

Chapter 6

Water Column Biogeochemistry below the Euphotic Zone

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6.1 Introduction

The main focus of the International JGOFS research initiatives was on the cycling of carbon and of associated elements within the surface layer, and their downward export from the upper ocean. Relatively few coordinated measurements and experiments were made below the photic zone so our understanding and modeling of the biogeochemistry of the ocean's interior is still in its infancy. However from the numerous data acquired in the 1990s during JGOFS and JGOFS-like process studies it is possible to extract sufficient information to make preliminary statements about the biogeochemistry of the water column below the euphotic zone. An important preliminary result of these studies is that we now are beginning to realize that the biogeochemistry of the surface ocean, of the ocean's interior, and of the surface sediments appears to be more coupled than was thought fifteen years ago. Moreover, the rate of sedimentation of particulate biogenic carbon into the ocean's interior can be very fast; particles can travel from the surface waters to the abysses in only a few days or weeks, and once the organic matter that is produced in the photic zone (Falkowski et al. 2003, this book) reaches the ocean's interior it is subjected to intense processes of biodegradation and recycling that release nutrients and dissolved CO_2 into subsurface waters. The subsequent upward transport of nutrients and dissolved CO_2 that have been produced and stored in the ocean's interior occurs at a slow rate; the dissolved CO_2 stored below the main ocean thermocline (the 'ventilation depth') will not return to the surface waters and to the atmosphere for centuries to millennia (Fig. 6.1). Whatever the exact time scale, it is clear that the biogeochemistry of the water column is largely driven by the biological pumping of CO_2 (and of other associated essential nutrients), a major process for exporting matter and energy from the photic zone towards the deep layers, and ultimately towards the sediments (see Lochte et al, this book).

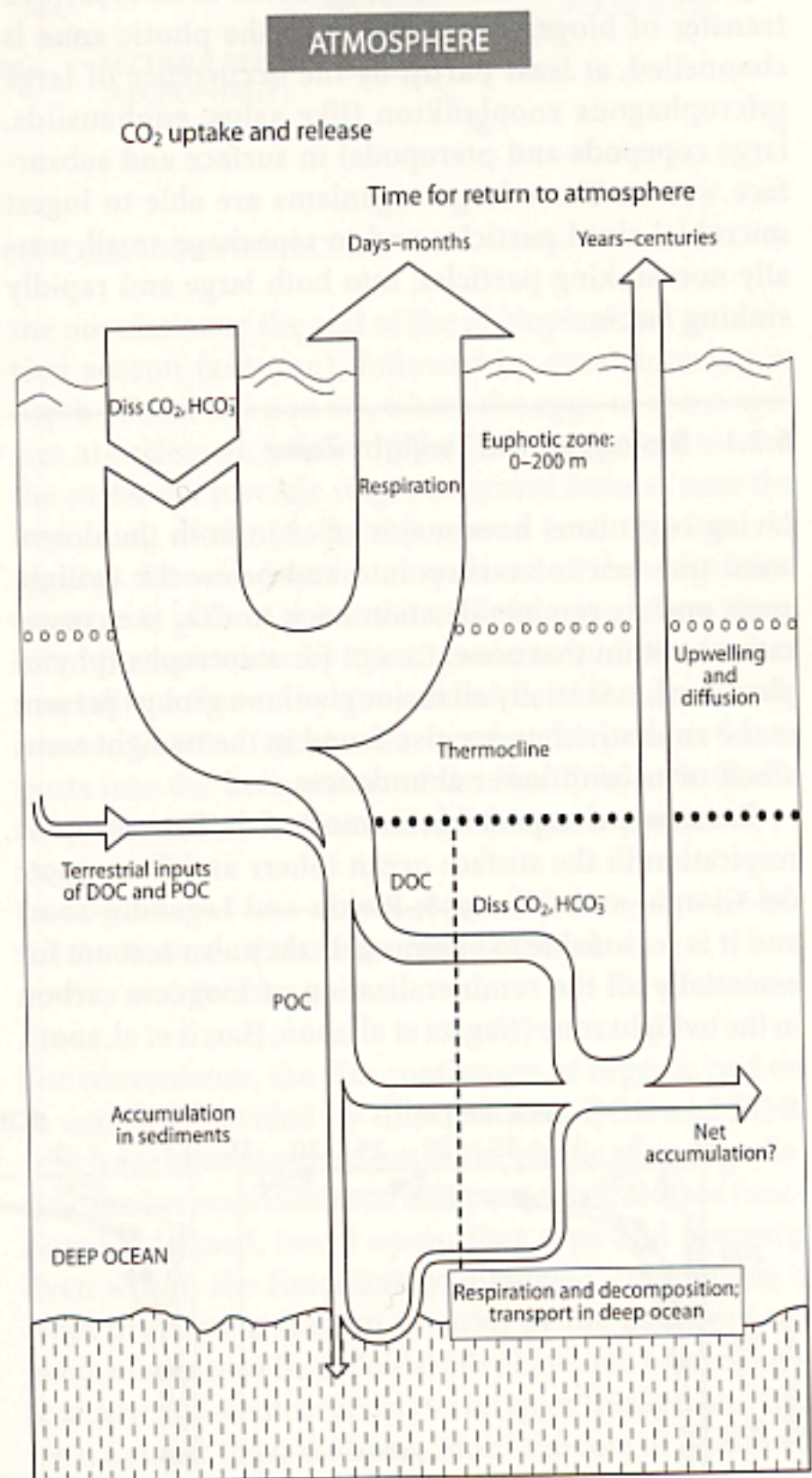


Fig. 6.1. A 1-D vision of the world ocean: the classical JGOFS scheme of the biological pump of CO_2 in the ocean with time scaling in the different layers of the ocean and in the sediment. This scheme first shows that the focus of JGOFS was really on the surface layer, which makes sense because about 90% of the cycle of carbon occurs in the surface layer. It also shows the biological pump is responsible for the transfer of carbon (and of associated elements) to the ocean's interior and ultimately to the sediments

6.2 The Twilight Zone: Biology, Biogeochemical Processes and Fluxes

The 'twilight' zone, immediately below the photic zone between 100 and 1 000 m, is a key layer for remineralization/respiration and biotic processes resulting in an intensive oxygen consumption and in a dramatic decrease of the vertical distributions of the concentrations in dissolved and particulate biogenic matter (Fig. 6.2). As demonstrated by the bifurcation model (Fig. 6.3, Legendre and Le Fèvre 1989; Le Fèvre et al. 1998), the transfer of biogenic matter out of the photic zone is channelled, at least partly, by the occurrence of large microphagous zooplankton (like salps, euphausiids, large copepods and pteropods) in surface and subsurface waters. These large organisms are able to ingest microbial-sized particles and to repackage small, usually non-sinking particles, into both large and rapidly sinking faeces.

6.2.1 Biology of the Twilight Zone

Living organisms have major roles in both the downward transport of carbon into and below the twilight zone, and its remineralization back to CO_2 (i.e., respiration) within that zone. Except for autotrophs (phytoplankton), essentially all major plankton groups present in the euphotic zone are also found in the twilight zone, albeit often with lower abundances.

Bacteria are responsible for most of the heterotrophic respiration in the surface ocean (Sherr and Sherr 1996; del Giorgio and Cole 1998; Rivkin and Legendre 2001) and it is reasonable to assume that they also account for essentially all the remineralization of biogenic carbon in the twilight zone (Nagata et al. 2000; Harris et al. 2001).

