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Corrigendum

Corrigendum to "An Investigation of size-fractionated organic matter from Lake Superior and a tributary stream using radiocarbon, stable isotopes, and NMR" by Zigah, P.K., Minor, E.C., Abdullah, H.A.N., Werne, J.P. and Hatcher, P.G.: A reanalysis using recent radiocarbon blank information [Geochim. Cosmochim. Acta 127 (2014) 264–284]

Abstract

This paper applies new information concerning the process blank for radiocarbon analysis of dissolved organic carbon using UV-oxidation and subsequent accelerator mass spectrometry analysis. Recent analyses at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) Facility show that reported values for such samples should be updated to reflect a process blank of 22 ± 6 micrograms of carbon with a fraction modern of 0.3 ± 0.2. The effects of this blank upon $\delta^{13}C$ were also assessed and found to be generally less than 0.2‰. While this process blank does not change interpretations of stable carbon isotope results, it does affect interpretations of carbon cycling in Lake Superior, with the lake's bulk dissolved organic carbon (Bulk DOC, <0.7 μm), initial DOC (Init DOC, <0.2 μm) and low molecular weight DOC (LMW DOC, <1000 kDa) appearing more enriched in bomb radiocarbon than previously reported. This paper also applies a previously published process blank to particulate organic carbon data, and this application generally, but not always, leads to more enriched $\Delta^{14}C$ values.

1. Introduction

Dissolved organic carbon (DOC) in oceans and lakes is often the dominant organic carbon pool present in these waters (Wetzel, 2001). Its cycling is critical to the understanding of the interchange between carbon in the atmosphere and in water systems as well as in understanding the underpinnings of the microbial food web and interactions between dissolved organic matter and the light available for biota within aquatic systems. Measurements of the radiocarbon content within DOC provide key constraints on the interactions between carbon pools in the global carbon cycle on timescales of centuries to millennia based upon the decay rate of radiocarbon and on timescales of decades based upon tracing the radiocarbon that entered the atmosphere during above-ground nuclear testing in the middle of the twentieth century (e.g., Druffel et al., 1992; review by McNichol and Aluwihare, 2007). It is useful to compare $\Delta^{14}C$ values for DOC with the co-occurring inorganic carbon pool within an aquatic system (here the dissolved inorganic or DIC pool) and with the particulate organic carbon (POC) that includes biota and acts as a main conduit for organic carbon from surface waters to the sediments. This was a main focus of Zigah et al. (2014) ("An Investigation of size-fractionated organic matter from Lake Superior and a tributary stream using radiocarbon, stable isotopes, and NMR").

Initially the measurement of radiocarbon within DOC, especially marine DOC, was limited by the challenges involved with low concentrations of DOC and high concentrations of matrix species such as sodium and chloride ions. These, coupled with stringent sample handling requirements to minimize carbon contamination from other sources, hindered routine measurements, which required either

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specialized high-temperature combustion instrumentation (e.g. Druffel et al., 1992) or large volumes of sample for acidification to remove inorganic carbon followed by direct UV-oxidation (Bauer et al., 1998) or freeze-drying, acidification, and subsequent combustion (e.g., Zigah et al., 2011) to provide carbon dioxide for graphitization. The method for radiocarbon analysis of DOC samples was optimized considerably by improvements to the acidification and subsequent UV-oxidation of DOC coupled to AMS analyses (Beaupre et al., 2007).

A modified version of the Beaupre et al. (2007) approach was employed by NOSAMS and made available on a cost-center basis in the late 2000s and was used for radiocarbon studies in Lake Superior (Zigah et al., 2011, 2012a, 2012b, 2014, 2017; Kruger et al., 2016). An initial DOC method blank was tested by applying field filtration protocols to a Milli-Q water sample and then subjecting this sample to acidification, UV-oxidation, graphitization and AMS analysis at NOSAMS. This process blank yielded 8.6 μmol C L^{-1} with a fraction modern of 0.6190, and, if Lake Superior DOC samples were blank corrected using this data, they would exhibit $\Delta^{14}C$ values roughly 38‰ higher than uncorrected values (Zigah et al., 2012a). The majority of this blank's carbon was attributed at the time to carbon within the MilliQ source water used for the process blank (Zigah et al., 2012a) and thus in early papers both uncorrected and blank corrected values were reported. In later papers (e.g., Zigah et al., 2014, 2017; Kruger et al., 2014), DOC values were not blank corrected with process blanks, in part due to the presumed low carbon blanks of the UV-oxidation procedure as reported by Beaupre et al. (2007) (0.2 μmol C L^{-1}), and because lake DOC samples would not be subject to the carbon within 1 L of lab MilliQ water, to which we attributed much of the carbon in the full process blank described in Zigah et al. (2012a). A more recent evaluation of the Beaupre system in use at UCI reports a line blank of 0.25–0.83 μmol C with a typical value of 0.33 μmol (Walker et al., 2019).

