Chapter 16

Modeling DOM Biogeochemistry

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I. INTRODUCTION

In the 1970s and 1980s it was realized that planktonic food webs were far more complex than had previously been appreciated, and that microorganisms

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constitute the majority of biomass and respiration in most planktonic systems (Pomeroy, 1974; Williams, 1981; Azam *et al.,* 1983). This new paradigm of the "microbial loop" developed contemporaneously with a heightened interest in the ocean's role in the global carbon cycle, following the realization that changes in ocean biogeochemistry may have forced changes in atmospheric CO_2 during glacial periods (Broecker, 1982) and that a large "missing sink" for atmospheric CO_2 existed, in which the ocean biota might play a role (Wong, 1978; Walsh *et al.,* 1981). Although the literature of ocean biogeochemical modeling has sometimes been concerned with one or the other of these developments without explicitly linking the two (i.e., the microbial food web is highly parameterized in some ocean biogeochemical models, and some microbial food web models are concerned primarily with organismal interactions rather than biogeochemical cycles), at least some investigators drew the connection quite early on (e.g., Pace *et al.,* 1984).

These developments predated the "discovery" of dissolved organic carbon (DOC) measured by high-temperature catalytic oxidation (HTCO) but not detected by other methods, in the late 1980s (Sugimura and Suzuki, 1988). This development heightened interest in DOC in the biogeochemical modeling community and led to the first global-scale simulations of oceanic DOC. While the original results of Sugimura and Suzuki (1988) are now considered erroneous (Suzuki, 1993), they opened the door to a different view of dissolved organic matter (DOM). In particular, it is now known that there is a substantial pool of DOM with a turnover time much less than the ocean overturning time scale ($\sim$1000 years), but long enough to allow carbon and nutrients to be remineralized far from where they were incorporated into organic matter.

After elevated levels of DOC and dissolved organic nitrogen (DON) were reported using HTCO methods (Suzuki *et al.,* 1985; Sugimura and Suzuki, 1988), a number of modeling experiments were undertaken to assess the implications of these observations for the global carbon cycle (e.g., Bacastow and Maier-Reimer, 1991; Najjar *et al.,* 1992; Paillard *et al.,* 1993). These experiments are of considerable interest in terms of understanding the evolution of the field, although their contemporary relevance is somewhat diminished by new information that calls into question some the assumptions employed. Most importantly, these authors took the concentration estimates of Suzuki and coworkers to be substantially accurate, and assumed that a "Redfield equivalent" pool of dissolved organic phosphorus (DOP) would eventually be observed as well. Neither of these assumptions remained tenable for long. By 1993, it had become clear that the HTCO-DOC estimates of Sugimura and Suzuki (1988) were excessive, although a pool of DOC not measured by other methods does exist (Suzuki, 1993; Hedges and Lee, 1993). Furthermore, the DON estimates of Suzuki *et al.* (1985) were shown to be erroneous, and no clear evidence for either DON or DOP not measurable by non-HTCO methods exists (Hansell, Chapter 15).

The conclusions drawn in the early global modeling experiments must therefore be reconsidered in light of an HTCO-DOC pool that is (a) considerably smaller than originally assumed, although not negligible and with similar vertical distribution, and (b) considerably out of Redfield ratio, i.e., strongly enriched in C relative to N and P. More recently, it has been shown that the equatorial nutrient-trapping and anoxicity that Bacastow and Maier-Reimer (1991) and Najjar *et al.* (1992) attempted to remedy by adding a DOM component to their models may be largely an artifact of the coarse resolution of the ocean circulation models employed, and can be eliminated simply by increasing resolution with no modification to the biogeochemical model (Aumont *et al.*, 1999). Matear and Holloway (1995) also showed that these artifacts could be remedied by changing circulation fields without including any DOM component in the biogeochemical model. However, the basic conclusion of Toggweiler (1989), that advection of DOM will substantially alter the distribution of nutrients, oxygen and dissolved inorganic carbon (DIC) relative to an ocean model with only sedimentation of particulate organic matter (POM), remains sound and relevant. The need for prognostic, mechanistic models of the processes that create and consume this pool is acute, and the fact that its elemental composition deviates from Redfield ratio underscores the need for a more sophisticated treatment of variable stoichiometry in biogeochemical models.

II. ECOSYSTEM MODELING STUDIES

A. Compartments and Currencies

The bulk DOM pool is still largely uncharacterized (Benner, Chapter 3) and cycling of elements through DOM is poorly understood from a mechanistic perspective (Kirchman *et al.*, 1993a; Azam, 1998). Reducing the complexity of DOM biogeochemistry to representative and quantifiable structures in models is therefore difficult, and a diversity of approaches and model structures have been utilized (Table I). Early ecosystem modeling studies examined the role of the microbial loop in recycling of nutrients and as a pathway for carbon transfer to higher trophic levels. The models of Fasham *et al.* (1990) and Taylor and Joint (1990) included labile DOM and heterotrophic bacteria (HBAC) as state variables, but no slow-turnover DOM pools. More recently, interest has focused on the biogeochemical role of longer-lived pools of DOM and, in particular, their contributions to export from the euphotic zone. Despite its heterogeneous nature, modelers have endeavored to categorize DOM into different classes to distinguish material that turns over rapidly from that which accumulates and can potentially be exported. High-molecular-weight organic matter requires enzymatic hydrolysis in order to provide the simple monomers that can be taken up by bacteria (Chróst, 1990), and so in principle should be utilized more slowly than monomers. The "HSB" model developed

Table I
Model Characteristics

Reference	Type	State variables	DOM pools	<Currencies> POM	DOM
Fasham *et al.*, 1990	0D	NPZDB	L	N	N
Billen and Becquevort, 1991	0D	B	L, S	C	C
Connolly and Coffin, 1995	0D	ZDB	L, S	C	C
Kawamiya *et al.*, 1995	1D	NPZD	S	N	N
Six and Maier-Reimer, 1996	3D	NPZD	S	P (C)	C
Anderson and Williams, 1998	0D	NPZDB	L, S	N (C)	N, C
Levy *et al.*, 1998	1D	NPZDB	L, S	N	N
Anderson and Williams, 1999	1D	B	L, S, R	C	C
Bissett *et al.*, 1999	1D	NPZDB	L, R	N (C)	N, C
Walsh *et al.*, 1999	3D	NPZDB	L, S	N (C)	C
Tian *et al.*, 2000	1D	NPZDB	L	N (C)	C
Vallino, 2000	0D	NPZDB	L, S	N, C	N, C

Note. State variables: nutrient (N), phytoplankton (P), zooplankton (Z), detritus (D), and bacteria (B) are listed if present. Others not listed. DOM pools: labile (L, turnover rate hours to days), semilabile (S, weeks to months), refractory (R, decades and longer); terminology may differ in original texts. Currencies: parentheses indicate fixed C/N or C/P ratios.

by the Brussels group (Billen, 1990; Billen and Becquevort, 1991; Lancelot *et al.*, 1991) exploited this principle by including two polymeric pools, with fast and slow rates of hydrolysis by bacterial ectoenzymes, which are converted to a common monomeric pool which is consumed rapidly by bacteria. However, the correlation between molecular weight and lability is surprisingly weak in natural DOM (Benner, Chapter 3). High-molecular-weight material can be highly bioreactive, while conversely the bulk of oceanic DOM comprises small molecules that cycle slowly or are relatively unavailable to microorganisms (Amon and Benner, 1994, 1996; Kepkay, 2000).

The simplest distinction between different DOM pools can be made simply on the basis of turnover rates, without necessarily invoking underlying causes. The early work of Ogura (1975) indicated that DOM decomposition in coastal seawater occurred in two distinct phases with rates of 0.1–1 and 0.007 day^{-1}, with a third fraction remaining unutilized. Experiments with DOM derived from phytoplankton in the laboratory also suggest a relatively small number of fractions, although the rate coefficients are quite variable (Pett, 1989; Chen and Wangersky, 1996). The bulk DOM pool can be usefully categorized into labile, semilabile, and

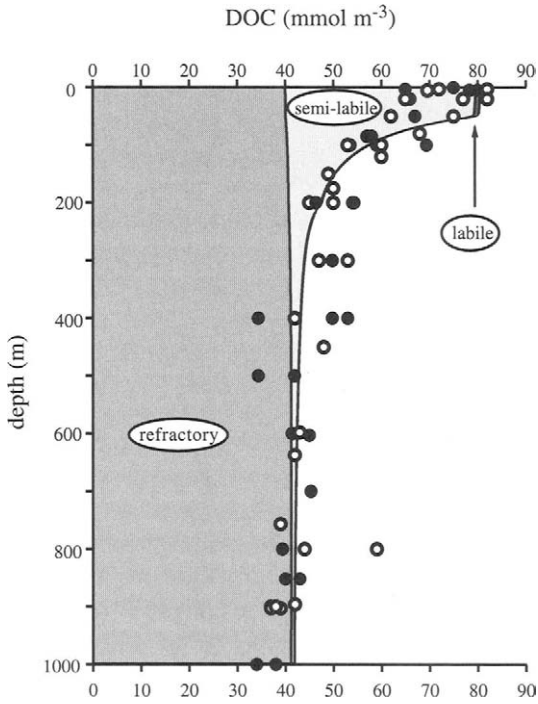

Figure 1 Vertical profile of DOC as simulated by the model of Anderson and Williams (1999), split into its component parts: labile, semilabile, and refractory. Data are for various profiles in the Atlantic (solid points) and Pacific oceans (open points) (see Anderson and Williams, 1999, for details).

refractory fractions (Kirchman *et al.*, 1993a; Carlson and Ducklow, 1995; Cherrier *et al.*, 1996) on the basis of turnover rates. Labile material is consumed rapidly, on time scales of hours to days, semilabile material degrades on seasonal time scales, while refractory material degrades very slowly and may be biologically inert. Anderson and Williams (1999) modeled vertical profiles of DOC in the ocean using a model based on these three fractions (Fig. 1). Many other models have employed two pools representing labile and semilabile compounds without necessarily assuming that this distinction is exactly analogous to, for example, monomers vs polymers (e.g., Connolly and Coffin, 1995; Anderson and Williams, 1998; Levy *et al.*, 1998; Walsh *et al.*, 1999; Vallino, 2000). The terminology regarding different fractions has been variously applied in the literature, e.g., the semilabile pool as defined above has been described as both labile (e.g., Six and Maier-Reimer, 1996) and refractory (e.g., Walsh and Dieterle, 1994; Levy *et al.*, 1998). Few models contain long-lived refractory pools (Anderson and Williams, 1999; Bissett *et al.*, 1999a).

