Is the Downward Dissolved Organic Matter (DOM) Flux Important in Carbon Transport?

J.R. Toggweiler

Geophysical Fluid Dynamics Laboratory/NOAA
Princeton University
Princeton, NJ 08542, U.S.A.

Abstract. A new method for measuring the concentration of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) in seawater has recently been applied to the study of the material balance in the oceanic water column. These measurements suggest that the downward transport of organic carbon and nitrogen in the dissolved organic phase is every bit as important as the downward transport in sinking particles. It appears that DOC and DON are the most important organic substrates supporting the consumption of oxygen and the remineralization of nitrate below the thermocline. Although still controversial, these findings are supported by a model study which shows that the vertical transport of organic matter cannot be attributed solely to the fast-sinking particles caught in sediment traps. A characterization of the vertical flux as such produces a model nutrient distribution which bears little resemblance to observed distributions.

INTRODUCTION

Sediment traps and large volume filtration systems have now been in use for more than a decade. These technologies give oceanographers a means of directly sampling the vertical flux of particulate material from the upper ocean. In the pre-trap era oceanographers could only infer what the characteristics of the sinking particles were from the distributions of biologically altered chemicals in the ocean, such as the nutrients O_2 and CO_2, and the composition of sediments on the seafloor. The distributions of these elements have suggested that most of the organic material which falls from the productive layers of the upper ocean is consumed within the upper kilometer or two of the ocean (Wyrtki 1962; Fiadeiro and Craig 1978).

65

Before the advent of direct sampling it was widely assumed that the sinking material represented some kind of degraded residue from the biological production in the upper ocean. Broecker and Peng (1982, p.1 of their text on chemical oceanography) characterize the sinking material as follows: "While much of the plant material is consumed by animals living in the surface ocean, some insolubles and indigestibles (i.e., fecal matter) move into the deep sea under the influence of gravity."

After a decade of direct sampling, it is quite clear that this characterization is incorrect. Upper ocean sediment trap results, summarized by Martin et al. (1987), show that most of the sinking organic matter flux in the open ocean is consumed in the upper 200–300 m. Most of the material which escapes consumption in the upper kilometer sinks straight to the bottom. Bishop et al. (1987) show that the decrease in the flux of organic carbon with depth in the upper few hundred meters is highly correlated with animal biomass. Subsurface animal populations apparently find and consume the sinking material very shortly after it falls out of the productive upper layers, suggesting that this material is hardly "indigestible." In the North Atlantic, bottom cameras have recorded the arrival of intact phytoplankton aggregations, which fall to the bottom in conjunction with the collapse of the spring bloom at the surface (Billet et al. 1983). The blanket of fresh material over the sediment surface disappears within a few weeks as the benthos feast on this manna from the upper ocean.

If sedimenting particulate matter is in fact readily digestible, and is consumed primarily near the surface and at the bottom, what accounts for the remineralization of nitrate and phosphate, and the consumption of oxygen in the interior of the ocean? Two recent papers by Suzuki et al. (1985) and Sugimura and Suzuki (1988) have unveiled a new method for measuring the total concentrations of DON and DOC in seawater. These papers report that the concentrations of DOC and DON are about four times higher in surface water and two times higher in deep water than previously thought. These papers also show that DOC and DON concentrations decrease strongly with depth, mirroring the increases in dissolved inorganic carbon and nitrate. In this review I will try to show that the new DOC and DON results appear to fill this void in our characterizations of the downward organic matter fluxes in the ocean. Downward advection and mixing of DOC and DON may well be more important in balancing the upward fluxes of CO_2 and nitrate from the deep sea than downward fluxes of sinking particles. While advection and mixing are inherently less efficient modes of vertical transport than particle sinking, these processes may simply move much bigger pools of organic matter.

Phytoplankton and other organisms in the upper ocean food webs are known to excrete dissolved organic compounds. We know that dissolved organic matter represents the primary substrate supporting bacteria in the

ocean. How does the new DOC and DON data fit our conceptions of oceanic ecosystems? The C:N ratio in Suzuki and Sugimura's DOM is relatively low, about 7–8. It does not make much sense, ecologically, that the phytoplankton would excrete so much nitrogen bound up in a form that will be passively mixed out of the upper ocean. I would like to conclude by reviewing some ideas and speculations regarding the origin and destruction of oceanic DOM.

BACKGROUND

The measurement of dissolved organic carbon in seawater is, theoretically, a straightforward process. One first filters the water to remove the particulate carbon and then drives off inorganic CO_2 by acidification. The remaining carbon is oxidized using a strong chemical oxidant, UV radiation, or some combustion process, and the CO_2 yield from the oxidation is determined by IR spectroscopy. To measure DON one oxidizes a water sample and measures total nitrate. The difference between the nitrate concentrations in oxidized and unoxidized samples represents the DON.

Historically, the measurement of DOC in seawater has been fraught with disagreement and contention. Estimates of the DOC content of seawater have covered a great range (for a review see Sugimura and Suzuki 1988). In recent years, chemical oceanographers in the West have generally settled on wet chemistry oxidation techniques and have favored a lower range of DOC concentrations. These "standard" techniques yield deep water concentrations which fall in the 30–50 µmol/l range, while surface water runs as high as 100 µmol/l. Oceanographers in the Soviet Union, using a dry combustion technique, have maintained that DOC levels might be twice this high.

Total organic carbon (TOC = DOC + POC on unfiltered samples) was measured during some of the GEOSECS cruises using a standard wet oxidation technique. (The particulate organic carbon (POC) represents at most 10% of the TOC in surface water, and a few percent in subsurface water.) This semi-global data set shows the highest TOC values in mid and low latitude surface waters. TOC decreases strongly in the upper few hundred meters and remains largely invariant in deeper waters. High latitude surface waters have TOC contents intermediate between mid latitude surface water and deep water.

