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

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ABSTRACT

We report radiocarbon measurements of dissolved inorganic carbon (DIC) in surface water samples collected daily during cruises to the central North Pacific, the Sargasso Sea and the Southern Ocean. The ranges of $\Delta^{14}\text{C}$ measurements for each cruise (11–30‰) were larger than the total uncertainty (7.8‰, 2-sigma) of the measurements. The variability is attributed to changes in the upper water mass that took place at each site over a two to four week period. These results indicate that variability of surface $\Delta^{14}\text{C}$ values is larger than the analytical precision, because of patchiness that exists in the DIC $\Delta^{14}\text{C}$ signature of the surface ocean. This additional variability can affect estimates of geochemical parameters such as the air–sea CO_2 exchange rate using radiocarbon.

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1. Introduction

Bomb radiocarbon (^{14}C) was produced in the late 1950s and early 1960s by thermonuclear weapons testing in the stratosphere and caused ^{14}C levels in tropospheric CO_2 to nearly double by 1964 (Nydal and Lovseth, 1983). After 1965, levels of ^{14}C in the atmosphere have decreased because of gas exchange with CO_2 in the surface ocean and incorporation into the terrestrial biosphere. Maximum $\Delta^{14}\text{C}$ values measured in surface water dissolved inorganic carbon (DIC) were attained in the 1970s, indicating that the turnover time of CO_2 in the atmosphere with respect to transfer to the surface ocean is ~ 10 years (Druffel and Suess, 1983). Measurements of $\Delta^{14}\text{C}$ in water column profiles made since 1970 have been used to calculate the inventory of bomb ^{14}C in various oceanic regions (Broecker and Peng, 1994; Duffy and Caldeira, 1995). The timescale of modification of ^{14}C is of the order of years, much longer than that for temperature, which is quasi-conservative over a few weeks. This means that ^{14}C will “remember” a mixing event from a storm, entraining colder, usually lower ^{14}C water for a longer time than will SST.

Daily measurements of surface DIC $\Delta^{14}\text{C}$ 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 $\Delta^{14}\text{C}$ 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 $\Delta^{14}\text{C}$ 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 $\Delta^{14}\text{C}$ values (McDuffee and Druffel, 2007) half way through the cruise.

We report daily surface DIC $\Delta^{14}\text{C}$ 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 $\Delta^{14}\text{C}$ 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 $\Delta^{14}\text{C}$ 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 CO_2 exchange rate and bomb ^{14}C 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

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Fig. 1. Time series of a) $\Delta^{14}\text{C}$ and b) $\delta^{13}\text{C}$ 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.

cruises: Alcyone-5 from October 8 to November 5, 1985, Eve-1 from June 6 to July 4, 1987, and Avon from May 28 to June 13, 1999. Samples were collected from a single site in the Sargasso Sea ($31^{\circ}50' \text{ N}$, $63^{\circ}30' \text{ W}$, 100 km southeast of Bermuda, bottom depth 4380 m) during two cruises: Hydros-6 from May 29 to June 22, 1989 and SarC from June 14 to 29, 2000. Additionally, surface samples were collected from a site in the Southern Ocean (54°S , 176°W , bottom depth 5340 m) during the Boomerang cruise from December 14–31,

1995 (salinity was only available through day 12). The DIC $\Delta^{14}\text{C}$ 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 $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$, 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 ($\pm 0.2^{\circ}\text{C}$). 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 HgCl_2 solution to prevent biological remineralization of organic matter.

Water samples were processed for DIC $\Delta^{14}\text{C}$ 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 $\Delta^{14}\text{C}$ in per mil (Stuiver and Polach, 1977). Statistical uncertainties for the individual conventional and AMS $\Delta^{14}\text{C}$ measurements were ± 2.5 – 3.0‰ ; the total uncertainty determined from replicate analyses of a standard seawater was $\pm 3.9\text{‰}$. Stable carbon isotope measurements ($\delta^{13}\text{C}$) were performed at WHOI or UCI on splits of CO_2 from the processed ^{14}C samples with a total uncertainty of $\pm 0.06\text{‰}$.

Alkalinity and [DIC] measurements were obtained by closed vessel titration of large volume ($\sim 100 \text{ ml}$) 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 $4 \mu\text{eq/kg}$ for alkalinity and $6 \mu\text{mol/kg}$ for [DIC]. Alkalinity measurements from the Avon and SarC cruises were high by about $25 \mu\text{eq/kg}$ due to the long storage time of samples prior to analysis ($> 1 \text{ year}$) and are not reported.

