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Key Points:

- DOC in the deep Eurasian Basin appears to contain at least 8% bomb $^{14}\mathrm{C}$
- Modern DOC appears to be selectively lost in the Beaufort Sea and slope water
- A relationship between DOC Δ^{14} C and total hydrolysable amino acids in the Beaufort suggests that chemical composition controls DOC cycling

Supporting Information:

Supporting Information S1

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Radiocarbon in dissolved organic and inorganic carbon of the Arctic Ocean

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Abstract Dissolved organic carbon (DOC) in the ocean is thousands of ¹⁴C years old, yet a portion of the DOC cycles on much shorter time scales (days to decades). We present ¹⁴C measurements of DOC in the Arctic Ocean and estimate that \geq 8% of the DOC in the deep Eurasian Basin contains bomb ¹⁴C. While this is a limited data set, there appears to be selective loss of modern DOC in the surface and halocline waters of the open Beaufort Sea versus the Beaufort slope. At one of the Beaufort Sea stations, there is a linear relationship between DOC Δ ¹⁴C values and previously measured total hydrolysable amino acid concentrations as reported by Shen et al. (2012), indicating that deep DOC contains small amounts of bioavailable DOC. The ¹⁴C data show that not all of the deep DOC is recalcitrant.

1. Introduction

The Arctic Ocean has a large continental shelf region and the largest input of freshwater per unit volume of any ocean. Dissolved organic carbon (DOC) in surface waters of the Arctic is the highest of any ocean, due to the large flux of terrigenous DOC from Arctic rivers [*Amon et al.*, 2012; *Benner et al.*, 2005; *Hansell et al.*, 2004]. This flux of DOC is expected to increase as the Earth continues to warm, causing release of organic C from expansive Arctic permafrost watersheds [*Anderson and Amon*, 2015; *Benner et al.*, 2004].

There are four main water masses in the Arctic Ocean: (1) polar surface water, (2) halocline water (30–200 m), (3) Atlantic derived water (200–800 m), and (4) deep Atlantic water. Polar surface water is cold and fresh, having been derived from Arctic rivers and sea ice melt. The halocline water is formed on the continental shelves from freezing and brine release and is laterally advected into the Arctic Basin [*Aagaard et al.*, 1981]. Water from the Pacific Ocean flows into the Beaufort Sea between 75 and 100 m depth (Upper Halocline Water), while water from the Atlantic Ocean enters from the Fram Strait and Barents Sea (Lower Halocline Water). The Beaufort Sea (in the southern Canadian Basin) and Eurasian Basin are separated by the Lomonosov Ridge whose sill depth is about 1500 m, keeping the deep waters of the Canada Basin and Beaufort Sea relatively isolated [*Ostlund et al.*, 1987] (Figure 1).

Radiocarbon provides quantitative information on the time scale of DOC cycling in the global ocean. Though the existing data are sparse, the available ¹⁴C ages of DOC reveal that the difference between the average, prebomb (<1957) deep North Atlantic (4900±60 ¹⁴C years) and deep North Pacific (6000 ¹⁴C years) is approximately 1100 ¹⁴C years [*Druffel et al.*, 2016], and that between the deep North Atlantic and the deep Beaufort Sea (5100±180 ¹⁴C years) [*Griffith et al.*, 2012] is not significant. Reported DOC Δ^{14} C measurements in Arctic rivers are mostly modern (~0‰) and contain recently fixed C from plant litter and upper soil horizons [*Amon et al.*, 2012; *Benner et al.*, 2004; *Raymond et al.*, 2007].

We analyzed samples for DOC Δ^{14} C and δ^{13} C from the Beaufort Sea (bottom depth >1000 m depth) and slope (bottom depth from 100 to 1000 m) and the Eurasian Basin to evaluate the distribution and cycling of DOC in the Arctic Ocean. We estimate that $\geq 8\%$ of the DOC in the Eurasian Basin is of postbomb origin. We find that DOC concentrations and Δ^{14} C values in the upper Beaufort Sea and slope are linearly correlated with salinity. Samples from one station in the Beaufort Sea has total hydrolysable amino acid measurements [*Shen et al.*, 2012] that are strongly correlated with DOC Δ^{14} C values, which indicates that deep DOC contains little bioavailable DOC.