The technique used by Suzuki et al. (1985) and Sugimura and Suzuki (1988) for measuring DOC and DON is a high temperature combustion process which utilizes a special platinum catalyst. Various investigators have tried to use high temperature combustion methods to measure DOC in the past (R. Barber, personal communication) but only Suzuki and Sugimura seem to have made them work reliably. Other investigators are now
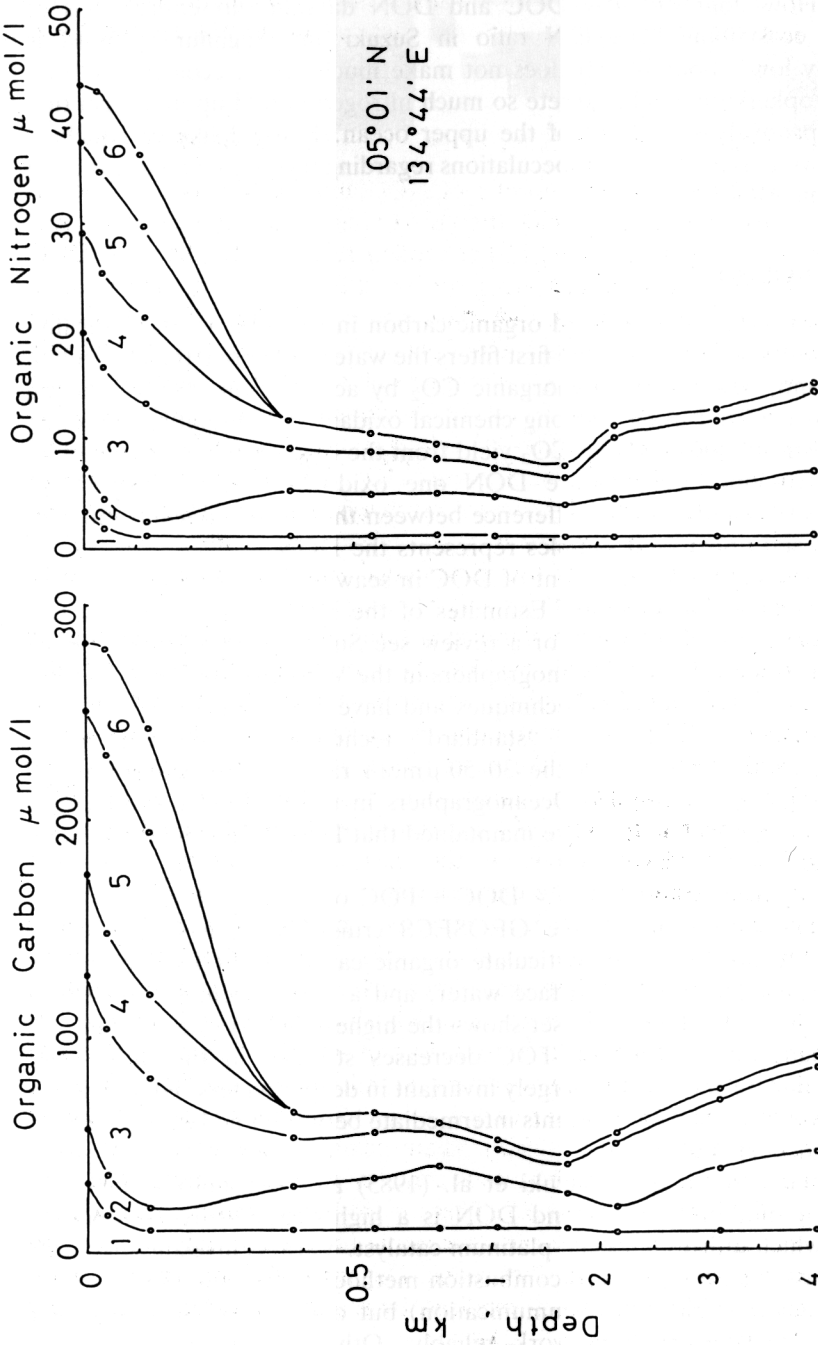
Fig. 1—Vertical profiles of DOC and DON at 5°N, 135°E, in the equatorial North Pacific. DOC and DON are subdivided into molecular size pools as follows (units – daltons): 1: < 1800; 2: 1800–4000; 3: 4000–20,000; 4: 20,000–60,000; 5: 60,000–100,000; 6: > 100,000. From Sugimura and Suzuki (1988).

attempting to replicate these results using similar equipment. Because no one else has yet done so, one must be cautious in fully accepting these results.

CHARACTERISTICS OF SUZUKI AND SUGIMURA'S DOM POOL

Figures 1 and 2 show vertical profiles of DOC and DON at two stations in the western North Pacific in which the DOM is separated by molecular size. Molecular size ranges are given in the caption to figure 1. The total DOC and total DON concentrations are given by the envelope of size fraction curves. Surface water concentrations are about 300 μmol/l for DOC and 40 μmol/l for DON. The surface DON values are particularly noteworthy because they are almost as large as nitrate values in the subsurface nitrate maximum. Surface water DOC and DON measurements made using the standard techniques yield only 60–90 μmol/l and 4–10 μmol/l, respectively. At each station in figures 2 and 3 the DOC and DON concentrations decline through the upper kilometer, reaching minimum values between 1000 and 1500 m. Concentrations increase below these depths. This sort of structure in the lower parts of the thermocline and deep water is not seen in DOM profiles made using the standard techniques.

Note that most of the water column structure below a few hundred meters can be attributed to size fraction 3. Taking into account the relative scales used in the DOC and DON plots, one sees that the largest amounts of DON relative to DOC are in fraction 3. Component 6, the largest size fraction, would appear to be the most labile; it totally disappears in the upper 400 m at the equatorial station and is hardly present in the 20°N station. Component 1, the smallest, appears to be the most refractory, since its top to bottom concentrations are the least variable. Component 2 has its highest concentrations in the deepest water.

