# Use of Keeling plots to determine sources of dissolved organic carbon in nearshore and open ocean systems

*Behzad Mortazavi*[1] *and Jeffrey P. Chanton*

Florida State University, Department of Oceanography, Tallahassee, Florida 32306-4320

*Abstract*—We apply a Keeling mixing model commonly used in atmospheric sciences to oceanic dissolved organic carbon (DOC) $^{14}$C and concentrations to demonstrate that DOC distribution across spatial transects or depth profiles can be modeled as two-component mixtures; one component consists of an old refractory pool to which a newly synthesized component pool is added. We then use the Keeling approach to determine the $\Delta^{14}$C signature of excess DOC added to background concentrations in nearshore and open ocean systems. Our analysis indicates enrichment in $^{14}$C of excess DOC in coastal waters relative to offshore waters, particularly in spring when river discharge increases. These findings are consistent with the export of $^{14}$C-enriched terrestrial DOC to the ocean and inconsistent with the idea of selective degradation of young terrestrial DOC in estuaries, resulting in export of old refractory component to the ocean. In the middle Atlantic Bight region, during the spring, excess DOC has a $^{14}$C signature similar to that of DOC in the major rivers, whereas during the peak primary productivity of the summer season, excess DOC has a signature more similar to that of dissolved inorganic carbon. Variability in the $\Delta^{14}$C of excess DOC in the open ocean was lower than that of the coastal ocean. Minima in $\Delta^{14}$C values of excess DOC in the open ocean were measured during periods of high particulate organic matter (POC) flux, indicating that POC can interact with DOC and selectively remove $^{14}$C-enriched components from the surface ocean. The Keeling plot provides a powerful approach for determining the isotopic composition of excess DOC from an entire DOC profile or transect.

Dissolved organic carbon (DOC) constitutes the largest reduced carbon pool in the ocean ($1.7 \times 10^{18}$ g C; Druffel et al. 1992). DOC in the ocean originates through primary production by cellular exudation, through viral lysis, and as a result of release during grazing by higher trophic levels. In the coastal ocean, rivers are a significant input source of DOC and globally deliver 0.25 Gt C of DOC (Spitzy and Ittekkot 1991). A fraction of the DOC supplied to the water column is respired, a fraction is incorporated by the food web, and a fraction is mixed below the subsurface layer following the breakdown of water column stratification (Carlson et al. 1994). The incorporation of surface water DOC into the deep ocean effectively sequesters carbon in the oceans prior to its oxidation and return to the atmosphere after several mixing cycles within the world ocean (Druffel et al. 1992).

The radioisotopic form of C, $^{14}$C with a half life of 5,730 yr, has proven to be a useful tool for investigating sources, residence time, and transformations of inorganic and organic carbon pools in the ocean (Williams and Druffel 1987; Bauer et al. 1992; Druffel et al. 1992). The $^{14}$C of DOC has also been used to provide isotopic constraints on carbon exchange between different reservoirs (Bauer et al. 1995). Results from coastal regions, for example, indicate that ocean margins are a significant DOC source to the deep open ocean (Bauer and Druffel 1998). In deep ocean environments, $^{14}$C of DOC and DOC concentration profiles in the sediments and overlying water provided evidence that deep ocean sediments are a source of relatively young DOC to the water column (Bauer et al. 1995).

According to the current paradigm, DOC in the ocean consists of an old or background refractory pool, with relatively constant concentration and $\Delta^{14}$C value as represented by the deep DOC pool, and a younger component present at varying concentrations in the upper ocean (Fig. 1A; Druffel et al. 1992; Carlson and Ducklow 1995; Cherrier et al. 1996; Bauer et al. 1998*a*). DOC at depth $z$ ([DOC]$z$) consists of an older background and relatively constant component ([DOC]b), to which an excess of more recently synthesized material is added ([DOC]xs):

$$[\text{DOC}]z = [\text{DOC}]\text{b} + [\text{DOC}]\text{xs} \qquad (1)$$

The goal of this paper is to introduce the oceanographic community to a model that can be used to determine the isotopic composition of DOC added in excess over background concentration ([DOC]xs in Eq. 1) that is based on concentration and isotopic measurements along a transect or profile. This model, developed in 1958 by Keeling (1958), is used by atmospheric chemists to determine the isotopic composition of excess $CO_2$ added by nighttime respiration relative to the background tropospheric $CO_2$ concentration (e.g., Mortazavi and Chanton 2002).

