

DISSOLVED ORGANIC MATTER IN THE OCEAN: COMMENTS ON A CONTROVERSY

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have been accepted as gospel by some, as heresy by others.*

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If these recent DOC and DON results are correct, there is a lot of explaining to do concerning the source of the DOM, its relative stability to chemical and microbial oxidation, and its molecular composition.

Recent measurements of dissolved (including colloidal) organic carbon (DOC) and nitrogen (DON) concentrations in the northwestern Pacific (Sugimura and Suzuki, 1988; Suzuki *et al.*, 1985) are 50 to 400% higher than previous results found for oceanic surface and deep waters (Figures 1, 2). These elevated concentrations, as yet unconfirmed, have been accepted as gospel by some, as heresy by others, with the skeptics somewhere in between.

Briefly, Sugimura and Suzuki (1988) and Suzuki *et al.* (1985) inject 200 μl of filtered, acidified seawater onto a 3% Pt on Al_2O_3 catalyst at 680°C and measure the resultant CO_2 (from DOC) by infra-red absorption or the resultant NO (from DON) by oxidation to NO_2 with subsequent spectrophotometric determination. Their DOC values (180-490 μM in the upper 300 m; 35 to 85 μM from 400 to 4100 m) and DON values (30 to 45 μM in the upper 300 m; 4 to 15 μM from 400 to 4100 m) display oceanographic consistency: DOC and DON are inversely correlated with the apparent oxygen utilization (AOU) (Figure 2), where there are near uniform values of DON plus inorganic nitrogen ($\text{NO}_3^- + \text{NO}_2^- + \text{NH}_3$) and of DOC plus the carbon equivalent of AOU from the surface to the deep sea. Profiles of DOC, DON, AOU and NO_3^- with these same general shapes were previously postulated in order to explain the N (and P) cycle(s) relative to AOU values (Miyaki *et al.*, 1982; 1985).

Believers would welcome high DOC and/or DON values to explain such anomalies as unknown protonated compounds (e.g., organic acids) which could account for the discrepancy between potentiometric and manometric measurements of total CO_2 in surface seawater (Bradshaw and Brewer, 1988); also it may explain the imbalance between reduced carbon exported out of the euphotic zone (as measured by sediment traps) and the higher amounts expected from *in situ* production inferred from seasonal oxygen signals. The skeptics should be concerned because potentially significant increases in trace metal complexation could result from elevated

dissolved organic matter (DOM) contents, and modification of global dissolved oxygen budgets vis-à-vis mineralization of this "excess" DOC and DON could occur in surface waters. The heretics simply do not believe that previous oxidation techniques have missed such a large fraction of the DOM and they are concerned because, at present, there is no evidence for the requisite dissolved organic phosphorus (DOP) (Suzuki, personal communication) or an equivalent PO_4^{3-} in surface waters as would be expected from Redfield C:N:P restraints.

If these recent DOC and DON results are correct, and for the purpose of this essay we will assume this is the case, there is a lot of explaining to do concerning the source of the DOM, its relative stability to chemical and microbial oxidation, and its molecular composition. These are not new queries, but they now assume a vital importance in oceanic carbon and nitrogen budgets and cycling, and in effect have stimulated a reawakening of an often dreary litany of the previously accepted, monotonic distributions of DOC and DON.

Chemical and Biochemical Stability of DOC

Some of the facts known about the stability of DOC are:

(1) DOC concentrations measured by different wet combustion techniques, for example, peroxydisulfuric acid, chromic acid, or short wavelength ultraviolet radiation (Armstrong *et al.*, 1966; Menzel and Vaccaro, 1964; Duursma, 1961) are comparable in both surface and deep waters and show little or no changes below the upper 300-500 m, nor do they correlate well with or reflect other oceanographic features or biological processes such as the oxygen minimum, surface primary productivity, and discrete water parcels (Williams *et al.*, 1980; Menzel and Ryther, 1968; Gershay *et al.*, 1979; Ogura, 1970; Holm-Hansen *et al.*, 1966; Duursma, 1961)(see Figure 1). The same holds true for elevated DOC values measured by various high temperature catalytic combustion techniques (e.g., Gershay *et al.*, 1979; Sharp, 1973; Gordon and Sutcliffe, 1973;