3. Results and discussion

3.1. North central Pacific

At the NCP site, the $\Delta^{14}\text{C}$ measurements of surface samples in June 1987 (Eve, 28 days on station) averaged $134 \pm 7\text{‰}$ ($n=15$) (Fig. 1a) (Table 1). Values were low on days 1–6 (average $124 \pm 3\text{‰}$, $n=3$) and higher and more variable on days 8–28 ($137 \pm 5\text{‰}$, $n=12$). A similar pattern was noticed for the $\delta^{13}\text{C}$ values (Fig. 1b), which were low on days 1–6 ($0.95 \pm 0.01\text{‰}$) and higher and more variable on days 8–28 ($1.21 \pm 0.07\text{‰}$). 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 ($< 55 \text{ m}$) 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 $\delta^{13}\text{C}$ variability. Alkalinity and salinity values were also higher after day 7 ($2323 \mu\text{eq/kg}$, 35.20‰ , respectively), though [DIC] remained constant throughout the cruise ($2030 \mu\text{mol/kg}$) (Fig. 2a,b).

In June 1999 (Avon, 17 days on station), daily $\Delta^{14}\text{C}$ measurements at the NCP site averaged $89 \pm 7\text{‰}$ ($n=17$); values were higher during the first 6 days (average $96 \pm 3\text{‰}$, $n=5$) and lower and more

Table 1

Average values and standard deviations for daily isotopic, chemical and SST measurements of surface water samples collected on six cruises to the NCP, SS and SOce sites

Site	Cruise	Date	Days on station	Aver $\Delta^{14}\text{C}$	$\pm$	Range $\Delta^{14}\text{C}$ values	Aver $\delta^{13}\text{C}$	$\pm$	Range $\delta^{13}\text{C}$ values	Aver Alk	$\pm$	Aver [DIC]	$\pm$	Aver SST	$\pm$	Aver salinity	$\pm$
				‰		‰	‰		‰	$\mu\text{eq/kg}$		$\mu\text{mol/kg}$		$^{\circ}\text{C}$		psu	
NCP	Alcyone	Nov-85	25	147.1	6.0	17.4				2330	22	2003	4	24.7	1.0	36.60	0.05
NCP	Eve	Jun-87	28	134.4	7.4	24.3	1.15	0.12	0.35	2317	15	2030	5	21.6	1.8	35.11	0.22
NCP	Avon	Jun-99	17	88.7	6.9	29.9	0.78	0.29	1.20			2043	6	23.8	0.4		
SS	Hydros	Jun-89	25	121.8	4.4	11.1				2387	17	2078	2	24.7	1.0	36.60	0.05
SS	SarC	Jun-00	14	80.6	8.4	24.2	1.03	0.06	0.20			2088	14	27.4	1.1	36.55	0.09
S. Ocean	Soce	Dec-95	18	18.8	7.5	25.5	1.85	0.20	0.75	2291	7	2091	8	8.5	0.5	34.32	0.09

Fig. 2. a) Alkalinity and [DIC], b) salinity, and c) SST values for surface water samples collected during each of the six cruises as described in the Fig. 1 caption.

variable from days 7–17 ($86 \pm 5\%$, $n=12$) (Fig. 1a). The $\delta^{13}\text{C}$ values from days 1–6 averaged $0.96 \pm 0.11\%$, and were lower and more variable thereafter ($0.69 \pm 0.32\%$) (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 $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values during this time. Values of [DIC] were constant throughout the cruise and averaged $2043 \pm 6 \mu\text{mol/kg}$. Alkalinity and salinity measurements are not available.

Previously reported $\Delta^{14}\text{C}$ measurements from a November 1985 cruise (Alcyone, 25 days on station) to the NCP site (Druffel et al., 1989) averaged $147 \pm 6\%$ ($n=12$) (Fig. 1a). Values appeared more scattered after day 13, though this trend was not statistically significant. Salinity, alkalinity and SST values were higher during the first half of the cruise (averaging $35.44 \pm 0.02\%$, $2355 \pm 27 \mu\text{eq/kg}$, $24.6 \pm 0.4 \text{ }^{\circ}\text{C}$) than during the second

half ($35.31 \pm 0.04\%$, $2319 \pm 8 \mu\text{eq/kg}$, $23.4 \pm 0.4 \text{ }^{\circ}\text{C}$) (Fig. 2a,b,c). A storm and high winds (~ 50 kts) occurred during days 10–13 of the cruise, and likely caused increased mixing in the surface water mass (Druffel et al., 1989). Values of [DIC] were constant throughout the cruise and averaged $2003 \pm 4 \mu\text{mol/kg}$.

