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Daily variability of dissolved inorganic radiocarbon at three sites in the surface ocean

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1. Introduction

Bomb radiocarbon (14C) was produced in the late 1950s and early 1960s by thermonuclear weapons testing in the stratosphere and caused 14C levels in tropospheric CO2 to nearly double by 1964 (Nydal and Lovseth, 1983). After 1965, levels of 14C in the atmosphere have decreased because of gas exchange with CO2 in the surface ocean and incorporation into the terrestrial biosphere. Maximum Δ14C values measured in surface water dissolved inorganic carbon (DIC) were attained in the 1970s, indicating that the turnover time of CO2 in the atmosphere with respect to transfer to the surface ocean is ~10 years (Druffel and Suess, 1983). Measurements of Δ14C in water column profiles made since 1970 have been used to calculate the inventory of bomb 14C in various oceanic regions (Broecker and Peng, 1994; Duffy and Caldeira, 1995). The timescale of modification of 14C is of the order of years, much longer than that for temperature, which is quasi-conservative over a few weeks. This means that 14C will “remember” a mixing event from a storm, entraining colder, usually lower 14C water for a longer time than will SST.

Daily measurements of surface DIC Δ14C were reported previously for sites in the North central Pacific (NCP) (Druffel et al., 1989) and the Sargasso Sea (SS) (McDuffee and Druffel, 2007). The Δ14C results from the NCP in November 1985 showed more variability after a 4-day storm, but accompanying chemical and physical data were not sufficient to determine the cause of the Δ14C variability. Daily measurements of chemical and physical parameters at the SS site indicated a change in water mass that was coincident with an increase in variability of Δ14C values (McDuffee and Druffel, 2007) half way through the cruise.

We report daily surface DIC Δ14C values obtained for cruises to the NCP and SS sites, and a site in the Southern Ocean. We wanted to determine if the variability of surface Δ14C values was greater than the total uncertainty of the measurements, because of changes in the water mass that occurred during the course of each cruise. Our results highlight the fact that the surface ocean Δ14C signature varies by a larger amount than previously indicated by uncertainties assigned to the individual values (3–4‰). This is relevant because surface radiocarbon values are used to calculate such quantities as air–sea CO2 exchange rate and bomb 14C inventory in the ocean, and additional error in the radiocarbon can impart larger error into these biogeochemical parameters.

2. Methods

Surface water samples were collected from a single site in the North central Pacific (NCP, 31 °N, 159 °W, bottom depth 5220 m) during three
1995 (salinity was only available through day 12). The DIC Δ¹⁴C results of depth profiles taken during the Alcyone-5, Eve-1, Hydros-6 (Druffel et al., 1992) and Boomerang cruises (Druffel and Bauer, 2000) were reported earlier.

Seawater samples were collected from 0–0.5 m depth using a plastic bucket and rope for DIC Δ¹⁴C and δ¹³C, and concentration ([DIC]), alkalinity and salinity measurements. Results obtained using this collection method are equivalent to those obtained using Niskin bottle collection (Druffel, unpublished data). Sea surface temperature (SST) measurements were made using a mercury thermometer (±0.2 °C). Samples were collected during daylight hours, usually between 1100 and 1400 h local time. Seawater samples for isotopic, [DIC] and alkalinity analyses were poisoned with saturated HgCl₂ solution to prevent biological remineralization of organic matter.

Water samples were processed for DIC Δ¹⁴C analysis using conventional counting (Alcyone, Eve and Hydros cruises) (Griffin and Druffel, 1985) and accelerator mass spectrometry (AMS) (SOce, Avon and SarC cruises) (McNichol et al., 1994; Southon et al., 2004). Radiocarbon measurements are reported as Δ¹³C in per mil (Stuiver and Polach, 1977). Statistical uncertainties for the individual conventional and AMS Δ¹⁴C measurements were ±2.5–3.0‰; the total uncertainty determined from replicate analyses of a standard seawater was ±3.9‰. Stable carbon isotope measurements (δ¹³C) were performed at WHOI or UCI on splits of CO₂ from the processed ¹⁴C samples with a total uncertainty of ±0.06‰.

