

AN ALTERNATE METHOD OF DILUTING DISSOLVED ORGANIC CARBON SEAWATER SAMPLES FOR ^{14}C ANALYSIS

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ABSTRACT. We present a time-saving modification to the ultraviolet (UV) oxidation method for analyzing dissolved organic carbon (DOC) concentration, $\Delta^{14}\text{C}$, and $\delta^{13}\text{C}$ measurements in seawater and standard materials. A low background ($\sim 0.2 \pm 0.2 \mu\text{M}$) was reported for pre-irradiated Milli-Q (MQ) water that was used to dilute samples for DOC ^{14}C analysis (Beaupré et al. 2007). We use MQ water without pre-irradiation (background $\sim 0.9 \pm 0.2 \mu\text{M}$) to dilute the sample. This method is suitable for small-volume, high-concentration samples (mass of sample DOC overwhelms mass of MQ water DOC). An acceptable precision of $\Delta^{14}\text{C}$ measurements (5–9‰) is maintained. This revised method reduces the preparation time for diluted DOC $\Delta^{14}\text{C}$ samples from 2 days to 1 day.

INTRODUCTION

Beaupré et al. (2007) presented a modified method for ultraviolet (UV) oxidation of bulk marine non-volatile dissolved organic carbon (DOC) for isotopic analysis, which had an analytical blank of $\sim 0.2 \mu\text{M}$. Although designed for 1-L samples, the method's low blank reduced the theoretical detection limit for DOC ^{14}C analyses to $\sim 30 \text{ mL}$ of seawater via dilution with pre-irradiated Milli-Q (MQ) water. DOC concentrations and $\Delta^{14}\text{C}$ values of diluted samples are calculated by mass balance assuming carbon was derived solely from the sample and the MQ water. Therefore, inherently larger uncertainties in DOC concentrations and $\Delta^{14}\text{C}$ values propagate from the following measurements and their associated uncertainties: the volume of the seawater sample; the volume, DOC concentration, and DOC $\Delta^{14}\text{C}$ value of MQ water; the total mass and $\Delta^{14}\text{C}$ value of carbon extracted from the mixture. Despite these concerns, concentration and $\Delta^{14}\text{C}$ measurements of a 500-mL seawater sample diluted to 1 liter with pre-irradiated, acidified MQ water was statistically indistinguishable from 1-L aliquots of the same seawater (Beaupré et al. 2007). Two days are required to process 1 sample, however, because an additional day is needed to pre-irradiate the MQ water used for dilution.

In order to increase small-sample throughput, we tested the effects of diluting samples with MQ water that was not pre-irradiated. Our results indicate that this approach is effective for sufficiently concentrated samples without sacrificing precision. We show that regular monitoring of the DOC concentrations and Fm values of non-irradiated MQ (raw MQ) water is required to obtain reliable results. This revised method reduces the preparation time for diluted DOC ^{14}C samples from 2 days to 1 day.

METHODS

The dilution method used to oxidize small DOC samples to CO_2 was reported previously (Beaupré et al. 2007), and requires accurate quantification of both the MQ and sample volumes. Briefly, the height of sample water added to a quartz reactor bottle was measured using a custom cathetometer ($\pm 0.5 \text{ mm}$), and converted to water volume based on prior calibration ($\pm 5 \text{ mL}$). The sample was then diluted with MQ water to a combined volume of $\sim 1 \text{ L}$. One mL of 85% phosphoric acid was then added to the water, reducing the pH to ~ 2.5 . A Pyrex[®] magnetic spin bar and heat exchanger were then inserted into the reactor. The dissolved inorganic carbon was sparged from the water using He gas. The sample was then irradiated using a 1200-W medium-pressure mercury arc UV lamp for

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4 hr, sparged again with helium, and the resultant CO₂ gas distilled twice through dry-ice/isopropyl alcohol slush traps and collected in a calibrated volume using liquid nitrogen. The mass of CO₂ was measured manometrically and stored in flame-sealed tubes for ¹⁴C and δ¹³C analysis. Splits of CO₂ for ¹⁴C analysis were converted to graphite on an iron catalyst (Vogel et al. 1987) and then analyzed at the UCI Keck Carbon Cycle Accelerator Mass Spectrometry (KCCAMS) facility's compact AMS system (NEC 0.5MV 1.5 SDH-2 AMS) (Southon et al. 2004). ¹⁴C analyses are reported as fraction modern (Fm).