Williams and Druffel (1987) have reported that the ^{14}C age of the deep water DOC extracted by the standard techniques is about 6000 years. Williams and Druffel speculate that about half of the deep water DOC is composed of extremely refractory material which has cycled through the ocean many times. It would have lost most of its ^{14}C to decay and would have to be almost completely resistant to microbial oxidation. A small subcomponent may have a terrestrial origin (Mantoura and Woodward 1983). Jackson and Williams (1985), again using the standard techniques, have found that a large and ubiquitous component of the marine DOM has a very high C:N ratio of about 25. There is probably considerable overlap between the refractory component responsible for the old radiocarbon ages and the component with high C:N ratios. Degens (1970) reports that most of the marine DOM compounds oxidized by the standard techniques have molecular weights less than 5000 Daltons.
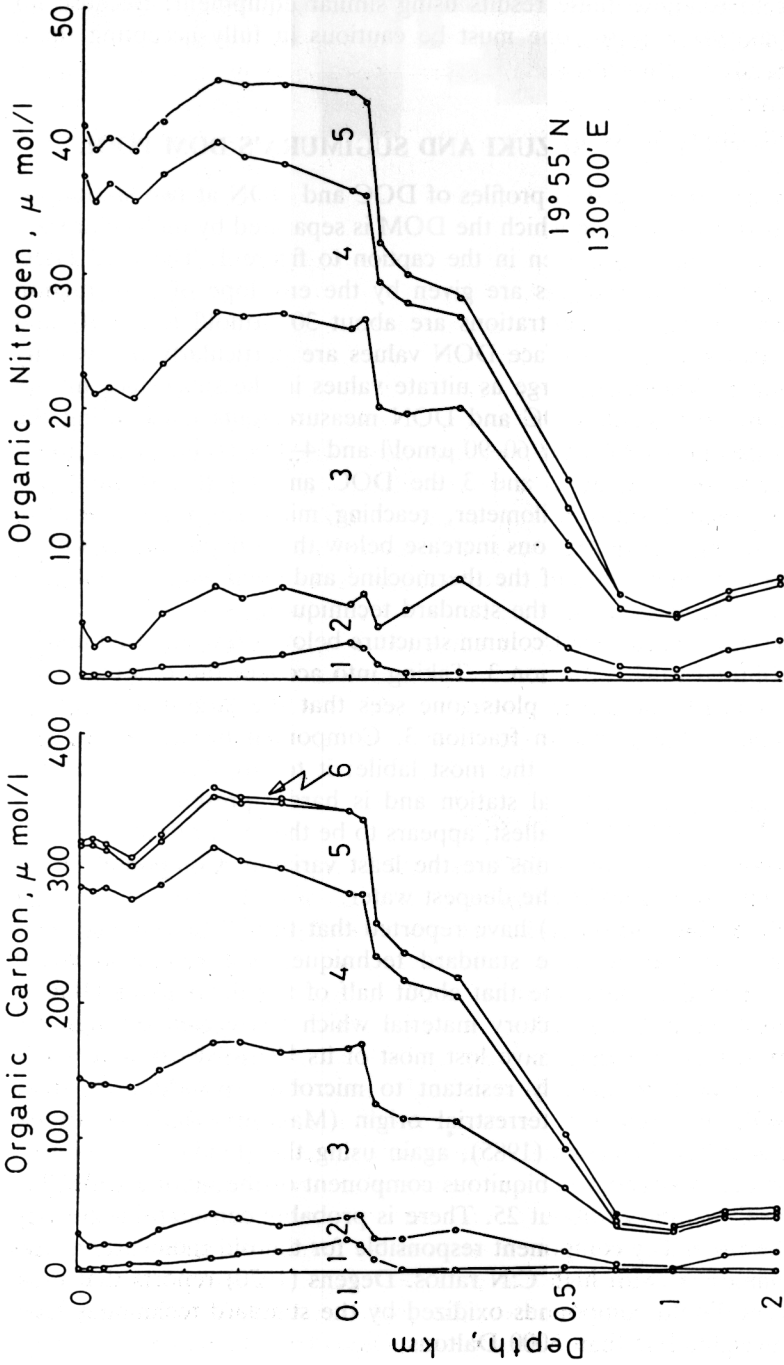
Fig. 2—Vertical profiles of DOC and DON at 20°N, 130°E, in the western North Pacific. DOC and DON are subdivided into the molecular size pools identified in the caption to Fig. 1. From Sugimura and Suzuki (1988).

Given what we know about oceanic turnover rates, the vertical distributions of Suzuki and Sugimura's DOM size fractions suggest that the bulk of their material persists in the ocean for some limited amount of time, perhaps several hundred years. In contrast to the material described by Williams and Druffel, this material appears to be susceptible to microbial breakdown. The largest size fraction has a fairly low C:N ratio of about 6. Most of the DOM compounds analyzed by Suzuki and Sugimura have molecular weights well in excess of 5000 Daltons.

If we assume that the high temperature combustion method extracts the refractory DOC characterized by Williams and Druffel (1987) and Jackson and Williams (1985), it would appear from the limited water column characterizations above that this very old material would have to be concentrated in Suzuki and Sugimura's smaller size fractions 1 and 2, the fractions with the smallest vertical gradients. Fractions 1 and 2 have molecular sizes up to 4000 Daltons and when combined account for about 20 to 50 μmols of DOC per liter of seawater. The C:N ratios of the DOM in fractions 1 and 2 are somewhat higher than in the larger fractions, but not nearly as high as in the material identified by Jackson and Williams. On the basis of water column characterizations, concentrations, molecular size, and C:N ratios, the size fractions 1 and 2 appear to have much in common with the refractory DOM extracted using the standard techniques. The remaining DOM extracted by Suzuki and Sugimura, the mystery substance, consists of larger molecules with lower C:N ratios that are produced and broken down in the ocean over relatively short time scales.

PROPERTY/PROPERTY ANALYSIS

Figure 3 reproduces a plot of DOC vs. AOU (apparent oxygen utilization) from Sugimura and Suzuki (1988) for three western N. Pacific stations. The slope of a line drawn through the data points is close to −1. Sugimura and Suzuki cite this correlation as evidence that the disappearance of DOC "sufficiently explains the amount of AOU in the water." The correlation between AOU and DOC, taken at face value, is inconsistent with the sediment trap results; surely the sinking POC is responsible for some part of the oxygen consumption. Below I will show that a simple correlation between AOU and DOC is misleading because it does not take into account the "preformed" concentrations of these substances.

A preformed concentration represents the concentration of a chemical substance which is present in a given water mass when the water mass was last at the surface. The preformed AOU is, by definition, zero because one usually assumes that surface waters have oxygen contents which are in equilibrium with the atmosphere. The preformed DOC is an unknown because we do not have any DOC measurements from high latitudes which
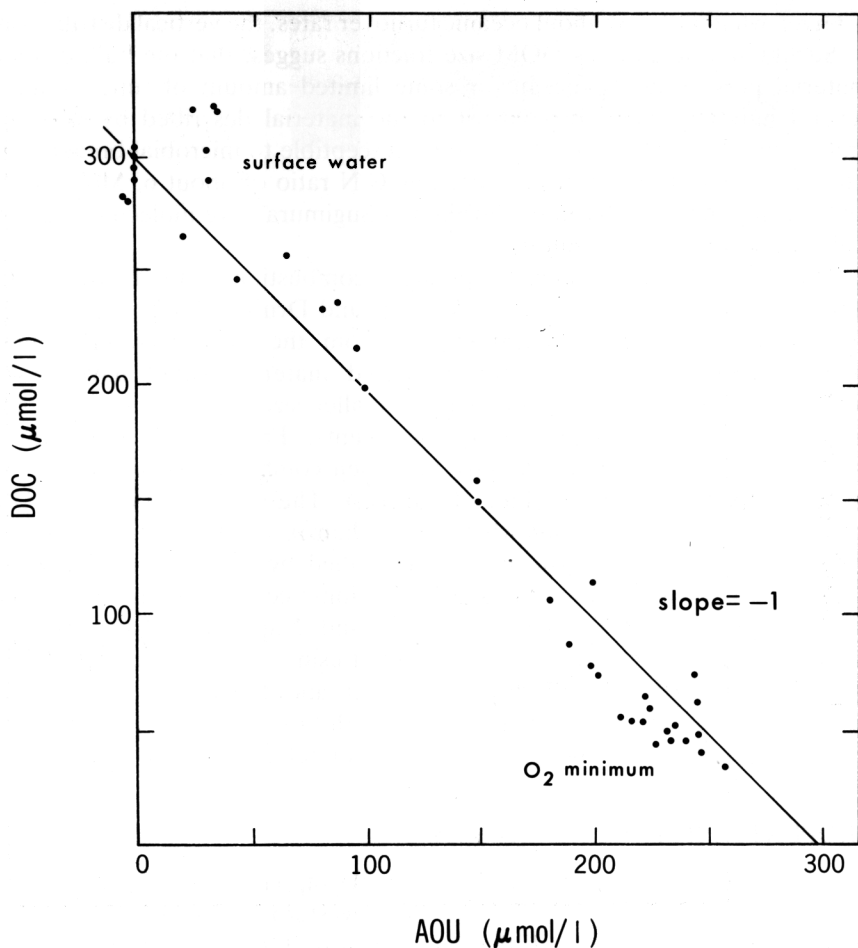
Fig. 3—Plot of DOC vs. AOU from three stations in the western North Pacific. From Sugimura and Suzuki (1988).