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Figure 1. Sampling locations in the Arctic Ocean (this work and CB4 [*Griffith et al.*, 2012]) and in the northern North Atlantic (A16) [*Druffel et al.*, 2016]. The arrow points to the Lomonosov Ridge (~1500 m depth) that separates the Eurasian and Canada Basins.

2. Methods

Radiocarbon in DOC and dissolved inorganic carbon (DIC) was measured in seawater samples from three cruises to the Arctic. On the R/V *Oden* in August 2012, 14 depths were sampled from a station in the Amundsen Basin near the pole (88°8.96'N, 78°14.56'E). On the *CCGS Amundsen* in August 2009, eight samples were collected from station A98 in the southern Beaufort Sea (70°47.612°N, 139°36.070°W). On the *USCGC Healy* in October 2012, samples from six stations (H35, H40, H42, H49, H60, and H64) were taken from the Beaufort Sea and slope. Sample locations are shown in Figure 1 and reported in Table S1 in the supporting information.

DOC samples shallower than 400 m were filtered using precombusted (540°C 2 h) GFF (0.7 μ M) filters; the *Healy* Stn 42 (H42) and *Amundsen* station (A98) samples were not filtered; thus, TOC (total organic carbon) was measured. All DOC samples were collected in precombusted 1 L Amber Boston Round glass bottles and frozen at -20°C. DIC samples were collected in 250 mL Wheaton[®] glass bottles and preserved with 50 μ L saturated HgCl₂ solution.

DOC samples were diluted with low carbon (DOC = $1.0 \pm 0.3 \mu M$), 18.2 M Ω Milli-Q water, acidified with 85% phosphoric acid, purged with ultrahigh purity helium gas, and UV oxidized (UVox) for 4 h [*Beaupré et al.*, 2007; *Griffin et al.*, 2010]. Samples for DIC Δ^{14} C analyses were prepared using the headspace-extraction technique [*Gao et al.*, 2014].

The CO₂ was converted to graphite on iron catalyst and analyzed for ¹⁴C at the Keck Carbon Cycle Accelerator Mass Spectrometry Laboratory at the University of California at Irvine [Southon et al., 2004; Xu et al., 2007]. Total uncertainty for DOC Δ^{14} C values is ±4‰ [Druffel et al., 2013; Walker et al., 2016]. Total uncertainties for DIC Δ^{14} C values range from 1.1 to 3.2‰ (see Table S2 in the supporting information). Total uncertainties for DOC concentrations are ±1.0 µM. Stable C isotopes (δ^{13} C) were measured on splits of the CO₂ samples using a Thermo Electron Delta Plus mass spectrometer, and most values have a total uncertainty of ±0.2‰; earlier samples (Oden, H42, and A98) have a total uncertainty of ±0.5‰.

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Figure 2. DOC Δ^{14} C measurements from (a) the *Oden* station in the Amundsen Basin and northern North Atlantic (A16 cruise) [*Druffel et al.*, 2016] and (b) the Beaufort Sea (*Healy and Amundsen*) and CB4 [*Griffith et al.*, 2012] (see Figure 1). DIC Δ^{14} C values in samples from (c) the *Oden* station and northern North Atlantic and (d) the Beaufort Sea. Error bars are shown, and where they are not shown, the error is smaller than the symbol size.

3. Results

3.1. DOC $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ Values

Surface DOC Δ^{14} C values ranged from -293% (51 m) to -230% (21 m) in the Beaufort Sea and slope and were -212% (20 m) and -129% (60 m) in the Amundsen Basin (Figures 2a and 2b and Table S2 in the supporting information). DOC Δ^{14} C values decreased steadily with depth to -485% by 2950 m in the Beaufort Sea. Below 200 m in the Amundsen Basin, DOC Δ^{14} C values ranged from -449 to -402%(Figure 2a). Previously published DOC Δ^{14} C values from 75°N in the Beaufort Sea [*Griffith et al.*, 2012] and in the North Atlantic south of Iceland [*Druffel et al.*, 2016] are included for comparison and are similar to our data (Figures 2a and 2b).