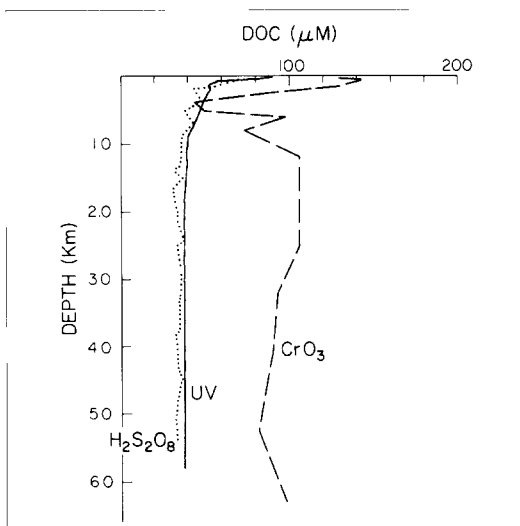


Figure 1. Profiles of DOC (μM) in the North Pacific using different oxidative techniques: UV-radiation (—, 31°N, 159°W, Williams and Druffel, 1987), peroxodisulfuric acid (· · ·, 31°N, 168°W, L. Gordon, personal communication, Geosecs Stn. 204), and chromic acid (- - -, 32°N, 142°E, Plunkett and Rakestraw, 1955).

Skopintsev *et al.*, 1966; Starikova and Yablokova, 1974) prior to the Suzuki and Sugimura (1988) results (Figure 2). An exception is the high DOC values found by Plunkett and Rakestraw (1955) using chromic acid oxidation of dried seawater from which most of the chloride ion had been removed by precipitation with thallium (Tl^+) (Krogh, 1934) (Figure 1).

(2) Virtually all of the standard organic compounds added to seawater yield 70 to 100% recoveries upon wet or UV oxidation, including such "refractory" and/or high molecular weight substances as albumin, palmitic acid, pyridine, "humic" substances, and powdered chitin (an N-acetyl-D-glucosamine polymer). These recoveries temper speculations that during wet or UV oxidation of natural seawater concurrent oxidation of seawater halides reduces the oxidation potential thus leading to incomplete oxidation of the seawater DOC, or that the residual DOC measured by Sugimura and Suzuki (1988) is transparent to UV and hence is not oxidized;

(3) Surface water DOC, when allowed to incubate with the indigenous bacterial populations, is reduced to the concentration levels of DOC in deep waters (Barber, 1968), suggesting that this baseline fraction of the DOC measured by wet or UV oxidation is chemically reactive but is only very slowly utilized by bacteria;

(4) Recent determinations of the natural radiocarbon content of DOC in samples from the surface to 5720 m in the north central Pacific (Williams and Druffel, 1987) give mean apparent ages for UV-oxidizable DOC of 1300 yrs B.P. ($\Delta^{14}\text{C} = -150\text{‰}$) at the surface and 6000 years B.P. ($\Delta^{14}\text{C} = -525\text{‰}$) from 900 to 5720 m. These values suggest that at least a portion of this DOC is recycled within the ocean on a $>10^3$ - 10^4 year time scale. These "old" ages are also reflected in

humic, fulvic and hydrophilic acids isolated on XAD macroreticular resins from seawater samples collected at 180 m, south of Hawaii (Druffel *et al.*, in preparation; Thorn *et al.*, 1987); and (5) Copper complexation studies in the NE Pacific provide strong evidence for 2 types of organic copper complexing ligands: a weaker ligand whose concentrations show no apparent variation with depth (0-1500 m) and a strongly-bound ligand that displays a subsurface maximum at the depth of the primary productivity maximum (50-75 m) and is zero by 200 m (Coale and Bruland, 1988).

Thus it appears that the deep-sea DOC oxidized by wet or UV oxidation techniques is relatively inert to rapid biochemical utilization, is mixed conservatively within the deep-sea, and comprises about 50% of the wet or UV oxidizable DOC in the surface mixed layer, the remainder being more labile organic compounds of recent origin (Druffel *et al.*, in preparation, Williams and Druffel, 1987).

Thus we are left with a paradox. What is the quality of the "extra" DOC (and DON) reported by Sugimura and Suzuki (1988) and Suzuki *et al.* (1985)? We know that this DOM does not oxidize readily, yet is utilized relatively rapidly by marine microbial community—at least judging from its covariance with AOU, NO_3^- and dissolved O_2 , and the observation that it exhibits diurnal variations in productive waters (Y. Suzuki; personal communication).

