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Daily variability of dissolved inorganic radiocarbon in Sargasso Sea surface water

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Abstract

Surface water samples were collected daily in June 2000 at a site in the Sargasso Sea to observe variability of $\Delta^{14}\text{C}$ values in dissolved inorganic carbon (DIC). Temperature, salinity, DIC concentration, alkalinity, and $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ values of DIC were measured in the samples. Ten $\Delta^{14}\text{C}$ measurements averaged $81 \pm 8\text{‰}$ and had a range of 24‰ over the sixteen-day cruise. $\Delta^{14}\text{C}$ values were more variable during the latter half of the cruise. Salinity and temperature measurements in the mixed layer throughout the cruise indicate that there were changes in water mass that occurred at our site. We conclude that the daily range of DIC $\Delta^{14}\text{C}$ values in the surface ocean at our site is several times greater than the annual change in surface waters in the Sargasso Sea during the last two decades of the 20th century. This points to the importance of obtaining multiple measurements of the surface ocean to adequately define the true variability of DIC $\Delta^{14}\text{C}$ measurements.

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1. Introduction

Natural $^{14}\text{C}/^{12}\text{C}$ ratios (<AD 1880) in DIC in the non-polar surface ocean were approximately 4–7‰ lower than that in the atmosphere (Bien et al., 1963; Broecker et al., 1960; Linick, 1980). This is known as the reservoir age of the surface ocean (330–580 ^{14}C years) (Stuiver et al., 1986). The depletion of $\Delta^{14}\text{C}$ values in surface seawater with respect to that in the atmosphere is caused primarily by mixing between surface and subsurface waters that are depleted in ^{14}C , and in small part to the long equilibration time of $^{14}\text{CO}_2$ between air and sea (~ 10 years). Knowing

the short-term variability of surface ocean DIC $\Delta^{14}\text{C}$ is important for establishing the uncertainty in the reservoir age of DIC at a given location. To date, this variability has not been adequately investigated.

An understanding of the natural variability of DIC $\Delta^{14}\text{C}$ in surface waters is necessary for interpretation of $\Delta^{14}\text{C}$ results obtained as a part of carbon cycling studies. Dissolved inorganic carbon is the precursor of all organic material produced in the surface ocean by photosynthesis. Because organic matter is transported to the deep sea in the form of fecal pellets and marine snow, knowledge of the variability of $\Delta^{14}\text{C}$ values in surface DIC is important for interpreting the $\Delta^{14}\text{C}$ measurements of organic matter at depth in the ocean.

An earlier study of surface DIC $\Delta^{14}\text{C}$ results of samples taken every 2–4 days in the central North Pacific Ocean in October 1985 revealed that the $\Delta^{14}\text{C}$

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values were more variable during and after a storm (Druffel et al., 1989). They suggested that high winds caused increased variability of surface $\Delta^{14}\text{C}$ and higher DIC concentrations.

This study reports isotopic and chemical measurements of daily surface water samples collected from a site in the Sargasso Sea during June 2000. Our results indicate that variability of DIC $\Delta^{14}\text{C}$ values observed during the cruise was likely associated with changes in the water mass at our site.

2. Collection site and methods

Samples were collected daily from a single site in the Sargasso Sea, 100 km southeast of Bermuda ($31^{\circ}50'$, $63^{\circ}30'W$, bottom depth 4380 m), from 14 to 29 June 2000. This site had previously been occupied from 29 May to 20 June 1989 and DIC $\Delta^{14}\text{C}$ results of a depth profile were reported earlier (Druffel et al., 1992).

Using a plastic bucket and rope deployed over the side of the *R/V Knorr*, seawater samples were collected from a depth of 0–0.5 m for DIC $\Delta^{14}\text{C}$, $\delta^{13}\text{C}$, concentration ([DIC]), alkalinity and salinity measurements. Sea surface temperature (SST) measurements were made using a mercury thermometer ($\pm 0.2^{\circ}\text{C}$). Samples were taken daily between 1200 and 1300 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.