Phytoplankton production is often limited by nutrient elements such as N or P, so one of these is usually employed as a model currency. Nitrogen is in some cases the only model currency (e.g., Fasham *et al.*, 1990; Kawamiya *et al.*, 1995; Levy *et al.*, 1998). However, the growth of heterotrophic bacteria may be carbon- or energy-limited (Kirchman, 1990; Carlson and Ducklow, 1996). Fasham *et al.* (1990) derived a relationship to balance the uptake of DON and ammonium based on assumed C/N ratios of bacteria and DOM of 5 and 8, respectively. Flows of carbon in multielement models are often calculated by assuming fixed C/N (or C/P) ratios for state variables. Ratios in zooplankton and bacteria are commonly different (lower) than those in phytoplankton and DOM. Elemental ratios in zooplankton and bacteria, and to a lesser extent phytoplankton, are relatively constant, whereas ratios in DOM are more variable, for example having highest C/N ratios during accumulation in spring (Williams, 1995). It is therefore necessary to stoichiometrically balance N cycling with DOC uptake and respiration by bacteria (e.g., Anderson, 1992; Goldman and Dennett, 2000).

Two approaches have been used to overcome difficulties with variable DOC/DON: DOC can be included in models without associated DON, or DOC and DON can be included as separate state variables permitting varying C/N. DOC and DON are, of course, inextricably linked; although N-free DOC exists, organic compounds contain C and so there is no DON without DOC. The first approach is useful for modeling accumulation and turnover of DOC, but neglects the role of DON in recycling of nutrients. This approach does not permit nitrogen to enter slow-turnover DON pools, and may therefore result in overestimation of remineralization rates. Bacterial growth is assumed to be limited by DOC, and nitrogen requirements are taken from the inorganic pool (Fig. 2). The second approach is to have separate state variables for DOC and DON, giving rise to a dynamic C/N. Models of this type (e.g., Moloney and Field, 1991; Anderson and Williams, 1998; Vallino, 2000) permit a detailed examination of the roles of DOM in nutrient

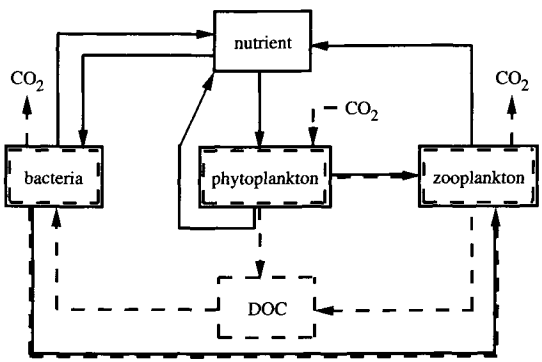

Figure 2 Ecosystem model structure which includes DOC but not DON. Solid lines, N or P flows; dashed lines, C flows.

cycling and accumulation and export of DOC and DON, but parameterization of the interactions between C and N is far from simple.

B. Modeling Production of DOM

DOM is produced from a variety of sources, so ecosystem models need to be complex if production processes are to be fully addressed. Most ecosystem models contain phytoplankton, zooplankton, and detritus, thus providing the potential for sources to be adequately defined. Models which do not include a full ecosystem, but do contain HBAC and DOM as state variables, have been used to study DOM cycling. Billen and Becquevort (1991) modeled bacterial production in Antarctic coastal waters using observed phytoplankton biomass to estimate production of DOC. Anderson and Williams (1999) defined DOC production rate in the euphotic zone as a fixed fraction of primary production and examined the fate of the organic carbon in a deep-water column. Some modeling studies that do include a full ecosystem include external as well as internal sources of DOM. Parsons and Kessler (1986) included a riverine source of DOC in an estuarine model. Walsh and Dieterle (1994) included a sedimentary source in their shallow-water model. Bissett *et al.* (1999a) included a source from dinitrogen fixation without having an explicit population of N_2-fixers.

There are a large number of processes by which DOM is produced (Fig. 3), most of which are poorly understood. As a first approximation, these processes can be

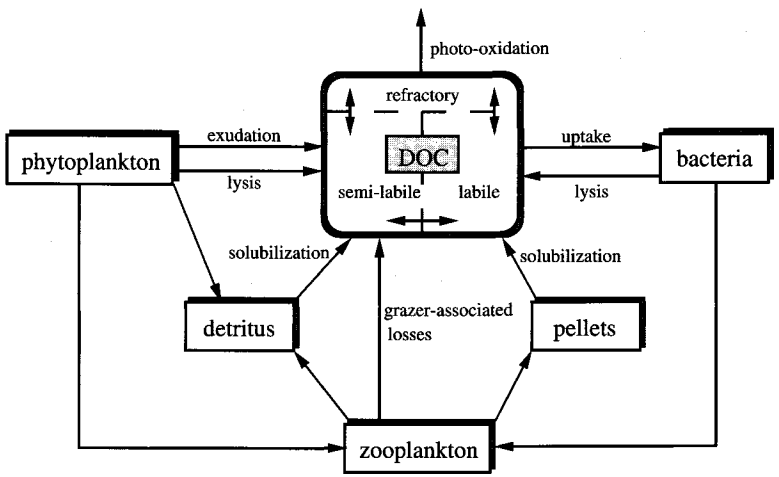

Figure 3 Idealized food web illustrating the four main DOC production terms (phytoplankton exudation, grazer-associated losses, lysis, detrital solubilization) and the two principal loss routes (bacterial uptake, photo-oxidation).

Table II

Sources of DOM in Models That Include an Ecosystem

Reference	Phytoplankton	Zooplankton	Lysis	Detritus
Fasham *et al.*, 1990	0.05pp	0.025Z	—	0.05D
Connolly and Coffin, 1995[a]	0.15pp	{0.07–0.14}g	—	{0.1–0.3}D
Kawamiya *et al.*, 1995	0.135pp	—	—	$0.5(0.03 + 0.0693T)D$[b]
Six and Maier-Reimer, 1996	0.03(P-0.01)	0.06(Z-0.01)	—	—
Anderson and Williams, 1998	$(0.05 + 0.34)$pp[c]	0.23g	$0.04B + 0.015P$	0.05D
Levy *et al.*, 1998	0.05pp	{0.005–0.025}Z	—	{0.008–0.075}D
Bissett *et al.*, 1999	0.05P	{0.33–0.46}g	—	—
Walsh *et al.*, 1999	0.04pp	0.5g	0.0075P	0.132D
Tian *et al.*, 2000	{0.02–0.04}P	0.4g	—	—[d]
Vallino, 2000	0.564pp	—	—	49.6D[e]

Note. P, phytoplankton; Z, zooplankton; B, bacteria; D, detritus; T, temperature; pp, primary production; g, grazing rate. All rates are per day. Brackets indicate a range of values; parentheses have their standard meaning in mathematical expressions.

[a] Includes only partial ecosystem (input observed pp).

[b] An equivalent amount is remineralized directly to DIN.

[c] First term (0.05) leakage (C, N), second term exudation (C only).

[d] Includes breakdown of large (sinking) to small (nonsinking) particles.

[e] Final value after optimization from a first guess of 0.1 day^{-1}, with a range of 0–50, indicating that this parameter was essentially unconstrained by the data.

divided into four categories: phytoplankton exudation, grazer-associated losses, lysis, and detrital turnover. Different models have included different combinations of these terms, and parameterized them in different ways (Table II).

1. Phytoplankton Exudation

Phytoplankton exudation may involve both passive "leakage" and active release. Leakage results from the permeability of the plasma membrane to low-molecular-weight compounds (Bjørnsen, 1988). Metabolic instabilities in algae may cause "extra" carbon to be actively exuded as DOC (Williams, 1990). High release rates

may be a common feature of oligotrophic waters, possibly a result of continued use of photosynthetic machinery after nutrient exhaustion (Norrman *et al.,* 1995; Obernosterer and Herndl, 1995). Exuded polymers may serve a number of functions, few if any of which are well understood (Decho, 1989; Hoagland *et al.,* 1993). Literature estimates of percentage extracellular release (PER) of DOC have a mean of about 13% of primary production, although considerably higher estimates exist (Baines and Pace, 1991; Nagata, 2000). There is significant uncertainty about a mean value due to both methodological considerations and adequacy of data coverage; oceanic environments are underrepresented (Baines and Pace, 1991; Nagata, 2000). The balance of the data seem to suggest that passive leakage is not the dominant mechanism, i.e., that exudation is more closely related to primary production rather than to phytoplankton biomass (Baines and Pace, 1991), although some studies suggest the opposite (e.g., Fuhrman *et al.,* 1980).