To reduce the processing time of analyzing diluted samples for ¹⁴C DOC analysis, we used raw MQ water for preparing standard solutions and for diluting seawater samples. Raw MQ water was obtained from a Millipore Synergy[®] UV system using a Synergy Pak 2 as the primary filter and an Express 20 as the final filter. The water source for the MQ system was the plumbed deionized water system in our building (Croul Hall). The raw MQ water was collected on the same day that samples were processed. To correct for carbon added to the standard or sample from raw MQ water, the concentrations and Fm values of ~1-L aliquots of MQ water were measured separately, approximately once per every 5 samples. It is assumed that different purification systems, source water, and filters used will vary in mass of and Fm of carbon.

The calculation of Fm of a sample is based on simple mass balance equations:

$$\text{total mass} = \text{sample mass} + \text{blank mass} \quad (1)$$

$$(\text{total mass} \times \text{Fm}_{\text{total}}) = (\text{sample mass} \times \text{Fm}_{\text{sample}}) + (\text{blank mass} \times \text{Fm}_{\text{blank}}) \quad (2)$$

Errors are propagated from Equations 1 and 2 as the single standard deviation of the measurements. In this method, the concentration of DOC in raw MQ water is sufficient for directly measuring the Fm_{blank} values by AMS. In contrast, direct measurement of the DOC Fm in pre-irradiated MQ water is not possible because the concentration is too low (0.2 ± 0.1 μM yields only 2 ± 1 μg C per 1-L aliquot). Instead, the Fm value of pre-irradiated MQ water is based on how much the measured ¹⁴C content of a set of standards added to pre-irradiated MQ water differ from their respective consensus ¹⁴C values.

Standard organic compounds were used to test the feasibility of using raw MQ water as a diluent. They were also used to compare the direct and indirect methods of determining their Fm value. The isotopic standards chosen, based on their importance in ¹⁴C analyses and their range in Fm values, are as follows: NBS oxalic acid 1 (Hox1; NIST-SRM-4990B), NBS oxalic acid 2 (Hox2; NIST-SRM-4990C), International Atomic Energy Agency (IAEA) C-7 and C-8 (oxalic acid). Grains of these standards were weighed, transferred to the reactor containing raw MQ water, and processed as for samples.

In addition to MQ blanks and standards, a 1-gallon seawater sample was analyzed in 4 aliquots: two 100% seawater samples and 2 samples diluted with raw MQ water. This sample was collected near Station M, our deep-sea time-series site, located 220 km west of Point Conception, California (34°50'N 123°00'W) (Smith and Druffel 1998; Beaupré and Druffel 2009) at 2007 m depth. The sample was stored at -20 °C after collection. On the day of processing, the water was quickly thawed in a hot (~60 °C) water bath on the first day of the series of oxidations. The water remained chilled between oxidations (~3 °C); all oxidations were performed within 4 days of the initial thawing. Raw MQ water was used to rinse the reactor, heat exchanger, and spin bar.

RESULTS AND DISCUSSION

The concentration of C and Fm values of CO₂ produced from UV-oxidized MQ water are presented in Table 1 and Figure 1. The concentration of blank C in ~1-L samples of raw MQ water varied from 0.7 to 1.3 μM C. The Fm values for the blank C also varied, ranging from 0.209 to 0.481. There were 3 general groupings of MQ blank C results: group I (oxidized from 5/8/08 to 9/16/08), group II (oxidized from 11/12/08 to 6/8/09), and group III (oxidized from 7/21/09 to 8/4/09). The average μM of C for all groups are within 1 standard deviation. The average Fm value for group III (0.232 ± 0.020 sd) was lowest, while that for group II (0.408 ± 0.044) was highest (Table 1).

Table 1 Time history of concentration and Fm values of MQ water used for dilution of seawater and standard samples.