DOC δ^{13} C values ranged between -21.3 and -23.7‰ at all Arctic stations (Figure S1 in the supporting information), consistent with previously published Arctic Ocean DOC δ^{13} C values [*Benner et al.*, 2005;



versus TDAA (% TOC) measured in the same water samples and reported by *Shen et al.* [2012]. The line is a least squares regression with equation

y = 0.0023x + 1.57, where r = 0.94 (p < 0.0001).

Griffith et al., 2012; Opsahl et al., 1999]. One exception was the slope station H60, where values were lower than those for all other stations (-25.1 to -23.9%) (Figure S1b in the supporting information).

3.2. DOC Concentrations

Concentrations of DOC ranged from 65 to $85 \,\mu M$ in the polar surface waters (upper 60 m) at our Arctic stations (Figure S2 and Table S2 in the supporting information). Values decreased to $38-45 \,\mu M$ below 1500 m depth at the deep stations (*Oden*, A98, and H42).

3.3. DIC Δ^{14} C Values

Surface DIC Δ^{14} C values ranged from -35% to 19‰ in the Beaufort Sea and slope and was 52‰ in the Amundsen Basin (Figures 2c and 2d).

Values were generally higher between 200 m and 1000 m in the Beaufort Sea and slope (20‰ to 80‰). Below 1500 m, DIC Δ^{14} C values decreased from 26‰ to -112% in the Beaufort Sea, whereas the decrease with depth was smaller in the Amundsen Basin (-79% to -59%).

4. Discussion

Four trends are apparent in the Δ^{14} C data from the Arctic. First, bomb ¹⁴C appears to be present in the deep (>1500 m) DOC and DIC of the Eurasian Basin (*Oden* data from the Amundsen Basin). An estimate of the percentage of the deep DOC pool that contains bomb ¹⁴C is presented. Second, an evaluation of past and present deep DIC Δ^{14} C values in the Beaufort Sea leads us to surmise that there is natural variability of this isotopic tracer in the deep water. Third, an inverse correlation between salinity and DOC Δ^{14} C values in the Beaufort Sea and slope illustrates the contribution of modern DOC to the region via rivers and marine primary production. Fourth, TOC-normalized yields of total dissolved amino acids (TDAAs), an indicator of bioavailable dissolved organic matter in the Arctic [*Shen et al.*, 2012], show a strong correlation with TOC Δ^{14} C values at the A98 station in the Beaufort Sea (Figure 3). This relationship demonstrates that older DOC (lower Δ^{14} C) has very low TDAA yields, indicating low concentrations of bioavailable DOC.

4.1. Bomb ¹⁴C in DOC and DIC of the Eurasian Basin

Elevated concentrations of DOC (~85 μ M) in surface waters of the Eurasian Basin (Figure S2a in the supporting information) are indicative of a contribution of terrigenous DOC, which is also indicated by high DOC Δ^{14} C values (-129 and -212‰) (Figure 2a). Below 200 m depth, there was minimal decrease in DOC concentrations and Δ^{14} C values in the Eurasian Basin, with the exception of the 2000 m value (-449‰) that was lower than the others (average -410±8‰ n=5) (Figure 2a).

Bomb-produced DIC ¹⁴C (Figure S3a in the supporting information) and tritium were found throughout the entire water column in samples collected in 1991 from the Eurasian Basin [*Schlosser et al.*, 1994]. Thus, the DIC Δ^{14} C values we report clearly contain bomb ¹⁴C (Figure 2c). Given the presence of bomb DIC Δ^{14} C and tritium here, and the presence of bomb ¹⁴C in DOC of deep North Atlantic waters feeding the Eurasian Basin [*Druffel et al.*, 2016], it is reasonable that deep DOC in the Eurasian Basin also contains bomb ¹⁴C. The deep Eurasian Basin directly exchanges with the Norwegian and Greenland Seas through the Fram Strait (sill depth 2600 m). Based on mass balances of ¹⁸O, tritium, salinity, and DIC Δ^{14} C values, it was estimated that the deep Eurasian Basin exchanges water with the subarctic Atlantic on a time scale of 10–100 years [*Ostlund et al.*, 1987], which would allow for bomb ¹⁴C and tritium to flow northward into the deep Eurasian Basin.

