC export flux at 75 m, the base of the model's euphotic zone. The figure shows that atmospheric  $p\text{CO}_2$  can vary by as much as 80 ppm if  $b$  is changed globally from 1.4 to 0.6—values that are within the range estimated from sediment traps. From Kwon (2008)


- Developing new methods and standards, and well-defined operational procedures for existing methods (e.g., assessment of accurate POC fluxes, prokaryotic production, respiration rates), especially in the context of the low rates of processes in the twilight zone.

An overarching view developed at the workshop was the requirement for a multidisciplinary approach involving observations and perspectives from physics, chemistry, and biology.

The presentations shown during the workshop provide useful overviews

for other researchers and students and are available at <http://www.eur-oceans.eu/events>.

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## REFERENCES

- Aumont O., and L. Bopp. 2006. Globalizing results from ocean in situ iron fertilization studies. *Global Biogeochemical Cycles* 20: GB2017, doi:10.1029/2005GB002591.
- Boyd, P.W., and T.W. Trull. 2007. Understanding the export of marine biogenic particles: Is there

consensus? *Progress in Oceanography* 4:276–312, doi:10.1016/j.pocean.2006.10.007.

Buitenhuis, E.T., C. Le Quéré, O. Aumont, G. Beaugrand, A. Bunker, A. Hirst, T. Ikeda, T. O'Brien, S. Piontkovski, and D. Straile. 2006. Biogeochemical fluxes through mesozooplankton. *Global Biogeochemical Cycles* 20, GB2003, doi:10.1029/2005GB002511.

Gehlen, M., L. Bopp, N. Emprin, O. Aumont, C. Heinze, and O. Ragueneau. 2006. Reconciling surface ocean productivity, export fluxes and sediment composition in a global biogeochemical ocean model. *Biogeochemistry* 3:521–537.

Herndl, G.J., T. Reinthaler, E. Teira, H. van Aken, C. Veth, A. Pernthaler, and J. Pernthaler. 2005. Contribution of *Archaea* to total prokaryotic production in the deep Atlantic Ocean. *Applied and Environmental Microbiology* 71:2,303–2,309.

Klaas, C., and D.E. Archer. 2002. Association of sinking organic matter with various types of mineral ballast in the deep sea: Implications for the rain ratio. *Global Biogeochemical Cycles* 16:63–1–63–14.

Kwon, E.Y. 2008. *Optimization and Sensitivity Analysis of a Global Ocean Biogeochemistry Model*. PhD Dissertation, University of California, Irvine.

Le Quéré, C., C. Rödenbeck, E.T. Buitenhuis, T.J. Conway, R. Langenfelds, A. Gomez, C. Labuschagne, M. Ramonet, T. Nakazawa, N. Metzl, N. Gillett, and M. Heimann. 2007. Saturation of the Southern Ocean  $\text{CO}_2$  sink due to recent climate change. *Science* 316:1,735–1,738, doi:10.1126/science.1136188.

Martin, J., G. Knauer, D. Karl, and W. Broenkow. 1987. VERTEX: Carbon cycling in the Northeast Pacific. *Deep-Sea Research* 34:267–285.

Passow, U. 2002. Transparent exopolymer particles (TEP) in aquatic environments. *Progress in Oceanography* 55:287–333.

Ploug, H., M.H. Iversen, M. Koski, and E.T. Buitenhuis. 2008. Production, oxygen respiration rates, and sinking velocity of copepod fecal pellets: Direct measurements of ballasting by opal and calcite. *Limnology and Oceanography* 53:469–476.

Steinberg, D.K., B.A.S. Van Mooy, K.O. Buesseler, P.W. Boyd, T. Kobari, and D.M. Karl. 2008. Microbial vs. zooplankton control of sinking particle flux in the ocean's twilight zone. *Limnology and Oceanography* 53:1,327–1,338.

Stemmann, L., G.A. Jackson, and D. Ianson. 2004a. A vertical model of particle size distributions and fluxes in the midwater column that includes biological and physical processes—Part I: Model formulation. *Deep-Sea Research Part I* 51:865–884.

Stemmann, L., G.A. Jackson, and G. Gorsky. 2004b. A vertical model of particle size distributions and fluxes in the midwater column that includes biological and physical processes—Part II: Application to a three year survey in the NW Mediterranean Sea. *Deep-Sea Research Part I* 51:885–908.