UCID#	Date UV oxidized	DOC μM	Fraction modern (Fm)	±
Group I				
10824	5/8/08	0.9	0.291	0.019
10840	5/21/08	1.2	0.333	0.014
10841	5/22/08	1.0	0.297	0.019
10845	6/5/08	0.9	0.257	0.027
10961	7/8/08	0.7	0.291	0.032
11091	8/20/08	1.1	0.361	0.020
11097	8/28/08	1.0	0.335	0.023
11093	9/16/08	0.9	0.257	0.025
average μM ± sd		1.0 ± 0.1	average Fm ± sd 0.303 ± 0.038	
Group II				
11107	11/12/08	0.8	0.365	0.026
11490	1/7/09	0.7	0.378	0.029
11501	2/3/09	0.6	0.426	0.041
11511	3/3/09	0.6	0.420	0.033
11663	3/13/09	0.7	0.359	0.035
11814	4/22/09	1.1	0.481	0.019
11824	6/8/09	0.8	0.429	0.026
average μM ± sd		0.8 ± 0.2	average Fm ± sd 0.408 ± 0.044	
Group III				
12003	7/21/09	1.0	0.209	0.024
12004	7/24/09	1.3	0.242	0.019
12119	8/4/09	1.1	0.244	0.024
average μM ± sd		1.1 ± 0.2	average Fm ± sd 0.232 ± 0.020	

Changes made to the oxidation line may have affected the MQ blank (Figure 1). A new UV lamp was installed in October 2008, and was synchronous with the beginning of group II MQ blank values. Secondly, the He tank, ascarite CO₂ scrubber, and KI solution were replaced in July 2009, synchronous with the beginning of group III MQ blank values. Each of these changes were made only once during the study, so it is not yet clear what changes have the most influence on the MQ blank values. It is important to process MQ blanks on a regular basis and whenever changes are made to the vacuum line.

The reasons for the variability may also involve the water that is supplied to the deionized water system. The sources of municipal water in Irvine, California, are from the Colorado River and deep local wells. The mixing of the 2 main sources of water changes throughout the year. Although there

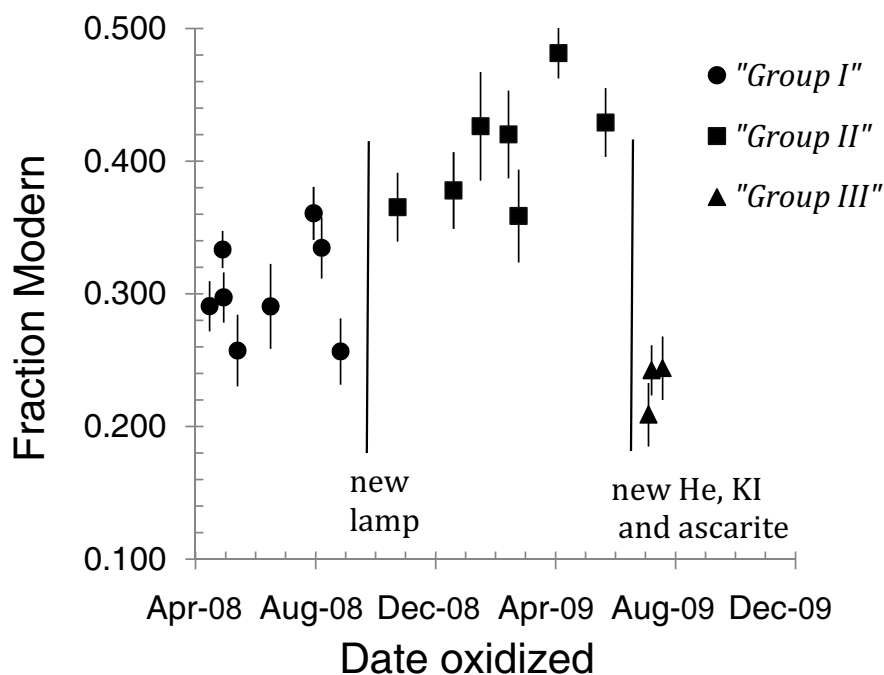


Figure 1 Date of oxidation of MQ blank water samples (~ 1.0 L) versus Fm value of the MQ blank C. Three groups of Fm values are apparent (Table 1) (see text for detail). Changes to the vacuum line are described and indicated by vertical lines.

is no significant correlation between the individual mass and Fm values, there appears to be a trend toward higher DOC values during spring and summer periods, with low to intermediate Fm values (groups I and III), as opposed to winter and spring periods that have low DOC values and higher Fm values (Figure 1). The time lapse between the groups was always more than a month; therefore, a gradual change in MQ blank would not have been observed. After MQ blanks are run over a longer period of time, definitive seasonal trends may emerge.