Here we reinterpret Lake Superior radiocarbon results from Zigah et al. (2014) using revised blank values reported by NOSAMS for the acidification, UV-oxidation, graphitization, and AMS procedure. For comparison with this blank corrected DOC, we also apply the process blank for POC from Zigah et al. (2011) to the POC data initially presented in uncorrected form. The corrections discussed here do not impact HMW DOC values or the NMR data presented in Zigah et al. (2014) (see Tables 1 and 2)

2. Methods

NOSAMS provided a revised blank value for the acidification, UV-oxidation, graphitization, and accelerator mass spectrometry (AMS) analysis of DOC water samples, which was found to be 22 ± 6 micrograms of carbon per liter (1.8 ± 0.5 μmol C L^{-1}) with a fraction modern of 0.3 ± 0.2. This value is based on NOSAMS analysis of modern and dead DOC standards analyzed between 2008 and 2018. This value was used to blank-correct Lake Superior results reported in Zigah et al. (2014) for Init DOC (<0.2 μm), Bulk DOC (<0.7 μm), and LMW DOC (<1000 Da, determined by mass balance calculations). Note that based upon this data, the full process blank for Bulk DOC (Zigah et al., 2011), where 1 L of lab MilliQ water was filtered and analyzed for radiocarbon, contains 6.8 μmol/L of carbon from the filtration process and initial MilliQ water. The MilliQ water used in this process blank was from an older water purification system and we believe it may have contributed a considerable amount of the carbon seen in the full process blank. Thus, we use the NOSAMS blank value rather than our full Bulk DOC process blank for the correction of UV-oxidized DOC radiocarbon data.

From Zigah et al. (2011), the method blank for large volume POC is 0.95 μmol C/L with a $\Delta^{14}C$ value of −95‰. We used this data in a mass balance equation (1) where the radiocarbon values (Δ^{14}Cmeasured and Δ^{14}Cblank) and carbon concentrations within the measured sample (Cmeasured) and the process blank (Cblank) were used to calculate the corrected POC radiocarbon value (Δ^{14}CPOC) initially presented in uncorrected form in Zigah et al. (2014).

$$\Delta^{14}C_{POC} = ((\Delta^{14}C_{measured} \times C_{measured}) - (\Delta^{14}C_{blank} \times C_{blank}))/(C_{measured} - C_{blank}) \quad (1)$$

A recent evaluation of the DIC process blank demonstrates that it contains approximately 1.3 μmol C L^{-1} with a $\Delta^{14}C$ of −75.5‰ (Gospodinova et al., 2016). This blank does not have a significant impact on the values reported here, where the minimum carbon concentration in DIC samples is 720 μmol C/L and the resulting $\Delta^{14}C$ correction is on the order of 0.1‰.

Table 1
Concentration, stable carbon, and radiocarbon isotopic compositions of size fractionated OM and DIC in isothermal Lake Superior in June 2010 and in the Lake Superior tributary Amity Creek (AC) in June 2008 (storm flow). Concentrations and Δ^{14}C-original are from Zigah et al. (2014). Blank corrected values have been adjusted as described in the text. Bold indicates a change in interpretation when blank-corrected values are used.