Bacterial abundances tend to decrease from ca 5 to 10×10^8 cells l^{-1} in the upper ocean to ca. 5 to 10×10^7 at 1 000 m (Ducklow 1993; Turley and Mackie 1994; Patching and Eardly 1997; Nagata et al. 2000). Areal abundances and biomass however can be 2- to 4-fold greater in the 100 to 1 000 m depth interval than the upper 100 m. The few studies on the production of twilight-zone bacteria show that the rates tend to be ca. 1 to 10 $\text{ng C l}^{-1} \text{d}^{-1}$, or about 10^2 - to 10^3 -fold lower than in the upper ocean (Hoppe et al. 1993; Biddanda and Benner 1997; Patching and Eardly 1997; Hoppe and Ullrich 1999; Dixon and Turley 2000; Turley and Stutt 2000; Nagata et al. 2000 and references cited therein). Areal production is typically 2- to 10-fold lower in the 100 to 1 000 m depth interval than in the upper 100 m. Karner et al. (2001) reported that two groups of archaea (pelagic euryarchaeota and crenarchaeota) were very abundant below the euphotic zone at the Hawaii Ocean Time-Series station. The fraction of pelagic crenarchaeota increased with depth, reaching ca. 40% of the total picoplankton. The high proportion of cells containing significant amounts of rRNA suggests that most pelagic deep-sea microorganisms are metabolically active. This strongly supports the premise that the heterotrophic microbial community in the twilight zone is active, with high rates of autochthonous production that is fuelled by the input of surface-derived dissolved and particulate organic material.

Compared to bacteria, relatively little is known about microzooplankton in the twilight zone (Turley et al. 1988; Turley and Carstens 1991; Patterson et al. 1993). Studies have described the distributions of testate foraminifera or radiolaria (Swanberg et al. 1986) and tintinnids (Krsinic 1988), and a recent study reported that twilight-zone heterotrophic nanoflagellates actively ingest bacterial-size prey (Cho et al. 2000). The exponential decrease in bacterial biomass with depth (e.g., Nagata et al. 2000, 2001) suggest that mortality is due to a combination of

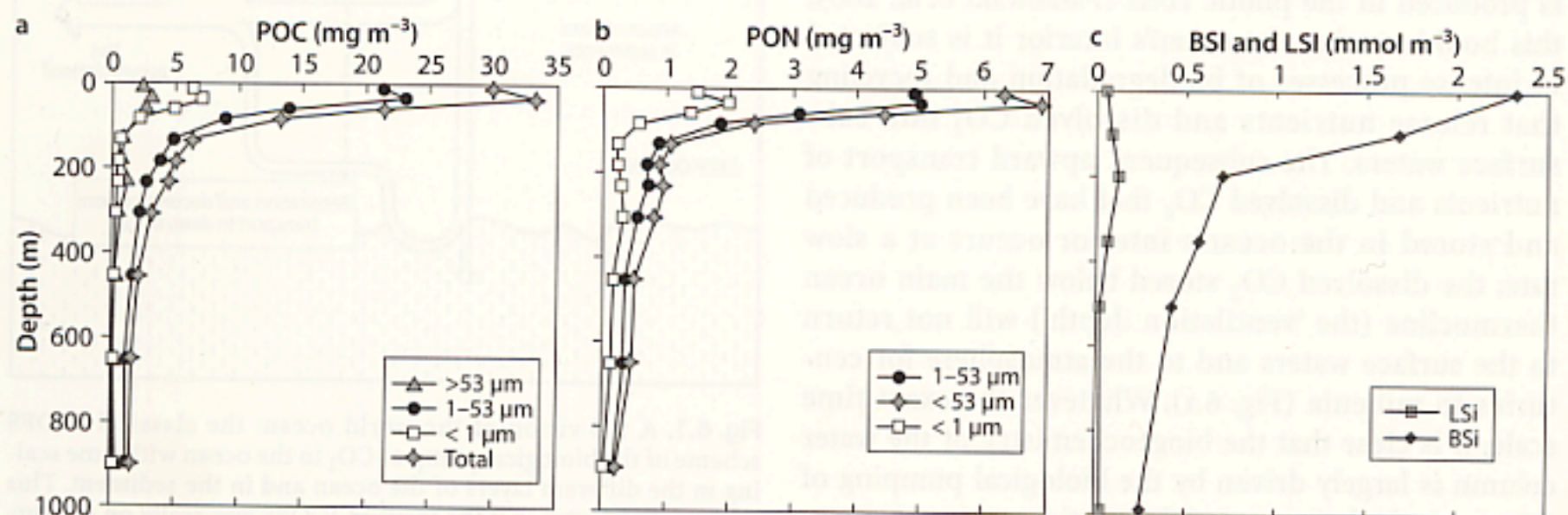
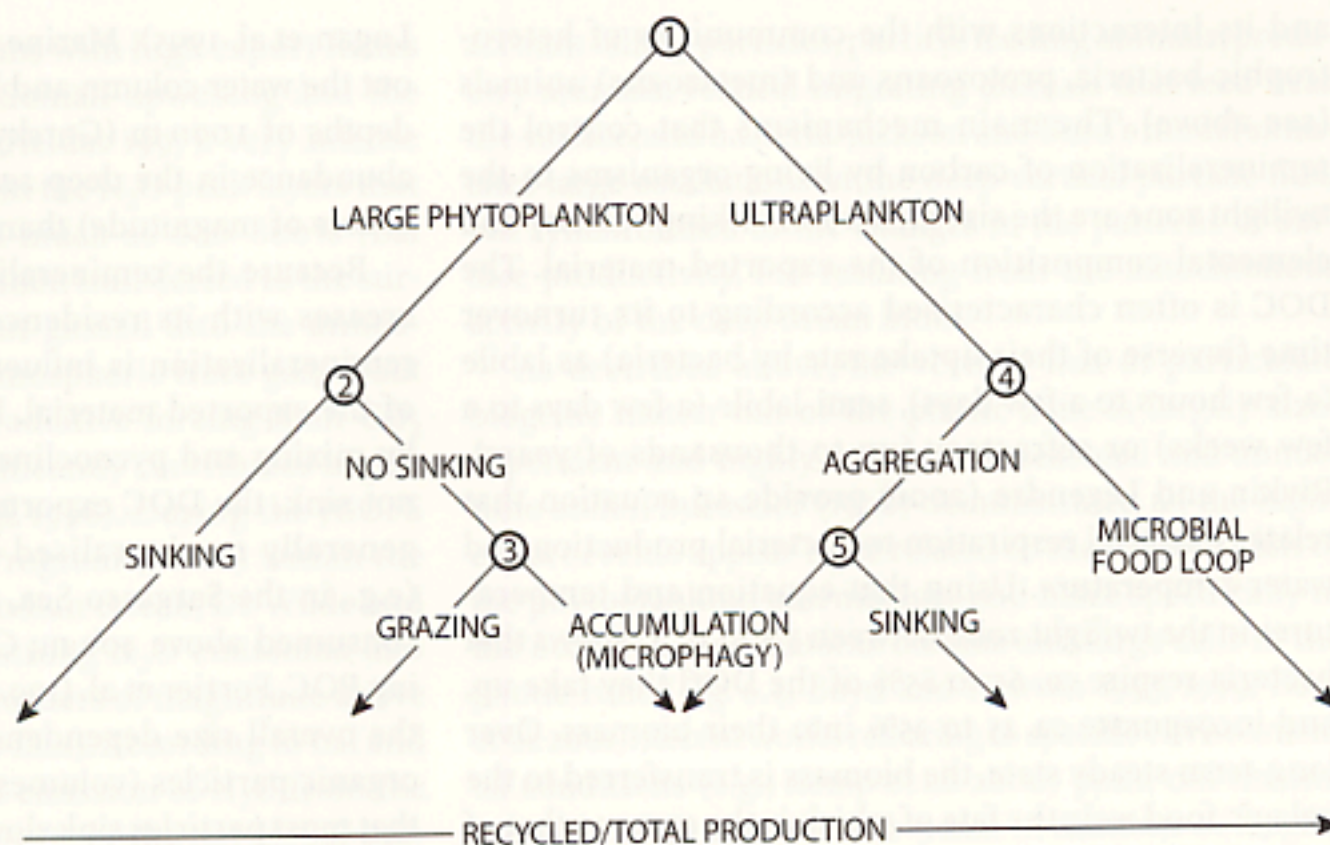