were made using Suzuki and Sugimura's technique. For this reason property/ property diagrams constructed using oxygen or AOU as one of the properties (e.g., figure 3) are especially vulnerable to misinterpretation. Figure 3 gives the impression that the properties of the subsurface water masses evolved from the local, zero AOU, 300 μmol/l DOC mid latitude surface water. All that one can reasonably conclude from figure 3 is that the subsurface water masses evolved from one, or several, preformed compositions which lie on the left-hand axis of the plot.
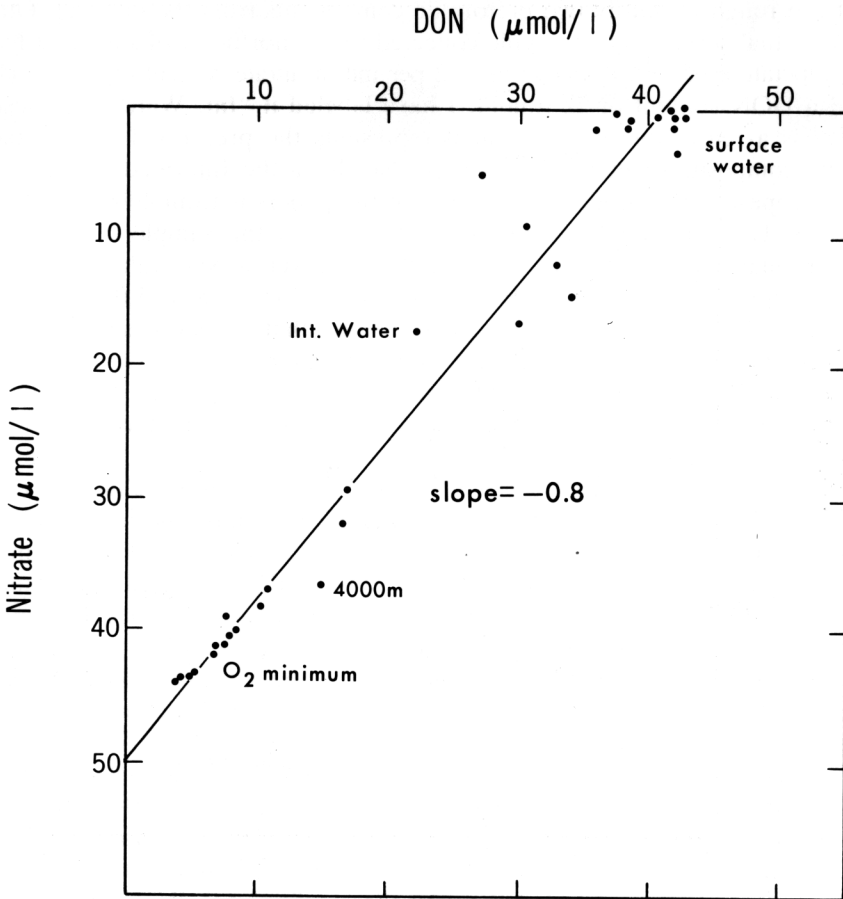
Fig. 4—Plot of DON vs. nitrate from data tabulated in Suzuki et al. (1985). The data include two vertical profiles at 20° and 40°N along approximately the 140°E meridian, and several surface water samples.

Figure 4 shows a plot of DON vs. nitrate made up from data tabulated in Suzuki et al. (1985). Surface water and O_2 minimum water define the end points in figure 4. Water from the thermocline, intermediate water, and deep water fill in the middle regions of the trend. The slope of the line drawn through these points is −0.8. This is a more meaningful correlation than the AOU vs. DOC correlation in figure 3 because there is enough data available for DON and nitrate to suggest what the preformed components might be.

I can roughly identify two preformed components from the data set. One is an actual surface water sample collected to the northeast of Japan. It has a temperature of 2.6°, a salinity of 33.2 per mil, a nitrate content of 17 µmol/l, and a DON content of 22 µmol/l. I have labeled it "Int. Water," because there is a reasonable chance that it represents the preformed nitrate and DON compositions of the low salinity North Pacific Intermediate Water. The deepest sample collected in either of the papers is from 4000 m at 5°N and 134°E. I have interpolated the DON value for this sample from figure 13c in Sugimura and Suzuki (1988) and have taken a NO_3 value from the same depth at the nearest GEOSECS station (241, almost 5,000 km due east). I label this point "4000 m" and assume that it retains some of the preformed composition of Antarctic Bottom Water.

Because the North Pacific O_2 minimum lies below the low-salinity intermediate water and above the deep water, the O_2 minimum end member composition for DON and NO_3 evolves from these two preformed components, not the local surface water. The observations that the two preformed components lie close to the trend line joining the local surface water and O_2 minimum water reflects, I think, two facts: (a) low and mid latitude surface waters are the source of most of the long-lived DON, and (b) the DON and nitrate compositions of the outcropping deeper water masses are only weakly altered at the surface. The DOM which breaks down in the O_2 minimum may be produced in the local surface water but the actual pathway by which it reaches the ocean's interior probably includes a detour through higher latitudes.