	Concentration-original (μM)	Concentration -blank corrected (μM)[a]	Δ^{14}C-original data (‰)	Δ^{14}C-blank corrected (‰)	^{14}C ages (BP yrs)
AC < 1 m					
Storm-flow POC (>0.7 μm)*	532 ± 1	531 ± 1	11 ± 2	11 ± 4	Modern
Storm-flow Bulk DOC (<0.7 μm)*	885 ± 8		62 ± 4		Modern
ONT 4 m					
DIC	820 ± 2		48 ± 4		Modern
POC (>0.7 μm)	11 ± 1	10 ± 1	−10 ± 4	−2 ± 5	**Modern**
Bulk DOC (<0.7 μm)	109 ± 2		−19 ± 5	−7 ± 7	**Modern**
Init DOC (<0.2 μm)	92 ± 1		52 ± 4	66 ± 6	Modern
HMW DOC (>1 kDa)	11 ± 2		34 ± 4		Modern
LMW DOC (<1 kDa)	82 ± 2		54 ± 4	70 ± 7	Modern
WM 5 m					
DIC	830 ± 4		46 ± 4		Modern
POC (>0.7 μm)	4.8 ± 0.2	3.9 ± 0.2	−15 ± 2	4 ± 4	**Modern**
Bulk DOC (<0.7 μm)	88 ± 1		57 ± 4	76 ± 7	Modern
Init DOC (<0.2 μm)	69 + 1		17 ± 4	32 ± 7	Modern
HMW DOC (>1 kDa)	6 ± 1		23 ± 5		Modern
LMW DOC (<1 kDa)	63 ± 2		16 ± 5	33 ± 9	Modern
WM 127 m					
DIC	829 ± 3		45 ± 4		Modern
POC (>0.7 μm)	5.6 ± 0.4	4.7 ± 0.4	12 ± 4	32 ± 5	Modern
Bulk DOC (<0.7 μm)	94 ± 1		51 ± 4	68 ± 7	Modern
Init DOC (<0.2 μm)	93 ± 1		20 ± 3	37 ± 7	Modern
HMW DOC (>1 kDa)	8 ± 1		49 ± 4		Modern
LMW DOC (<1 kDa)	85 ± 1		17 ± 4	36 ± 8	Modern
EM 5 m					
DIC	827 ± 2		39 ± 4		Modern
POC (>0.7 μm)	4.1 ± 0.2	3.2 ± 0.2	33 ± 5	73 ± 6	Modern
Bulk DOC (<0.7 μm)	90 ± 2		45 ± 4	62 ± 7	Modern
Init DOC (<0.2 μm)	90.4 ± 0.2		47 ± 5	65 ± 8	Modern
HMW DOC (>1 kDa)	11 ± 1		60 ± 4		Modern
LMW DOC (<1 kDa)	80 ± 1		45 ± 5	66 ± 9	Modern
EM 210 m					
DIC	830 ± 3		39 ± 4		Modern
POC (>0.7 μm)	4.5 ± 0.2	3.6 ± 0.2	33 ± 5	82 ± 5	Modern
Bulk DOC (<0.7 μm)	88 ± 2		50 ± 3	67 ± 7	Modern
Init DOC (<0.2 μm)	90 ± 2		42 ± 4	60 ± 8	Modern
HMW DOC (>1 kDa)	9 ± 1		38 ± 4		Modern
LMW DOC (<1 kDa)	81 ± 2		42 ± 4	63 ± 9	Modern

* Data from Zigah et al. (2011).

[a] Bulk and Init DOC concentrations were determined by TOC analysis and HMW DOC by elemental analysis after freeze-drying. LMW DOC was determined by mass balance. Carbon added during UV–Vis oxidation, graphitization, etc. would not be reflected in these DOC concentrations and would change them by ≤3%. POC was analyzed by elemental analysis. As there was a C blank determined from the POC filtration blank, and as POC concentrations are very low within Lake Superior, we do report blank-corrected values for POC.

To the authors' knowledge there are no reported full-process radiocarbon blanks for the isolation of HMW DOC by ultrafiltration, in part because of the effort involved and in part because it is difficult to determine an appropriate solution for the blank as membranes leach differently as a function of ionic strength and pH. It is assumed that due to the much higher sample sizes (in terms of total carbon) in the highly concentrated HMW samples, they will be much less affected by carbon contributions from the oxidation, graphitization and radiocarbon analyses. The potential contribution from

Table 2
Concentration, stable carbon, and radiocarbon isotopic compositions of size fractionated OM and DIC in thermally stratified Lake Superior in August 2010 and in the Lake Superior tributary Amity Creek (AC) in September 2010 (base flow). Blank corrected values have been adjusted as described in the text. Bold indicates a change in interpretation when blank-corrected values are used.

