CONCENTRATIONS AND RADIOCARBON SIGNATURES OF DISSOLVED ORGANIC MATTER IN THE PACIFIC OCEAN

Ellen R. M. Druffel
Woods Hole Oceanographic Institution, Woods Hole, MA

Peter M. Williams
Scripps Institution of Oceanography, La Jolla, CA

Yoshimi Suzuki
Meteorological Research Institute, Yatabe, Tuskuba, JAPAN

Abstract. We present evidence suggesting that only a portion of the dissolved organic carbon (DOC) in the seawater analyzed previously by Williams and Druffel (1987) was oxidized by the UV-radiation method. High temperature catalytic (HTC) methods (Sugimura and Suzuki, 1988) used to reoxidize the central North Pacific gyre water samples reveal that the total DOC (DOC) is about twice that of the UV-oxidizable DOC (DOCuv). Indications from the original study suggest that this additional DOC contains higher concentrations of radiocarbon than in the DOCuv. This HTC method suggests that the DOC is responsible for most of the dissolved organic carbon there are 2 to 3 times more DOC in our seawater samples than previously measured. If correct, correlations between DOC and AOU indicate that DOCuv is older and thus more refractory with respect to photooxidation, yet is more chemically reactive with respect to photooxidation, than the fraction resistant to UV (DOCuv).

Introduction

For the past twenty years, measurements of DOC in seawater have been commonly achieved by two methods: photooxidation of UV-radiation from Hg-arc lamp (Armstrong et al., 1966) and by wet oxidation using peroxodisulfuric acid (Menzel and Vacarro, 1964). Plunkett and Rakestraw (1955) obtained high DOC results using wet oxidation with chromic acid after removal of most of the chloride ion. Higher, but erratic, DOC values were also reported earlier using a variety of high temperature techniques (see references in Williams and Druffel, 1988). Sugimura and Suzuki (1988) measured non-volatile DOC using direct injection of acidified seawater onto a high temperature platinum-on-alumina catalyst. They found DOC concentrations up to 3 times higher than those measured using wet oxidation techniques. Oxidation of chloridic acid ion by the aforementioned wet oxidation techniques may lower the oxidation potential in these systems below the threshold value necessary to combust the more resistant DOC. Sugimura and Suzuki's (1988) data, not yet rigorously confirmed, imply that virtually all of the AOU (apparent oxygen utilization) in the western North Pacific Ocean can be accounted for by the oxidation of DOC and dissolved organic nitrogen (DON).

Methods

Concentrations of DOC were measured in filtered (1.0 μm GFC glass fibre) water samples collected from 31°N, 159°W during the Alcyone-5 cruise aboard the R/V Melville (October 1985). Frozen and thawed aliquots of both UV-oxidized (DOCuv) and unoxidized (DOCunox) water samples were injected into an oxygen stream onto a 3% Pt-on-alumina catalyst at 680°C (Sugimura and Suzuki, 1988), with subsequent detection of the resultant CO2 by incinerated adsorption. The error of DOCuv and DOCunox measurements is estimated from replicate analyses of the same water samples to be ± 3 μM.

Results

Residual DOC (DOCuv) was detected in all of the 19 UV-oxidized seawater samples analyzed, with values ranging from 46-144 μM (Table 1). The subtraction of the original DOC values from DOCuv measured in the corresponding 19 unoxidized samples are remarkably close to the DOCuv values (Table 1). If these results are a true representation of DOC concentration, then the DOC pool in the central North Pacific Ocean is about twice as large as had previously been believed (Figure 1). It also means that there is indeed variation in the DOC depth profile, where UV- and wet-oxidation techniques had indicated an invariant DOC profile at depths > 1000 m.

Figure 2 shows DOCuv (in μM) plotted versus AOU (in μM), which was calculated from oxygen, salinity and potential temperature measured during the Eve-1 cruise at the same location (31°N, 159°W) in June 1987. The plot of results from the upper part of the water column (3-482 m) shows a slope of 1.0 (d[AOU]/d[DOCuv]), which is close to the value of 1.3 obtained by Redfield et al., (1963) for organic carbon and oxygen utilization in the water column. The similarity to Redfield ratios imply that DOC is responsible for most of
Table 1. DOC in original seawater measured by UV (2σ = ± 1.5 uM) and HTC (2σ = ± 3.0 uM) oxidation, and DOC remaining (DOC_{uv}) in the UV-oxidized samples measured by HTC oxidation. All samples were collected from 31°N, 159°W in October 1985 (Williams & Druffel, 1987).