The slope of −0.8, relating DON and nitrate, reflects the fact that 80% of the nitrate remineralization below the thermocline is due to the oxidation of DON. The remineralization of PON in sinking particles contributes only 20%. This same 80/20 partitioning must hold for the consumption of oxygen and remineralization of CO_2 below the thermocline as well.

We can now go back to figure 3 and ask how preformed DOC affects one's interpretation of this diagram. From the characteristics of the DON I infer that the preformed DOC in North Pacific Intermediate Water and Antarctic Bottom Water is lower than the DOC in mid latitude surface water. Therefore, I expect that the DOC and AOU composition of O_2 minimum water evolves from preformed components which lie well off the trend in figure 3. Based on the DON vs. NO_3 slope (−0.8), the C:N ratio in the DOM (7), and the stoichiometry of oxygen consumption relative to nitrate release (1/9), I would say that the true $\Delta AOU/\Delta DOC$ slope is about −1.6, not −1.0. One can extrapolate a line with this slope from the cluster of O_2 minimum points to the zero AOU axis. From the intercept I predict an average preformed DOC value of roughly 175 µmol/l for the O_2 minimum water.

One cannot partition nitrate remineralization and oxygen consumption in the upper thermocline between DOM and sinking particles using this data. The zone in which most of the particulate organic matter is remineralized is shallower than 300 m (Martin et al. 1987). Water in this depth range has nitrate concentrations less than 7 or 8 μmol/l. The DON vs. NO_3 plot in figure 4 has no well-defined trend in this part of the plot. For this reason, the property/property plots in figure 4 do not preclude an important role for particles in the upper thermocline.

It seems to me that a large part of Suzuki and Sugimura's DOM is produced, in the Pacific at least, within warm surface waters and is broken down over several hundred years in subsurface waters. Long-term ocean mixing processes, which exchange properties between low and mid latitude surface water and deep water, dominate the DON vs. nitrate plot. The true measure of the role of DOM vs. particles in the vertical exchange is obscured in the AOU vs. DOC plot by the resetting of the AOU component to zero and the lack of DOC data from high latitudes.

MODELING STUDIES

Modeling studies have just begun to address the question of how the characterization of the vertical flux of organic matter affects the distribution of nutrients and CO_2 in the ocean and the ocean's chemical cycles. Initial results indicate that it does indeed make a great deal of difference how the flux is characterized. If the upward flux of nutrients into the surface layers of the ocean solely gave rise to a sinking flux of organic particles, which were remineralized according to the vertical scaling demonstrated by Martin et al.'s sediment traps, the ocean's nutrient distribution would be radically altered and the ocean's particle production would be higher than is currently measured.

This conclusion was reached in a 3-D model study by R. Najjar at Princeton University, as reported in Toggweiler et al. (1987) and Sarmiento et al. (1988). The physical model used in these experiments is an idealized, two-hemisphere, flat-bottomed sector model of a single ocean basin. It is driven by zonally and meridionally averaged winds, and zonally averaged surface temperatures and salinities.

Chemically, the model contains only phosphorus and has no external sources or sinks. If one ignores the effects of denitrification and nitrogen fixation, nitrate could be substituted for PO_4 in this model with a suitable stoichiometric correction. In order to avoid having to predict the surface nutrient field, the model restores the predicted phosphate concentration at each surface layer grid point toward the observed zonally averaged surface concentration in each latitude band as compiled from the GEOSECS data

set. The same fraction of phosphate removed from the model surface box per time step is removed from all model boxes in the upper 100 m. The total amount of phosphate removed from the upper 100 m at a given location represents the model's predicted new production for the euphotic zone at that point. The flux of phosphate from the upper 100 m is then numerically partitioned into all subsurface layers immediately below according to the sediment trap-derived scaling function in Martin et al. (1987). The model is initialized with a uniform phosphate field in which the concentration in every grid box is equal to the global average.

Figure 5 shows a zonally averaged north–south section of phosphate predicted by the model. Figure 6 shows the phosphate distributions along

PHOSPHATE (μmol/kg) ZONALLY AVERAGED
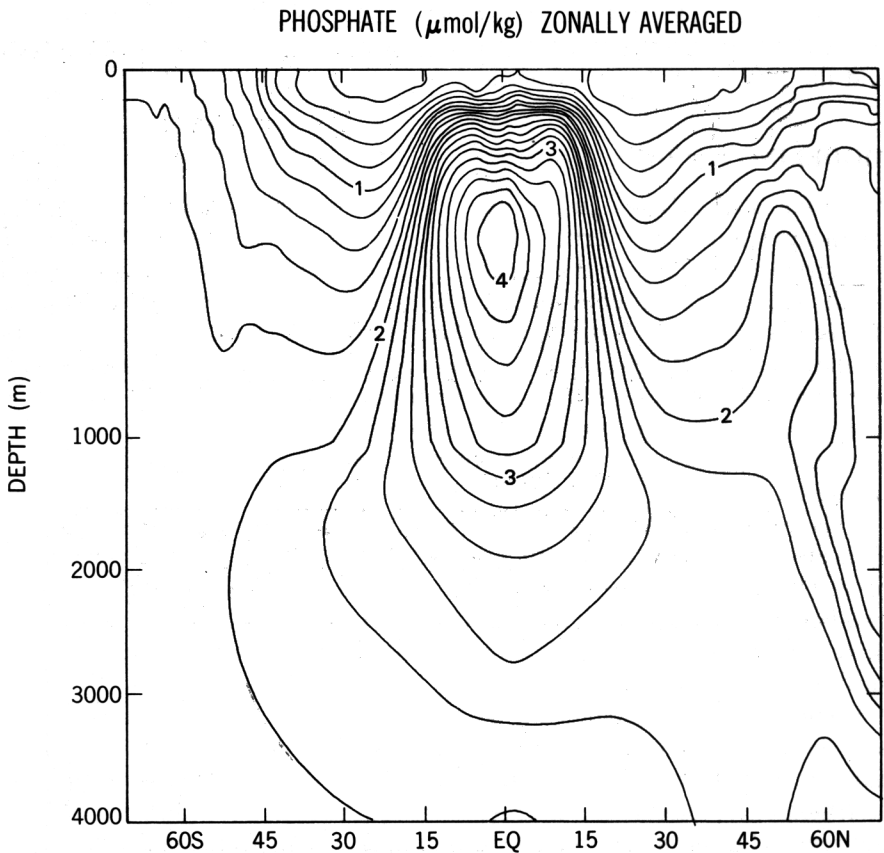
Fig. 5—North-south section of phosphate predicted by a 3-D nutrient cycle model run in an idealized sector ocean basin. See text for description. Results shown are zonally averaged (units: μmols/kg). From Toggweiler et al. (1987).