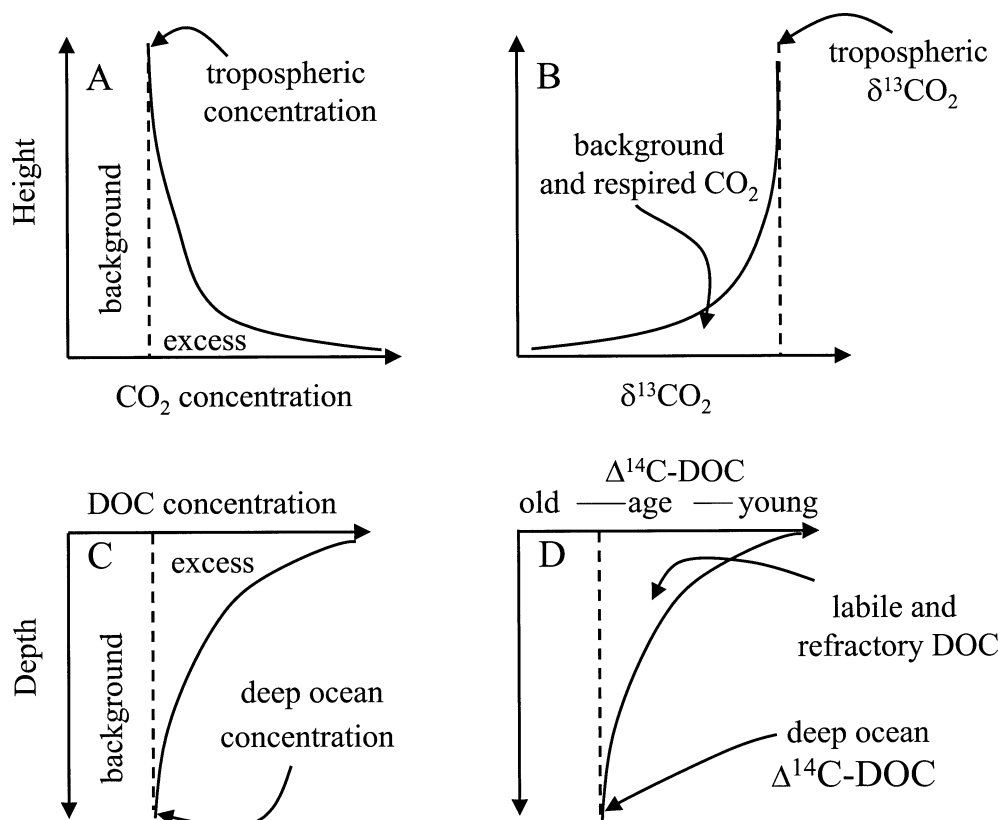In forest canopies during the night, there is an increase in $CO_2$ concentration relative to the background tropospheric

Fig. 1.   Conceptual diagram of (A) $CO_2$ buildup and (B) $^{13}C$ depletion in a forest canopy during the night. The depletion in $^{13}C$ results from addition of respired $CO_2$ with a signature of $-27‰$ to a background tropospheric concentration of $\sim 370$ ppm and $\delta^{13}C$ of $-8‰$. An (C) oceanic DOC concentration and (D) $^{14}C$ profile shows an enrichment near the surface ($-100‰$; Williams and Druffel 1987) because of the addition by the food web of young $^{14}C$-enriched DOC to a background refractory and $^{14}C$-depleted DOC ($-500‰$; Williams and Druffel 1987) of relatively constant concentration (adapted from Cherrier et al. 1996).

concentration as a result of soil and foliage respiration (Fig. 1A). Concurrent with the increase in $CO_2$ concentration, there is a depletion in the $^{13}C$ isotopic ratio of $CO_2$ within the canopy because respiration adds $CO_2$ with a signature of approximately $-27‰$, less than a background tropospheric value of $-8‰$ (Fig. 1A,B). A similar conceptual model can be used to describe oceanic DOC concentration and $\Delta^{14}C$ profiles. A DOC profile shows an increase in concentration (Cherrier et al. 1996) and an enrichment in $^{14}C$ near-surface waters (Druffel et al. 1992) as a result of the addition by the food web of young DOC, enriched in $^{14}C$, over a background of old DOC depleted in $^{14}C$ that is relatively constant in concentration and $^{14}C$ content (Fig. 1C,D).

Our first objective was to test the hypothesis that the relation between oceanic $\Delta^{14}C$ DOC and concentration can be described with a two-component mixing model, in which one component consists of background DOC of relatively constant concentration and $^{14}C$ content and a second component consists of a younger fraction (excess DOC) that is added to this background component. Although others have used a two-component model for discrete samples at unique depths (Druffel et al. 1992), our study differs in that we are expanding the approach across broad horizontal and vertical scales. Our

analysis does not require prerequisite knowledge of the background DOC concentration and its isotopic ratio but, instead, can be used to resolve the isotopic composition of the excess DOC in a system. Our second objective was to use this model to contrast the spatial and temporal variability in the $\Delta^{14}C$ of excess DOC at coastal and open ocean sites. Our approach toward accomplishing these goals was to (1) contrast oceanic DOC Keeling plots with data compiled from the literature on DOC concentrations and $\Delta^{14}C$-DOC depth profiles or horizontal transects in nearshore and open ocean waters and (2) use the model to compare the $\Delta^{14}C$ signature of excess DOC in coastal and open ocean waters.