Fig. 6.2. Typical vertical profiles in the 0–1 000 m layer of the ocean. **a** Particulate organic carbon (POC) and **b** particulate organic nitrogen (PON) with size-fractionation, in the 0–1 000 m layer in the North Pacific, station PAPA (reprinted from Deep-Sea Research II 46, Boyd et al. (1999) Transformations of biogenic particulates from the pelagic to deep ocean realm, pp 2761–2792, © 1999, with permission from Elsevier Science). **c** Biogenic silica (BSi) and lithogenic silica (LSi) in the Southern Ocean (reprinted from Deep-Sea Research I 37, Tréguer et al. (1990) The distribution of biogenic and lithogenic silica and the composition of particulate organic matter in the Scotia Sea and the Drake Passage during autumn 1987, pp 822–851, © 1990, with permission from Elsevier Science).

Fig. 6.3.
The 'bifurcation model' of Legendre et Le Fèvre (1989) for the export production in the ocean. Although a pre-JGOFS concept this model has proven to be useful in JGOFS process studies, to correctly understand the major pathways of the export of biogenic matter under physical and biological forcing (reproduced with permission from W. H. Berger et al. (1989) (ed.) *Productivity in the ocean: present and past*. © John Wiley & Sons)



active ingestion of bacteria by heterotrophic protists (Cho et al. 2000) and viral lysis (Hara et al. 1996). Twilight-zone zooplankton and fish have been well studied relative to microheterotrophic components of the food web (Gjosaeter and Kawaguchi 1980; Barnett 1975; Gasser et al. 1998; Tseitlin and Rudjakov 1999; Silguero and Robinson 2000; Yamaguchi and Ikeda 2000; Luo et al. 2000).

Several groups of metazoans, mostly crustacean zooplankton but also some fish and other taxa, migrate upwards, generally to feed in the richer surface waters (Longhurst and Harrison 1988; Hay et al. 1997; Al-Mutari and Landry 2001; Hidaka et al. 2001). There are two general types of vertical migrations, i.e., nycthemeral (or daily) migrations, which occur on a circadian or 24-h cycle, and ontogenic (or seasonal) migrations, that take place over the annual cycle. The same organisms may undergo the two types of migrations during different phases of their life cycle. The typical pattern of nycthemeral migrations is upward movement of the population around sunset and return to depth around sunrise, but the reverse pattern also exists. Depending on the taxa, their size and life stage, nycthemeral migrations vertically range over a few tens to hundreds m, and the upper migration depth ranges from surface to hundreds of meters. During the nycthemeral migrations, the organisms actively transport carbon downwards, mostly from the euphotic into the twilight zones, where they remineralise organic carbon, release (respire) CO₂ and excrete DOC. This downward transport of organic and inorganic carbon may be a significant contribution to carbon export to the twilight zone in some areas (Longhurst and Harrison 1988; Longhurst et al. 1990; Hay et al. 1997; Steinberg 2000; Al-Mutari and Landry 2001; Hidaka et al. 2001) and may account for a large fraction of the bacterial demand for carbon substrates (Steinberg 2000; Nagata et al. 2000; Hidaka et al. 2001). Seasonal migrations generally include a downward movement of

the population at the end of the phytoplankton production season (autumn), followed by overwintering at depth (down to 1 000 m), where the eggs of some species are released, followed by a slow movement toward the surface of juvenile stages or gravid females near the beginning of the productive season (end of winter or spring). The downward component of the migration transports carbon below the twilight zone, where there is both respiration by the organisms and often mass mortality followed by the oxidation of the dead body masses. Morales (1999) estimates that this process transports into the deep waters of the North Atlantic Ocean as much carbon as the sinking of organic particles.

6.2.2 Nature of the Exported Material and Processes

For convenience, the size continuum of organic carbon in oceans is divided by filtration into DOC and POC, which are both exported out of the photic zone. The distinction between dissolved and particulate is often functionally defined, based upon filter type and porosity. Even within the functionally 'dissolved' component, a large proportion (i.e., 30 to 50%) of the dissolved organic matter may be colloidal (Kepkay 2000). Using new (but now non-controversial) techniques (Hedges and Lee 1993; Cauwet 1994; Williams 2000) the role of dissolved organic matter in the carbon cycle of the world ocean is in the process of being reassessed.

The concentration of dissolved organic carbon decreases from the surface values of ca 60 to 80 μM (depending on the region; Williams 2000) to a relatively constant 38 to 40 μM below 1 000 m (Hansell and Carlson 1998; Williams 2000). The shape of the profile and the turnover rate of organic carbon in the twilight zone depend upon the nature of the exported material,

and its interactions with the communities of heterotrophic bacteria, protozoans and (metazoans) animals (see above). The main mechanisms that control the remineralization of carbon by living organisms in the twilight zone are the size structure, sinking velocity and elemental composition of the exported material. The DOC is often characterised according to its turnover time (inverse of their uptake rate by bacteria) as labile (a few hours to a few days), semi-labile (a few days to a few weeks) or refractory (up to thousands of years). Rivkin and Legendre (2001) provide an equation that relates bacterial respiration to bacterial production and water temperature. Using that equation and temperatures in the twilight zone between 3 and 15 °C shows that bacteria respire ca. 65 to 85% of the DOC they take up, and incorporate ca. 15 to 35% into their biomass. Over long-term steady state, the biomass is transferred to the pelagic food web, the fate of which is the same as that of other forms of particulate matter (see below). The organic particles (POC) may be solubilised by diffusible exoenzymes liberated by their attached bacteria (Alldredge and Youngbluth 1985; Hoppe et al. 1993), or they may alternatively be fragmented into smaller particles by various processes and/or consumed by metazoans or protozoans. Using an empirical equation given by Rivkin and Legendre (2001) and the same range of temperatures as above shows that marine protozooplankton (phagotrophic flagellates and ciliates) in the twilight zone respire ca. 40 to 55% of the carbon they consume, so that ca. 45 to 60% are eventually transferred to larger pelagic organisms or exported below the twilight zone. Hence, respiration in the twilight zone is an inverse function of the size of the material exported from the euphotic zone.