north–south GEOSECS tracks in the western Pacific and western Atlantic for comparison. Figure 7 shows a map of the predicted phosphate concentration at 180 m and a map of the model's new production, where the phosphorus flux units have been scaled up by a factor of 130 to be equivalent to a flux of organic carbon. The model develops an intense, shallow nutrient maximum beneath the tropics, in which phosphate concentrations exceed 8 μmols/kg adjacent to the eastern boundary. In the ocean, observed phosphate maxima, in contrast, are much deeper, have concentrations which rarely exceed 3 μmols/kg, and are not so focused within the tropics.
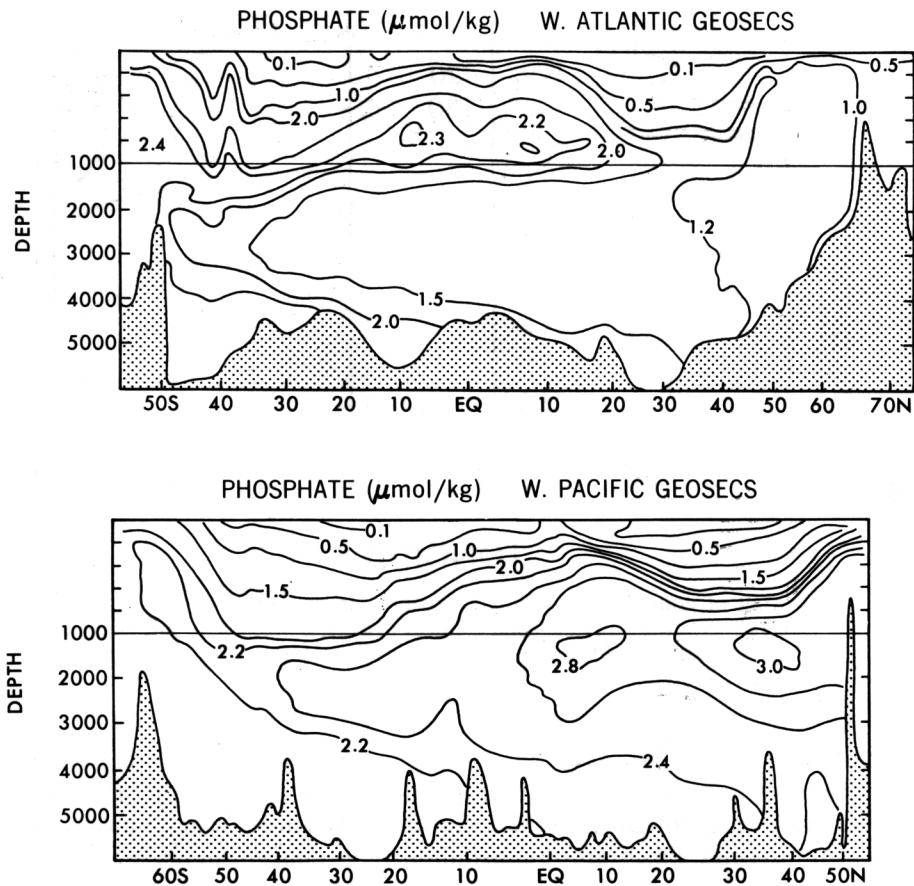

Fig. 6—North-south sections of phosphate along the W. Atlantic (upper) and W. Pacific (lower) GEOSECS tracks (units: μmols/kg).
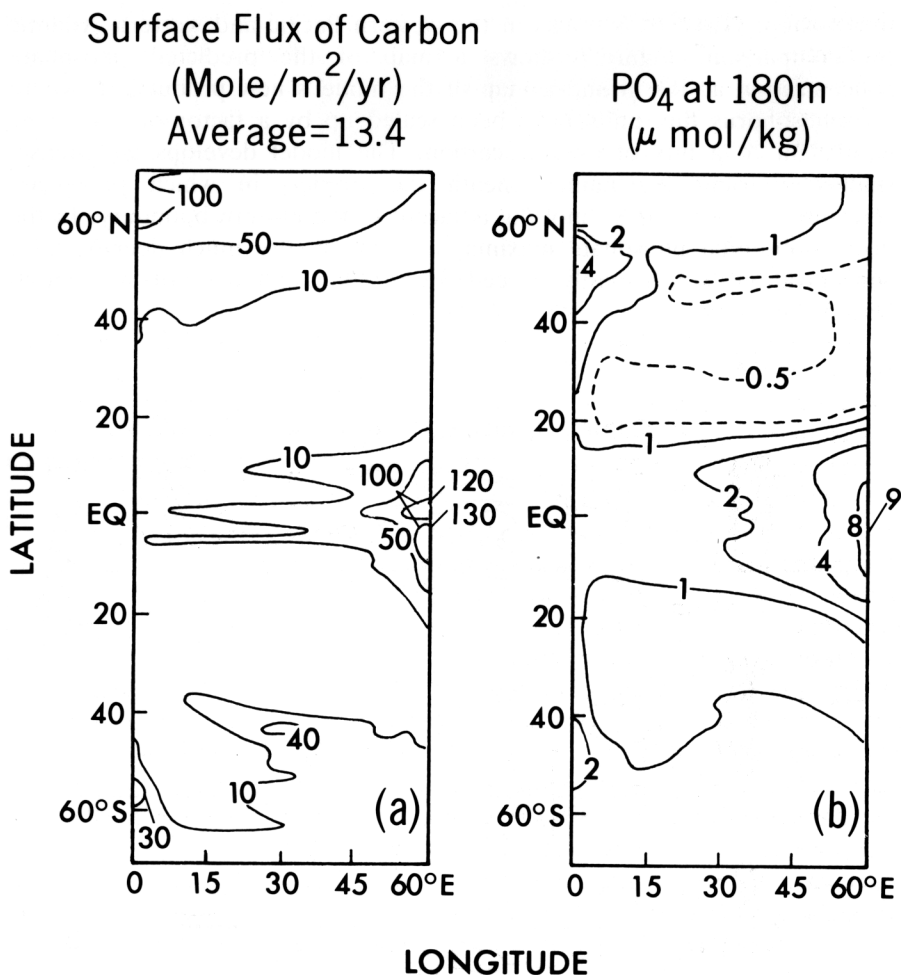
Fig. 7—(a) Map of equivalent particulate organic carbon flux (new production) at 100 m predicted by the model (units: mols C/m²/yr). (b) Map of phosphate concentrations at 180 m predicted by the sector model (units: μmols/kg). From Sarmiento et al. (1988).