Bjørnsen (1988) argued for the representation of exudation as a "property tax" (some fraction of biomass per unit time) rather than an "income tax" (a fraction of photosynthesis) and estimated the rate as about 5% of carbon biomass per day. Models have variously used both approaches (Table II). Rates of production may differ for carbon and nitrogen. A range of compounds including simple sugars and amino acids may be leaked from cells, containing both C and N, whereas exudation due to an overflow of photosynthate might be expected to be dominated by nonnitrogenous compounds. Anderson and Williams (1998) distinguished in their model between leakage, which occurred in the C/N ratio of the phytoplankton, and exudation which was only carbon. The Bissett *et al.* (1999a) exudation term supplied only DOC. Vallino (2000) optimized model parameters to fit mesocosm data and found that a very high C/N in phytoplankton exudate (43200), as well as an exuded fraction of greater than 50% of photosynthesis, achieved the best results. Anderson and Williams (1998) adjusted the exuded fraction in their model in order to simulate the seasonal accumulation of DOC at a station in the English Channel and similarly found that a high DOC exudation rate (PER of 29%) was required. A few models have treated exudation rate as being inversely related to photosynthetic or phytoplankton growth rate (e.g., Pace *et al.,* 1984; Bratbak and Thingstad, 1985), but this approach has not been favored in the more recent literature and does not appear to be supported by the available data (Baines and Pace, 1991). Anderson and Williams (1998) compared two formulations of exudation—a constant fraction of photosynthesis, or a fraction of the difference between nutrient-limited and nutrient-saturated growth rates (cf. Bratbak and Thingstad, 1985). They were unable to assert that either of these parameterizations was more useful than the other.

2. Grazer-Associated DOM Production

There are several mechanisms of grazer-associated DOM production, including so-called "sloppy feeding" (release of dissolved compounds when prey cells are

broken by mouthparts of crustacean zooplankton), direct exudation of DOM, and egestion and dissolution of fecal material. Sloppy feeding losses are negligible if prey can be ingested whole and are likely restricted to metazoa (Nagata, 2000). Rapid pellet dissolution may provide an important mechanism of DOC production (Jumars *et al.*, 1989). Strom *et al.* (1997) estimated that between 16 and 37% of algal C is released as DOC during grazing by phagotrophic protozoa.

The most common modeling approach is to direct a fixed fraction of grazed material to DOM. Values assigned in this manner typically range between 0.2 and 0.4 (Table II), giving rise to large fluxes of DOM via zooplankton. Another approach has been to direct a fraction of zooplankton losses (excretion, mortality) to DOM. Several models do not have any explicit term for production of DOM by zooplankton, but direct losses to "particulate" detritus which is subsequently solubilized to DOM. Including this lag may cause small differences in the dynamic behavior of models, but it is unlikely that these differences are meaningful given the overall uncertainty regarding definitions of particulate and dissolved. Most modelers will likely continue to assign losses to "DOM" or "detritus" depending on assumptions about the size of the grazers that dominate in a particular ecosystem; in open ocean ecosystems, a flow that is predominantly directly to DOM is appropriate (Nagata, 2000).

3. Lysis

Planktonic microorganisms may be lysed by a variety of agents including viruses, bacteria, and under certain circumstances their own intrinsic hydrolytic enzymes (autolysis). Lytic processes potentially explain a great deal of DOM production, especially the more refractory fractions, as cell walls and membranes are sources of important components of DOM (Tanoue *et al.*, 1995; McCarthy *et al.*, 1998). There have been relatively few attempts to model the details of these processes. Models of viral infection have been developed (e.g., Murray and Jackson, 1992), although these have not yet been incorporated into biogeochemical models that fully account for the fate of the DOM produced in this process, with the exception of the very comprehensive treatment by Blackburn *et al.* (1996). These authors modeled four biochemical pools: protein, carbohydrate, nucleic acid, and phospholipid. The DOM released during viral lysis was divided about equally between protein and nucleic acid with only minor contributions from carbohydrate and phospholipid, which were largely retained in "ghost" cells. Thingstad (2000) modeled multiple bacterial strains with a common protozoan predator but host-specific viruses, and showed that the overall rate of viral infection and the importance of lysis in biogeochemical cycles depends strongly on the diversity of the bacterial community.

Plankton models often include a nonspecific mortality term to account for phytoplankton loss processes other than grazing and sedimentation. This term may be

directed to POM, DOM, or inorganic nutrients. The first models to have assigned some of this loss term to DOM appear to have been Taylor and Joint (1990), who applied a first-order loss term to all of their biota groups and assigned some fraction of this to DOC, and Moloney and Field (1991), who defined a population of "senescent" cells that were then subject to lysis to DOC. More recent models that assign some of the loss to lysis to DOC include Anderson and Williams (1998) and Walsh *et al.* (1999). More commonly, this term is applied to particulate organic carbon (POC), which is subsequently subject to solubilization and/or remineralization.

4. Solubilization of Particles

It has been observed that the rate of solubilization of particles by hydrolytic enzyme activity may be orders of magnitude greater than the rate at which the DOM produced is respired (Smith *et al.,* 1992), implying that most particle mass enters the dissolved phase as DOM. Particle turnover is therefore often passed directly to DOM in models (e.g., Fasham *et al.,* 1990; Anderson and Williams, 1998; Levy *et al.,* 1998; Vallino, 2000), although other models recycle it at least in part directly to inorganic nutrients (e.g., Bissett *et al.,* 1999a). Fluxes are modeled as first-order rate processes in many models. Modeling the underlying mechanisms of this process is in its infancy. A basic theory exists for fragmentation of aggregates by turbulence, although there are a number of ill-constrained parameters involved (Hill, 1996). The importance of turbulence in the fragmentation process is in dispute, however, because the turbulent energy required exceeds that normally found in the ocean by several orders of magnitude (Alldredge *et al.,* 1990; Hill, 1998). Solubilization of POM to DOM is in general a biological process, for which few quantitative models exist. Vetter *et al.* (1998) determined the steady-state distribution of a freely released extracellular enzyme and its hydrolysate in an idealized aggregate with a single bacterium at its center. This simple model provides little quantitative information about rates of solubilization, but can be used to estimate the ratio of hydrolysate respired by attached bacteria to that lost to the environment as DOM, which was one to two orders of magnitude greater. The flux of hydrolysate to the cell depends strongly on the diffusivity of the enzyme, with smaller enzymes producing less benefit because hydrolysis occurs, on average, further from the cell. Within the range of diffusivities and partition (between solid and liquid phase) coefficients considered, the flux of hydrolysate increased linearly with increasing release of enzyme, i.e., there was no optimal rate of release. This simple model demonstrates that it is possible for bacteria in porous aggregates to survive by releasing hydrolytic enzymes and that literature estimates of "uncoupled solubilization" from field experiments are reasonable.

5. Lability of DOM Produced

In models with multiple DOM pools, production of DOM must be allocated between the various pools. Phytoplankton exudation is usually assumed to consist solely of labile molecules (e.g., Billen and Becquevort, 1991; Anderson and Williams, 1998; Walsh *et al.*, 1999). However, there is marked variability between models in how other fluxes are allocated. Billen and Becquevort (1991) assumed that DOC produced by lysis and sloppy feeding was partitioned equally between their two polymeric fractions. Walsh *et al.* (1999) allocated 40% of DOC-related grazing losses to the labile pool, with the remainder to semilabile. Connolly and Coffin (1995) assumed that both bacteria and phytoplankton biomass contain 15% labile and 20% semilabile C, part of which is released as DOC during zooplankton grazing. Various modeling studies have adjusted the allocation of organic fluxes to different pools in order to achieve acceptable fits to data. Anderson and Williams (1998) were able to simulate the seasonal DOC increase in the English Channel (34 μmol L^{-1}) by partitioning 90% of DOM produced by various processes (lysis, sloppy feeding, detrital turnover) to the semilabile pool (with the remainder labile). Lowering this fraction required unrealistically high phytoplankton exudation rates in order to generate sufficient DOC to match observations. In a mesocosm experiment, Vallino (2000) found the best fit to data when 67% of detrital turnover went to the semilabile pool. By contrast, in the Mediterranean Sea, Levy *et al.* (1998) found that only 15% of DOC fluxes needed to be allocated to the semilabile pool.

Processes contributing to the production of refractory DOM are poorly understood and have not been extensively modeled. Anderson and Williams (1999) allocated a small fraction of the turnover of labile and semilabile pools to the refractory pool; a value of 0.35% led to a balance between production and ultraviolet (UV) photooxidation (see Section II.C.3). Bissett *et al.* (1999a) assumed that 4.0 % of DOC consumption was released as refractory material.

C. Modeling Utilization and Remineralization of DOM

The primary loss mechanism for DOM is uptake by heterotrophic bacteria. Measurements of bacterial production and growth efficiency show that bacterial respiration accounts for a large fraction of primary production in most oceanic ecosystems (Ducklow, 1999). Some eukaryotic microorganisms (Sherr, 1988; Marchant and Scott, 1993) and metazoa (Wright and Manahan, 1989) can take up dissolved or colloidal organic matter, but it is not known how widespread or quantitatively significant this process is, and it has not to our knowledge been explicitly incorporated into models. The other sink is abiotic photooxidation by solar ultraviolet radiation. Direct photooxidation of DOC to DIC (photomineralization) may be as great as photolysis to monomers and subsequent respiration by bacteria (Miller

and Zepp 1995; Miller and Moran 1997), although it is not known how quantitatively important this process is in the open ocean. Photochemical effects have been incorporated into several ecosystem models (Bissett *et al.,* 1999a; Anderson and Williams, 1999).