Four different standards dissolved in raw MQ water were analyzed, and results for the C-8 analyses are shown in Figure 2. Before the MQ blank correction was applied, the AMS measurements (open points) were significantly higher than the consensus Fm value of 0.1503, indicating the presence of a more ^{14}C -enriched C blank. After the correction for MQ blank was applied (solid points), agreement was achieved within 2σ of the reported error for all samples ($n = 14$). Similar results were obtained for OXI, OXII, and C-7 standards, where corrected Fm values were within 2σ uncertainty of the consensus values for samples as small as 0.01 mg C.

When both the indirect and direct methods were used to correct a subset of our standards for MQ blank C, the corrected Fm values differed by an average of 0.0011 ($n = 10$), which is within 1σ uncertainty of the measurements.

Results for the seawater sample from 2007 m at Station M are presented in Table 2. The 2 undiluted aliquots had Fm values of 0.375 ± 0.003 and 0.380 ± 0.003 , and agreed within 2σ uncertainty. The diluted samples had Fm values of 0.367 ± 0.005 and 0.388 ± 0.009 , and were diluted by $\sim 55\%$ and 75% , respectively. Both of these Fm values are within 2σ of the average value for the 2 undiluted samples (0.377 ± 0.003). This agreement indicates that analysis of seawater samples diluted with raw MQ water produces satisfactory ^{14}C results.

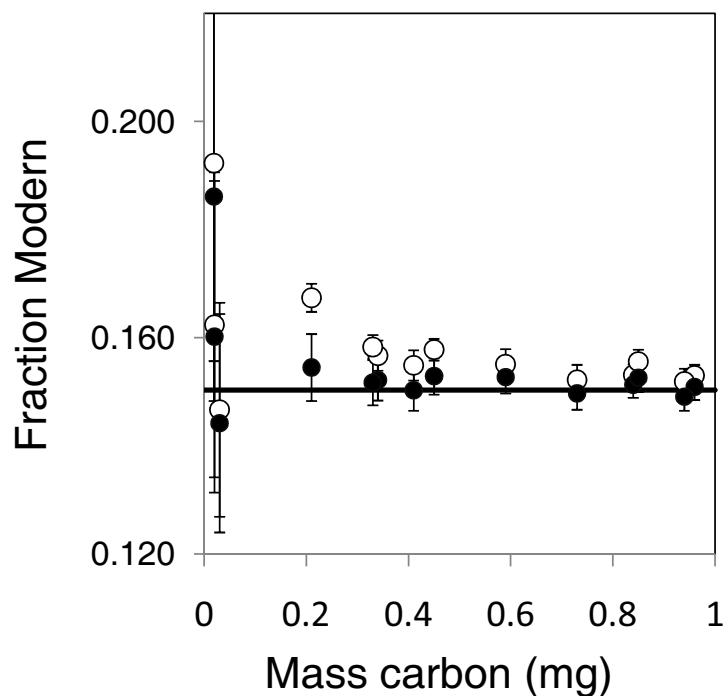


Figure 2 Mass of carbon in C-8 oxalic acid standards (mg) versus Fm value. Open points are AMS measurements and solid points are corrected for the presence of MQ blank C. The horizontal line is the consensus Fm value of 0.1503. Note the increased error of Fm with decreasing sample size.

Table 2 ¹⁴C analyses of seawater sample collected at Station M in October 2004.

UCID#		Mass total C (μg)	Mass blank C (μg)	Mass sample C (μg)	Sample μM C	AMS-measured Fm	Corrected Fm	±Fm
12006	diluted with MQ water	266	8	258	46.3	0.363	0.367	0.005
12117	diluted with MQ water	140	12	128	43.5	0.376	0.388	0.009
12005	100% seawater	nd ^a				0.375		0.003
12118	100% seawater	549			45.7	0.380 ^b		0.003

^and = not determined.

^bAverage of 2 analyses from splits of the same CO₂ gas.

This revised method requires frequent monitoring of MQ blanks. However, fewer MQ blanks will need to be run as the method becomes more routine. Also, many fewer standards will need to be run when correcting with the direct method.

The major advantage of this method is that it expedites the analysis of DOC-enriched samples. Other steps could be taken to reduce the amount of time required to run DOC ¹⁴C analysis. These steps may include the construction of smaller quartz reactors that could be arranged around a single UV source and run in batch mode, a higher powered UV lamp that would reduce oxidation time, and pre-irradiation of MQ water off-line of the DOC reactor.

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