Methods

The isotopic composition of DOC at depth $z$ ($\Delta^{14}DOCz$) results from the relative contributions of background DOC with an isotopic value of $\Delta^{14}DOCb$, and the newly added component (or a mixture of components added in constant proportions) with an isotopic value of $\Delta^{14}DOCxs$.

$$([DOC]z)(\Delta^{14}DOCz) = ([DOC]b)(\Delta^{14}DOCb)$$
$$+ ([DOC]xs)(\Delta^{14}DOCxs) \quad (2)$$

If a two-component mixing model is applicable, then by substituting $[DOC]z - [DOC]b$ for $[DOC]xs$ (Eq. 1) in Eq. 2 and by dividing both sides of Eq. 2 by $[DOC]z$, one finds that there should be a linear relation between $\Delta^{14}DOCz$ and $1/[DOC]z$.

$$\Delta^{14}DOCz = (1/[DOC]z)([DOC]b\Delta^{14}DOCb$$
$$- [DOC]b\Delta^{14}DOCxs)$$
$$+ \Delta^{14}DOCxs \qquad (3)$$

The intercept ($\Delta^{14}DOCxs$) of a plot of $\Delta^{14}DOCz$ as a function of $1/[DOC]z$ will correspond to the isotopic signature of excess DOC that has been added to background concentrations. The regression line will have a slope that is a composite of three parameters: $[DOC]b$, $\Delta^{14}DOCb$, and $\Delta^{14}DOCxs$. Because of a lack of specific knowledge of the background DOC concentration and isotopic composition, the slope does not provide any additional information. The regression analysis, however, is a powerful approach that can be used to determine $\Delta^{14}DOCxs$. The great dynamic range in $\Delta^{14}C$ of DOC, −525‰ in deep ocean DOC (Bauer et al. 1998*a*), to +257‰ in York River estuary (Raymond and Bauer 2001*a*), compared to the 2–3‰ range in $\Delta^{13}C$ DOC (Bauer et al. 2002), provides a clear advantage for using $^{14}C$ instead of $^{13}C$ in Eq. 3. Admittedly, describing excess DOC as a single component is an oversimplification. However, if the individual components of excess DOC in a region or along a profile are supplied in relatively constant ratios, or as long as one component dominates within the timescale of mixing, we can obtain a linear fit to the data and calculate the $\Delta^{14}C$ isotopic value of the DOC in excess of background values.

*Statistical considerations*—The assumptions associated with the standard linear regression (Model I) are violated when we assume that the independent variable ($1/[DOC]z$) has no errors associated with it and is under the experimenter's control (Sokal and Rohlf 1981) and that the errors in the dependent variable ($\Delta^{14}DOCz$) are independent of errors in the dependent variable (Sokal and Rohlf 1981; Pataki et al. 2003). We, therefore, used a Model II regression (geometric mean regression, Sokal and Rohlf 1981) to estimate the intercept of the Keeling plots. The slope of the Model II regression is calculated as the slope of the Model I regression divided by the $R$ coefficient of the $X$ and $Y$ variables, and the standard error of the intercept of a Model I regression is used to approximate the error estimate for the Model II intercept (Sokal and Rohlf 1981; Pataki et al. 2003).

A Student's *t*-test (Sokal and Rohlf 1981) was used to test whether the intercepts of two Keeling plots were identical ($H_0$) or significantly different ($H_1$).

$$t = (I1 - I2)/[(SE\ I1)^2/n1 + (SE\ I2)^2/n2]^{1/2}$$

I1 and I2 are the intercepts of two Keeling plots, and (SE I1) and (SE I2) are the standard errors of the intercept for the two Keeling plots. The degrees of freedom will be ($n1 + n2 - 4$), where $n1$ and $n2$ are the sample sizes in the regression lines. At $P < 0.05$, the null hypothesis was rejected in favor of $H_1$.

A Student's *t*-test (Sokal and Rohlf 1981) was used to test whether the intercept of a Keeling plot was identical ($H_0$) or significantly different ($H_1$) than mean $\Delta^{14}C$ of dissolved inorganic carbon (DIC).

$$t = (I - M)/[(SE\ I)^2/n1 + (SD\ M)^2/n2]^{1/2}$$

I is the intercept of the Keeling plot and M is the mean value of the surface water $\Delta^{14}C$ DIC and (SD M) is the standard deviation of the mean. The degrees of freedom will be ($n1 + n2 - 3$), where $n1$ is the sample size used in the regression and $n2$ is the sample size for $\Delta^{14}C$ DIC values. At $P < 0.05$, the null hypothesis was rejected in favor of $H_1$.

*Results and discussion*—The main objective of this research was to test the hypothesis that a two-component mixing model can be used to determine $\Delta^{14}C$ in excess DOC across spatial transects and depth profiles in marine systems. Our approach toward evaluating this hypothesis was to examine DOC $^{14}C$ and concentration data to see whether they fit a two-component mixing model similar to that used by atmospheric chemists. The results of this analysis were then used to examine the temporal and spatial variability of $\Delta^{14}C$ in excess DOC at coastal and open ocean sites. This is the first attempt to systematically compare $\Delta^{14}C$ in excess DOC from all existing oceanic DOC profiles or transects.