1. Turnover of Semilabile DOM

Semilabile material is variously defined in different models, so it is unsurprising that parameterizations of its turnover vary. Connolly and Coffin (1995, p. 682) describe it as compounds that are "readily used, but are less optimal for bacterial growth." They assumed that semilabile material was utilized only after exhaustion of labile substrates and with a lower growth efficiency. Another definition is "molecules whose eventual assimilation by the bacteria requires ectoenzyme hydrolysis to the labile pool" (Anderson and Williams, 1998). Many models therefore employ Michaelis–Menten kinetics to describe turnover, which is usually passed to labile pools (Table III). However, estimates of the kinetic parameters are rare. Billen (1990) estimated parameter values from degradation of DOM derived from an algal culture; Walsh and Dieterle (1994) used these parameters in their model. Lamy *et al.* (1999) fit the HSB model directly to time-series data from experimental microcosms using nonlinear regression. Connolly *et al.* (1992) and Connolly and Coffin (1995) derived values for a variety of coastal and freshwater environments; values from Santa Rosa Sound were applied to the English Channel by Anderson and Williams (1998).

2. Bacterial Utilization of Labile DOM

The predominant model of uptake of dissolved organics by bacteria is a hyperbolic form similar to Michaelis–Menten kinetics, which has been widely used in ecosystem models (Davidson, 1996). Monod (1942) showed that the relationship of growth rate of bacteria in culture to substrate concentration has the form

$$\mu = \frac{\mu_{\max} S}{K_S + S}, \qquad [1]$$

where S is the substrate concentration, $\mu_{\max}$ is the maximal growth rate, and K_S is the substrate concentration at which $\mu = \mu_{\max}/2$. Monod's formulation has been widely adopted by the modeling community, although it lacks a strong theoretical basis (Button, 1998) and there is evidence that other hyperbolic functions give a better fit to observed growth rates (Bader, 1982). Monod's result was derived for cultures grown on simple monomers such as glucose, which some early models assumed to be the predominant form of substrate (e.g., Bratbak and Thingstad, 1985). As models have come to consider other forms of substrate the basic formulation has been retained, although experimental evidence of its applicability is limited.

Table III

Models of DOM Cycling and Turnover

Model	Bacterial model	Parameters	Semilabile turnover	Parameters	UV
Fasham *et al.*, 1990	FDM (see text)	$v_B = 2.0\ day^{-1}$ $K = 0.5\ \mu M\ N$	—	—	—
Billen and Becquevort, 1991	Monod fn DOC	$\omega_C = 0.3$ $v_B = 4.3\ day^{-1}$ $K = 0.8\ \mu M\ C$	Monod fn DOC	$v_S = 6\ day^{-1}$ $K = 208\ \mu M\ C$	—
Connolly and Coffin, 1995	Monod fn DOC	$\omega_C = 0.5$ $v_B = 5.0\ day^{-1}$ $K = 4.2\ \mu M\ C$	Monod fn DOC	$\omega_C = 0.2$ $v_S = 10\ day^{-1}$ $K = 20.8\ \mu M\ C$	—
Kawamiya *et al.*, 1995	—	—	Temperature dependent rate	$0.03\ day^{-1}$ at 0°C	—
Six and Maier-Reimer, 1996	—	—	Monod fn phosphate	$v_S = 0.025\ day^{-1}$ $K = 0.5\ \mu M\ P$	—
Anderson and Williams, 1998	CN stoichiometry	$\omega_C = 0.27$ $v_B = 3.6\ day^{-1}$ $K = 25\ \mu M\ C$	Monod fn DOC	$v_S = 4.0\ day^{-1}$ $K = 417\ \mu M\ C$	—
Levy *et al.*, 1998	FDM	$v_B = 2.0\ day^{-1}$ $K = 0.5\ \mu M\ N$	fixed rate	$v_S = 1.0\ year^{-1}$	—
Bissett *et al.*, 1999	Min[C, N terms], C:Monod, N:after FDM	$v_B = 2.0\ day^{-1}$ $K = 130\ \mu M\ C$	—	—	Y
Walsh *et al.*, 1999	Monod fn DOC	$\omega_C = 0.5$ $v_B = 1.6\ day^{-1}$ $K = 0.8\ \mu M\ C$	Monod fn DOC	$v_S = 0.6\ day^{-1}$ $K = 0.83\ \mu M\ C$	Y
Tian *et al.*, 2000	Monod fn DOC	$\omega_C = 0.15$ $v_B = 0.5\ day^{-1}$ $K = 12.5\ \mu M\ C$	—	—	—
Vallino, 2000	CN stoichiometry	$\omega_C = 0.804$ $v_B = 40.0\ day^{-1}$ $K = 48.8\ \mu M\ C$	Fixed rate	$0.128\ day^{-1}$	—

Note. "UV" indicates models that include photolysis and/or photomineralization. ω_C, carbon gross growth efficiency; v_B, maximum bacterial growth rate (in some cases may be the product of maximum uptake rate and gross growth efficiency); v_S, maximum semilabile uptake rate; K, half-saturation constant.

The basic formulation of Monod has been extended in ecosystem models to address the simultaneous use of organic and inorganic nitrogen (Fasham *et al.*, 1990; Ducklow, 1994). The N-based model of Fasham *et al.* (1990) defines a ratio of inorganic to organic nitrogen uptake for balanced growth, given by

$$\eta = \frac{\omega_C \theta_{DOM}}{\omega_N \theta_B} - 1, \qquad [2]$$

where ω_x is the growth efficiency for carbon or nitrogen, and θ_{DOM} and θ_B are C/N ratios of DOM and bacteria, respectively. This model assumes that if there is sufficient NH_4^+, dissolved inorganic nitrogen (DIN) and DON are taken up in fixed ratio ($\eta = 0.6$). If not, DIN and DON jointly limit the bacterial growth rate. This model does not include carbon and does not consider the dependence of NH_4^+ excretion on substrate C/N; excretion occurs at a constant biomass-specific rate ($0.05\ day^{-1}$).

Excretion of nitrogen by bacteria is thought to decrease at high substrate C/N ratio (Goldman *et al.*, 1987) as N is conserved for growth and respiration costs are met using C-rich substrates. Net nitrogen excretion, E_B, can be described by the following expression (Goldman *et al.*, 1987; Anderson, 1992; Goldman and Dennett, 2000):

$$E_B = U_C \left(\frac{1}{\theta_{DOM}} - \frac{\omega_c}{\theta_B} \right), \qquad [3]$$

where U_C is DOC uptake. A negative E_B requires ammonium uptake to supplement DOC as a growth substrate. Net excretion occurs only at low C/N, and supplementation of DON by ammonium occurs only if there is insufficient DON to meet N demand. If sufficient C is available then no net excretion of N occurs. Depending on the C/N of DOM, either C or N is predicted to limit growth; above a threshold C/N ratio θ_B/ω_c, N is limiting. At high C/N there may be insufficient NH_4^+ to permit full utilization of DOC for growth, and DOC can accumulate (Anderson and Williams, 1998; see also Thingstad *et al.*, 1997). Net regeneration of NH_4^+ is predicted to occur only when nonnitrogenous C sources are scarce and N-rich DOM is being utilized. Simple relationships between regeneration of ammonium by bacteria and respiration may not occur (Ducklow, 1994).

Values of ω vary considerably among models (Table III), typically between 0.25 and 0.50. A recent review of bacterial growth efficiency in the open ocean indicates a mean value of 0.15 for carbon (del Giorgio and Cole, 2000). The model of Vallino *et al.* (1996) provides a more mechanistic basis for modeling bacterial respiration and growth efficiency, but ecosystem models to date have not generally moved beyond assuming constant values. Blackburn *et al.* (1996) used a two-component model of bacterial respiration, with a constant fraction of DOC

uptake respired in addition to a constant mass-specific basal metabolism. Values of the half saturation constant for labile DOC uptake also show marked differences between models. Moreover, there is evidence that bacteria physiologically adapt to changing substrate levels, e.g., by altering the maximal uptake rate (Kirchman *et al.,* 1993b, 1995), a phenomenon not currently considered in models. A mathematical treatment of the mechanisms underlying such adaptation is given by Button (1998).

A slightly different approach to dual element modeling was taken by Bissett *et al.* (1999a). The equations of Fasham *et al.* (1990) were used to define rates of DON and NH_4^+ uptake, except that the value of θ_{DOM} (and therefore η) was variable, and a separate Monod function was defined for DOC. The rate of carbon uptake was then set to be the minimum of the carbon- and nitrogen-limited rates of carbon uptake. If the former, nitrogen uptake was adjusted downward to achieve balanced growth. DIN uptake was reduced first, and if DON uptake was in excess once DIN uptake was eliminated, the "excess" N was transformed into NH_4^+, permitting remineralization of N when the ambient substrate pool was N rich.

The model of Thingstad *et al.* (1997, 1999) indicates that labile DOC may not be consumed rapidly by bacteria because of a "malfunctioning microbial loop." These models contain a steady-state representation of the bacteria–phytoplankton–phosphate–flagellate system, which is subject to external grazing pressure from ciliates and higher predators. Biomass of HBAC can be limited by a combination of nutrient stress and predation so that an increase in the total nutrient content (and therefore phytoplankton biomass and production) of the system can result in accumulation of labile DOC (Thingstad *et al.,* 1997). Lags between peaks of primary and secondary (bacterial) production during blooms can be explained even if the DOM is labile (Thingstad *et al.,* 1999). This work provided a theoretical and experimental demonstration of how a combination of predation and mineral nutrient limitation, rather than the availability of organic substrates, may control bacterial production and thus consumption of labile DOM.