An estimate of the fraction of DOC that contains bomb ¹⁴C would be useful for comparison with estimates made for other oceans. An estimate of the prebomb DOC Δ^{14} C value in the deep North Atlantic is \leq -456‰ [Druffel et al., 2016], which is significantly lower than the average deep DOC Δ^{14} C value at the Eurasian station (-416\% n=6). If we assume that \leq -456\% represents the prebomb DOC Δ^{14} C value in the deep Eurasian Basin, we can estimate the fraction of DOC that contains bomb ¹⁴C using a mass balance approach. Assuming that the primary source of bomb ¹⁴C to the deep water is from solubilization of particles produced in the overlying surface waters (DIC Δ^{14} C = 50%) (Figure 2c), then we estimate that >8 ± 1% of the deep DOC in the Eurasian Basin is postbomb (-416%=0.92 · -456%+ 0.08 · 50%). If the source of the bomb ¹⁴C was instead from solubilization of particles and DOC produced in the northern North Atlantic surface water (DIC Δ^{14} C = 50‰) [Druffel et al., 2016] and transported via meridional overturning circulation, the same estimate of $\geq 8 \pm 1\%$ bomb ¹⁴C in the deep DOC is obtained. This percentage of bomb ¹⁴C is the same as that estimated for deep North Atlantic DOC [Druffel et al., 2016]. This estimate is most likely a lower bound because the prebomb estimate of deep DOC (-456%) for the North Atlantic may contain some bomb ¹⁴C, and deep water is also aging as it is transported to the deep Arctic Ocean. The presence of bomb ¹⁴C highlights a dynamic and "actively" cycling fraction of deep DOC in two ocean basins, the North Atlantic and the Eurasian Basin of the Arctic Ocean.

4.2. DOC and DIC Δ^{14} C of the Beaufort Sea and Slope

Deep DOC Δ^{14} C values in the Beaufort Sea and slope decrease linearly from -403 at 1525 m to -485‰ at 2950 m and are similar to values obtained for the CB4 profile in the Beaufort Sea in 2008 [*Griffith et al.*, 2012] (Figure 2b). Deep DIC Δ^{14} C values in the Beaufort Sea and slope also decrease with depth (Figure 2d). The decrease of DOC and DIC Δ^{14} C with depth in the Beaufort Sea is partially the result of isolation of the Beaufort Sea with respect to mixing with the Eurasian Basin by the shallow Lomonosov Ridge (sill depth 1500 m). *Ostlund et al.* [1987] estimated that the deep Beaufort Sea exchanges on a time scale of 500–700 years with the deep northern North Atlantic. The question of whether the deep DOC pool in the Beaufort Sea contains a small amount of bomb ¹⁴C cannot be resolved with the limited data available.

The DIC Δ^{14} C values in the Beaufort Sea are shown for our cruises (H42 and A98) and for earlier cruises from the Beaufort Sea/Canada Basin in 1985, 1989, 1992, and 2008 [*Griffith et al.*, 2012; *Jones et al.*, 1994; *Macdonald and Carmack*, 1991] (Figure S3b in the supporting information). The DIC Δ^{14} C values from 1985 were generally lower than those from the later cruises. The amount of postbomb ¹⁴C has clearly increased with time in the upper 1000 m of the water column [*Key et al.*, 2004]. Below 2000 m, the 1985 values ranged from –148 to –124‰, and from 1989–2012 values ranged from –112 to –79‰. It is difficult to determine if there is bomb ¹⁴C in the deep Beaufort Sea. This basin is ventilated very slowly [*Ostlund et al.*, 1987], and it seems more likely that there is significant natural variability in the DIC Δ^{14} C signal in this deep basin, similar to that seen in the central North Pacific [*Druffel et al.*, 2008].