Our approach to test the applicability of the Keeling plot approach for DOC in the ocean was to examine DOC Keeling plots for samples collected along a transect or a depth profile. If the DOC data can be treated as a background component of relatively constant concentrations and isotopic composition, to which a single component or multiple components in a constant blend is added, then a linear relation should exist between 1/DOC and $\Delta^{14}C$ (Eq. 3), with an intercept that corresponds to the isotopic composition of excess DOC. The Keeling analyses yielded highly significant regressions for every profile, including coastal and open ocean samples ($0.82 < r^2 < 0.99$, e.g., Fig. 2; Table 1). Examples from the North Central Pacific, the Gulf of Mexico, and the North Atlantic (Fig. 2; Table 1) suggest that Keeling plots provide a useful means for determining the $^{14}C$ content of DOC in excess of the background concentrations from an entire data set compiled along a transect or a depth profile. The Keeling plot intercepts for the North Central Pacific, the Gulf of Mexico and the western North Atlantic (Fig. 2) were significantly different from each other at $P < 0.05$.

*Spatial and temporal variability of $\Delta^{14}C$ in excess DOC*—Coastal ocean: The Keeling analysis for coastal transects off Delaware and Chesapeake Bay and the Cape Hatteras region (Transects 4, 5, and 6 from Bauer et al. 2002) show a clear temporal variability in the $\Delta^{14}C$ signature of excess DOC for the spring and summer seasons (Table 1; Fig. 3). During the spring period of high river discharge, the $\Delta^{14}C$ of excess DOC exceeded $\Delta^{14}C$ DIC values. The largest deviations were measured at the outflow region of the Chesapeake and Delaware Bays. It is only during the summer months and at the station farthest from the river outflow (Transect 6, summer 96) that $\Delta^{14}C$ values of excess DOC were similar to DIC values, indicating that excess DOC during this period predominantly resulted from in situ primary production. At all other times and locations in the Middle Atlantic Bight (MAB), $\Delta^{14}C$ of
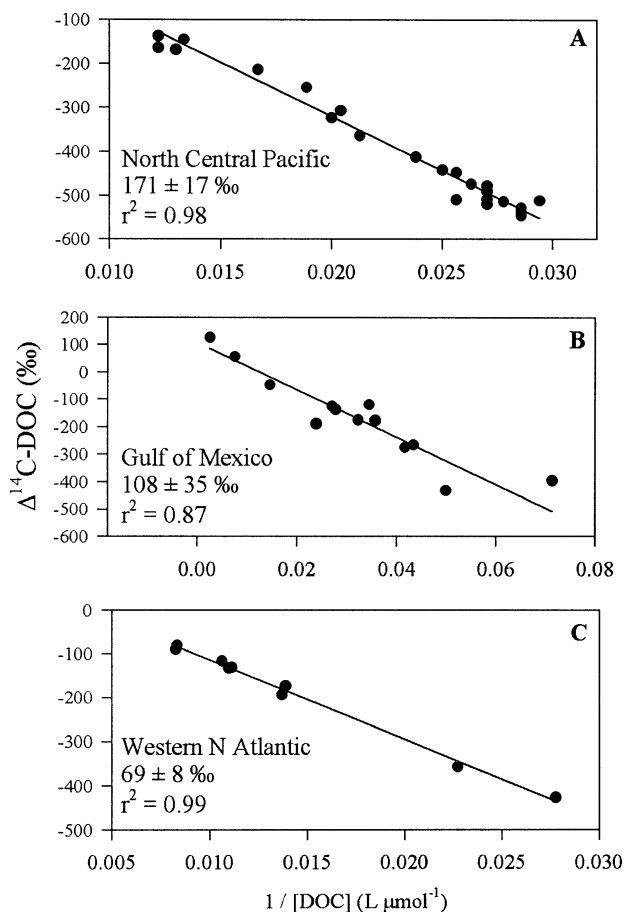
Fig. 2. Keeling plots for (A) the North Central Pacific (Druffel et al. 1992), (B) the Gulf of Mexico (Santschi et al. 1995), and (C) the western North Atlantic Transects 2 and 3 collected July 1996 (Bauer et al. 2002). A Model II regression was used to estimate the intercept of the regression line (*see Methods*). For each plot, the intercept ($\pm 1$ SE) and the correlation coefficient is shown.

excess DOC and mean $\Delta^{14}$C DIC values were significantly different at the $\alpha = 0.05$ level (Student's *t*-test).

Bauer et al. (2002) observed a positive shift in the $\Delta^{14}$C of total DOC by 20–133‰ from March to August 1996. They speculated that this enrichment might have resulted directly or indirectly from increased phytoplankton production during the summer season. The Keeling approach clearly highlights the temporal shift in the source of excess DOC between spring and summer seasons in the coastal regions of the north Atlantic (Fig. 3). During the summer, the higher DOC concentrations and younger $\Delta^{14}$C DOC values measured by Bauer et al. (2002) in the MAB associated with lower salinity waters would appear to be the result of riverine nutrient input to the MAB and stimulation of primary production, as observed by Lohrenz et al. (2002), rather than the result of DOC input from alluvial sources. Summer primary productivity in the MAB exceeds the spring rates by 60% (Lohrenz et al. 2002). The input of recently assimilated DOC to the water column was apparent at the southernmost portion of the MAB during summer 1996, where $\Delta^{14}$C in excess DOC was similar to the mean $\Delta^{14}$C in water column DIC (Student's *t*-test, $P > 0.05$; Fig. 3).