Alkalinity and [DIC] measurements were obtained by closed vessel titration of large volume (~100 ml) samples using an automated titration system (Bradshaw et al., 1981; Brewer et al., 1986) in the laboratory of C. Goyet (WHOI) or D. McCorkle (WHOI). Measurements were determined using a nonlinear curve fitting approach (DOE, 1994) and standardized using certified reference materials obtained from Andrew Dickson (Scripps Institution of Oceanography). The standard deviation of pairs of replicate analyses of culture water was 4 µeq/kg for alkalinity and 6 µmol/kg for [DIC]. Alkalinity measurements from the Avon and SarC cruises were high by about 25 µeq/kg due to the long storage time of samples prior to analysis (~1 year) and are not reported.

### 3. Results and discussion

#### 3.1. North central Pacific

At the NCP site, the Δ¹⁴C measurements of surface samples in June 1987 (Eve, 28 days on station) averaged 134±7‰ (n=15) (Fig. 1a) (Table 1). Values were low on days 1–6 (average 124±3‰, n=3) and higher and more variable on days 8–28 (137±5‰, n=12). A similar pattern was noticed for the δ¹³C values (Fig. 1b), which were low on days 1–6 (0.95±0.1‰) and higher and more variable on days 8–28 (1.21±0.07‰). McNichol and Druffel (1992) reported T-S data from 7 CTD casts (0–210 m depth) taken throughout this cruise that showed a cooler, less saline (by 0.20 psu) water mass (<55 m) present from days 1–6, than afterward (days 8–28). This shift to a new water mass between days 6 and 8 is likely the source of the surface water δ¹³C variability. Alkalinity and salinity values were also higher after day 7 (2323 µeq/kg, 35.20‰, respectively), though [DIC] remained constant throughout the cruise (2030 µmol/kg) (Fig. 2a,b).

In June 1999 (Avon, 17 days on station), daily Δ¹⁴C measurements at the NCP site averaged 89±7‰ (n=17); values were higher during the first 6 days (average 96±3‰, n=5) and lower and more

### Table 1

<table>
<thead>
<tr>
<th>Site</th>
<th>Cruise</th>
<th>Date</th>
<th>Days on station</th>
<th>Average Δ¹⁴C ± Range</th>
<th>Average δ¹³C ± Range</th>
<th>Aver Alk ±</th>
<th>Aver [DIC] ±</th>
<th>Aver SST ±</th>
<th>Aver salinity ±</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCP</td>
<td>Alcyone</td>
<td>Nov-85</td>
<td>25</td>
<td>147.1 ± 6.0</td>
<td>17.4</td>
<td>2330</td>
<td>22</td>
<td>2003</td>
<td>4 ± 16</td>
</tr>
<tr>
<td>NCP</td>
<td>Eve</td>
<td>Jun-87</td>
<td>28</td>
<td>134.4 ± 7.4</td>
<td>24.3</td>
<td>2317</td>
<td>15</td>
<td>2030</td>
<td>5 ± 16</td>
</tr>
<tr>
<td>NCP</td>
<td>Avon</td>
<td>Jun-99</td>
<td>17</td>
<td>88.7 ± 6.9</td>
<td>29.9</td>
<td>2387</td>
<td>17</td>
<td>2078</td>
<td>2 ± 16</td>
</tr>
<tr>
<td>SS</td>
<td>Hydros</td>
<td>Jun-89</td>
<td>25</td>
<td>121.8 ± 4.4</td>
<td>11.1</td>
<td>2387</td>
<td>17</td>
<td>2078</td>
<td>2 ± 16</td>
</tr>
<tr>
<td>SS</td>
<td>SarC</td>
<td>Jun-00</td>
<td>14</td>
<td>80.6 ± 6.4</td>
<td>24.2</td>
<td>2387</td>
<td>17</td>
<td>2078</td>
<td>2 ± 16</td>
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<tr>
<td>S. Ocean</td>
<td>Soce</td>
<td>Dec-95</td>
<td>18</td>
<td>18.8 ± 7.5</td>
<td>25.5</td>
<td>2291</td>
<td>7</td>
<td>2001</td>
<td>8 ± 16</td>
</tr>
</tbody>
</table>