3. Photochemical Effects

The photochemistry of DOM has been an area of increasing interest in recent years, although most models do not contain such processes. The basic equations of aquatic photochemistry have been reviewed by Miller (1998) and Mopper and Kieber (Chapter 9) and will not be repeated here. The absorption spectrum of absorbing or "colored" DOM (CDOM) has a negative exponential shape, increasing monotonically toward shorter wavelengths. Most of the photochemical reactivity is in the ultraviolet B range (UVB, approximately 280–320 nm). A number of models exist that describe photochemical production of various compounds from DOM (e.g., Sikorski and Zika, 1993; Gnanadesikan, 1996; Preiswerk

and Najjar, 2000), but are not discussed here as they do not explicitly model the DOM pool itself. For a general treatment of the theory of modeling meteorological and solar forcing of photochemistry in the upper ocean see Doney *et al.* (1995).

Anderson and Williams (1999) included refractory DOM (RDOM) as one of three fractions in their model. This RDOM was not subject to direct bacterial oxidation, but was photooxidized to labile DOM which was available to bacteria. Using a photochemical breakdown rate at the ocean surface (α_0) of 0.0015 day^{-1} and an attenuation coefficient for UVB (k_{uv}) of 0.33 m^{-1}, they found that a steady state was attained with an RDOM production rate of 0.35% of labile and semilabile DOM utilization by bacteria. The depth-integrated rate of photooxidation in this one-dimensional model can be approximated as $\alpha_0 R_0 / k_{uv}$ (their Eq. [7]), where R_0 is the concentration of RDOM at the ocean surface. This model suggested that a 10% increase in UV radiation at the ocean surface would decrease the global ocean stock of RDOM by less than 1% over 200 years. Klepper *et al.* (1994) estimated that increased UV-induced DOM photolysis would decrease ocean carbon storage in 2070 by more than 25% relative to their baseline simulation of no change in ocean circulation or biogeochemistry with CO_2-induced climate change. This effect was the largest of the seven "feedback" terms that they quantified, but was considered the most uncertain. Few details about the model are given, so it is difficult to evaluate these conclusions. The model incorporates in at least rudimentary form the ocean's overturning circulation, which is impossible in the type of model employed by Anderson and Williams (1999), and is highly relevant to the question of global DOM photooxidation rates.

Bissett *et al.* (1999b) coupled a complete ecosystem model to a spectral model of inherent and apparent optical properties, by specifying a certain fraction of the DOC produced within the ecosystem model as "colored" and subject to photochemical reactions. Estimating these fractions is difficult, and their values in nature are largely unknown (Nelson and Siegel, Chapter 11). Bissett *et al.* (1999b) had observations of spectral attenuation coefficients with which to compare the model output, although their model is very complex and difficult to constrain. Modeled values of CDOM absorption in the Sargasso Sea were maximal at 60–80 m depth in autumn, which is consistent with observations (Siegel and Michaels, 1996). Ratios of the downwelling attenuation coefficients at 412 and 487 nm, which is an approximate index of attenuation due to CDOM relative to phytoplankton (Siegel and Michaels, 1996) were in the range of 1–1.2 and were generally lower than observed values except at the surface in summer. This may imply low rates of photooxidation or it may be the modeled seasonal cycle of DOC itself that is in error, rather than the photochemical model. This model was also the first to our knowledge to consider direct photomineralization to CO_2.

III. MODELING THE ROLE OF DOM IN OCEAN BIOGEOCHEMISTRY

A. Major Classes of Ocean Models

At basin to global scale, ocean models generally belong to one of two classes: ocean general circulation models (OGCMs) and box-diffusion models. The former represent the integration of the equations of motion, or a partially linearized approximation, on a grid whose resolution is generally on the order of 1–3° for basin- to global-scale models. The latter divide the ocean up into a number of boxes that exchange heat and chemical tracers according to specified rates of advective exchange and mixing coefficients ("eddy diffusivities"). The processes that are represented by these coefficients are also relevant to OGCMs, as the grid is too coarse to represent mixing processes explicitly, and the results are frequently highly sensitive to how these "sub-grid-scale" processes are represented (e.g., Danabasoglu *et al.,* 1994; McWilliams, 1996). An important innovation in box-diffusion models has been the inclusion of an "outcrop" box in the high latitudes that extends from the surface to greater depths than the surface boxes in lower latitudes (e.g., Siegenthaler and Joos, 1992). This permits rapid exchange of oxygen and carbon between the atmosphere and the low-latitude deep ocean via the high latitudes, as these fluxes occur in the ocean primarily along isopycnal surfaces.

B. Early Results: Equatorial Nutrient-Trapping

Experiments with both OGCMs and box-diffusion models were conducted in the wake of the "discovery" of HTCO-DOC to assess the effects of DOC production on the large-scale distribution of nutrients, oxygen, and DIC (e.g., Bacastow and Maier-Reimer, 1991; Najjar *et al.,* 1992; Paillard *et al.,* 1993). It is important to note that not all of these simulations employed prognostic biological models: in many cases they simply estimated "new production" (NP, which is actually net community production) either by restoration of the model nutrient fields to climatological values as these are altered by upwelling and advection (Najjar *et al.,* 1992) or as a function of nutrient concentration (Paillard *et al.,* 1993) or nutrient concentration and irradiance (Bacastow and Maier-Reimer, 1991; Matear and Holloway, 1995). This NP is then redistributed downward to simulate sedimentation, usually according to the hyperbolic expression of Martin *et al.* (1987). Early experiments with DOM assigned some fraction of NP to the DOM pool rather than to the sedimentation flux, allowing it to be mixed and advected in the same fashion as dissolved inorganic nutrients.

Bacastow and Maier-Reimer (1991) assigned a decay rate for DOM of 0.02 year^{-1} (turnover time, $\tau = 50$ years). Najjar *et al.* (1992) did not specify

τ, but their model gives values of the same order. This results in a significant penetration of DOM into the mesopelagic and alters the vertical distribution of nutrients and oxygen relative to particle-only simulations. An important component to these experiments was the search for solutions to the equatorial "nutrient-trapping" problem. It had been found that sedimentation-only biogeochemical models produced large accumulations of (inorganic) nutrients and depletions of oxygen in the equatorial thermocline that were not consistent with observations (Toggweiler, 1989). Assigning some of the NP to DOM rather than to the sedimentation scheme (which results in remineralization directly below the point at which the particles are formed) seemed to remedy this problem, resulting in nutrient maxima that were deeper, weaker, and less restricted to the equatorial region (Toggweiler, 1989; Bacastow and Maier-Reimer, 1991; Najjar *et al.*, 1992).

These simulations employed OGCMs with horizontal resolution on the order of 3–4°, which is inadequate for accurate simulation of the equatorial current system. These early results have been called into question on the grounds that artificialities in the circulation fields are as likely an explanation for the nutrient-trapping problem as the use of particle-only biogeochemical models. Matear and Holloway (1995) used a simple POM-based biogeochemical model similar to that used by Bacastow and Maier-Reimer (1991) and an adjoint technique that allows particular model parameters or fields to vary in order to force selected fields closer to observations or other *a priori* constraints. By retaining the circulation fields of the basic model but allowing the new production rate at a given nutrient concentration and remineralization length scale (RLS) for sinking particles to vary, they found that an increased RLS and reduced NP could alleviate nutrient-trapping without an explicit DOM component, but not with realistic values of these terms. By retaining the base values of the biogeochemical parameters but allowing the circulation fields to vary, they found that small changes in circulation could achieve the same result and concluded that uncertainties about the modeled circulation were too large for definitive conclusions to be drawn regarding the relative roles of DOM and POM. More recent experiments by Aumont *et al.* (1999) have shown that increasing the resolution of the circulation model largely eliminates nutrient trapping without any change in the biogeochemical model. Note that the authors of the original studies appear to have been well aware that this might prove to be the case (Toggweiler, 1989; Najjar and Toggweiler, 1993). A more extensive discussion of the effects of advection schemes and grid resolution on biogeochemical models is given by Oschlies (2000).

C. DOM Turnover Times

The decay rates employed in the early simulations of Bacastow and Maier-Reimer (1991) and Najjar *et al.* (1992) were called into question by Archer *et al.*

(1997) and Yamanaka and Tajika (1997), using HTCO-DOC data not available at the time of the earlier experiments. Using a steady-state model of DOC production and consumption and an OGCM simulation of the tropical Pacific circulation, Archer *et al.* (1997) defined a "grow in" time scale for semilabile DOC. This model reduced the production and remineralization rates to a single value (based on the observed differences between surface and deep concentrations), assuming that oligotrophic surface waters with the highest observed DOC concentrations are near steady-state with respect to production and consumption of DOC, while recently upwelled waters are not. This simple model generated optimal values of τ between 30 and 120 days, suggesting that the bulk of semilabile DOC is not nearly as refractory as assumed in earlier studies. Yamanaka and Tajika (1997) used a slightly more complex model to estimate the ratio of DOC to POC produced ("production ratio") and the decay rate of semilabile DOC. They found that τ's of 0.3–1 year, and production ratios of 1–2 were the most consistent with observed surface concentrations and penetration depths of semilabile DOC. These values increase and decrease, respectively, by about a factor of 2 if POM solubilization produces labile rather than semilabile DOM. An innovative aspect of this analysis is that while either the observed surface concentrations or penetration depths generate a range of approximately equivalent solutions, the two sets of observations provide orthogonal constraints (in terms of positive or negative correlation between turnover time and production ratio for statistically equivalent solutions). Only a narrow range of solutions are consistent with both. The authors note, however, that estimates of the penetration depth are imprecise, and that more observations in the 100 to 400 m depth range would make these solutions more robust. These estimates of the mean lifetime of semilabile DOM are also consistent with the 1D model results of Anderson and Williams (1999); these authors found the poorest fit to data in the 200 to 400 m depth range. It has also been shown that alleviation of nutrient trapping is possible with turnover times in this lower range (Anderson and Sarmiento, 1995), using the same circulation fields employed by Najjar *et al.* (1992).