During the spring, excess DOC in the MAB region has $^{14}$C values that are more similar to DOC from the York river estuary (208–257‰, Raymond and Bauer 2001*a*), a major subestuary of the Chesapeake Bay, and indicates DOC accumulation in surface waters of decadal-aged material of presumably terrestrial/riverine origin. The Keeling analyses indicate that accumulation of young $^{14}$C-enriched DOC in the shelf from spring to summer resulted from increased phytoplankton production. The increase in DOC concentration and the $^{14}$C enrichment of excess DOC during the summer was less than the $^{14}$C enrichment of excess DOC in the spring (Fig. 3), when high river flow discharge exported terrestrial DOC to the MAB.

Our analysis agrees with that of Bauer et al. (2002), who suggested the contribution to shelf waters of $^{14}$C-enriched organic matter of terrestrial and riverine origin. We also agree with the hypothesis of Raymond and Bauer (2001*b*) that rivers discharging to the Atlantic Ocean export $^{14}$C-enriched terrestrial organic matter (Fig. 3). However, our analysis is not consistent with the Raymond and Bauer postulation that the young riverine DOC component can be selectively degraded and result in export of an older, more refractory component with an apparent age of 1,500 yr to the ocean (Raymond and Bauer 2001*b*). The $\Delta^{14}$C in excess DOC in the MAB has a modern signature that varies from 309‰ during the spring to 70‰ in the summer (Fig. 3).

The MAB receives freshwater from the Hudson, Delaware, and Chesapeake estuaries that carry high loads of DOC, and much of this DOC is of terrestrial origin, consisting of refractory organic matter that can be transported to the shelf region (Aluwihare et al. 2002). Less than 5% of the DOC is believed to be imported from a combination of rivers, estuaries, atmospheric deposition, and sediment porewater flux, whereas the rest is supplied from George's Bank (Vlahos et al. 2002). Although these DOC mass balance calculations suggest that, on an annual time scale, only a minor fraction of total DOC is derived from rivers and estuaries, on a seasonal time scale, the $\Delta^{14}$C values of excess DOC suggest that, during spring, decadal-aged DOC can contribute significantly to the excess DOC accumulating in the surface waters of the MAB region (Table 1; Fig. 3).

There is an apparent accumulation both inshore and alongshelf of excess DOC produced in shelf waters, as well as discharged to the MAB from the dominant rivers and estuaries (Bauer et al. 2002; Vlahos et al. 2002). Mass balance calculations suggest that DOC in the MAB resulted in total export of between 18.7 and 19.6 Tg C yr$^{-1}$, and as much as 67% of this DOC appeared to be recycled material that is believed to be refractory (Vlahos et al. 2002). Because of the short residence time of the MAB region, 50–300 d (Wallace 1994), excess DOC during spring, with a riverine/estuarine $\Delta^{14}$C signature, is potentially available for export to the open ocean.

The Keeling model can also be applied to size-fractionated DOC. Santschi et al. (1995) determined the apparent ages of size-fractionated dissolved organic carbon for samples collected in the Gulf of Mexico (GOM) and the Cape Hatteras region. Their results indicated that the 1-kDa to 0.2-$\mu$m colloidal organic carbon size fraction (COC1) had an apparent age of 380–4,500 yr. The Keeling intercepts for the COC1

Table 1. $\Delta^{14}$C in excess DOC determined from DOC transects or profiles in coastal regions and open ocean systems. The Keeling intercepts were determined with a Model II regression (*see Methods*). The number of samples in a transect or a profile used to determine the Keeling intercepts and the coefficient of determination for the regression is indicated ($n$, $r^2$). The Gulf of Mexico and the Cape Hatteras Keeling intercepts were determined for the ultrafiltered DOC fraction (1 kDa to 0.2 $\mu$m). All others are for total DOC. Transect numbers are from primary literature. The concentration range is $\mu$mol C L$^{-1}$.