**Fig. 1.** Time series of a) Δ¹⁴C and b) δ¹³C measurements of surface water DIC taken during three cruises to the North central Pacific (NCP) (October–November 1985; June 1987; June 1999), two cruises to the Sargasso Sea (SS) (June 1989; June 2000) and a cruise to the Southern Ocean (December 1995). See text for details.
variable from days 7–17 (86±5‰, n=12) (Fig. 1a). The δ13C values from days 1–6 averaged 0.96±0.11‰, and were lower and more variable thereafter (0.69±0.32‰) (Fig. 1b). Data from CTD casts made during this cruise showed a shift toward higher surface salinity values between days 8 and 11 (data not shown), which is consistent with a change in Δ14C and δ13C values during this time. Values of [DIC] were constant throughout the cruise and averaged 2043±6 μmol/kg. Alkalinity and salinity measurements are not available.

Previously reported Δ14C measurements from a November 1985 cruise (Alcyone, 25 days on station) to the NCP site (Druffel et al., 1989) averaged 147±6‰ (n=12) (Fig. 1a). Alkalinity values averaged 2091±8 μmol/kg and 2291±7 μeq/kg, and were slightly more variable during the second half of the cruise (1.05±0.08‰) than during the first 8 days (1.01±0.02‰) (Fig. 1b). The DIC measurements averaged 2085±9 μmol/kg (days 1–15) until the last day when an increase of 45 μmol/kg was noted. SST values increased 3 °C over the course of the cruise. Temperature–salinity data from five CTD casts (on days 2, 7, 11, 14 and 16) in the upper 250 m revealed large shifts in salinity between 2 and 25 m depth on days 7, 11, 14 and 16. Temperature values below ~20 m were 2–3 °C warmer after day 7 (McDuffee and Druffel, 2007).

3.2. Sargasso Sea

At the Sargasso Sea site in June 1989 (Hydros, 25 days on station), Δ14C measurements averaged 122±4‰ (n=7) (Fig. 2a) and were slightly lower during the first part of the cruise (days 1–14, 119±3‰, n=4) than during the second part (days 20–25, 125±3‰, n=3). There were no δ13C analyses of these water samples. Alkalinity, salinity and SST measurements were less variable before day 8 (2399±5 μeq/kg, 36.56±0.01‰, 23.5±0.2 °C) than afterward (2381±19 μeq/kg, 36.61±0.06‰, 25.3±0.6 °C) (Fig. 2a,b and c). There was a general warming trend with time. During the first 7 days of the cruise, the surface waters were more homogenous (i.e., low temperature, constant salinity) than afterward (data not shown). Values of [DIC] were constant and averaged 2078±2 μmol/kg.

McDuffee and Druffel (2007) report Δ14C measurements for the SS site, in June 2000 (SarC, 14 days on station) that averaged 81±8‰ (n=10). Values were high from days 1–8 (87±4‰, n=4) and lower and more variable thereafter (76±8‰, n=6) (Fig. 1a). Similar to the Δ14C values, the δ13C values were more variable during the second half of the cruise (1.05±0.08‰) than during the first 8 days (1.01±0.02‰) (Fig. 1b). The DIC measurements averaged 2085±9 μmol/kg (days 1–15) until the last day when an increase of 45 μmol/kg was noted. SST values increased 3 °C over the course of the cruise. Temperature–salinity data from five CTD casts (on days 2, 7, 11, 14 and 16) in the upper 250 m revealed large shifts in salinity between 2 and 25 m depth on days 7, 11, 14 and 16. Temperature values below ~20 m were 2–3 °C warmer after day 7 (McDuffee and Druffel, 2007).