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>DOC_{uv} (uM)</th>
<th>DOC_{HTC} (uM)</th>
<th>DOC_{HTC} - DOC_{uv} (uM)</th>
<th>DOC_{uv} (uM)</th>
<th>DOC_{uv} (uM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>90</td>
<td>210</td>
<td>120</td>
<td>-15</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>84</td>
<td>218</td>
<td>144</td>
<td>134</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>82</td>
<td>218</td>
<td>130</td>
<td>136</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>58</td>
<td>206</td>
<td>144</td>
<td>148</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>53</td>
<td>184</td>
<td>132</td>
<td>131</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>54</td>
<td>173</td>
<td>110</td>
<td>119</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>51</td>
<td>153</td>
<td>96</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>482</td>
<td>56*</td>
<td>108</td>
<td>48</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>637</td>
<td>46</td>
<td>96</td>
<td>48</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>757</td>
<td>43</td>
<td>94</td>
<td>48</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>40</td>
<td>90</td>
<td>46</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>903</td>
<td>43*</td>
<td>1152</td>
<td>50</td>
<td>293</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1152</td>
<td>293</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1308</td>
<td>40</td>
<td>98</td>
<td>52</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>1769</td>
<td>42*</td>
<td>106</td>
<td>66</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>2069</td>
<td>38</td>
<td>108</td>
<td>69</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>3378</td>
<td>38</td>
<td>110</td>
<td>72</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>3631</td>
<td>43*</td>
<td>110</td>
<td>68</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>4227</td>
<td>38</td>
<td>112</td>
<td>72</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>5227</td>
<td>38</td>
<td>112</td>
<td>72</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>5670</td>
<td>43*</td>
<td>108</td>
<td>65</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>5720</td>
<td>38</td>
<td>110</td>
<td>70</td>
<td>72</td>
<td></td>
</tr>
</tbody>
</table>

* One of the seven initial samples oxidized by UV. The 482 m 14C sample was lost (Williams and Druffel, 1987).

** Result not reported in original study (Williams and Druffel, 1987).

Fig. 1. DOC (o, *) (Williams and Druffel, 1987) and DOC_{HTC} (■) measured in seawater collected from the North Pacific gyre (31°N, 159°W) during the Alcyone-5 cruise in October 1985. Apparent oxygen utilization values (DOC) were calculated from a detailed oxygen profile measured on a subsequent cruise to the same site in June-July 1987.

Fig. 2. DOC_{HTC} (D, ■) and DOC_{uv} (O, *) versus AOU. Open symbols represent near surface samples (HTC: 3-482, uv: 3-300 m) and closed symbols represent all deeper samples.

The differences between our results and those of Sugimura and Suzuki (1988) indicate that one or more of the following may be taking place at our site: 1) Other species are being oxidized, especially in the deep sea (i.e., DON, particulate organic carbon and nitrogen); 2) There is a possible additional process for oxygen utilization in the deep sea, i.e., lateral advection and subsequent oxidation of DOC-rich water from continental margins which may not be present at the western North Pacific sites; or 3) DOC was lost prior to the HTC analysis during slow freezing (24 hours) and/or thawing of our unpurified seawater samples, especially in the upper several hundred meters. However, higher DOC values were measured at the oxygen minimum at 31°N, 159°W (10 µM) than at the oxygen minima in the western North Pacific (40 µM, Sugimura and Suzuki, 1988), suggesting that more of the chemically resistant DOC was present in the NCP intermediate waters. The plot of AOU vs. DOC_{uv} (Figure 2) reveals a slightly higher slope for the shallow samples (1.3, 0-300 m), which may indicate the presence of another oxidizable substrate (i.e., DON) or differing DOC_{uv} values measured in 1987 from the samples measured in 1985 (oxygen was not measured on the October 1985 cruise). The slope of infinity for the deep samples (482-5720 m) indicates that DOC_{uv} in the deep sea is not oxidizable on the timescale of oxygen utilization, an assertion which is supported by the low 14C results (~520/0) for DOC_{uv} in the deep sea (Williams and Druffel, 1987).

In order to understand the source(s) of DOC, we must determine the 14C signature and composition of this pool of organic matter. There was evidence in the DOC_{uv} concentrations and 14C measurements from the original study (Williams and Druffel, 1987) of the nature of the DOC. First, the initial seven of 26 seawater samples oxidized by UV yielded 7-14% higher DOC values than succeeding samples from the same site collected on a subsequent cruise to the same site in June-July 1987.
A14C results reflect the added DOC calculated using the mass balance relationship: depth (Figure 3). Assuming that these higher additional analyses of DOC are needed before conclusions can be drawn. res Libby C half-life of 5568 years.

Second, the A14C values of the DOC oxidized in six (the 482 m sample was lost) of the anomalous samples were significantly higher (by 20-100\%/.., 3-140) than values from succeeding samples from the same depths in the other regions (Figure 3). Assuming that these higher A14C values reflect the added DOC, the A14C values for DOC oxidized in 60 to the first 7 samples oxidized are calculated using the mass balance relationship:

\[ \Delta^{14}C_{ca} = \left( \Delta^{14}C_{ch} - \Delta^{14}C_{n} \right) \frac{f}{f_a} \]  