| | Year collected | Keeling intercept | Concentration range | $\delta^{14}$C range |
|---|---|---|---|---|
| Bauer et al. 2002 | | | | |
| NW Atlantic N transect | Apr 94 | 98±36(8, 0.95) | 46–102 | −442, −160 |
| NW Atlantic C transect | Apr 94 | 309±35(7, 0.98) | 51–115 | −451, −39 |
| NW Atlantic S transect | Apr 94 | 119±53(7, 0.93) | 50–112 | −438, −98 |
| North Atlantic transect 1+2 | Mar 96 | 136±19(8, 0.99) | 49–85 | −418, −172 |
| North Atlantic transect 3 | Mar 96 | 95±38(10, 0.92) | 47–107 | −418, −120 |
| North Atlantic transect 4 | Mar 96 | 222±88(7, 0.85) | 94–42 | −420, −117 |
| North Atlantic transect 5 | Mar 96 | 210±59(8, 0.91) | 46–126 | −432, −77 |
| North Atlantic transect 6 | Mar 96 | 154±74(7, 0.85) | 38–102 | −401, −85 |
| North Atlantic transect 1 | Aug 96 | 155±24(8, 0.98) | 41–75 | −414, −159 |
| North Atlantic transect 2+3 | Aug 96 | 69±8 (9, 0.99) | 36–121 | −427, −80 |
| North Atlantic transect 4 | Aug 96 | 84±19(8, 0.99) | 39–119 | −404, −69 |
| North Atlantic transect 5 | Aug 96 | 83±16(9, 0.99) | 39–156 | −408, −29 |
| North Atlantic transect 6 | Aug 96 | 70±17(7, 0.99) | 38–90 | −420, −138 |
| Santschi et al. 1995 | | | | |
| Gulf of Mexico | 1992–1993 | 108±35(13, 0.87) | 14–404 | −432, −126 |
| N Atlantic Cape Hatteras | Jun 93 | 141±34(6, 0.99) | 20–44 | −427, −101 |
| Bauer et al. 1998*a* | | | | |
| NE Pacific Station M | Jul 91 | −13±72(9, 0.86) | 33–62 | −558, −302 |
| NE Pacific Station M | Feb 92 | 105±56(9, 0.93) | 38–70 | −559, −287 |
| NE Pacific Station M | Jun 92 | 152±61(10, 0.93) | 38–72 | −573, −238 |
| NE Pacific Station M | Oct 92 | 111±33(9, 0.98) | 37–72 | −550, −250 |
| NE Pacific Station M | Feb 92 | 124±52(6, 0.97) | 37–67 | −546, −244 |
| NE Pacific Station M | Jul 93 | 31±33(5, 0.99) | 36–74 | −543, −257 |
| Bauer et al. 1998*b* | | | | |
| NE Pacific Station M | Jun 95 | 44±61(11, 0.88) | 36–72 | −568, −275 |
| NE Pacific Continental Rise | Jun 95 | 71±55(8, 0.94) | 35–65 | −568, −287 |
| NE Pacific Upper Slope | Jun 95 | 163±104(5, 0.90) | 43–56 | −466, −324 |
| Druffel et al. 1992 | | | | |
| North Central Pacific | Jun 87 | 162±39(19, 0.92) | 34–72 | −536, −179 |
| Sargasso Sea | May 91 | 78±39(23, 0.82) | 40–75 | −414, −210 |

size fractions, however, indicate that in both the GOM and the Cape Hatteras region, excess COC1 has a $\Delta^{14}$C signature similar to that of the $\Delta^{14}$C of DIC (Fig. 3), thus indicating that excess COC1, despite the century-old apparent age of the COC1 total pool, is of contemporary origin. This result suggests that the dominant mechanism for formation of new COC1 is through assimilation of new carbon rather than the breakdown of "aged" organic matter.

Open ocean: The variability in $\Delta^{14}$C in excess DOC at the open ocean sites was lower than the variability at the coastal sites (Table 1; Fig. 3). In the open ocean, the greatest variability in water column $\Delta^{14}$C in DOC occurs at depths above 700 m, where the seasonal effects of primary production and remineralization are greatest (Bauer et al. 1998*a*). In the open ocean, the major source of DOC to the deep ocean derives from soluble or solubilized forms of organic matter produced in the euphotic zone by living organisms. This is in contrast to the coastal sites that also receive temporally varying inputs of DOC from rivers and estuaries.