4.3. Comparison of DOC Δ^{14} C and δ^{13} C and Salinity

Earlier studies reported an inverse relationship between salinity and DOC concentration in the upper 200 m of the Beaufort Sea, slope, and shelf (salinity \leq 33.5 practical salinity unit), showing evidence of a strong input of terrigenous DOC from the Mackenzie and Yukon Rivers into the Chukchi Sea, Bering Strait, and Beaufort Sea [*Hansell et al.*, 2004; *Mathis et al.*, 2005]. Our data from the Beaufort Sea and slope also show a significant inverse linear relationship between DOC concentrations and salinity values \leq 33.5 (Figure S4a in the supporting information) (r = 0.62, p < 0.003), though the data distribution is skewed to high salinities. The *y* intercept of the salinity versus DOC least squares fit is $145 \pm 24 \,\mu$ M DOC, similar to an estimate ($154 \pm 7 \,\mu$ M) reported previously [*Hansell et al.*, 2004; *Mathis et al.*, 2005]. Our data agree with previous work showing terrigenous DOC loss as water moves offshore [*Anderson and Amon*, 2015; *Opsahl et al.*, 1999].

Extending this approach to DOC Δ^{14} C, we find a significant inverse linear relationship between DOC Δ^{14} C values and salinity values \leq 33.5 (r = 0.49, p < 0.03) (Figure S4b in the supporting information). The y intercept is 1 ± 122‰, consistent with studies that report high DOC Δ^{14} C values in major Arctic rivers (-100 to 100‰) [*Amon et al.*, 2012; *Benner et al.*, 2004; *Raymond et al.*, 2007]. However, rapid removal of ¹⁴C modern lignin and selective preservation of older lignin in the upper water column (<300 m) has been observed [*Benner et al.*, 2004]. There was no linear relationship between DOC δ^{13} C values and salinity (Figure S4c in the supporting information).

It is important to point out that using salinity versus DOC concentration to estimate river end-members ignores other sinks and sources of DOC in the Arctic Ocean [*Anderson and Amon*, 2015]. First, there is significant loss of DOC in the rivers themselves (about 30%) before the water reaches the estuaries, illustrating the labile nature of this portion of river DOC [*Holmes et al.*, 2008; *Letscher et al.*, 2011]. It also appears that the average Δ^{14} C of riverine DOC is composed of an age spectrum that is subject to selective degradation of the most bioavailable (and ¹⁴C-enriched) DOC. Second, high primary production in Arctic waters produces bioavailable marine DOC, such as TDAA, whose concentrations have varied seasonally by a factor of 3–4 [*Davis and Benner*, 2005, 2007] in the western Arctic. This causes variability of the slope of the salinity versus DOC concentration relationship and possible incorrect identification of the river DOC source. Third, DOC from melting sea ice [*Smith et al.*, 1997] would cause the salinity versus DOC relationship to underestimate the DOC river end-member. More work is needed to constrain these additional δ^{13} C and Δ^{14} C DOC isotopic source end-members in order to inform us about C cycling in Arctic Ocean water.

4.4. Comparison of the Molecular Composition and Δ^{14} C of DOC

Total dissolved amino acids serve as quantitative indicators of bioavailable DOC that is produced by plankton and respired by microbes in the Arctic [*Davis and Benner*, 2007]. High concentrations and DOC-normalized yields of TDAA are found in the Beaufort Sea, and even higher values are found in the more productive Chukchi Sea to the west [*Davis and Benner*, 2005, 2007; *Shen et al.*, 2012]. Yields of TDAA were measured in the water samples [*Shen et al.*, 2012] that were also analyzed for DOC Δ^{14} C from the *Amundsen* cruise (station A98) (Figure 3). The samples from 40 to 425 m depth contain relatively high TDAA (% TOC) values (0.75–1.06%) and high DOC Δ^{14} C values (–350 to –232‰) compared to those in deeper water, demonstrating the presence of young, bioavailable DOC [*Shen et al.*, 2012]. Samples with the lowest DOC Δ^{14} C values (–398 to –441‰ from ≥1025 m depth) have low TDAA yields (<0.7%), indicating minimal bioavailable DOC in deep waters that originated from the North Atlantic Ocean. Removal of labile DOC (e.g., high TDAA) with high Δ^{14} C values would leave behind a recalcitrant DOC pool, with lower Δ^{14} C values and TDAA yields.