where \(^{14}C_{ca}\) represents values in the 6 anomalously high samples, \(^{14}C_{ch}\) in subsequent analyses (low) from the same depths, and \(f\) and \(f_a\) are the fractions of DOC in each of the two pools of DOC. The calculated values of \(^{14}C_{ca}\) decrease with depth, from +270 \pm 40\%/.. at 20 m to -350 \pm 30\%/.. at 5670 m (see in Figure 3). These high values (young ages) for \(^{14}C_{ch}\) are counter intuitive, as previous conjectures held that the chemical as well as biological stability of organic matter is proportional to radiocarbon age. Initial results suggest the presence of bomb \(^{14}C\) in the deep sea DOC pool, which most likely has its source from sinking particulate matter produced in the euphotic zone and subsequent dissolution at depth. As these are the only estimates available of DOC oxidation, it is tempting to extend this approach one step further and assume that all of the DOC, as listed in Table 1, is the same \(^{14}C\) value\] we calculated for the additional DOC (Figure 3). The range for the A14C of DOC oxidized in 60 to the first 7 samples oxidized is shown in Figure 3 (3631 m point excluded). This assumption is an oversimplification of the actual case, as DOC more likely contains a variety of \(^{14}C\) values, which decrease with depth. This indicates that the average turnover time of DOC in the deep sea may be much shorter (3-3000 yrs B.P.) than previously reported (-520\%/.., 5000 yrs B.P.; Williams and Druffel, 1987).

The \(^{14}C\) results of the 3 anomalous deep (>1000 m) samples averaged -21.3 \pm 2.2\%/.., 0.4\%/.., and -20.9 \pm 0.3\%/.. (SD) (Williams and Druffel, 1987). Additional analyses of DOC res before conclusions can be drawn.

In an effort to date individual fractions of the DOC, humic substances (fulvic, humic and hydrophilic acids) were isolated from filtered seawater collected at 180 m in the North Pacific by sorption onto XAD macroreticular resins (Ronald Malcolm, personal communication). We assume that humic materials are completely oxidized by UV-radiation based on the complete recovery of humic substances added to UV-oxidized seawater (P.W. Williams, unpublished results). Precise percent age yields of the humic substances isolated by R. Malcolm were not determined. However, humic plus fulvic acids isolated from seawater on XAD resins constitute about 5 to 20\% of the DOC in deep and surface waters (Harvey et al., 1983; Meyers-Schulte and Hedges, 1986). Humic acids, however, were less abundant than either the fulvic or hydrophilic acids (Table 2), and we will assume that 20\% of the DOC \(_{uv}\) was collected on the XAD-2, -8 and -4 resins.

The A14C values (Table 2) were -410 and -400\%/.., for the fulvic acids (XAD-8 and -2, respectively) and -310\%/.. for the humic acids (XAD-2). An intermediate value (-362\%/..) was obtained for the hydrophilic acid fraction (XAD-8, -4). For comparison, A14C of DOC at 200 m at 31\°N, 159\°W was -314\%/.. (Williams and Druffel, 1987). The average A14C values are higher and \(^{13}C\) are lower in the humic acid fraction (-310\%/.., -23.30\%/..) than those in the fulvic acid (-405\%/.., -21.75 to -22.63\%/..), or hydrophilic (-362\%/.., -20.37\%/..) acid fractions. These data suggest that there are significant differences in the sources to and/or degradative processes acting on these various classes of humic substances.

-410\%/.., -21.75 to -22.63\%/.. or hydrophilic

** Contaminated with modern carbon subsequent to elution from XAD-8 column.
Assessment of the problem

First, the labile compounds (total [free plus combined] dissolved amino acids and carbohydrates, THAA and TCHO) measured in the same samples used for the DOC analyses makeup approximately 19% and 15% of the DOC, respectively (DOCr_s) in: The DOC if it were not soluble, but instead existed as particulate (.05-1.0 μm diameter) form. 3_6, 83-97, 1985.

THAA and TCHO; A C = 100%/o ) and 20% humic carbon (fulvic, humic and hydrophilic acids, A C = ~386/9°,) when measured in UV-irradiated seawater, which illustrates the presence of significant amounts of biologically utilizable DOC in this media. It would be consistent with the chemical stability of DOC if it were not instead existing in colloidal (.005-.05 μm diameter) and/or small particle (.05-1.0 μm diameter) form.

The results reported here, an attempt to further our limited knowledge of the age and identity of DOC in the ocean. These results must be augmented by 1) confirmation of the HTC technique using other methods (i.e., combustion of dried seawater), and 2) direct isotopic (δ13C, δ14C) measurements of DOC/HC, using the gas produced by HTC methods. It is imperative that characterization of DOC, and DOC, be pursued. Not until this is achieved will we understand the sources, sinks and transformations of DOC, perhaps the largest actively-exchanging reservoir of carbon on earth.

Acknowledgements. We thank Dr. L. Keiser and colleagues for analyzing δ13C in the humic material at the University of Toronto Isotrace AMS Facility and Dr. R. Malcolm (U.S.G.S., Denver) for providing the humic material. We are very grateful to M.N. Hill, pp. 26-77, Interscience, New York, 1963.

Griffin, A.J.T. Jull, D. Donahue, L. Toolin

References


Yoshimi Suzuki, Meteorological Research Institute, Nagamine 1-1, Yatabe, Tsuchu, Ibaraki 305, JAPAN.

Peter M. Williams, Scripps Institution of Oceanography, La Jolla, CA 92033.

(Rceived: January 4, 1989; Accepted: June 30, 1989)