3.2. Sargasso Sea

At the Sargasso Sea site in June 1989 (Hydros, 25 days on station), $\Delta^{14}\text{C}$ measurements averaged $122 \pm 4\%$ ($n=7$) (Fig. 1a) and were slightly lower during the first part of the cruise (days 1–14, $119 \pm 3\%$, $n=4$) than during the second part (days 20–25, $125 \pm 3\%$, $n=3$). There were no $\delta^{13}\text{C}$ analyses of these water samples. Alkalinity, salinity and SST measurements were less variable before day 8 ($2399 \pm 5 \mu\text{eq/kg}$, $36.56 \pm 0.01\%$, $23.5 \pm 0.2 \text{ }^{\circ}\text{C}$) than afterward ($2381 \pm 19 \mu\text{eq/kg}$, $36.61 \pm 0.06\%$, $25.3 \pm 0.6 \text{ }^{\circ}\text{C}$) (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 $2078 \pm 2 \mu\text{mol/kg}$.

McDuffee and Druffel (2007) report $\Delta^{14}\text{C}$ measurements for the SS site, in June 2000 (SarC, 14 days on station) that averaged $81 \pm 8\%$ ($n=10$). Values were high from days 1–8 ($87 \pm 4\%$, $n=4$) and lower and more variable thereafter ($76 \pm 8\%$, $n=6$) (Fig. 1a). Similar to the $\Delta^{14}\text{C}$ values, the $\delta^{13}\text{C}$ values were more variable during the second half of the cruise ($1.05 \pm 0.08\%$) than during the first 8 days ($1.01 \pm 0.02\%$) (Fig. 1b). The [DIC] measurements averaged $2085 \pm 9 \mu\text{mol/kg}$ (days 1–15) until the last day when an increase of $45 \mu\text{mol/kg}$ was noted. SST values increased $3 \text{ }^{\circ}\text{C}$ 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 $2\text{--}3 \text{ }^{\circ}\text{C}$ warmer after day 7 (McDuffee and Druffel, 2007).

3.3. Southern Ocean

At the Southern Ocean site in December 1995 (SOce, 18 days on station), surface $\Delta^{14}\text{C}$ results averaged 19 ± 8 ($n=17$) (Fig. 1a), and values were lowest during days 2–4 (range $5\text{--}8\%$). The $\delta^{13}\text{C}$ values averaged $1.8 \pm 0.2\%$ ($n=17$) and values were slightly more variable during days 8–11 ($1.6 \pm 0.3\%$) (Fig. 1b). SST values were lower during days 3–6 ($7.7 \pm 0.6 \text{ }^{\circ}\text{C}$) than afterward ($8.7 \pm 0.3 \text{ }^{\circ}\text{C}$) (Fig. 2c). Salinity values were variable ($34.32 \pm 0.09\%$) during the period for which data was available (days 1–12) (Fig. 2b). The [DIC] and alkalinity values averaged $2091 \pm 8 \mu\text{mol/kg}$ and $2291 \pm 7 \mu\text{eq/kg}$, respectively, throughout the cruise (Fig. 2a). Data from five CTD casts revealed overall higher salinity values between 30 and 200 m depth on days 1 and 18 of the cruise than on days 3, 10 and 15.

3.4. Implications for surface ocean variability in DIC $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$

Variability of the six $\Delta^{14}\text{C}$ time series, as measured by the standard deviation of the averages, ranged from $\pm 4.4\%$ (SS 1989) to $\pm 8.4\%$ (SS 2000) (Table 1). The range of $\Delta^{14}\text{C}$ 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 $\Delta^{14}\text{C}$ values, NCP 1999 and S. Ocean 1995 (25.5%), also had the largest ranges of $\delta^{13}\text{C}$ 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 $\Delta^{14}\text{C}$ 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 $\Delta^{14}\text{C}$ measurements in samples collected from the upper ocean (0–300 m) during each of the six cruises (Druffel and Bauer, 2000; Druffel et al., 2008; Druffel et al., 1992) plotted versus density (sigma- t). The average and standard deviation of all surface values for each cruise are plotted as symbols with error bars, whereas $\Delta^{14}\text{C}$ 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 $\Delta^{14}\text{C}$ values with depth than that from the 1999 cruise (filled

squares), in large part because atmospheric $\Delta^{14}\text{C}$ values in the 1980s (160–270‰) were higher than in the 1990s (95–150‰). Surface ocean $\Delta^{14}\text{C}$ values were lower in 1999 (NCP) and 2000 (SS) (Fig. 3a, b), because more bomb ^{14}C had penetrated deeper into the main thermocline, and were replaced by ^{14}C -poor waters from below, causing a smaller gradient of $\Delta^{14}\text{C}$ values with depth.