Sediment traps are classically used for collecting the sinking particulate organic carbon including large size material named 'marine snow' by Suzuki and Kato (1953). This sticky and fibrous material, >500 µm in length, is able to scavenge particles that easily adhere to it, forming aggregates. Polysaccharide-rich transparent exopolymeric (TEP) material acts as a 'biological glue' and greatly enhances the formation of these aggregates (Alldredge and Gotschalk 1988; Kiorboe et al. 1998; Mari 1999; Mari et al. 2001). Colonization of marine snow aggregates by a wide diversity of marine heterotrophs, ranging from bacteria to zooplankton, has been reported (Alldredge and Youngbluth 1985; Smith et al. 1992; Silver et al. 1998; Azam 1998; Kiorboe 2000). Microbial communities within and upon the marine snow can undergo complex successive changes on time scales of hours to days, with significant alteration of the chemical and biological properties of the particles (Alldredge and Silver 1988; Steinberg et al. 1997; Silver et al. 1998). Aggregates may also break apart, spilling their organic content into the water, so that modeling the fate of marine snow in the water column becomes a real challenge (Jackson 1995;

Logan et al. 1995). Marine snow is distributed throughout the water column and has been recently observed at depths of 1 000 m (Gorsky et al. 2000). Nonetheless its abundance in the deep sea is invariably lower (several orders of magnitude) than in the surface waters.

Because the remineralization of organic matter increases with its residence time in the twilight zone, remineralization is influenced by the sinking velocity of the exported material. DOC is exported downwards by mixing and pycnocline ventilation. Because it does not sink, the DOC exported from the euphotic zone is generally remineralised in the upper twilight zone (e.g., in the Sargasso Sea, the exported DOC is mostly consumed above 400 m; Carlson et al. 1994). Concerning POC, Fortier et al. (1994) provide a figure that shows the overall size dependency of the sinking velocity of organic particles (volumes from 10^1 to $>10^{11}$ µm³), and that most particles sink slowly (about 100 m d⁻¹), including the faecal pellets of most crustacean zooplankton. Because of this, only a few types of exported particles sink fast enough to escape remineralization within the twilight zone (e.g., phytoplankton aggregates, faecal pellets of Antarctic krill, salps and houses of twilight-zone appendicularians; Fortier et al. 1994).

So, the elemental composition of organisms (expressed as the ratio of carbon to various elements, e.g., N, P, Si) differs for different food web components. For example, when bacteria, protists and zooplankton use resources with elemental ratios higher than their own (e.g., $C:N_{\text{Bacteria}} < C:N_{\text{DOM}}$), they remineralise and release into the environment the excess C as inorganic (CO₂) and/or organic compounds. Because the C:N of dissolved and particulate organic matter increases with depth (Loh and Bauer 2000; Kaehler and Koeve 2001), the proportion of the ingested or assimilated organic material that is respired also increases with depth.

The structure and activity of the food webs in both the euphotic and twilight zones will influence the composition, and the rates and patterns of degradation and remineralization of particulate and dissolved biogenic carbon. The combined effect of the above described processes of organic matter transformation and partitioning leads to the remineralization, within the twilight zone, of most of the organic carbon exported from the euphotic zone. It can be estimated that almost none the exported DOC and only ca. 10% of the POC exported from the euphotic zone reach the bottom of the twilight zone at about 1 000 m.

6.2.3 Microbial Production of Nitrous Oxide

As soon as sub-oxic conditions prevail in subsurface and deep waters, active microbial production of nitrous oxide (N₂O), a green-house gas, occurs either by nitrification or by denitrification (Naqvi et al. 1998). This is es-

pecially the case for ecosystems with high export fluxes of organic matter (e.g., the Somali upwelling and the Gulf of Aden, De Wilde and Helder 1997). Very intense production of N_2O occurred in the N_2O peak layers that can be supersaturated by as much as 600–800% (Lal et al. 1996). Dissolved N_2O is then transferred to the surface layer, and ultimately out-gassed into the atmosphere. N_2O is a long-lived atmospheric trace gas, about 20 times more effective in radiative forcing than CO_2 on a per mole basis, and significantly contributes to global warming (Houghton et al. 1996). During the JGOFS Netherlands Indian Ocean Program (NIOP) within the upwelling areas of the NW Indian Ocean, De Wilde and Helder (1997) documented strong N_2O emissions into the atmosphere (they were 3 orders of magnitude above the global mean oceanic N_2O flux). According to Lal and Patra (1998) the total annual emission of N_2O from the Arabian Sea accounts for 13–17% of the net global oceanic source, estimated at about $4.4 \text{ Tg } N_2O \text{ yr}^{-1}$ by Nevison et al. (1995).

6.3 The Fluxes of Biogenic Matter vs. Depth

6.3.1 The Export Flux out of the Euphotic Zone

Siegenthaler and Sarmiento (1993) estimated that the export flux of dissolved organic carbon out of the photic zone might represent as much as 60% of the total export flux, but the exact contribution of dissolved organic carbon to the total export flux of carbon towards the ocean's interior is still a matter of discussion (Williams 1995; Emerson et al. 1997).

The export flux of particulate organic carbon can be estimated using proxies like ^{234}Th (Murray et al. 1996; Buesseler 1998) and barite (Dymond and Collier 1996; Dehairs et al. 1997). It can also be simulated by coupled physical-biogeochemical models (Sarmiento et al. 1998; Pondaven et al. 1999). Buesseler (1998) showed that the export flux of organic carbon represents more than 50% of the annual primary productivity in high latitude systems, differing from the oligotrophic gyres of the Atlantic or of the Pacific oceans, where it is usually less than 10% (Fig. 6.4). Vertical fluxes of particulate matter are not necessarily unidirectional: zooplankters and micronektoners are responsible for active upward or downward migrations that can bypass sediment traps (Angel 1989; Zhang and Dam 1997). Most models that simulate the vertical distributions and the fluxes of biogenic particulate matter in the water column rely on a curve fit of particle flux as an exponential function of depth, avoiding the difficulty of simulating the internal dynamic of the deep ecosystem. New and promising modeling approaches are now emerging (Jackson and Burd 2002) that consider the large diversity of the organic matter that populates the 'twilight zone' taking into

account falling particles, particle feeding animals, predatory animals, vertical migrating animals that feed near the surface, and bacteria. Jackson and Burd's model simulates large oscillations in the deep vertical particle flux, not synchronized to the changes in the patterns of surface productivity, but resulting from the autochthonous activity of the deep ocean biota.