D. DOM AND ATMOSPHERIC CO_2

There are several examples of global ocean box models applied to questions about atmospheric CO_2. Models of ocean–atmosphere CO_2 exchange on glacial–interglacial time scales tend to underestimate the glacial–interglacial difference (ΔCO_2, ~100 ppm). Paillard *et al.* (1993) attempted to determine whether including DOM in the ocean model would alleviate this, but found that it actually increased the discrepancy (decreased ΔCO_2 in the model) because it reduced the overall geochemical stratification of the model ocean, i.e., less transport of carbon to the deep ocean. Decreasing the turnover time of the DOM would bring ΔCO_2

more in line with the particle-only model, while increasing it tends to further "smooth out" the glacial–interglacial cycle. The biogeochemical model resembles those of Bacastow and Maier-Reimer (1991) and Najjar *et al.* (1992) in that DOM was assumed to have Redfield C/N/P ratios and a lifetime of order 100 years.

Keller and Goldstein (1995) used a variant of the model of Siegenthaler and Joos (1992) to assess the long-term consequences of a pulse of CO_2 into the atmosphere or an injection into the oceanic thermocline. They found that at steady state (the simulations ran for 1500 years) a negligible fraction (0.21%) of the "excess" carbon was found in the DOC pool. Sensitivity studies showed that an increased upwelling velocity caused a significant increase in the total DOC, due to increased input of nutrients to the surface layer. They assumed Redfield stoichiometry for DOM and modeled remineralization as a first-order process with a turnover time that appears to have been on the order of 100 years. Klepper *et al.* (1994) used a box-diffusion model to analyze biogeochemical feedbacks to rising atmospheric CO_2, but provide so few details that it is difficult to determine what if any effect DOM had on their results.

E. Diagnostic Models of the North Atlantic

Schlitzer (1989) constructed a simple model of the North Atlantic Ocean and estimated values of new production, particle flux, and air–sea exchange of CO_2 in each box by fitting the model to historical observations of nutrients, oxygen, DIC, and alkalinity. He then attempted to add a DOC component to the model based on the very limited data available at the time, by (1) using pre-HTCO values, (2) using values derived from the Sugimura and Suzuki (1988) Pacific data, with their surface concentrations in the first model layer ($\sigma_\theta < 25.5$) and their deep concentrations in the other layers, and (3) calculating DOC from apparent oxygen utilization based on the correlation reported by Sugimura and Suzuki (1988). The result of this experiment was that with the pre-HTCO DOC concentrations, solutions could be derived that were consistent with the range of data constraints available, whereas when the results of Sugimura and Suzuki (1988) were used this was not possible. In experiment (2), the distributions of total C, N, and P were "incompatible with the circulation pattern of the model and with [North Atlantic Deep Water] formation rates greater than 5 Sv" (Schlitzer, 1989, p. 12,791). The method used allows the circulation to change to give the best fit of the model to biogeochemical fields, but the changes required in this case were outside acceptable bounds. In experiment (3), the optimal solution was better but still unacceptable; new production was much less than the smallest literature values, and diapycnal mixing coefficients were negative in some places. Note that this experiment was conducted considerably before Suzuki's (1993) retraction of his early results. As a cautionary note, however, like other early modeling efforts in the

"post-HTCO" era, Schlitzer (1989) appears to have assumed large pools of DON and DOP as well as DOC.

Walsh *et al.* (1992) also attempted to estimate meridional fluxes of DOM in the North Atlantic from a handful of early (and probably erroneous) HTCO-DOC estimates, using zonally integrated transport estimates for various depth strata (cf. Rintoul and Wunsch, 1991). They too found mass-balance difficulties, such as ratios of carbon and oxygen flux that were far out of Redfield ratio. The concentration estimates are generally high, but if this is attributed largely to blank-correction problems (Suzuki, 1993) the net meridional transport estimates may not be entirely fanciful. They estimated the net (southward) flux of DOC as about $1\text{–}4 \times 10^{13}$ mol year^{-1}, which would imply that DON could not balance the apparent poleward transport of DIN estimated by Rintoul and Wunsch (1991) with reasonable C/N ratios.

F. Basin-to-Global Scale Ecosystem Modeling

None of the studies discussed above employed prognostic biological models (e.g., state variables for phytoplankton and zooplankton). Prognostic ecosystem models including a DOM component have been coupled to OGCMs in the North Atlantic (Fasham *et al.*, 1993; Sarmiento *et al.*, 1993), the North Pacific (Kawamiya *et al.*, 2000), the equatorial Pacific (Toggweiler and Carson, 1995), the Arabian Sea (Ryabchenko *et al.*, 1998), and, in only one case that we are aware of, globally (Six and Maier-Reimer, 1996). Not all of these models included an explicit population of heterotrophic bacteria; Six and Maier-Reimer (1996) and Kawamiya *et al.* (2000) used concentration-dependent rate equations for remineralization of DOM.

In the simulations of Fasham *et al.* (1993) and Sarmiento *et al.* (1993), DON constituted a small fraction of total N in the North Atlantic ($\sim$0.01 μM N, much less than particulate detritus or plankton biomass), reflecting the fact that the ecosystem model employed (Fasham *et al.*, 1990) simulates only labile DON. Fasham *et al.* (1993) noted that at both Bermuda (subtropical) and Ocean Weather Station "India" (OWSI, subarctic) about half of the annual supply of DON came from breakdown of detritus. Although this result is sensitive to parameter choices, it was not anticipated by the authors of the model. This source was most dominant below about 40 m depth. Convective overturning was the dominant process for removal of DON from the euphotic zone (more than an order of magnitude greater than vertical mixing or downwelling when averaged over the model grid), consistent with observations collected near Bermuda (Carlson *et al.*, 1994; Hansell and Carlson, 2001). Convective losses were much greater at Bermuda than at OWSI, although annual mean surface concentrations were quite similar. This may reflect the lack of production in winter in the subarctic and periodic restratification in

winter in the subtropics, but caution is required in interpreting these results as the OGCM may overestimate the vertical exchange of nitrogen by wintertime convection (McGillicuddy *et al.,* 1998).

Kawamiya *et al.* (2000) simulated realistic concentrations of DON (6–8 μM) in the tropical Pacific Ocean. Their model included a prognostic phytoplankton and zooplankton model; DON consumption was parameterized by a first-order remineralization term. Their model equations indicate a temperature-dependence of this rate, but the temperature-dependence parameter was assigned a value of zero, implying a constant specific remineralization rate of 0.01 day^{-1}. Solubilization of particulate organic nitrogen (PON) was temperature-dependent with a base rate of 0.05 day^{-1}, and rates of $\sim$0.3 day^{-1} at the temperatures characteristic of the tropics. A simple calculation gives the steady-state concentration of DON as a function of temperature, PON concentration, and the rate of production of DON by processes other than solubilization; the modeled values of 6–8 μM are consistent with values of these expected for tropical–subtropical surface waters. The specific rate of PON solubilization is consistent with measurements of ectoenzyme activities on particles (Smith *et al.,* 1992), and calculations based on fluxes of particles collected in sediment traps (Christian *et al.,* 1997) or on thorium disequilibria (Murnane, 1994). Kawamiya *et al.* (2000) compared their modeled DON distributions with data collected by Libby and Wheeler (1997) between 10°S and 10°N and about 95–140°W, noting the model's reproduction of a minimum at the equator and a zonal gradient (increasing westward) north of the equator, which they attributed to greater mixed layer depths in the central tropical Pacific.

Six and Maier-Reimer (1996), like Kawamiya *et al.* (2000), employed prognostic phytoplankton and zooplankton models, but did not model bacteria and used first-order remineralization of DOC, with a maximal rate of 0.025 day^{-1}. The actual rate was a function of inorganic nutrient concentration; i.e., it was assumed that nutrient limitation of HBAC would reduce the rate of remineralization (see also Thingstad *et al.,* 1997). They did not include solubilization of POC as a source of DOC. Like Kawamiya *et al.* (2000), their simulated DOC concentrations were within the range of observed values (15–40 μM at the surface, not counting the refractory "background" fraction). The highest concentrations were in the summer hemisphere, with strong enrichments to $\sim$60° latitude in the summer months and maximal concentrations around 20°. DOC dominated the poleward transport of organic matter that balances equatorward transport of mineral nutrient; these transports were maximal at 10–15°N or S. These simulations showed little seasonality of surface DOM concentrations at latitudes less than about 20°, while at higher latitudes most of the surface-layer DOM appears to be turned over on annual time scales. These results could be highly sensitive to the choice of temperature or nutrients as the factor determining the remineralization rate, as these are negatively correlated in surface waters at large space and time scales.