We observe a strong linear correlation between the TDAA yield and DOC Δ^{14} C values (r = 0.94, n = 8, p < 0.0001). This relationship may provide a method for quantifying modern DOC loss in the Arctic Ocean. Additional analyses of TDAA yield and DOC Δ^{14} C on the same water samples are needed in order to achieve this goal.

A positive correlation was observed between lignin phenol concentrations and DOC Δ^{14} C values in Arctic rivers [*Amon et al.*, 2012]. This correlation is also observed in various locations and depths in the Arctic Ocean [*Benner et al.*, 2004], suggesting that lignin phenols are bioavailable components of DOC.

A recalcitrant component of marine DOC is dissolved black C (DBC), which has very low Δ^{14} C values [*Ziolkowski and Druffel*, 2010]. Dissolved black C was measured in DOC (solid phase extracted) from H40 (176 m depth) and a site close to the Alaskan coast (H29, 125–175 m, 71°26.01′N, 152°2.50′W) during the *Healy* cruise; DBC concentrations of 1.7 and 1.6 μ *M*, respectively, were reported [*Coppola and Druffel*, 2016]. The Δ^{14} C values of these DBC samples were $-262 \pm 115\%$ and $-824 \pm 5\%$, respectively. These results indicate that DBC from these two locations is similar in concentration, though its isotopic composition is very different, suggesting [*Coppola and Druffel*, 2016] variable isotopic signatures of DBC sources to this slope region.

5. Implications for the DOC Cycle in the Arctic Ocean

We estimate that $\ge 8\%$ of the deep DOC in the Eurasian Basin is postbomb organic matter produced during the last 60 years. This agrees with results from three locations in the North Atlantic Ocean [*Druffel et al.*, 2016]. This is consistent with studies that report a wide range of ¹⁴C ages in compound fractions within deep DOC from the Pacific and the Atlantic Oceans [*Loh et al.*, 2004; *Repeta and Aluwihare*, 2006; *Ziolkowski and Druffel*, 2010]. Thus, a fraction of DOC is more dynamic and labile than most of the DOC in the deep ocean and that not all of the deep DOC is recalcitrant.

Yet the average ¹⁴C age of DOC in the deep Eurasian Basin (Δ^{14} C = -419‰, 4360 ¹⁴C years) is much older than the average turnover time of DOC (1/k, where $k = \Sigma(1/^{14}$ C age)), because DOC is a heterogeneous

mixture of postbomb and refractory C. The average turnover time is estimated by using the two fractions of DOC (8% postbomb and 92% refractory) with different ¹⁴C ages (30 and 4900 ¹⁴C years) to obtain a value of 350 years (= 1/(0.08/30 + 0.92/4900)). In other words, the average turnover time of DOC in the deep Eurasian Basin is much shorter than its ¹⁴C age, indicating that a portion of DOC is rapidly being added to and lost in the deep ocean.

The strong correlation between TDAA (% DOC) and DOC Δ^{14} C values reveals that molecular composition is important for understanding the bulk isotopic signature of DOC. It is necessary to include both of these measurements, including other molecular composition assays, on the same water samples in future studies.

Unlike the North Atlantic Ocean, there are no temporal DOC Δ^{14} C data for the Arctic [*Druffel et al.*, 2016]. Reoccupations of Arctic stations for DOC Δ^{14} C and δ^{13} C, TDAA, and lignin measurements will allow calculation of the flux rate of labile marine and terrestrial organic C into the deep Arctic Ocean. The Arctic region is warming, and sea ice is melting, which will likely increase primary production [*Arrigo and VanDijken*, 2011]. It is projected that DOC concentrations will increase and that DOC Δ^{14} C values will change as a result of global climate change [*Anderson and Amon*, 2015]. The DOC Δ^{14} C data presented both here and in *Griffith et al.* [2012] provide a near baseline to which future measurements can be compared.

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