As described above, the vertical flux of particulate biogenic matter out of the photic zone is largely size-dependent and highly variable on seasonal and annual time scales. Buesseler (1998) demonstrated all the high-export events appear to be related to the composition of the phytoplankton assemblages and more specifically to the occurrence of diatoms blooms and large cells in the photic zone (Fig. 6.4; Boyd and Newton 1995, 1999; Bory et al. 2001). Recent works referring to specific environmental conditions (e.g., Kemp et al. 2000) point out the importance of giant diatoms (2–5 mm in diameter or length) to export fluxes. These algae are part of the shade flora (Smetacek 2000) that grow slowly in the less well lit waters at the base of the euphotic zone or in frontal systems

The export production of organic carbon out of the photic zone has to be balanced by an equivalent flux of limiting nutrients (i.e., new production) into the photic zone over the long-term steady state (i.e., annual or longer time periods). This paradigm, proposed by Eppley and Peterson (1979) over two decades ago, is a well known and important concept for biogeochemists. It is important to recall that Eppley and Peterson's original concept was based on the nitrogen cycle, and that the polar oceans and, specifically the Southern Ocean, "where growing seasons are short while ambient nutrients are high", were excluded from their conceptual approach. Since the 1980s this concept has been system-

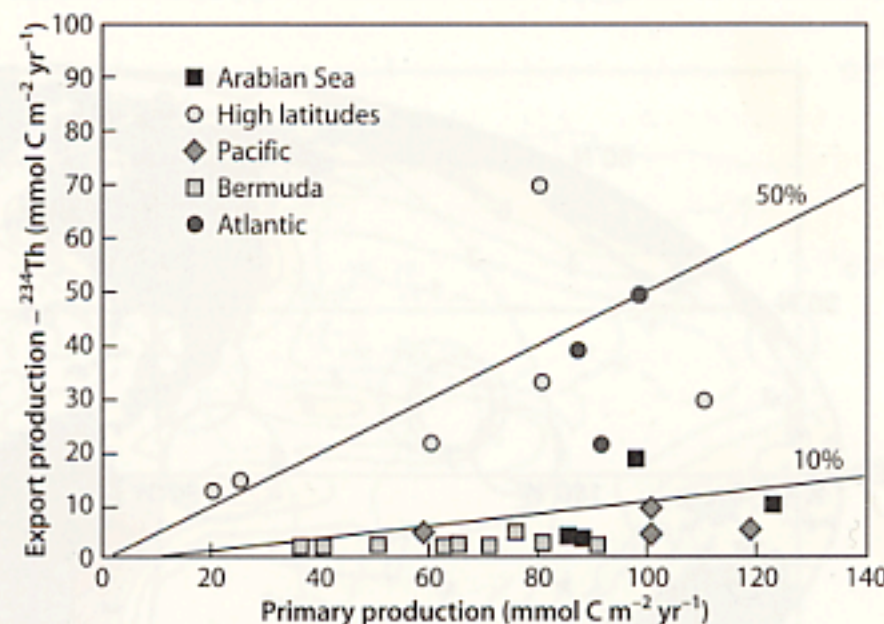


Fig. 6.4. The relative importance of export flux of particulate organic carbon, POC (estimated by the ^{234}Th method) vs. primary productivity, PP. Much of the ocean is characterized by low export of POC relative to PP, except for the high latitudes ecosystems. Diatoms and large cells are responsible for large export events out of the euphotic layer (modified by permission of American Geophysical Union from Buesseler KO (1998) The decoupling of production and particulate export in the surface ocean. *Global Biogeochem. Cycles* 12:207–210. © 1998 American Geophysical Union)

atically but simplistically extrapolated by a number of authors to the carbon cycle. Its validity has been tested during the numerous JGOFS process studies. As shown by Garside and Garside (1993) for the North Atlantic Bloom Experiment, although the concept is valid at appropriate time scales (a year), the balance between export and new production is not matched at short time scales (days to months). It is also clear that extrapolation from nitrogen to carbon is not straightforward because the cycles of carbon and of nitrogen in the euphotic zone (as well as those of carbon and silicon) can be decoupled (see Falkowski et al., this book). This has profound consequences for the assumption about elemental ratios of the exported biogenic material, which can vary from the Redfield ratios (Sambrotto et al. 1993; Maier-Raimer 1996; Karl et al. 2001; Kaehler and Koeve 2001; Koertzing et al. 2001). Indeed, the structure of the food web can influence both the quantity (Boyd and Newton 1995; Rivkin et al. 1996) and quality (i.e., C:N ratios) of the exported material (Walsh 1996; Daly et al. 1999; Agusti et al. 2001), and thus predicting that carbon export from the cycling or flux of other elements may lead to large systematic errors. This also has important major consequences for paleoproductivity reconstructions (Ragueneau et al. 2000).

Based on monthly mean total production maps (estimated from CZCS chlorophyll and *f*-ratios), Behrenfeld and Falkowski (1997) and Falkowski and Raven (1997) estimated that the total export flux was 16 Gt C yr⁻¹ (1300 Tmol C yr⁻¹). A revised estimate of about 11 Gt C yr⁻¹ (916 Tmol C yr⁻¹) is now proposed by Falkowski et al. (2003, this book) using recent SeaWiFS data. Thus, export production might represent 20–40% of the recent estimates of the global marine primary production (Antoine et al. 1997; Falkowski et al. 1998; Laws et al.

2000). Based on inverse modeling of the distributions of physical and chemical parameters for the world ocean, including a large amount of available historical nutrient data (>20 000 stations, <http://www.awi-bremerhaven.de/GEO/Flux/model.html>), Schlitzer (2002) estimates the global marine export flux of biogenic carbon to be 10 Gt C yr⁻¹ (or 833 Tmol C yr⁻¹), a value that is very similar to Falkowski's most recent estimate. However, as regards the regional distribution of this export production, large discrepancies exist between the two approaches. Compared to Schlitzer's method the satellite-derived estimates give a much lower export flux in the Southern Ocean and a higher estimate in the oligotrophic open ocean areas (Fig. 6.5). The discrepancies between the two approaches remain unsolved to date. The export of CaCO₃ in Schlitzer's model roughly follows that of organic carbon and amounts to about 16% of the organic carbon flux. Schlitzer's estimate for the export flux of opal is 162.5 Tmol yr⁻¹, i.e., 58–81% of the global marine production of biogenic silica according to Nelson et al. (1995) and Tréguer et al. (1995).

6.3.2 The Export Flux towards the Ocean's Interior (>1 000 m)

Although they are still criticised (review in Gardner 1995; also see Yu et al. 2001), sediment traps have proven to be very useful tools to study the spatial and temporal variability of sinking biogenic matter in the deep ocean. Sediment traps have been deployed on moorings many times in the various provinces of the world ocean (Honjo and Manganini 1993; Honjo 1997; also see Ragueneau et al. 2000) and the regional distribution of the seasonal and annual fluxes of organic carbon mat-