Sugimura and Suzuki (1988) and Suzuki (personal communication) also found that the major portion of the DOC in surface water which is not oxidized by peroxydisulfuric acid is in the molecular weight range of 4000-22,000 Daltons and has a C/N ratio of 5.6 to 6.8 by atoms (as compared to a normal C/N ratio of 7-12 for wet or UV oxidizable DOC). This is approximately the same size range which accounts for an appreciable fraction of the missing DON (Suzuki *et al.*, 1985). The implications are clear: the "extra", N-enriched, organic matter, derived from phytoplankton, is attractive to heterotrophic microorganisms, is probably polymeric, and has oxidation potentials and/or rates exceeding those of the standard compounds used in evaluating the efficiency of the wet, UV, and earlier high temperature oxidation techniques.

One way out of this dilemma is to postulate that the "extra" DOC is a highly cross-linked polymer derived from proteinaceous precursors (such as glycoproteins etc. in cell walls) by photochemical and/or microbial transformations in surface waters. Such a polymer would either be very slowly oxidized (molecular layer by molecular layer) by wet chemical or UV irradiation techniques, or its threshold oxidation potential would be too high for wet chemical techniques to effect any oxidation in the presence of 0.5 molar chloride ion. In fact, it is difficult to believe that this hypothetical substance would be truly soluble with a molecular weight of 4000 to 22,000

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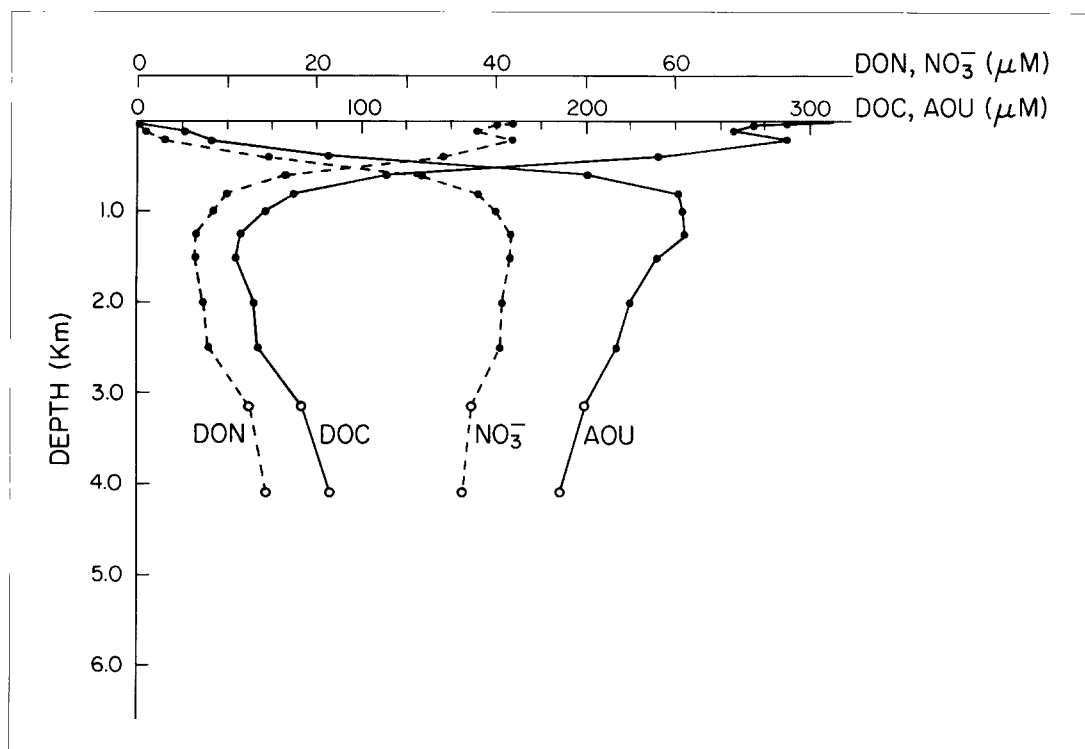


Figure 2. Profiles of DOC, DON, apparent oxygen utilization (AOU), and NO_3^- as measured by Sugimura and Suzuki (1988) at 20°N , 137°E (---) and 5°N , 135°E (-o-). The depth of the O_2 minimum at 20°N , 137°E is between 800 and 1000 m. Notice the similarity between this DOC profile and that of Plunkett and Rakestraw (Figure 1).

Daltons rather than being colloidal in nature.