	Concentration-original (μM)	Concentration-blank corrected (μM)[a]	Δ^{14}C-original data (‰)	Δ^{14}C-blank corrected (‰)	^{14}C ages (BP yrs)
AC < 1 m					
Base-flow DIC	1869 ± 6		42 ± 3		Modern
Base-flow POC (>0.7 μm)	25 ± 1	24 ± 1	−127 ± 4	−128 ± 5	1040 ± 35
Base-flow Bulk DOC (<0.7 μm)	815 ± 8		29 ± 4	38 ± 5	Modern
Base-flow Init DOC (<0.2 μm)	776 ± 2		−4 ± 3	5 ± 5	Modern
Base-flow HMW DOC (>1 kDa)	22 ± 1		36 ± 4	Modern	
Base-flow LMW DOC (< 1 kDa)	755 ± 1		−5 ± 4	−3 ± 6	Modern
ONT 4 m					
DIC	780 ± 2		65 ± 5	Modern	
POC (>0.7 μm)	19 ± 1	18 ± 1	49 ± 3	57 ± 4	Modern
Bulk DOC (<0.7 μm)	118 ± 1		−8 ± 5	4.1 ± 7	**Modern**
Init DOC (<0.2 μm)	112 ± 1		58 ± 4	72 ± 6	Modern
HMW DOC (>1 kDa)	27 ± 1		59 ± 3		Modern
LMW DOC (<1 kDa)	85 ± 1		58 ± 5	76 ± 7	Modern
WM 5 m					
DIC	780 ± 2		57 ± 2		Modern
POC (>0.7 μm)	nd[b]		53 ± 4	81 ± 5	Modern
Bulk DOC (<0.7 μm)	97 ± 1		40 ± 4	55 ± 7	Modern
Init DOC (<0.2 μm)	96 ± 1		59 ± 4	75 ± 7	Modern
HMW DOC (>1 kDa)	19 ± 1		48 ± 3	48 ± 3	Modern
LMW DOC (<1 kDa)	77 ± 1		62 ± 4	81 ± 8	Modern
WM 127 m					
DIC	806 ± 2		56 ± 3		Modern
POC (>0.7 μm)	4.2 ± 0.1	3.3 ± 1	12 ± 4	45 ± 5	Modern
Bulk DOC (<0.7 μm)	96 ± 1		56 ± 3	73 ± 7	Modern
Init DOC (<0.2 μm)	90 ± 1		53 ± 4	70.4 ± 8	Modern
HMW DOC (>1 kDa)	12.9 ± 0.3		nd	nd	nd
LMW DOC (<1 kDa)	77 ± 1		nd	nd	nd
EM 5 m					
DIC	775 ± 4		58 ± 3		Modern
POC (>0.7 μm)	9.3 ± 0.2	8.4 ± 1	37 ± 4	53 ± 3	Modern
Bulk DOC (<0.7 μm)	91 ± 1		2 ± 3	16 ± 7	Modern
Init DOC (<0.2 μm)	92 ± 2		44 ± 3	60 ± 7	Modern
HMW DOC (>1 kDa)	11.5 ± 0.2		57 ± 4		Modern
LMW DOC (<1 kDa)	79 ± 2		42 ± 4	60 ± 8	Modern
EM 210 m					
DIC	805 ± 2		69 ± 3		Modern
POC (>0.7 μm)	nd[b]		−94 ± 5	−94 ± 6	735 ± 40
Bulk DOC (<0.7 μm)	83 ± 1		28 ± 4	45 ± 7	Modern
Init DOC (<0.2 μm)	86 ± 1		52 ± 3	69 ± 8	Modern
HMW DOC (>1 kDa)	11 ± 1		64 ± 4		Modern
LMW DOC (<1 kDa)	74 ± 1		50 ± 4	70 ± 9	Modern

[a] Bulk and Init DOC concentrations were determined by TOC analysis and HMW DOC by elemental analysis after freeze-drying. LMW DOC was determined by mass balance. Carbon added during UV–Vis oxidation, graphitization, etc. would not be reflected in these DOC concentrations and would change them by ≤3%. POC was analyzed by elemental analysis. As there was a C blank determined from the POC filtration blank, and as POC concentrations are very low within Lake Superior, we do report blank-corrected values for POC.

[b] Note: "nd" indicates not determined; for blank correction an average original open water concentration of 6 μM (which was blank-corrected to 5 μM) was assumed here.