The intense phosphate maximum develops in the model because phosphate is trapped within converging subsurface layers associated with the wind-driven equatorial upwelling. When this high phosphate water upwells, it produces particles which are remineralized immediately below, leading to still more particle production, and so on. The model predicts new production well in excess of 50 mols C/m²/yr within the eastern equatorial zone. Outside of the tropics, the shallow nutrient remineralization leads to high upper

thermocline phosphate concentrations generally, and a basin-average new production of 13 mols $C/m^2/yr$, almost 10 times higher than the organic carbon fluxes actually caught in sediment traps (Martin et al. 1987).

In hindsight, the result is not entirely unexpected, given the intensity with which observed vertical fluxes of carbon decrease with depth immediately below the photic zone. Nutrients taken up in the euphotic zone are simply not moved very far by sinking particles. Furthermore, lengthening the scale over which the flux is remineralized in the model does not make the unrealistic features of the phosphate distribution disappear. It is not simply the vertical scale which produces the unrealistic features but also the vertical trajectory assumed in having the new production remineralized immediately below where it is produced.

The most realistic simulations have been derived when half of the new production is put into a long-lived dissolved organic phosphorus pool (breakdown rate = $1/200$ yr^{-1}), which is allowed to advect with the water. This mechanism allows much of the organic production and nutrients from the equatorial upwelling zone to be transported out of the tropics without being trapped. It also allows some of the DOM to be mixed into the deeper strata of the ocean before being remineralized. It deepens and disperses the phosphate maximum and lowers the basin-average particulate carbon flux into good agreement with sediment trap results.

We chose the parameters for the DOM experiment to yield a DOM pool consistent in size with that observed by Suzuki and Sugimura, assuming a C–P ratio of ~ 100 in the DOM. It is worth pointing out that this same result cannot be obtained by putting half the new production into a pool of small particles which can advect with the water. The particulate organic matter pool in the ocean is 10–100 times smaller than the DOM pool. If a significant fraction of the ocean's new production ended up in nonsinking particles, the turnover time for the pool would be measured in days, instead of years. Material this ephemeral could not advect or mix far enough to make any difference.

We readily acknowledge that the circulation field produced by the sector model in these experiments is not entirely realistic. We are currently repeating this set of experiments in a global general circulation model which includes real continental boundaries, bottom topography, and observed surface wind stresses. The global model has been thoroughly evaluated by running predictive simulations of the distributions of natural and bomb-produced radiocarbon (Toggweiler et al. 1989). An effect which has not been included in the model, and which might be very important, is downward organic matter transport along continental margins. Organic matter production along continental margins is much higher per unit area than in the open ocean. If there is a direct flux of organic matter from the surface to the deep sea, along continental margins over the globe which exceeds

the open ocean flux (Walsh 1983), downward particulate transport along the ocean's margins may circumvent the problem raised by the sediment trap observations.

SOURCES AND SINKS OF SUZUKI AND SUGIMURA'S DOM

Why should marine organisms produce DOM which ties up scarce nutrients in forms which are so difficult to break down? DOM is produced by most elements of marine food webs. Lancelot and Billen (1985) provide an excellent review of the literature on the production of DOM associated with primary production. They report that the release of photosynthetically produced DOC by healthy, growing phytoplankton ranges from 0 to 10% of the primary production. Several studies report higher percentages of release by organisms under low nutrient conditions, particularly when the phytoplankton are dominated by flagellates. Populations dominated by diatoms characteristically release low percentages of their primary production as DOC. Caron et al. (1985) report that heterotrophic microflagellates release 10% of the carbon they ingest as DOC.

Microbiologists maintain that DOC provides the main substrate for bacterial growth in the ocean (Ducklow 1983). It is usually assumed that the bacteria derive most of their energy by breaking down the primary exudates of the phytoplankton and animal populations. Microbiologists view the DOC on which the bacteria feed as a small, labile pool which turns over on time scales of hours or days. Estimates of bacterial biomass and production suggest that the fraction of the primary phytoplankton production which passes through the bacteria may be 20–50% (Ducklow 1983), somewhat greater than the DOM fraction detected by ^{14}C incubations.

One of the most thorny issues concerning the origin of marine DOM involves the transformation of the relatively simple compounds produced and utilized by marine organisms into the complex, long-lived, and uncharacterizable compounds which form the bulk of the ocean's DOM. Only 10–20% of the DOM can be characterized as identifiable compounds or classes of compounds (Williams 1975).

The primary exudates of the phytoplankton are mainly low molecular weight metabolites and polymeric carbohydrates (Lancelot and Billen 1985). The carbohydrates are quantitatively more important, giving the pool of excreted DOC a distinctly high C:N ratio. The metabolites are readily usable by bacteria whereas the high molecular weight carbohydrates must be broken down. In order to use the high molecular weight substrates, the bacteria produce extracellular enzymes to break these compounds down into small molecules which can be absorbed through their cell walls. The enzyme reactions are not 100% efficient, leading to condensation reactions between the carbon-rich primary exudates with the nitrogen-rich enzymes. This sort

of condensation reaction has been separately proposed by Duursma (1965) and Sieburth and Jensen (1969) as a possible source of the long-lived, low C:N, DOM in seawater.

The same enzymes which break down the primary exudates are probably capable of breaking down the condensation products as well. When the primary exudates are abundant, the production of condensation products may exceed the breakdown of these compounds, with the net result being an increase in the condensed organic matter pool. When the primary exudates are not available, the condensation products may be consumed, albeit slowly.

There are sedimentary and terrestrial analogues for the formation and breakdown of condensed DOM (Rice 1982; Melillo et al. 1984). Melillo et al. describe the nitrogen immobilization by decaying forest litter as a batch process. The decay of fresh, nitrogen-poor substrates results in nitrogen uptake from the surroundings, as bacterial enzymes are consumed in the decay process. Initially, the nitrogen concentration in the organic matter goes up, but nitrogen uptake eventually gives way to nitrogen release as the entire pool of organic material is consumed. The hypothesis outlined above for oceanic DOM represents the same type of process operating in a continuous mode. The seasonal batch processing of forest litter is replaced in the ocean by a physical separation between the zone of active condensed-DOM formation, where phytoplankton and animal exudates are being produced, and a zone of net destruction, where the exudates are not available.

This hypothesis could probably be put to the test with a well-resolved survey of an ocean basin which included some seasonal time series. A key prediction is a systematic variation in the C:N ratio. If the terrestrial analogy holds, the highest C:N ratios in the bulk DOM should be found in the surface waters, with the lowest C:N in the most condensed fractions. Suzuki and Sugimura's size fraction work suggests that there are distinct pools within the DOM which should be characterizable with new approaches. There is also a great need to know whether or to what degree dissolved organic phosphorus is included in the additional DOM extracted by Suzuki and Sugimura's technique.