The Molecular Composition Of DOC

There is not much known about the composition of DOC. The facts are that in surface waters about 15% of the "old" DOC (as measured by UV or wet oxidative techniques) can be identified as combined amino acids and carbohydrates, 1-2% as solvent-extractable lipids, and 20-50% as "humic substances" isolated on XAD-2, -8, and -4 macroreticular polystyrene resins (Williams and Druffel, 1987; Thorn *et al.*, 1987; Druffel *et al.*, in preparation). In deeper waters, the combined amino acids and carbohydrates plus lipids account for 7 to 8% of the DOC and the "humic substances" $\geq 10\%$. In addition, a number of trace organic compounds (urea, organometallics, Krebs cycle acids, etc.) have been identified, primarily in surface waters (Williams, 1986), and account for less than 1% of the DOC. The "new" Sugimura and Suzuki (1988) elevated DOC values would reduce these identifiable constituents by factors of 2 to 3 in surface and deep waters. Thus we are confronted with the challenge of identifying an additional 100 to 300 μM of DOC and 20-40 μM of DON in surface waters and 10 to 50 μM DOC and 1 to 5 μM DON below 300 m—most of which must be resistant to chemical or UV oxidation, relatively labile to rapid bacterial utilization and degradation, and presumably (see below) of marine origin.

The Source Of DOC

It has been assumed that the bulk of DOC (and DON) has its fundamental origin in surface ocean waters via such processes as phytoplankton excretion, lysis and solubilization of living and

detrital particulate organic matter (microplankters, fecal material, extracellular exudates, etc.) and "sloppy feeding" at various trophic levels. On the other hand, it has been postulated that 50% or more of the DOC in the oceans arises from river inputs of soluble organic matter which is conserved rather than removed during estuarine flocculation and degradative processes (Mantoura and Woodward, 1983). Current analytical data, however, does not support a significant riverine contribution to oceanic DOM. First, lignin (uniquely identified by its oxidation products [Hedges and Ertel, 1982]), whose origin is restricted solely to terrestrial sources, occurs in rivers, coastal waters, and in sediments bordering continental runoff areas (e.g., Hedges and Mann, 1979; Ertel *et al.*, 1986; Hedges *et al.*, 1986). It is not found, however, in open ocean water at 5 and 150 m at two locations in the eastern tropical Pacific (Meyers-Schulte and Hedges, 1986). Second, the $^{13}\text{C}/^{12}\text{C}$ $\delta^{13}\text{C}$ ratios of "old" open ocean DOC are -20 to -22 ‰ (Williams and Druffel, 1987; Meyers-Schulte and Hedges, 1986) while riverine (Amazon) DOC and POC have values of -28 (Williams and Gordon, 1970) and -26 to -32 ‰ (Hedges *et al.*, 1986), respectively. Third, diurnal variations in the low molecular weight fraction of the DOC (Suzuki, personal communication) demand a phytoplankton source, and thus limit the contribution of riverine DOC, at least in surface waters. These facts suggest that riverine contributions are less than 10% of the total marine DOC pool. Additional analyses of lignin oxidation products in surface and deep waters of the Pacific and Atlantic (whose river

sources are much higher than for the Pacific) should more precisely define the magnitude of terrestrial input to the dissolved organic matter pool.

What does all of this mean to the oceanographic community and where do we go from here? Confirmation of the elevated DOC and DON values of Sugimura and Suzuki (1988) and Suzuki *et al.* (1985) is the first mandate. This includes confirmation using other methods, e.g., closed-tube combustion of dried seawater samples. If these measurements reveal consistently higher DOC values, then a series of experiments must be run to determine the identity and source of this DOM and its resistivity to chemical and UV oxidation. Such experiments would include: exposing seawater solutions of proteinaceous-type compounds (including the indigenous microbial populations) to various periods of incubation with natural UV- β radiation and measuring the DOC by both UV and Suzuki methodologies; adding ^{14}C and ^3H -labelled bacteria and/or phytoplankters to seawater and determining whether or not the label is incorporated into UV-resistant fractions of the resultant, size-fractionated organics, both soluble and colloidal; and measuring the natural $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values in the additional DOC to estimate its source, its apparent "age" with respect to production and the rate at which it is entering the deep sea.

It also means that the role of DOM in the biogeochemical cycles of organic carbon, organic nitrogen, O_2 , inorganic N and P nutrients, CO_2 and trace metals will have to be re-evaluated. In addition, a closer evaluation of the role of this new DOM to phytoplanktonic growth must be done.

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