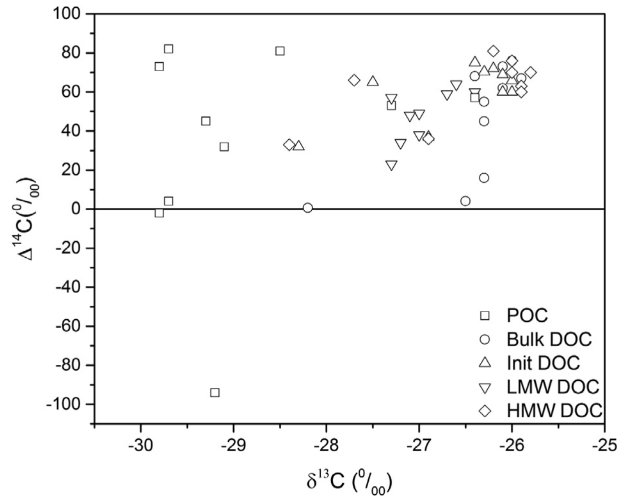

Fig. 1. Cross plot of $\Delta^{14}C$ (using blank corrected values where available, see also Tables 1 and 2) vs. $\delta^{13}C$ of OC size fractions including POC (>0.7 μm), Bulk DOC (<0.7 μm), Init DOC (<0.2 μm), LMW DOC (<1 kDa), and HMW DOC (1 kDa–0.2 μm) in Lake Superior water column covering both stratified and mixed lake conditions. POC shows wider variability in $\Delta^{14}C$ values and is more ^{13}C-depleted than the other OC size fractions.