G. Inverse Models of Flows within Food Webs

An "inverse method" is a statistical method for fitting a model to data, and can be applied to both diagnostic (e.g., Vézina and Platt, 1988; Jackson and Eldridge, 1992) and prognostic (e.g., Matear and Holloway, 1995; Spitz *et al.*, 1998; Fasham *et al.*, 1999; Vallino, 2000) models. Fitting of a linear, steady-state model of a planktonic food web was described by Vézina and Platt (1988), and applied to data sets collected in the English Channel and the Celtic Sea. This model estimates the flows of matter and energy among the model compartments (e.g., phytoplankton, zooplankton, heterotrophic bacteria) that best fit the data in a least-squares sense, subject to specified constraints (e.g., an upper limit to the fraction of gross photosynthesis that can be exuded as DOC), but does not specify the mathematical form of relationships among these compartments. This methodology has since been applied to data collected in various regions of the ocean (e.g., Jackson and Eldridge, 1992; Donali *et al.*, 1999; Vézina *et al.*, 2000), as well as freshwater (Vézina and Pace, 1994) and sea ice (Vézina *et al.*, 1997) ecosystems.

The solutions derived by Vézina and Platt (1988) suggest that a majority of DOC (~65%) came from heterotrophs (DON was assumed to come only from heterotrophs). A substantial fraction (11–19%) of DOC came from the heterotrophic bacteria. There were no *a priori* constraints placed on this flow (whereas other groups had upper limits set on the fraction of energy intake lost to DOC), so it is not surprising that in the optimal solutions this flow would have a positive value, and little can be concluded with certainty from it. The upper limit to detrital dissolution was set at 1% day^{-1}. Jackson and Eldridge (1992), applying the method to data collected in the Southern California Bight, discarded this constraint and found that this rate was about 6% day^{-1} for their data set. The flux of carbon to bacteria from DOM in the solutions of Vézina and Platt (1988) was 16.2 mmol C m^{-2} day^{-1} in the English Channel and 17.5 mmol C m^{-2} day^{-1} in the Celtic Sea. In the English Channel this is equivalent to 0.56% of the total DOC pool each day, or 36–40% of net primary production. In the Celtic Sea, the estimated flux of carbon to bacteria exceeded measured bacterial production by a factor of 21, implying a very low growth efficiency. In both systems, the calculated C/N molar ratio of the DOM consumed by bacteria was 14, and uptake rates of DON and NH_4^+ were similar.

In the Gulf of Riga, Donali *et al.* (1999) found that bacterial carbon demand significantly exceeded DOC supply in spring and autumn. Because the calculation takes account only of the mean flows during the period of the field observations, such imbalances do not violate mass balance constraints, but imply that a large amount of DOC (which was not measured) was present in the water prior to the cruises. These authors attributed this DOM to phytoplankton production rather than terrestrial input. In the subarctic Pacific, Vézina and Savenkoff (1999) calculated flows for cruises in September, February, and May. In May, steady-state solutions could not be derived, i.e., changes in the mass of some compartments over the

course of the cruise were necessary. They calculated a net DOC accumulation on the order of 100 mg m^{-2} day^{-1}, which would imply a seasonal accumulation of $\sim$10 μM. As with the data sets employed by Vézina and Platt (1988), heterotrophs dominated DOC production in all seasons, with the highest autotrophic input in spring. Heterotrophs also dominated DOC production in the Gulf of St. Lawrence, which was approximately half of gross primary production during winter–spring, with protozoa accounting for the largest fraction (Vézina *et al.*, 2000).

H. Coastal and Estuarine Systems

Coastal systems are not our area of expertise, and we have not attempted to cover exhaustively work in this area, especially that which is primarily concerned with anthropogenic DOM (e.g., Yassuda *et al.*, 2000). The principles of modeling DOM in coastal systems are essentially the same as in pelagic systems, except that one must consider allocthonous (e.g., fluvial) sources of DOM, and exchange of organic matter at the water–sediment interface. Some ecosystem models take account of the DOM flux from sediments in some fashion (e.g., Walsh and Dieterle, 1994). Decomposition of fluvial DOM has been modeled using a variety of approaches, few of which take explicit account of the biochemical composition of this material. Hopkinson *et al.* (1998) defined equations relating measurable quantities such as elemental composition and molecular weight to the chemical composition (e.g., aromaticity) and degree of carbon reduction of terrestrially derived DOM, which are expected to be correlated with bacterial growth rate and efficiency (Vallino *et al.*, 1996).

An important issue in oceanography is the lateral transport of autocthonously produced (plankton source) DOM, as well as inorganic nutrients and DIC, from coastal regions to the open ocean (e.g., Pace *et al.*, 1984; Walsh *et al.*, 1997; Tusseau-Vuillemin *et al.*, 1998). Walsh *et al.* (1997) used a Lagrangian model to estimate fluxes from the coastal zone to the open ocean, concluding that there are substantial fluxes of DOM from the Bering and Chukchi seas to the Pacific and Arctic oceans. Tusseau-Vuillemin *et al.* (1998) found that the continental shelf of the Gulf of Lions was a source of nitrate to the open Mediterranean in winter but a sink for oceanic DIN for much of the rest of the year. The shelf sink for DIN in summer may imply an export of DON, and this model could in principle be used to quantify fluxes of DOM (including fluvial DOM) from the margin to the open ocean. The magnitude of this flux, however, depends on exchanges at the sediment–water interface that the authors describe as "roughly parameterized."

Cifuentes and Eldridge (1998) developed a simple model of DOC dynamics along estuarine salinity gradients, which they used to identify additional allocthonous (e.g., wetlands) and autocthonous (e.g., phytoplankton) sources of DOC

when the model deviated from patterns expected for the central processes of mixing, advection and decomposition of fluvial DOM. These authors provide a useful analysis of the relationship between DOC decomposition time scales and estuarine mixing and advection time scales, noting that the behavior of DOC in strongly mixed estuaries will be quite different than in those where advection dominates. Accurate identification of nonfluvial sources will likely improve with improved models of mixing and DOC decomposition.

I. Small-Scale Spatial Structure

Virtually all of the models cited thus far treat the plankton community as homogeneous in space on scales ranging from a few meters to hundreds of kilometers. The interaction between bacteria and their substrates takes place on viscous scales orders of magnitude smaller. The basic concepts for understanding how organisms function on these scales have been reviewed by Jackson (1987) and Jumars *et al.* (1993). Significant results from these studies are that (a) oceanic turbulence does not enhance the flux of substrate to cells in the bacterial size range over that resulting from molecular diffusion alone, (b) motile bacteria "swim" along a biased random walk trajectory rather than a consistently up or down gradient path, and (c) the minimum size of phytoplankton cells that can be "found" by chemotactic bacteria is 2–5 μm.

Several investigators have addressed the question of whether bacteria can gain energetic advantage from chemotactic "clustering" around phytoplankton cells "leaking" DOM. Jackson (1989) addressed this question in relation to laminar sinking of phytoplankton cells, concluding that only in conditions where cells were large, abundant, and leaky did chemotaxis appear to confer significant energetic advantage for nonattached bacteria, with the caveat that the effects of turbulent fluid motion needed to be assessed before this question could be resolved. Bowen *et al.* (1993) showed that there is a small but significant gain from chemotaxis under realistic conditions of oceanic turbulence. Individual cells do not remain in a particular cell's halo for long except under the most quiescent conditions, and the fraction of cells found within enriched microzones is small, but chemotactic cells spend enough time within these microzones on average to derive a significant energetic advantage.

Blackburn *et al.* (1997) addressed the question of chemotaxis with a microbial food web model that was spatially structured (70×70 grid cells) but purely viscous (molecular diffusion only). Rather than exudation, they treated "events" of protozoan predation or cell lysis as the source of DOM. A chemically homogeneous and presumably labile pool of DOM was employed, whose concentration remained low (much less than plankton biomass). DOM concentration varied by more than two orders of magnitude in both time and space, although the total

volume simulated was less than 1 mL. This experiment provides an additional qualitative confirmation of the value of chemotaxis and shows that the aggregate behavior of the spatially structured model differs significantly from that of a homogeneous version of the same food web model. The spatial scales and diffusivities employed are at (or perhaps beyond) the limits of the viscous assumption, so the results should be taken as an illustration and not at as a realistic simulation of the "invisible world."

An important aspect of the Blackburn *et al.* (1997) study is that they addressed temporal as well as spatial variability of DOM production, whereas Jackson (1989) and Bowen *et al.* (1993) treated the phytoplankton cell as a continuous point source of DOM. In all of these experiments it is assumed that autotroph or micrograzer cells from which DOM is generated are much larger than bacteria (e.g., 20 μm). The "encounter rate" of bacteria with the enriched "microzones" scales linearly with the number of such microzones but with the third power of their diameter (Jumars *et al.*, 1993), so results calculated for a relatively small number of large microzones can not necessarily be extrapolated to oligotrophic waters with a larger number of smaller ones.

IV. DISCUSSION AND CONCLUSIONS

Over the past two decades there have been considerable advances in the methodologies of both seawater chemistry and numerical ocean modeling. The relatively small number of high-quality observations, as well as the fundamental weakness of our understanding of interactions within microbial communities (Nagata, 2000) and of the physiology of heterotrophic bacteria (Kirchman, 2000), limit what can be achieved with numerical models. For example, few estimates of the kinetic parameters defining degradation of semilabile DOM are available, and it is questionable how reliably it is possible to simulate this process in models. Estimates of the decay time scale of semilabile DOM in early models (e.g., Bacastow and Maier-Reimer, 1991; Najjar *et al.*, 1992) are much longer than those in more recent studies (e.g., Archer *et al.*, 1997; Yamanaka and Tajika, 1997). The rate of attenuation of DOM concentration with depth is important for biogeochemical cycling and model validation; more observations in the thermocline and mesopelagic zone (e.g., 100–500 m) would be useful.