The DIC $\Delta^{14}\text{C}$ samples were processed for carbon isotopic analysis according to standard methods (McNichol et al., 1994). Six of the sixteen samples were lost prior to analysis. Briefly, a 500-ml sample was acidified with 85% phosphoric acid while nitrogen gas was bubbled through the solution to strip it of CO_2 ; the CO_2 was collected cryogenically in a liquid nitrogen-cooled trap. The CO_2 was converted to graphite with hydrogen gas on cobalt catalyst at 550°C (Vogel et al., 1987) and measured at the Keck Carbon Cycle Accelerator Mass Spectrometry (AMS) Laboratory at UC Irvine (Southon et al., 2004).

Radiocarbon measurements are reported as $\Delta^{14}\text{C}$ in per mil for geochemical samples with age correction from time of collection to time of AMS analysis (Stuiver and Polach, 1977). Statistical uncertainties for the individual AMS $\Delta^{14}\text{C}$ measurements was ± 2.5 – 3.0‰ ; the total uncertainty determined from replicate seawater analyses was $\pm 3.9\text{‰}$. Stable carbon isotope results ($\delta^{13}\text{C}$) were performed on a Finnigan Delta Plus isotope ratio mass spectrometer at UCI on splits of CO_2 from the processed $\Delta^{14}\text{C}$ sample and the total uncertainty was $\pm 0.06\text{‰}$. 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 D. McCorkle (Woods Hole Oceanographic Institution). Alkalinity and [DIC] were determined using a nonlinear curve fitting approach (DOE, 1994) and standardized using certified reference materials (Dickson et al., 2003). The standard deviation of pairs of replicate analyses of culture water was $6\text{ }\mu\text{mol/kg}$ for [DIC]. Alkalinity measurements of samples from this cruise were $\sim 20\text{ }\mu\text{eq/kg}$ higher than values for samples obtained from a previous occupation to this site in 1989 (Druffel et al., 1992), likely due to the extended period between collection and analysis (1 year). Thus, we assign a larger uncertainty to the alkalinity values ($\pm 20\text{ }\mu\text{eq/kg}$).

3. Results

The $\Delta^{14}\text{C}$ measurements of daily surface samples ranged from 68‰ (day 10) to 92‰ (day 8) (Fig. 1a and Table 1). The $\Delta^{14}\text{C}$ values for days 3–8 averaged $87 \pm 3\text{‰}$, whereas the following two samples (days 10 and 11) had a significantly lower average $\Delta^{14}\text{C}$ value ($69 \pm 1\text{‰}$). The average $\Delta^{14}\text{C}$ value of the last six samples ($76 \pm 8\text{‰}$, days 10–16) is 11‰ lower than the average of the four initial samples, however this difference is not statistically significant.

The $\delta^{13}\text{C}$ values (Fig. 1b) were constant from days 3–11 ($1.0 \pm 0.03\text{‰}$), and slightly higher and more variable from days 12–16 ($1.08 \pm 0.08\text{‰}$). The trend displayed by the $\delta^{13}\text{C}$ values resembles that of the $\Delta^{14}\text{C}$ values (Fig. 1a).

Alkalinity (Alk) measurements (Fig. 2a) were constant (average $2423 \pm 8\text{ }\mu\text{eq/kg}$) until day 16 when Alk was significantly lower (by $70\text{ }\mu\text{eq/kg}$). The [DIC] values were also relatively constant (average $2085 \pm 9\text{ }\mu\text{mol/kg}$) until day 16 when the value increased significantly (by $46\text{ }\mu\text{mol/kg}$). SST values rose from day 2 to day 3, remained constant ($27.2 \pm 0.3^{\circ}\text{C}$) from days 3–10 (Fig. 2b), and then steadily increased to 29.8°C by day 15; SST was nearly 2°C lower on day 16. Salinity values decreased from 36.582‰ to 36.480‰ from days 1–8, and then increased to a maximum of 36.745‰ on day 14. The lowest surface salinity value (36.364‰) was observed on day 16.

Wind speeds measured during the cruise ranged from 0–6.0 m/s (Fig. 2c). Higher wind speeds (> 4.0 m/s) were recorded on days 1, 2, 8, 9, and 14. Data from multiple casts of a Seabird CTD revealed salinity and temperature measurements every 2 m at our site throughout the cruise. Fig. 3a shows large shifts in salinity in the upper 25 m of the water column on days 7, 11, 14 and 16. Temperatures near the surface increased

Fig. 1. Time series of DIC a) $\Delta^{14}\text{C}$ values (filled diamonds) and b) $\delta^{13}\text{C}$ values (open diamonds) of surface waters collected at the Sargasso Sea site, versus cruise day in June 2000 (ticks mark noon).

throughout the cruise, and values below 20 m were 2–3 °C higher after day 7 (Fig. 3b).