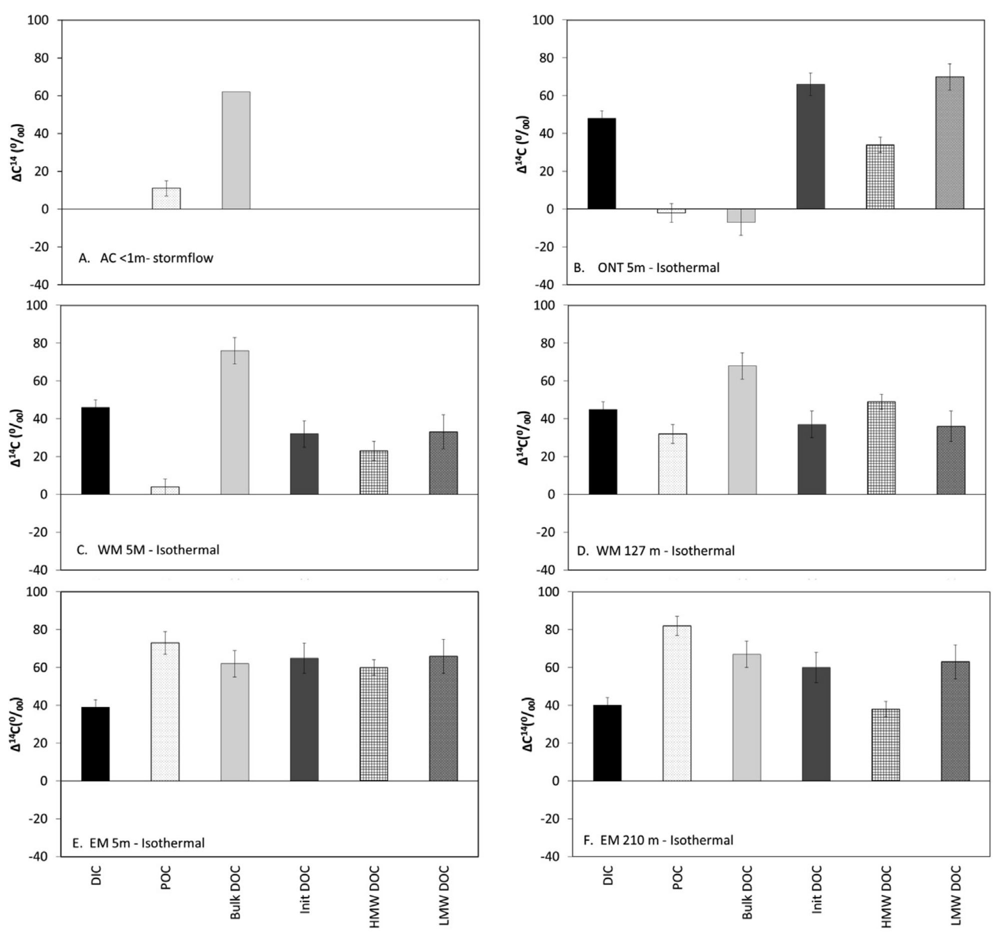

Fig. 2. Radiocarbon distributions of DIC and various organic carbon size fractions including POC (>0.7 μm), Bulk DOC (<0.7 μm), Init DOC (<0.2 μm), LMW DOC (<1 kDa), and HMW DOC (1 kDa – 0.2 μm) in the mixed Lake Superior water column (June 2010) and Amity Creek during stormflow condition (June 2008). POC data has been corrected using blank values published in Zigah et al., 2011 and Bulk DOC, Init DOC, and LMW DOC values have been blank corrected using the new data from NOSAMS.

the ultrafiltration process itself remains an open question at this time. As a very rough scaling of potential blank effects, we performed a radiocarbon mass balance estimate of "blank-corrected values" using the ultrafiltration carbon mass balance information and the $\Delta^{14}C$ value of bulk radiocarbon from our filtered Bulk DOC process blank (Zigah et al., 2012a). As an example, the EM deep-water (210 m) sample from August 2010 (Zigah et al., 2014 and Table 2) had an overall ultrafiltration carbon mass balance of 105%, indicating a potential blank that is 5% of the initial bulk water concentration (86 μmol C L^{-1}), thus a potential blank of 4.3 μmol C L^{-1}. If this blank is proportionally distributed between the high molecular weight and low molecular weight pools in the same manner as total C (Table 2), then the high molecular weight pool has a blank carbon concentration of 0.55 μmol C L^{-1}. Applying this in a radiocarbon mass balance equation (such as shown in equation (1)), leads to a HMW DOC $\Delta^{14}C$ value of 88‰, an enrichment of 24‰ relative to the reported value. As the assumptions involved in this "blank-correction" are highly speculative, we do not correct HMW DOC or LMW DOC values in the data presented here but the reader should realize that there is uncertainly in these numbers beyond that indicated by the precision terms in Tables 1 and 2.

3. Results

The revised results show the same broad trends reported in Zigah et al. (2014). Of the carbon pools in Lake Superior, the POC is most variable in terms of $\Delta^{14}C$ (Fig. 1), with a slightly increased range of values, −94 to 82‰ as compared to previously reported values of −94 to 53‰. As reported by Zigah