CONCLUSIONS

The new higher DOC and DON concentrations reported by Suzuki and Sugimura, although not yet reproduced by other investigators, may revolutionize our models of how the vertical material balance is maintained in the ocean. This work is revolutionary, not simply because it shows the pool of oceanic DOM is bigger, but also because it shows that this pool is much more dynamic and more integral to the ocean's chemical cycles than

previously thought. The DOM oxidized by Suzuki and Sugimura's technique appears to consist of larger molecules which contain more nitrogen than the DOM oxidized by standard methods. Oceanic distributions suggest that Suzuki and Sugimura's DOM is relatively long-lived in the ocean, but is considerably more degradable than the bulk DOM extracted by the standard methods. Relationships between DOM concentrations and concentrations of other geochemical properties suggest that 80% of the nitrate remineralization, organic matter respiration, and oxygen consumption below the thermocline is due to DOM which has been mixed downward from the upper ocean or advected laterally from high altitudes.

Given the potential impact of these new results, we know very little about mechanisms which govern the size of the ocean's DOM pools. Sugimura and Suzuki's DOC profiles, if extrapolated to the whole ocean, suggest that the ocean's DOC pool is at least twice as big as the atmospheric CO_2 reservoir. There are no obvious feedbacks controlling the size of this reservoir like those controlling the inorganic CO_2 pool (e.g., the effects of pH on $CaCO_3$ solubility). The ocean's DOM, therefore, represents a present-day wild card in our efforts to understand the ocean's chemical cycles.

REFERENCES

Billet, D.S.M.; Lampitt, R.S.; Rice, A.L.; and Mantoura, R.F.C. 1983. Seasonal sedimentation of phytoplankton to the deep sea benthos. *Nature* **302**: 520–522.

Bishop, J.K.B.; Stepien, J.C.; and Wiebe, P.H. 1987. Particulate matter distributions, chemistry, and flux in the Panama Basin: response to environmental forcing. *Prog. Ocean.* **17**: 1–59.

Broecker, W.S., and Peng, T.-H. 1982. Tracers in the Sea. Palisades, NY: Eldigio Press.

Caron, D.A.; Goldman, J.C.; Anderson, O.K.; and Dennett, M.R. 1985. Nutrient cycling in a microflagellate food chain. II. Population dynamics and carbon cycling. *Mar. Ecol. Prog. Ser.* **24**: 243–254.

Degens, E.T. 1970. Molecular nature of nitrogenous compounds in seawater and recent sediments. In: Organic Matter in Natural Waters, ed. D.W. Hood. *Inst. Mar. Sci. Alaska.* **1**: 77–106.

Ducklow, H. 1983. Production and fate of bacteria in the oceans. *Bioscience* **33**: 494–501.

Duursma, E.K. 1965. The dissolved organic constituents of seawater. In: Chemical Oceanography, eds. J.P. Riley and G. Skirrow, vol. 1, 1st ed. pp. 433–475. London: Academic Press.

Fiadeiro, M.E., and Craig, H. 1978. Three-dimensional modeling of tracers in the deep Pacific Ocean. I. Salinity and oxygen. *J. Marine Res.* **36**: 323–355.

Jackson, A.J., and Williams, P.M. 1985. Importance of dissolved organic nitrogen and phosphorus to biological nutrient cycling. *Deep-Sea Res.* **32**: 223–235.

Lancelot, C., and Billen, G. 1985. Carbon-nitrogen relationships in nutrient metabolism of coastal marine ecosystems. In: Advances in Aquatic Microbiology, eds. H.W. Jannasch and P.J. leB. Williams, vol. 3, pp. 263–321. London: Academic Press.

Mantoura, R.F.C., and Woodward, E.M.S. 1983. Conservative behavior of riverine dissolved organic carbon in the Severn Estuary: chemical and geochemical implications. *Geochim. Cosmochim. Acta* **47**: 1293–1309.

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

Melillo, J.M.; Naiman, R.J.; Aber, J.D.; and Linkins, A.E. 1984. Factors controlling mass loss and nitrogen dynamics of plant litter decaying in northern streams. *Bull. Amer. Sci.* **35**: 341–356.

Rice, D.L. 1982. Detritus nitrogen problem: new observations and perspectives from organic geochemistry. *Mar. Ecol. Prog. Ser.* **9**: 153–162.

Sarmiento, J.L.; Toggweiler, J.R.; and Najjar, R. 1988. Ocean carbon cycle dynamics and atmospheric pCO_2. *Phil. Trans. R. Soc. Lond. A* **325**: 3–21.

Sieburth, J.M., and Jensen, A. 1969. Studies on algal substances in the sea. II. The formation of gelbstoff (humic material) by oxidates of Phaeophyta. *J. Exp. Mar. Biol. Ecol.* **3**: 275–289.

Sugimura, Y., and Suzuki, Y. 1988. A high temperature catalytic oxidation method of non-volatile organic carbon in seawater by direct injection of liquid sample. *Marine Chem.* **24**: 105–131.

Suzuki, Y.; Sugimura, Y.; and Itoh, T. 1985. A catalytic oxidation method for the determination of total nitrogen dissolved in seawater. *Marine Chem.* **16**: 83–97.

Toggweiler, J.R.; Dixon, K.; and Bryan, K. 1989. Simulations of radiocarbon in a coarse resolution world ocean model. *J. Geophys. Res.*, in press.

Toggweiler, J.R.; Sarmiento, J.L.; Najjar, R.; and Papademetriou, D. 1987. Models of chemical cycling in the oceans: a progress report. Ocean Tracers Lab. Tech. Rep. #4, Atmospheric and Oceanic Sciences Program, Princeton Univ., 61 pp.

Walsh, J.J. 1983. Death in the sea: enigmatic phytoplankton losses. *Prog. Ocean.* **12**: 1–86.

Williams, P.J. leB. 1975. Biological and chemical aspects of dissolved organic material in seawater. In: Chemical Oceanography, eds. J.P. Riley and G. Skirrow, vol.2, 2nd ed., pp. 301–363. London: Academic Press.

Williams, P.M., and Druffel, E.R.M. 1987. Radiocarbon in dissolved organic matter in the central North Pacific Ocean. *Nature* **330**: 246–248.

Wyrtki, K. 1962. The oxygen minima in relation to ocean circulation. *Deep-Sea Res.* **9**: 11–23.