4. Discussion

Data from the isotopic, chemical and physical time series each displayed unique trends. The $\Delta^{14}\text{C}$ values were significantly lower during days 10–11 and 14 than those during days 3–8. If the lower $\Delta^{14}\text{C}$ values during days 10–11 were the result of increased vertical mixing between surface and subsurface waters caused by

increased wind during days 8–9, then a mass balance calculation can be used to assess the mixing necessary to achieve the low $\Delta^{14}\text{C}$ values. The average of DIC $\Delta^{14}\text{C}$ values obtained during days 1 and 2 on this cruise from 20 and 100 m depth ($63 \pm 8\text{‰}$; (Druffel et al., in preparation) was $24 \pm 11\text{‰}$ lower than the average $\Delta^{14}\text{C}$ value ($87 \pm 3\text{‰}$) of the surface samples from days 3–8 (Table 1). Calculations reveal that $75 \pm 20\%$ of the surface waters would have been replaced by subsurface waters from day 8 to day 10 to account for the decrease of the average $\Delta^{14}\text{C}$ value observed on days 10 and 11

Table 1
 $\Delta^{14}\text{C}$, $\delta^{13}\text{C}$, alkalinity, [DIC], salinity, SST and density (sigma-t) values for water samples collected from 0–0.5 m depth at the Sargasso Sea site in June 2000

Sample	Event	Day	Collection	$\Delta^{14}\text{C}$	$\delta^{13}\text{C}$	Alkalinity	[DIC]	Salinity	SST	Sigma-t
UCID#	#	#	Date	(‰)	(‰)	($\mu\text{eq/kg}$)	($\mu\text{mol/kg}$)	(‰)	(°C)	
	105	1	6/14/00			2427	2095	36.582	25.6	25.35
	114	2	6/15/00			2428	2097	36.547	25.5	24.39
4878	120	3	6/16/00	86	0.98	2426	2087	36.523	27.0	23.87
4885	127	4	6/17/00	86	1.01	2427	2087	36.550	27.6	23.69
4873	134	5	6/18/00	84	1.02	2417	2085	36.500	27.1	23.82
	141	6	6/19/00			2407	2082	36.449	26.7	23.91
	150	7	6/20/00			2422	2083	36.492	27.6	23.68
4896	160	8	6/21/00	92	1.03	2418	2083	36.480	27.0	23.84
	165	9	6/22/00			2443	2103	36.633	27.4	23.82
4893	173	10	6/23/00	68	1.01	2419	2087	36.543	27.1	23.85
4891	182	11	6/24/00	70	0.96	2416	2085	36.537	27.8	23.62
4895	193	12	6/25/00	84	1.13	2418	2071	36.604	28.0	23.60
	198	13	6/26/00			2421	2078	36.554	28.0	23.50
4890	213	14	6/27/00	69	1.04	2423	2071	36.745	28.5	23.54
4884	225	15	6/28/00	81	1.16	2433	2080	36.679	29.8	23.06
4877	235	16	6/29/00	86	1.00	2354	2131	36.364	28.0	23.42

Fig. 2. Time series of a) alkalinity ($\mu\text{eq/kg}$, open circles) and [DIC] ($\mu\text{mol/kg}$, filled circles), b) SST ($^{\circ}\text{C}$, black squares) and salinity (psu or ‰ , open squares) in surface waters, and c) wind speed (m/s) measured at the Sargasso Sea site, versus cruise day in June 2000 (ticks mark noon).

($69 \pm 1\text{‰}$). Because the highest winds (5.5–6 m/s) of the cruise occurred on day 8, it is feasible that lower $\delta^{14}\text{C}$ values in the surface samples could have been caused by increased mixing induced by the wind event. $\delta^{13}\text{C}$ values in subsurface waters are equal to or slightly lower

than surface values (by 0.2 ‰ Druffel et al., in preparation) because of remineralization of organic matter. Thus, the slight increase of $\delta^{13}\text{C}$ values we observe >day 11 (Fig. 1b) does not support increased vertical mixing during the second half of the cruise.