It seems likely that the variability of surface $\Delta^{14}\text{C}$ is the result of sampling of different water masses that are floating by a single geographic location. Most of the subsurface $\Delta^{14}\text{C}$ 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 $\Delta^{14}\text{C}$ and sigma- t for most of the cruises. This inverse relationship suggests that $\Delta^{14}\text{C}$ 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 $\Delta^{14}\text{C}$ values at a single point in time. This is in contrast to geochemical proxies, such as shells, corals, forams and varved sediments that integrate $\Delta^{14}\text{C}$ values over an extended period of time (weeks to years) depending on the sampling resolution. Most of the DIC $\Delta^{14}\text{C}$ data available for the world ocean has been obtained from discreet water samples, e.g. Geosecs, WOCE, TTO. The reported uncertainty for DIC $\Delta^{14}\text{C}$ 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 $\Delta^{14}\text{C}$ value at a given site over a several week period is approximately two times the reported uncertainty ($\sim 7\%$).

Therefore, depending on the application, users of post-bomb $\Delta^{14}\text{C}$ data should consider this short-term variability of surface ocean $\Delta^{14}\text{C}$ values and factor this into their analysis. For example, assessment of the bomb ^{14}C inventory in the water column requires numerous $\Delta^{14}\text{C}$ measurements from a given depth profile (Broecker et al., 1995). Calculation of the bomb ^{14}C inventory at our NCP site in 1999 reveals a value of 1.8×10^{14} atoms/m² with an error (based only on the ^{14}C measurement error of $\pm 3.5\%$) of $\pm 2.2\%$. Using a larger error for $\Delta^{14}\text{C}$ values of $\pm 7\%$, our uncertainty for the bomb ^{14}C inventory increases to $\pm 5\%$, which still is not large. Another example is how variability of surface ocean $\Delta^{14}\text{C}$ values affect estimates of air–sea CO_2 exchange rate. Using a multi-box isopycnal mixing model to calculate the steady state, pre-bomb $\Delta^{14}\text{C}$ value (-43.5%) in the surface waters of the Sargasso Sea (Druffel, 1997), the average air–sea CO_2 exchange rate is 18.9 moles/m²/y. To obtain a pre-bomb value one-sigma lower than this (-47%), an air–sea CO_2 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 CO_2 exchange rate of 28.6 moles/m²/y. Doubling the error for pre-bomb $\Delta^{14}\text{C}$ values ($\pm 7\%$) expands the range of air–sea CO_2 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 masses mix – e.g., tropical Pacific and subpolar/temperate boundaries.

Monthly surface $\Delta^{14}\text{C}$ 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 $\Delta^{14}\text{C}$ values (11–30‰) that we measured at our three sites in the NCP, SS and SOce

Fig. 3. $\Delta^{14}\text{C}$ 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 (sigma- t). The average and standard deviation of all surface values for each cruise are shown with error bars and $\Delta^{14}\text{C}$ values for subsurface samples (10–250 m depth) are plotted as symbols with no error bars (NCP – 1985 filled triangle, 1987 filled circle, 1999 filled square; SS – 1989 open triangle, 2000 open circle; SOce – 1995 “X”). Lines are least squares fits of the average surface and subsurface data for each cruise (NCP – 1985 solid black line, 1987 dashed black line, 1999 dotted black line; SS – 1989 solid grey line, 2000 dashed grey line; SOce – 1995 solid grey line).

are comparable to the range of $\Delta^{14}\text{C}$ values observed seasonally at selected sites.

In summary, our results show that a single measurement of DIC $\Delta^{14}\text{C}$ in surface seawater has a larger uncertainty than that accounted for by measurement error alone. The true range of $\Delta^{14}\text{C}$ 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 $\Delta^{14}\text{C}$ signature of the surface ocean, and the movement of surface water masses relative to geographic location.

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