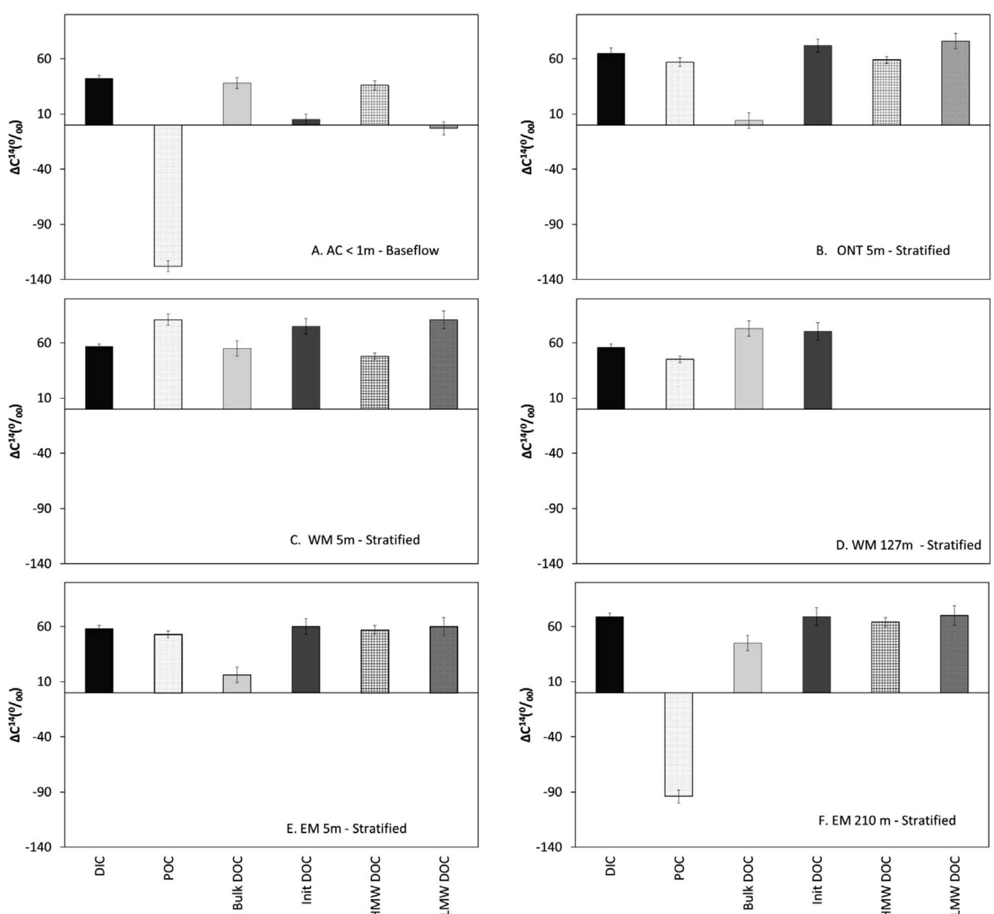

Fig. 3. The radiocarbon distributions of various organic carbon size fractions and DIC in the stratified Lake Superior water column (August 2010) and Amity Creek during baseflow condition (September 2010). POC values have been corrected using blank information from Zigah et al. (2011); Bulk, Init, and LMW DOC values have been blank corrected with the new data from NOSAMS and panel 3D has been corrected to reflect missing data for HMW and LMW DOC.

et al. (2014), the various size fractions of DOC generally contained positive (post-bomb) radiocarbon values and more variable $\delta^{13}C$ (Fig. 1). After blank correction, Bulk DOC remains the most variable of the DOC size fractions (with $\Delta^{14}C$ now ranging from −7 to 76‰). After blank correction and in contrast to previous reporting, nearshore values (site ONT Bulk DOC values for June and August 2010), while depleted in radiocarbon relative to other DOC fractions, are not distinguishable from modern values (Tables 1 and 2).

During spring mixing both uncorrected and corrected POC values at the western lake site (WM) show depletion in ^{14}C relative to co-occurring DIC, while at the eastern lake site (EM), the revised values show POC was enriched in ^{14}C relative to DIC in both surface and deep water samples. In the open lake, the POC relationship with the DOC pool is variable in terms of radiocarbon. During isothermal spring conditions blank-corrected POC $\Delta^{14}C$ was lower than that of co-occurring DOC size fractions at WM and higher than that of DOC size fractions at site EM. In stratified-water summer conditions, POC was similar in $\Delta^{14}C$ to Init DOC in the surface samples from the stratified summer lake, and lower than $\Delta^{14}C$ values in Init DOC at depth.

The general increase in $\Delta^{14}C$ values caused by the blank corrections changes relationships between both the particulate and dissolved organic carbon pools and dissolved inorganic carbon (DIC). All offshore sites now show isothermal values for Bulk DOC that are distinguishably enriched relative to co-occurring DIC (Fig. 2). The relationship between Bulk DOC and DIC radiocarbon values is more variable in the stratified period (Fig. 3). During the stratified season, surface water POC has radiocarbon values much more similar to DIC than in the isothermal period, though the stratified deep-water POC at the open water eastern basin site (EM) is considerably aged (Figs. 2 and 3).

Amity creek base flow and storm flow values do not vary much upon blank correction as they are fairly carbon rich relative to the lake samples. The main difference upon blank correction is that Init and LMW DOC in the baseflow creek are now defined as modern (not distinguishably pre-bomb), though they remain considerably depleted in radiocarbon relative to Bulk (>0.7 μm) and HMW DOC.

4. Discussion

Correction of Bulk, Init, and LMW DOC radiocarbon data using new NOSAMS blank values leads to more enriched $\Delta^{14}C$ values, with greater changes for the low-carbon open-water sites in Lake Superior. Correction of the POC values using a previously described process blank (Zigah et al., 2011) generally, but not always, yields more enriched $\Delta^{14}C$ values. The application of these corrections shifts relationships between the DOC, POC and DIC pools. The main observations presented in Zigah et al. (2014), however, remain valid. DOC size fractions remain generally modern (post-bomb) in both the open lake and in a tributary stream. POC, as compared to other water column carbon pools, has the most variable radiocarbon values, with pre-aged POC appearing in the baseflow stream sample and deep water at the open-lake eastern basin site during lake stratification.

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