Fig. 3. a) Salinity and b) temperature versus depth from CTD casts made during days 2, 7, 11, 14 and 16 of the SarC cruise. See text for detail.

Fig. 4. Time-series of surface DIC $\Delta^{14}\text{C}$ values from annually banded corals from Bermuda (Druffel, 1989) (small filled circles), and average DIC $\Delta^{14}\text{C}$ values (large filled circles) from the SarC cruise (this work) and the Hydros cruise in June 1989 (Druffel, in preparation; Druffel et al., 1992) (ticks mark 1 January). $\Delta^{14}\text{C}$ values of atmospheric CO_2 are also shown (○) (Levin et al., 2003). Error bars indicate the total uncertainty (Bermuda corals and air CO_2) and range of daily values (SS seawater DIC).

Instead, lateral change in water mass is the more likely explanation for the variability in isotopic, chemical and physical (SST) parameters we observed during the cruise. The large range of salinity values in the upper 25 m (Fig. 3a) indicates that the water mass was changing with time. At times, salinity values exceeded 37.0‰, indicating the presence of salinity maximum water that originates further south during excessive evaporation (Blanke et al., 2002; Worthington, 1976). It appears that high salinity water moved into the sampling site after day 2 (Fig. 3a). Also, temperature profiles show an increase of 2–3 °C between days 7 and 11 (Fig. 3b), which could not have been caused by insolation of a single water mass. Instead, the water mass at our site was continually changing, and with it, came waters with different characteristics, including variable $\Delta^{14}\text{C}$ signatures. The Alkalinity and [DIC] values also indicate a different water mass was present during the last day of the cruise because it is unlikely that these changes reflect a biological process in a single water mass.

The trend in $\Delta^{14}\text{C}$ values for the SarC cruise shows a range of 24‰ within a short time period (days). This is compared to the annual decrease of $\Delta^{14}\text{C}$ in Bermuda corals (Druffel, 1989) and surface seawater DIC from 1980–2000 of 3–4‰ per year (Fig. 4). This illustrates that the present, daily variability of $\Delta^{14}\text{C}$ at this site in the Sargasso Sea is several times greater than the annual change in this region. This is important for parameterization of ocean circulation and atmosphere/ocean coupled models that utilize seawater $\Delta^{14}\text{C}$ measurements e.g. Geosecs and WOCE, as a regulator of carbon

transfer and cycling between atmosphere and ocean. The true variability of surface ocean $\Delta^{14}\text{C}$ measurements ($\pm 12\text{‰}$) is actually much larger than the reported uncertainty ($\pm 4\text{‰}$).

In 2000, $\Delta^{14}\text{C}$ of atmospheric CO_2 was 94‰ (Levin et al., 2003), only 13‰ higher than the average value in the surface ocean of the Sargasso Sea ($81 \pm 8\text{‰}$) (Fig. 4). This difference is smaller than that observed during steady state conditions <A.D. 1880 (~ 40 to 50‰ Druffel, 1997). This indicates that by the year 2000, the Sargasso Sea surface ocean was no longer a net sink for bomb ^{14}C , as had been the case during the 1960s–1990s when the air-sea ^{14}C gradient exceeded 50‰ . Similar findings have been reported for soil organic matter, where pore-space CO_2 is higher in $\Delta^{14}\text{C}$ compared to atmospheric CO_2 because of remineralization of a bomb ^{14}C -enriched organic matter fraction (Trumbore, 2006).

5. Conclusions

1. The range of daily surface ocean DIC $\Delta^{14}\text{C}$ values (24‰) is several times greater than the annual change in surface waters in the mid-gyre region (3–4‰).
2. The observed changes in surface ocean DIC $\Delta^{14}\text{C}$ were likely the result of water mass changes that occurred at our sampling location throughout the cruise.
3. We show that single seawater measurements may not reflect the true $\Delta^{14}\text{C}$ value for the seawater in the Sargasso Sea and that numerous measurements taken over a several day period may be necessary to define the true range of values for that location.

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