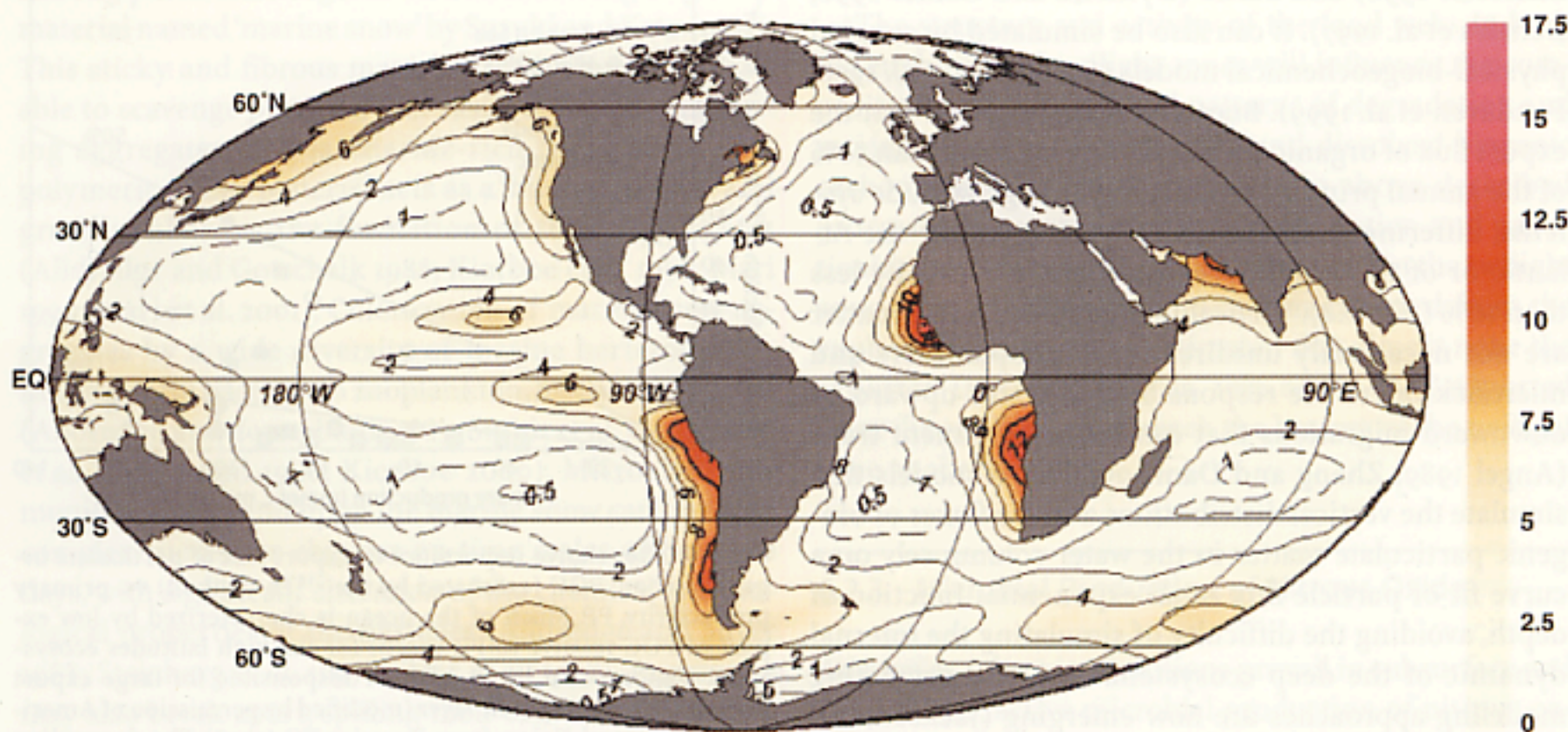


Fig. 6.5. Export production of particulate organic matter (in mol C m⁻² yr⁻¹) out of the surface layer for the world ocean, calculated by inverse modeling of the distributions of physical and chemical parameters for the world ocean, including a large amount of available historical nutrient data (>20 000 stations, <http://www.awi-bremerhaven.de/GEO/Flux/model.html>), Schlitzer (2002).

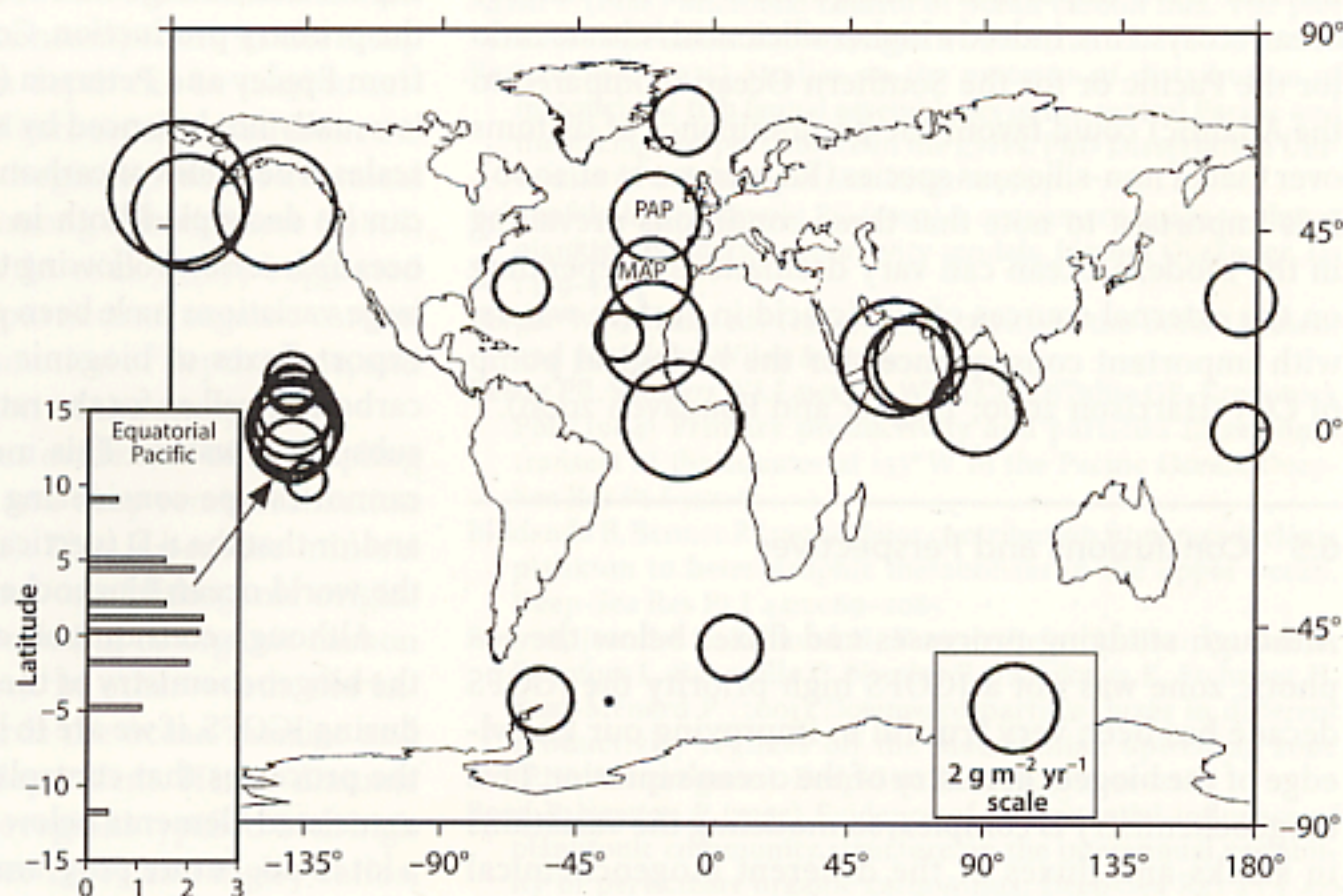
ter below 1 000–2 000 m (i.e., below the layer of fast remineralization and dissolution rates, see above) is now relatively well documented (Lampitt and Antia 1997). The polar seas are however still poorly sampled (Pondaven et al. 2000; Honjo et al. 2000). The proportion of the primary production that reaches the deep sea does not vary much with latitude (Jahnke 1996). Globally, the open ocean flux of organic carbon at 2 000 m, normalised using the empirical relationship due to Martin et al. (1987), is $0.34 \text{ Gt C yr}^{-1}$ that is $<1\%$ of the total net primary production (Lampitt and Antia 1997). Lampitt and Antia showed the organic carbon flux at 2 000 m (outside the Polar Domains) ranges between 0.38 and $4.2 \text{ g C m}^{-2} \text{ yr}^{-1}$ (Fig. 6.6); the monsoonal environments show the highest (1.7%) export ratio (calculated as the ratio of export flux of carbon at 2 000 m: the primary productivity in the surface layer). These authors found the lowest percentages (about 0.1%) in the Southern Ocean. Recently however (Pondaven et al. 2000; Ragueneau et al. 2000) values as high as 0.6% have been reported for the Southern Ocean, indicating a smaller range than previously thought. The global mean rain rate of opal at 3 000 m is estimated at $0.08 \text{ mol Si m}^{-2} \text{ yr}^{-1}$ (Tréguer et al. 1995). This rain rate ranges between 0.02 – $0.09 \text{ mol Si m}^{-2} \text{ yr}^{-1}$ and 0.05 – $0.51 \text{ mol Si m}^{-2} \text{ yr}^{-1}$, respectively for the North Atlantic Ocean on the one hand and for the two major High Nutrient Low Chlorophyll (HNLC) systems, the Southern Ocean and the Equatorial Pacific, on the other hand. Honjo (1997) showed that the ratio of silicon to calcium in biogenic particles collected by deep ocean sediment traps can be used as a proxy for the rate of removal of carbon-dioxide carbon from the upper ocean to the deep-ocean 'sink'. Based on this ratio Honjo (1997) has defined two types of biogeochemical oceans: the 'silicic acid ocean' (mostly the HNLC areas) corresponds to