Minima in the Keeling intercepts at Sta. M in the North Central Pacific were measured during intense periods of particulate organic matter (POC) flux in July 1991 and July 1993 (Bauer et al. 1998*a*). The seasonal shift in the isotopic composition of excess DOC could result from its interaction with the POC through adsorption and removal of certain components of DOC (Druffel et al. 1992; Bauer et al. 1998*a*). Minimum surface DOC concentrations at Sta. M were measured during a period when sinking POC flux was maximal (Bauer et al. 1998*a*). $\Delta^{14}$C values of subsurface POC were 20–30‰ enriched during the high-POC flux period (Druffel et al. 1996). The Keeling approach also suggests that the interaction between DOC and POC selectively removes DOC enriched in $^{14}$C during periods of high POC flux (Druffel et al. 1996; Bauer et al. 1998*a*). Another source of variability of $\Delta^{14}$C in DOC at the open ocean site can be observed along an offshore–inshore Pacific ocean transect (Fig. 3). The $\Delta^{14}$C-DOC enrichment near the coast indicates a possible terrestrial DOC contribution to the nearshore marine environment, similar to Atlantic observations.
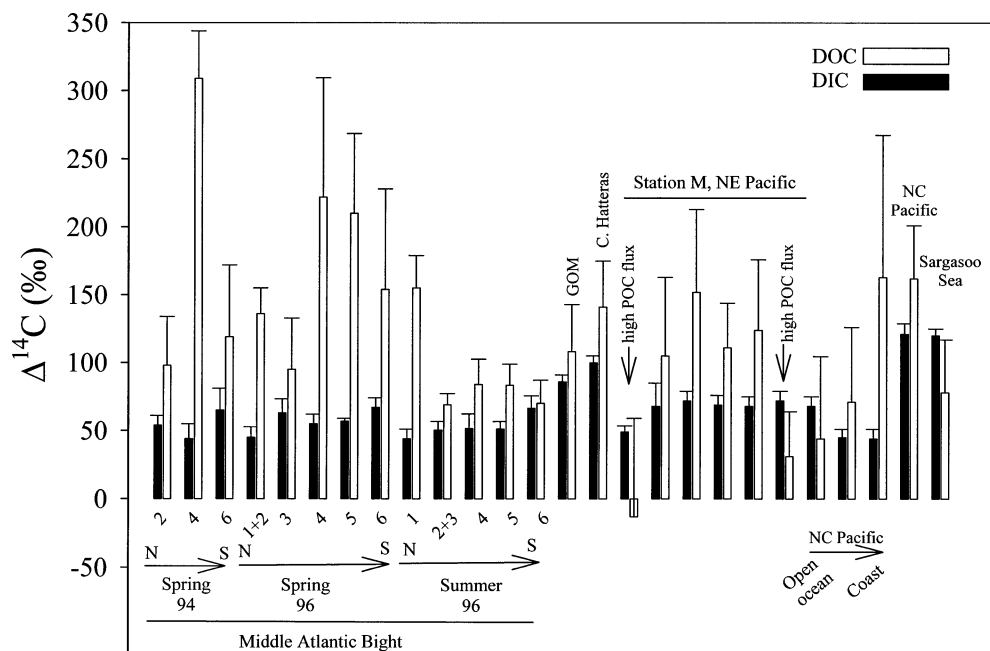
Fig. 3.   $\Delta^{14}C$ in excess DOC and associated error determined from the intercept of the Keeling plots and the $\Delta^{14}C$ of DIC for the Gulf of Mexico (GOM), Cape Hatteras, the Middle Atlantic Bight (MAB, numbers refer to the transect locations from Bauer et al. [2002], Transect 1 is in the northern MAB, whereas Transect 6 is located in the southern portion of the MAB, and Transects 4 and 5 correspond to the outflow region of the Delaware and Chesapeake Bays), Sta. M in the NE Pacific, an offshore–inshore transect in the North Central Pacific, the North Central Pacific, and the Sargasso Sea. The Gulf of Mexico and Cape Hatteras samples correspond to the ultrafiltered (1 kDa–0.2 $\mu$m) fraction of DOC. DIC values for the GOM and Cape Hatteras are from Santschi et al. (1995) and Severinghaus et al. (1996). DIC values for the MAB region are from Bauer et al. (2002). DIC values for Sta. M are from Masiello et al. (1998). DIC values for the transect from the open ocean to the coast in the North Central Pacific region are from Bauer et al. (1998*b*). DIC values for the North Central Pacific and Sargasso Sea profiles are from Druffel et al. (1992). There was a significant difference ($P < 0.05$) between the intercept of the Keeling plots and mean $\Delta^{14}C$ DIC values at all the MAB stations, except at Region 6 during summer 1996. Notice the spatial and temporal variability in $^{14}C$ of excess DOC and the deviation from the $\Delta^{14}C$ of DIC during high river flow periods in the MAB region. The intercept of the Keeling plots and mean $\Delta^{14}C$ DIC values in the North Central Pacific and the Sargasso Sea were significantly different ($P < 0.05$). We could not test for significant differences between the intercept of the Keeling plots and mean $\Delta^{14}C$ DIC values in the GOM, Cape Hatteras, Sta. M, NE Pacific, and open ocean to coast transect in the North Central Pacific because only few samples were collected for determination of the $\Delta^{14}C$ in DIC. The error bars for $\Delta^{14}C$ DIC values correspond to the standard deviation of replicate samples or to the analytical precision, in case replicate samples were not collected.

## Summary

Stable isotopes of C, N, and S have been used to constrain sources of organic matter in nearshore marine environments (e.g., Chanton and Lewis 2002). The prerequisite associated with these models is the knowledge of the isotopic value for "end-member" components. The Keeling plot approach uses a linear regression on measured variables to determine the end-member isotopic value of excess DOC relative to the background value. The large dynamic range in $\Delta^{14}C$ values in naturally occurring organic matter reservoirs allows $^{14}C$ to be used as a sensitive source indicator. In the future, by increasing the sampling frequency, the standard error of the intercept of the Keeling plots and the standard deviation of the estimates of mean surface water $\Delta^{14}C$ DIC can be reduced, which will lead to more robust statistics.

Results indicate a high degree of variability of $\Delta^{14}C$ in DOC available for export from the margins to the open ocean or from the surface to the subsurface layers following the breakdown of water column stratification. The Keeling approach offers a powerful and consistent approach for determining and quantitatively comparing the isotopic value of the excess DOC and the associated error term by considering an entire DOC transect or profile.

## *References*

ALUWIHARE, L. I., D. J. REPETA, AND R. F. CHEN. 2002. Chemical composition and cycling of dissolved organic matter in the mid-Atlantic Bight. Deep-Sea Res. **49:** 4421–4437.

BAUER, J. E., AND E. R. M. DRUFFEL. 1998. Ocean margins as a significant source of organic matter to the deep open ocean. Nature **392:** 482–485.

——, P. M. WILLIAMS, AND E. R. M. DRUFFEL. 1992. $^{14}$C activity of dissolved organic carbon fractions in the north-central Pacific and Sargasso Sea. Nature **357:** 667–670.