3.3. Southern Ocean

At the Southern Ocean site in December 1995 (SOoce, 18 days on station), surface Δ14C results averaged 19±8‰ (n=17) (Fig. 1a), and values were lowest during days 2–4 (range 5–8‰). The δ13C values averaged 1.8±0.2‰ (n=17) and values were slightly more variable during days 8–11 (1.6±0.3‰) (Fig. 1b). SST values were lower during days 3–6 (7.7±0.6 °C) than afterward (8.7±0.3 °C) (Fig. 2c). Salinity values were variable (34.32±0.09‰) during the period for which data was available (days 1–12) (Fig. 2b). The [DIC] and alkalinity values averaged 2091±8 μmol/kg and 2291±7 μeq/kg, respectively, throughout the cruise (Fig. 2a). Data from five CTD casts revealed overall higher salinity values between 30 and 200 m depth on days 7, 11, 14 and 16. Temperature values below ~20 m were 2–3 °C warmer after day 7 (McDuffee and Druffel, 2007).

3.4. Implications for surface ocean variability in DIC Δ14C and δ13C

Variability of the six Δ14C time series, as measured by the standard deviation of the averages, ranged from ±4.4‰ (SS 1989) to ±8.4‰ (SS 2000) (Table 1). The range of Δ14C values observed for the cruises was a minimum of 11.1‰ (SS 1989) and a maximum of 29.9‰ (NCP 1999) (Table 1). We note that the two cruises with the largest ranges of Δ14C values, NCP 1999 and SOoce 1995 (25.5‰), also had the largest ranges of δ13C values (1.2‰ and 0.75‰, respectively).

These results illustrate that, during all six cruises, repeated sampling at the same geographic location over the course of 2–4 weeks revealed surface Δ14C values that varied by more than the
total uncertainty of the measurement (7.8% 2-sigma). Changes in the upper water mass were observed during most of these cruises, as determined by temperature–salinity relationships in the CTD data sets.

The source(s) of the variability in the isotopic measurements are likely changes in vertical mixing and/or spatial heterogeneity. Fig. 3 displays Δ¹⁴C measurements in samples collected from the upper ocean (0–300 m) during each of the six cruises (Druffel and Bauer, 2000; Druffel et al., 1992) plotted versus density (σ-t). The average and standard deviation of all surface values for each cruise are shown as symbols with error bars, whereas Δ¹⁴C values for subsurface samples (10–250 m depth) are plotted as symbols with no error bars. Data from the earlier NCP cruises in 1985 (filled triangles) and 1987 (filled circles) show a larger gradient of Δ¹⁴C values with depth than that from the 1999 cruise (filled squares), in large part because atmospheric Δ¹⁴C values in the 1980s (160–270‰) were higher than in the 1990s (95–150‰). Surface ocean Δ¹⁴C values were lower in 1999 (NCP) and 2000 (SS) (Fig. 3a, b), because more bomb Δ¹⁴C had penetrated deeper into the main thermocline, and were replaced by Δ¹⁴C-poor waters from below, causing a smaller gradient of Δ¹⁴C values with depth.

It seems likely that the variability of surface Δ¹⁴C is the result of sampling of different water masses that are floating by a single geographic location. Most of the subsurface Δ¹⁴C values are slightly lower than their average surface value. The least squares fit through each data set (lines in Fig. 3a,b) suggests an inverse relationship between Δ¹⁴C and σ-t for most of the cruises. This inverse relationship suggests that Δ¹⁴C values are higher in surface waters that have limited contact with subsurface water, e.g., areas of little or no upwelling. The exception is the Southern Ocean where mixing with subsurface waters is prevalent. This is illustrative of the concept that mixing in the ocean occurs predominantly along surfaces of constant density. Discreet water sampling provides a snapshot of DIC Δ¹⁴C values at a single point in time. This is in contrast to geochemical proxies, such as shells, corals, forams and varved sediments that integrate Δ¹⁴C values over an extended period of time (weeks to years) depending on the sampling resolution. Most of the DIC Δ¹⁴C data available for the world ocean has been obtained from discreet water samples, e.g. Geosecs, WOCE, TTO. The reported uncertainty for DIC Δ¹⁴C values is based on repeated analyses of the same water sample and generally ranges from ±3–4‰ (Key, 1996; Key, 1997; McNichol et al., 1994; Ostlund and Stuiver, 1980; Stuiver and Ostlund, 1980). Our study shows that for surface samples, the total uncertainty of a DIC Δ¹⁴C value at a given site over a several week period is approximately two times the reported uncertainty (~7‰).