about 40% of the world ocean with nutrient rich surface waters and opal rich particle rains and sediments. The rest of the oceanic domain is the 'carbonate ocean' (mostly the central gyres) with nutrient poor surface waters and particle rains and sediments rich in calcium carbonate.

6.4 The Variable Composition of the World Ocean Waters along the Conveyor Belt

The JGOFS strategy was largely inspired by a 1-D (vertical) vision of the ocean biogeochemistry (Fig. 6.1). This vision has proven to be very fruitful in understanding the cycling of biogenic matter in the ocean; for a given site of the world ocean the export ratio of the flux of biogenic silica to that of organic carbon exported from the surface layer (Ragueneau et al. 2000) increases with depth, demonstrating preferential remineralization of organic carbon (the same is true for PON) in the twilight zone. Nonetheless large variations in the Si/C molar ratio (Fig. 6.7) are now reported at regional scales; the ratio ranges from 0.1 in the North Atlantic, to 0.3–0.4 in the Indian Ocean, to 0.7 in the Equatorial Pacific, reaching values >1 in the North Pacific. In other words, this Si/C ratio increases along the track of the conveyor belt. So, one important JGOFS output is that the world ocean biogeochemistry experiences drastic differences at regional scales. According to Broecker and Peng (1982), biogenic silica recycles more slowly than organic carbon (or organic nitrogen) causing silicic acid accumulation in subsurface and deep waters along the track of the conveyor belt. More specifically the chemical composition of the subsurface layers of the ocean also varies, with an increase in the silicic acid/nitrate ratio from the North

Fig. 6.6. Export flux of organic carbon in the deep ocean as measured from sediment traps. The flux is proportional to the area of each circle. Organic carbon flux normalized to a depth of 2 000 m exhibits a range of an order of magnitude in areas outside the Polar Domains (0.38 to $4.2 \text{ g C m}^{-2} \text{ yr}^{-1}$). Globally the average oceanic flux at 2 000 m deep is about 1% of the total net primary production (reprinted from Deep-Sea Res II 8, Lampitt RS, Antia AN (1997) Particle flux in deep seas: regional characteristics and temporal variability. pp 1377–1403, © 1997, with permission from Elsevier Science)



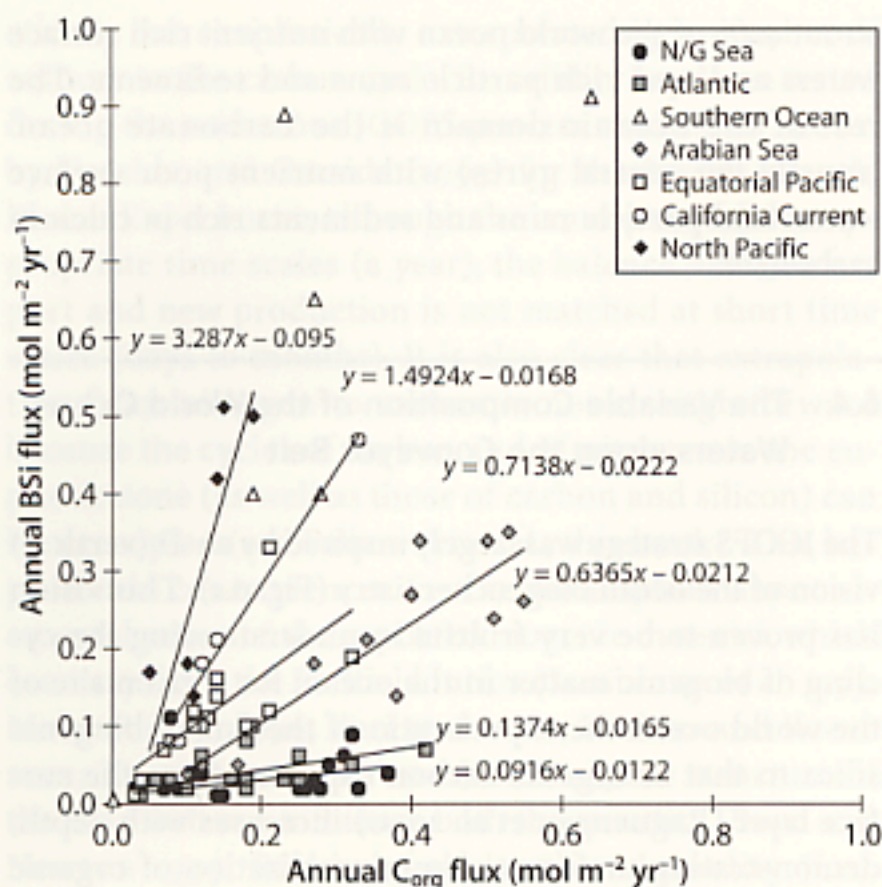


Fig. 6.7. Export fluxes (in $\text{mol m}^{-2} \text{yr}^{-1}$) of biogenic silica (BSi) and of particulate organic carbon (all depths below the euphotic zone) for various regions of the world ocean. Note that the Si/C ratio increases going from the Atlantic Ocean (the 'carbonate ocean' to the North Pacific and the Southern Ocean (the 'silicate ocean'), i.e., following the track of the Conveyor Belt (reproduced with permission from Ragueneau et al. 2000)

Atlantic to the Pacific Ocean and to the Southern Ocean. On average the nutrient source waters of the coastal upwelling of the Pacific Ocean have higher Si/N ratios than those of the Atlantic (Fig. 6.8). Inter-basin silicon fractionation has been described already by Codispoti (1983) through comparisons of nutrients in the two major oceans. Taking into account the JGOFS data for particulate matter we are now able to complete the explanation. These differences in the biogeochemistry of the ocean's interior have important consequences for the surface ocean ecosystems. Indeed a higher silicic acid/nitrate ratio for the Pacific or for the Southern Ocean (compared to the Atlantic) could favour the predominance of diatoms over that of non-siliceous species (Ragueneau et al. 2000). It is important to note that these conditions prevailing in the modern ocean can vary dramatically, depending on the external sources of silicic acid in surface waters, with important consequences for the biological pump of CO_2 (Harrison 2000; Tréguer and Pondaven 2000).

