Marine Chemistry 110 (2008) 185–189

Contents lists available at ScienceDirect

Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem

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

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ARTICLE INFO

Article history:
Received 5 October 2007
Received in revised form 11 April 2008
Accepted 11 April 2008
Available online 20 April 2008

Keywords:
Dissolved inorganic carbon
Radiocarbon
Surface ocean
Carbon-13
Daily variability

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 $\Delta^{14}C$ 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 $\Delta^{14}C$ values is larger than the analytical precision, because of patchiness that exists in the DIC $\Delta^{14}C$ 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.

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 $\Delta^{14}C$ 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 $\Delta^{14}C$ 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 $\Delta^{14}C$ 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 $\Delta^{14}C$ 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 $\Delta^{14}C$ 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 $\Delta^{14}C$ values (McDuffee and Druffel, 2007) half way through the cruise.

We report daily surface DIC $\Delta^{14}C$ 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 $\Delta^{14}C$ 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 $\Delta^{14}C$ 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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doi:10.1016/j.marchem.2008.04.004

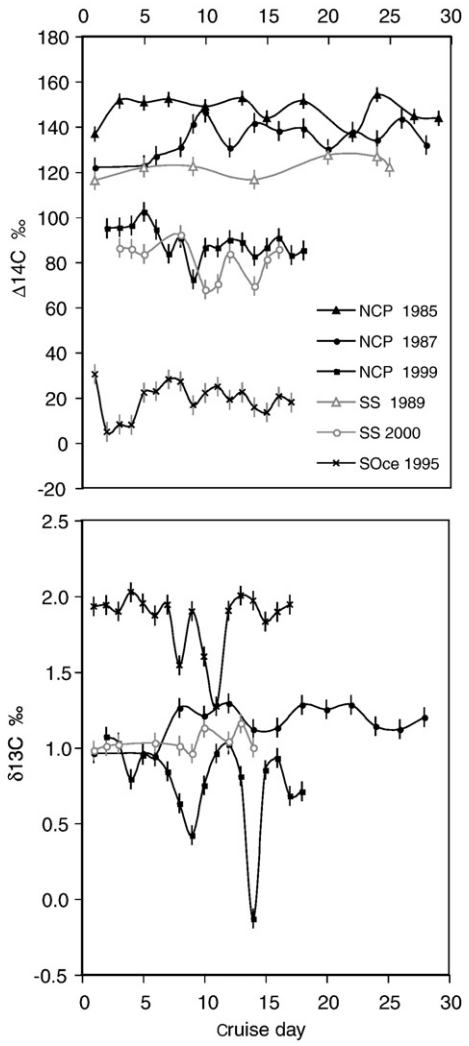

Fig. 1. Time series of a) $\Delta^{14}C$ and b) $\delta^{13}C$ measurements of surface water DIC taken during three cruises to the North central Pacific (NCP) (October–November 1985; June 1987; June 1999), two cruises to the Sargasso Sea (SS) (June 1989; June 2000) and a cruise to the Southern Ocean (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°50′ N, 63°30′ 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 $\Delta^{14}C$ 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 $\Delta^{14}C$ and $\delta^{13}C$, 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 (±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 $HgCl_2$ solution to prevent biological remineralization of organic matter.

Water samples were processed for DIC $\Delta^{14}C$ 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 $\Delta^{14}C$ in per mil (Stuiver and Polach, 1977). Statistical uncertainties for the individual conventional and AMS $\Delta^{14}C$ measurements were ±2.5–3.0‰; the total uncertainty determined from replicate analyses of a standard seawater was ±3.9‰. Stable carbon isotope measurements ($\delta^{13}C$) were performed at WHOI or UCI on splits of CO_2 from the processed ^{14}C 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 $\Delta^{14}C$ 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 $\delta^{13}C$ values (Fig. 1b), which were low on days 1–6 (0.95±.01‰) 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 $\delta^{13}C$ 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 $\Delta^{14}C$ 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
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 $\Delta^{14}C$	±	Range $\Delta^{14}C$ values	Aver $\delta^{13}C$	±	Range $\delta^{13}C$ values	Aver Alk	±	Aver [DIC]	±	Aver SST	±	Aver salinity	±
				‰		‰	‰		‰	μeq/kg		μmol/kg		°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