——, C. E. REIMERS, E. R. M. DRUFFEL, AND P. M. WILLIAMS. 1995. Isotopic constraints on carbon exchange between deep ocean sediments and sea water. Nature **373:** 686–689.

——, E. R. M. DRUFFEL, P. M. WILLIAMS, D. M. WOLGAST, AND S. GRIFFIN. 1998*a.* Temporal variability in dissolved organic carbon and radiocarbon in the eastern North Pacific Ocean. J Geophys Res., C **103:** 2867–2881.

——, ——, D. M. WOLGAST, S. GRIFFIN, AND C. A. MASIELLO. 1998*b.* Distributions of dissolved organic and inorganic carbon and radiocarbon in the eastern North Pacific continental margin. Deep-Sea Res. **45:** 689–713.

——, ——, ——, AND ——. 2002. Temporal and regional variability in sources and cycling of DOC and POC in the northwest Atlantic continental shelf and slope. Deep-Sea Res. **49:** 4387–4419.

CARLSON, C. A., AND H. W. DUCKLOW. 1995. Dissolved organic carbon in the upper ocean of the central equatorial Pacific Ocean, 1992: Daily and finescale vertical variations. Deep-Sea Res. **42:** 639–656.

——, ——, AND A. F. MICHAELS. 1994. Annual flux of dissolved organic carbon from the euphotic zone in the northwestern Sargasso Sea. Nature **371:** 405–408.

CHANTON, J. P., AND F. G. LEWIS. 2002. Examination of coupling between primary and secondary production in a river-dominated estuary: Apalachicola Bay, Florida, U.S.A. Limnol. Oceanogr. **47:** 683–697.

CHERRIER, J., J. E. BAUER, AND E. R. M. DRUFFEL. 1996. Utilization and turnover of labile dissolved organic matter by bacterial heterotrophs in eastern north Pacific surface waters. Mar. Ecol. Prog. Ser. **139:** 267–279.

DRUFFEL, E. R. M., P. M. WILLIAMS, J. E. BAUER, AND J. R. ERTEL. 1992. Cycling of dissolved and particulate organic matter in the open ocean. J. Geophys. Res. **97:** 15,639–15,659.

——, J. E. BAUER, P. M. WILLIAMS, S. GRIFFIN, AND D. M. WOLGAST. 1996. Seasonal variability of particulate organic radiocarbon in the northeast Pacific Ocean. J. Geophys. Res. **101:** 20,543–20,552.

KEELING, C. D. 1958. The concentration and isotopic abundances of atmospheric carbon dioxide in rural areas. Geochim. Cosmochim. Acta **13:** 322–334.

LOHRENZ, S. E., D. G. REDALJE, P. G. VERITY, C. N. FLAGG, AND K. V. MATULEWSKI. 2002. Primary production on the continental shelf off Cape Hatteras, North Carolina. Deep-Sea Res. **49:** 4479–4509.

MASIELLO, C. A., E. R. M. DRUFFEL, AND J. E. BAUER. 1998. Physical controls on dissolved inorganic radiocarbon variability in the California Current. Deep-Sea Res. **45:** 617–642.

MORTAZAVI, B., AND J. P. CHANTON. 2002. Carbon isotopic discrimination and control of nighttime canopy $\delta^{18}$O–CO$_2$ in a pine forest in the southeastern US. Glob. Biogeochem. Cycles **16:** 10.1029/2000GB001390.

PATAKI, D. E., AND OTHERS. 2003. The application and interpretation of Keeling plots in terrestrial carbon cylcle research. Glob. Biogeochem. Cycles **17:** 10.1029/2001GB001850.

RAYMOND, P. A., AND J. E. BAUER. 2001*a.* DOC cycling in a temperate estuary: A mass balance approach using natural $^{14}$C and $^{13}$C isotopes. Limnol. Oceanogr. **46:** 655–667.

——, AND ——. 2001*b.* Riverine export of aged terrestrial organic matter to the North Atlantic Ocean. Nature **409:** 497–500.

SANTSCHI, P. H. AND OTHERS. 1995. Isotopic evidence for the contemporary origin of high–molecular weight organic matter in oceanic environments. Geochim. Cosmochim. Acta **59:** 625–631.

SEVERINGHAUS, J. P., W. S. BROECKER, T. H. PENG, AND G. BONANI. 1996. Transect along 24°N latitude of $^{14}$C in dissolved inorganic carbon in the subtropical North Atlantic ocean. Radiocarbon **38:** 407–414.

SOKAL, R. R., AND F. J. ROHLF. 1981. Biometry. WH Freeman.

SPITZY, A., AND V. ITTEKKOT. 1991. Dissolved and particulate organic matter in rivers, p. 5–17. *In* R. F. C. Mantoura, J. M. Martin, and R. Wollast [eds.], Ocean margin processes in global change. Wiley.

VLAHOS, P., R. F. CHEN, AND D. J. REPETA. 2002. Dissolved organic carbon in the mid-Atlantic Bight. Deep-Sea Res. **49:** 4369–4385.

WALLACE, D. W. R. 1994. Anthropogenic chlorofluoromethanes and seasonal mixing rates in the Middle Atlantic Bight. Deep-Sea Res. **41:** 307–324.

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