6.5 Conclusions and Perspectives

Although studying processes and fluxes below the euphotic zone was not a JGOFS high priority the JGOFS decade has been very fruitful in improving our knowledge of the biogeochemistry of the ocean's interior. This biogeochemistry is complex, so modeling the variations in stocks and fluxes of the different biogeochemical components remains a challenge. The key elements are

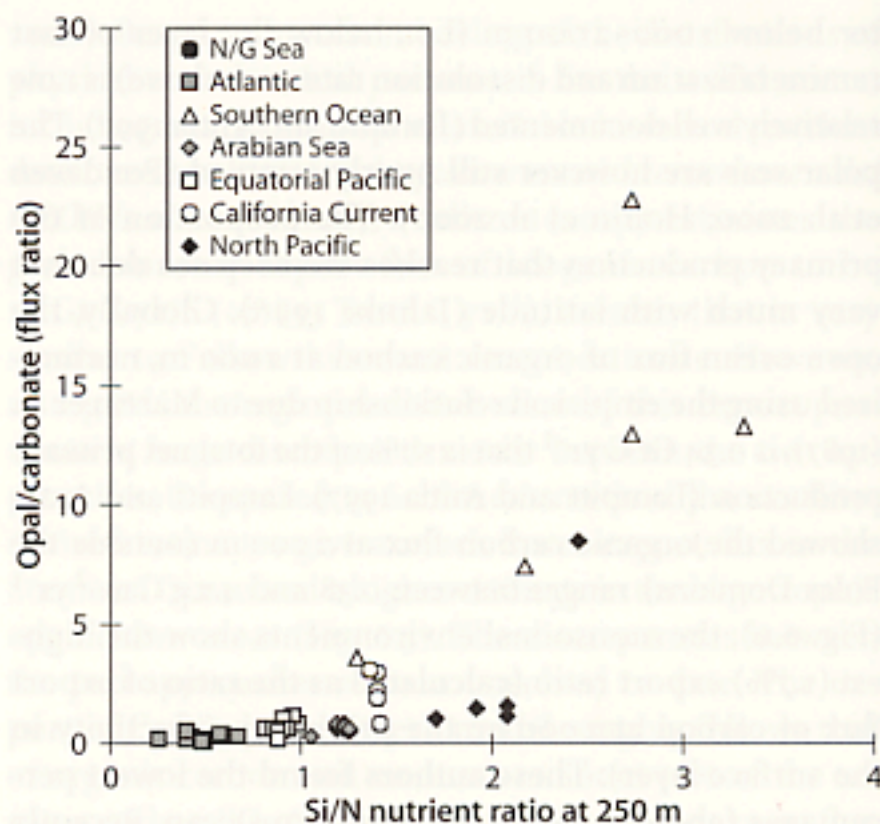


Fig. 6.8. Variations of the silicic acid/nitrate ratio in subsurface waters (250 m depth) at stations where the export fluxes have been measured (see Fig. 6.7). This Si/N ratio increases as the silicic acid concentrations in subsurface water increases with the age of the water masses (reproduced with permission from Ragueneau et al. 2000)

the dissolved and colloidal organic matter, the falling particles, the particle feeding animals, the predatory animals, the vertically migrating animals that feed near the surface, and the bacteria. It is clear that the biogeochemistry of the ocean's interior is much more linked to that of the surface layer than we thought in the 80s. The twilight zone is the key layer for remineralization/respiration processes that result in a drastic decrease of stocks and fluxes of biogenic matter vs. depth. The export flux of organic carbon out of the surface mixed layer is estimated at about 10 Gt C yr^{-1} , i.e., about 20% of the global marine primary production; at 2000 m depth the export flux of organic carbon decreases to about 1% of the primary production. Contrary to what was expected from Eppley and Peterson (1979), the export production is usually not balanced by new production at short time scales. The cycles of carbon, nitrogen and biogenic silica can be decoupled both in the surface layer and in the ocean's interior. Following the track of the conveyor belt, large variations have been evidenced in the ratios of the export fluxes of biogenic silica to particulate organic carbon as well as for the ratios of silicic acid to nitrate in subsurface waters. This means marine biogeochemists cannot escape considering the ocean at regional scales, and/or that the 1-D (vertical) vision typical of JGOFS for the world ocean biogeochemistry is no longer valid.

Although considerable advances in the knowledge of the biogeochemistry of the water column were achieved during JGOFS, if we are to better understand and model the processes that controls the fluxes of carbon and of associated elements below the photic zone we have still a lot to do. Future programs in biogeochemistry should take these considerations into account.

6.5.1 The Ventilation Depth and the ν -Ratio

The dissolved CO_2 stored below the main ocean thermocline will not return to the surface waters or to the atmosphere for centuries to millennia. So the export flux of carbon which is really relevant to the JGOFS perspective is definitely not the flux which escapes the photic zone (i.e., the export flux of carbon as defined by Eppley and Peterson 1979), but the flux which survives to degradation by mineralization and recycling within the twilight zone, and which goes down beyond the ventilation depth. This depth is variable regionally and seasonally, ranging from 50 m in low latitudes to 800 m in high latitudes where deep convection occurs especially during winter (see Fig. 10.2 in Falkowski and Raven 1997). For future studies the ventilation depth of a given system is a characteristic feature that should be systematically determined. In parallel to the classical Eppley and Peterson's f -ratio for the euphotic zone, determining the relative export flux for the ventilation depth, so called the ν -ratio ($\nu = F_A / P_D$, F_A being the annual flux of biogenic element at the ventilation depth, and P_D the time-integrated annual gross photosynthetic production in the surface layer) is of particular interest. For example in the Pacific sector of the Southern Ocean, where very deep convection occurs in the Southern Antarctic Circumpolar region during winter, the ν -ratio for organic carbon is estimated at 0.04, which is about 10 times lower than the annual average f -ratio (Nelson et al. 2002).

6.5.2 The Role of Mineral Ballasts in the Export of Carbon to the Ocean Interior

The idea that the rates of C, N and P remineralization (as well as that of oxygen consumption) in the deep waters of the ocean at a given depth can be used to calculate estimates of the flux of carbon exported from the surface layer emerged in the beginnings of the chemical oceanography (Riley 1954). Among others, Suess (1980), Betzer et al. (1984), and Martin et al. (1987) suggested that the remineralization of particulate organic carbon (POC) can be specified as a function of depth alone, and did not depend on the location of the study site.

But we now have numerous evidences of decoupling between surface production and deep remineralization (Armstrong and Jahnke 2001). This is because mineral ballasts, either of biogenic and/or of lithogenic origin, can play a major role in the sinking of organic carbon (Armstrong and Jahnke 2001). In other words the export of organic carbon towards the ocean interior and the sediment is ecosystem dependent. Hence diatoms are key players in high latitude regions typified with high export flux systems (Buesseler 1998) and high f -ratios, i.e., with low recycling of carbon in the surface layer. In

other words this means that the organic matter exported from the surface layer in association with biogenic silica is very labile, so it is rapidly degraded in the upper layer of the twilight zone, giving low ν -ratios at the ventilation depth. The contrary is true for low latitude systems typified with low f -ratios, where phytoplankters like coccolithophorids predominate. François et al. (2001) now give support to the idea that, in carbonate-dominated systems with low f -ratios, ν -ratios are high, i.e., a higher fraction of the exported organic carbon sinks to the deep ocean. If this is true calcium carbonate might be more efficient a transporter of organic carbon to the ocean interior than opal.

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