The question of what are the optimal biological structures for use in large-scale biogeochemical modeling studies is a subtle one. The one component which appears to be required is a semilabile DOM fraction, which provides a significant contribution to export flux in many areas. But what about labile and refractory fractions and indeed heterotrophic bacteria? One important argument for the inclusion of heterotrophic bacteria and the whole microbial loop is that these organisms provide the enzymes for hydrolysis of macromolecular and even monomeric

DOM. Without explicit treatment of bacteria it is necessary to resort to empiricism to model DOM turnover. However, this apparent advantage must be weighted against the reliability with which bacteria can be simulated, as well as our ability to mechanistically parameterize semilabile DOM turnover. Other reasons for explicit treatment of the microbial loop in models are that it may provide a link between the microbial and metazoan food webs and that bacteria compete with phytoplankton for inorganic nutrients (e.g., Bratbak and Thingstad, 1985). The question of whether to include refractory DOM in models would appear to be a matter of time scales. Anderson and Williams (1999) examined the response of this pool to increased UV and concluded that it was so slow that it may not be necessary to include refractory material dynamically in models for examining climate change within the next 200 years.

Processes by which DOM is created are represented in models in varying ways. In models that do not include explicit DOM state variables, terms representing exudation, respiration, and lysis and other forms of nongrazing mortality can have essentially identical mathematical form, although the choice of processes considered and terminology used to describe them varies. Here we have shown the wide diversity that exists in the ways models that consider DOM explicitly represent cycling of organic matter. One can speculate on various causes of this variability—differences between systems, varying objectives, or a lack of consensus on the importance of representing different processes in models. We suggest that the last of these causes is likely to be a significant source of model variability, highlighting the need for further process studies and improved models. Determining model sensitivities to choices of processes and parameters is a necessary first step, which requires data relative to which the models' sensitivities can be adequately assessed (e.g., relatively complete seasonal cycles of DOC concentration, direct measurement of rate processes such as exudation). Ultimately, evaluation of different model formulations' performance relative to common data sets will be required.

One of the earliest marine ecosystem models to consider DOM assumed that all organisms produce DOM (Pace *et al.,* 1984). Since then there have been both models that assumed just one or two processes were responsible, and models that specified a variety of different processes (Table II). The recent models of Anderson and Williams (1998), Walsh *et al.* (1999), and Tian *et al.* (2000) have incorporated a broad spectrum of processes. The mathematical formulation of these terms remains tentative and speculative, and the sensitivity of the models with respect to the formulation of these various sources need to be assessed carefully. Analysis of carbon flows within food webs seems to confirm that heterotrophs, not autotrophs, account for the largest fraction of DOC production. This conclusion needs to be examined for biases resulting from the structure of the food web models and the data to which they are fitted, but is consistent with other results and should be taken seriously by developers of ecosystem models.

Differences in terminology between studies also confound model comparison. The distinction between what is dissolved and what is particulate is not necessarily clear (Sharp, 1973). From a biogeochemical modeling perspective, the distinction between dissolved material and suspended particles with negligible sinking velocities is not necessarily meaningful, although the mechanisms and rates of utilization by bacteria may differ (Joint and Morris, 1982; Kepkay, 2000). Bissett *et al.* (1999a) gave three of their four fecal pellet fractions zero sinking velocity, but treated these differently than DOM and did not make them available to HBAC. Tian *et al.* (2000) considered only a single "dissolved" organic fraction and two of "particulate" detritus, but the smaller of these did not sink. The inclusion of additional fractions may stem from a desire to include a reasonably complete representation of the range of microbial processes. Vertical transport is a key issue in biogeochemical cycling, so more complete tests of these various formulations' performance are desirable.

There has been progress on the "demand" side (modeling the utilization of DOM by HBAC), for example, the models of Anderson and Williams (1998), Bissett *et al.* (1999a), and Vallino (2000) allow for both C- and N-limited growth and net uptake or remineralization of DIN. Spitz *et al.* (2001) found that the fit of their model (based on that of Fasham *et al.*, 1990) to data from the Bermuda Atlantic Time-Series station was significantly improved by including these processes. Nevertheless, the assumptions underpinning these models need further validation. A major weakness of most models is that the biochemical composition of DOM is not explicitly considered. The composition of the mixture of substrates utilized in nature is not well known, and the variable energy content of different biochemicals with similar stoichiometry is not accounted for in models (Vallino *et al.*, 1996; Weber, 2000). An important challenge for the near future will be to model the full C/N/P stoichiometry of bacterial growth. The biochemistry and biogeochemistry of N and P are quite different (Kirchman, 2000; Karl and Björkman, Chapter 6), and few models have addressed these differences. Furthermore, bacteria in aquatic ecosystems are a diverse group of organisms, and so care has to be exercised when using, for example, stoichiometric models. The physiological capacities of dominant bacterial groups can vary seasonally (Pinhassi and Hagström, 2000). Nutrient additions may stimulate particular types of bacteria, changing overall community composition (Fuchs *et al.*, 2000).

Only a few models have addressed the significance of UV radiation in DOM cycling, and those have focused on increases in lability resulting from photooxidation of refractory material. While exposing refractory DOM to UV radiation can increase its lability, there is also evidence that photochemical reactions can render labile DOM less available for bacterial consumption (Keil and Kirchman. 1994; Benner and Biddanda, 1998; Obernosterer *et al.*, 1999). Simulating the balance between these opposing effects of UV radiation on DOM lability presents a significant future challenge for modelers.

Among the most promising recent developments is the use of optimization techniques for statistical fitting of prognostic models to data (Spitz *et al.,* 1998, 2001; Fasham *et al.,* 1999; Lamy *et al.,* 1999; Vallino, 2000). These experiments have employed physical frameworks such as a mesocosm (Vallino, 2000) and a Lagrangian, drifter-tracking cruise (Fasham *et al.,* 1999) to minimize advective effects and make use of zero-dimensional models viable. The limited information available from these experiments results from the mismatch of model complexity and the available observational data, that is, the available analytical methodologies may not be adequate to place strong constraints on many of the terms in the models. Vallino (2000) applied a variety of parameter-estimation techniques to a model of a mesocosm experiment with four experimental treatments (control, +DOM, +DIN, and +DOM+DIN). The results are somewhat disconcerting: despite the extraordinary effort expended in finding the most statistically probable solutions for the model parameters, these solutions could not be generalized from one experimental treatment to another. It is therefore unlikely that the model accurately represented the mechanisms regulating the response of the microbial community to the different experimental treatments. It is simple to find fault with particular aspects of the model or the experimental treatments; it is quite another matter to demonstrate that these artificialities and not a fundamental lack of understanding of the underlying biology are responsible for the weakness of the solutions derived. There are many areas in which biogeochemical models have not yet addressed the underlying biological mechanisms. For example, the results of Thingstad (2000) suggest that the diversity of the bacterial community may represent an important control on biogeochemical cycles. Even for a single species, a more mechanistic treatment of bacterial growth is clearly possible (Vallino *et al.,* 1996; Button, 1998).

Nonetheless, the development of modeling in the study of dissolved organic matter in the oceans has advanced rapidly over the past decade. While there are many remaining uncertainties, and many of the results cited are quite tentative, a fair amount of progress has been made. A variety of sophisticated new models, have been developed in a simplified (0D or 1D) physical context, and their ability to simulate spatial and temporal variability of DOM and its effects on large-scale ocean biogeochemistry will hopefully be evaluated in the near future. There is a continuing need for improved parameterizations of the underlying processes, and coupling of these to contemporary models of the ocean circulation (cf. Doney, 1999). All of the global and most of the regional simulation experiments to date have employed fairly coarse-resolution models, and conclusions regarding biogeochemistry must be received cautiously until more realistic circulation fields are employed. Equatorial nutrient-trapping and anoxicity can be eliminated in particle-only models and may be an artifact of poor simulation of the equatorial circulation (Matear and Holloway, 1995; Aumont *et al.,* 1999). However, the "negative result" that DOM is not needed to eliminate these artifacts cannot be taken to imply that DOM plays a minor role in ocean biogeochemistry.

Inclusion of DOM in models can alter the biogeochemical stratification of the ocean and the partitioning of carbon between ocean and atmosphere, decouple the C, N, and P cycles, and change the structure of food webs and the grazing pressures on phytoplankton. Quantifying these effects is difficult due to lack of data and uncertainty about model structure. Early experiments in large-scale modeling were clustered at opposite extremes, i.e., biogeochemical models with highly parameterized biology and long DOM lifetimes, and microbial food web models with a single, labile DOM pool. Both the long lifetimes assumed by the former and the low concentrations generated by the latter are probably erroneous. Proper simulation of the role of DOM in biogeochemistry would appear to require at the least that the semilabile pool be simulated, and that its lifetime is on the order of 1 year. Some recent experiments have included a single pool with a first-order remineralization rate in the semilabile range, and generated realistic concentrations and spatial and seasonal variations (Six and Maier-Reimer, 1996; Kawamiya *et al.,* 2000). Dependence of these remineralization rates on temperature and inorganic nutrient concentration needs to be better understood, assuming that such dependence even exists. Rigorous evaluation of competing formulations against observations, combined with development more mechanistic models of the remineralization process (e.g., Vallino *et al.,* 1996) could potentially identify weaknesses in empirical formulations and also identify situations in which they are adequate to the task at hand. Models with both a semilabile pool and an explicit HBAC population have generated realistic depth profiles (Anderson and Williams, 1999), but need to be more extensively tested with regard to temporal variations. To understand biogeochemical fluxes on interannual to interdecadal time scales, more data in the mesopelagic zone are required, along with a better understanding of why some models fit the observations poorly in this region. Fluxes between the coastal zone and the open ocean are also poorly characterized; improved models of exchanges at the sediment–water interface and of decomposition of terrestrially derived DOM need to be explored.

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