Therefore, depending on the application, users of post-bomb Δ¹⁴C data should consider this short-term variability of surface ocean Δ¹⁴C values and factor this into their analysis. For example, assessment of the bomb Δ¹⁴C inventory in the water column requires numerous Δ¹⁴C measurements from a given depth profile (Broecker et al., 1995). Calculation of the bomb Δ¹⁴C inventory at our NCP site in 1999 reveals a value of 1.8 × 10¹⁴ atoms/m² with an error (based only on the Δ¹⁴C measurement error of 3.5‰) of ±2.2‰. Using a larger error for Δ¹⁴C values of ±7‰, our uncertainty for the bomb Δ¹⁴C inventory increases to ±5‰, which still is not large. Another example is how variability of surface ocean Δ¹⁴C values affect estimates of air–sea CO₂ exchange rate. Using a multi-box isopycnal mixing model to calculate the steady state, pre-bomb Δ¹⁴C value (~43.5‰) in the surface waters of the Sargasso Sea (Druffel, 1997), the average air–sea CO₂ exchange rate is 18.9 moles/m²/y. To obtain a pre-bomb value one-sigma lower than this (~47‰), an air–sea CO₂ exchange rate of 9.9 moles/m²/y is needed, and to obtain a value one-sigma higher (~40.0‰) requires an average air–sea CO₂ exchange rate of 28.6 moles/m²/y. Doubling the error for pre-bomb Δ¹⁴C values (~7‰) expands the range of air–sea CO₂ exchange rate values obtained to 2.3 to 40.4 moles/m²/y. We need to caveat that this example is for a pre-bomb ocean, based on uncertainties from post-bomb surface water masses, though pre-bomb variability is likely to be equally important at locations where different water mass mix – e.g., tropical Pacific and subpolar/temperate boundaries.

Monthly surface Δ¹⁴C values from post-bomb corals displayed a seasonal amplitude that ranged from 30–80‰ in the eastern equatorial Pacific (Guilderson and Schrag, 1998) to 10–20‰ in the subtropical Atlantic and Pacific (Druffel, 1987; Druffel, 1989; Guilderson et al., 2000). Thus, the ranges of daily Δ¹⁴C values (11–30‰) that we measured at our three sites in the NCP, SS and SOce

Fig. 3. Δ¹⁴C values in upper water samples (0–300 m depth) collected during a) four cruises to the Pacific, and b) two cruises to the Atlantic, plotted versus water density (σ-t). The average and standard deviation of all surface values for each cruise are shown with error bars and Δ¹⁴C values for subsurface samples (10–250 m depth) are plotted as symbols with no error bars. Data from the earlier NCP cruises in 1985 (filled triangles) and 1987 (filled circles) show a larger gradient of Δ¹⁴C values with depth than that from the 1999 cruise (filled squares).
are comparable to the range of $^{14}$C values observed seasonally at selected sites.

In summary, our results show that a single measurement of DIC $^{14}$C in surface seawater has a larger uncertainty than that accounted for by measurement error alone. The true range of $^{14}$C values that occur over a several day-to-several week period is approximately double the measurement precision. This is due to patchiness that exists in the DIC $^{14}$C signature of the surface ocean, and the movement of surface water masses relative to geographic location.

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