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BLANK CORRECTION FOR $\Delta^{14}C$ MEASUREMENTS IN ORGANIC COMPOUND CLASSES OF OCEANIC PARTICULATE MATTER

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ABSTRACT. Contaminant carbon (blank carbon) was studied for its impact on the carbon isotope measurements ($\Delta^{14}C$ and $\delta^{13}C$) of 3 organic compound classes of oceanic particulate organic matter. Two methods of blank correction and associated uncertainties were studied. First, the carbon blanks were quantified manometrically and the isotope ratios of the blank carbon were measured directly. Second, the isotope ratios of the blank carbon were estimated using the standard dilution method from the difference in $\Delta^{14}C$ values between unprocessed and processed standards. The 2 methods agreed within the uncertainties. The standard deviations of numerous $\Delta^{14}C$ measurements made on processed standard compounds were comparable to those of real samples. Blank correction using the standard dilution method is much less sensitive to the error in determination of blank carbon mass than is correction using the directly measured mass and $\Delta^{14}C$ values of the blank carbon. The standard dilution method is recommended for correcting $\Delta^{14}C$ analyses of small samples that involve incorporation of a significant amount of blank carbon.

INTRODUCTION

The advent of accelerator mass spectrometry (AMS) has made radiocarbon isotope measurements possible on very small samples. As sample size decreases, the importance of extraneous carbon, or the procedural blank, increases. If the sample size is sufficiently large, the effect of the blank is minimized. However, frequently it is not possible to obtain large samples of environmental materials. Blank corrections for isotope ratio measurements are different from those for quantitative analyses because the isotopic signature of the blank must be considered as well as its mass. In the unique case where the isotopic signature of the blank is the same as that of the sample, there is no need to correct the sample results.

Assuming that blank carbon has constant mass and isotopic signatures in all samples, the ^{14}C measurement can be easily blank-corrected. However, since blank correction requires information on the mass and the isotopic signature of the blank, the uncertainty in either or both of these terms may require processing of as many blanks and standards as samples.

An important additional issue in blank correction is the assignment of uncertainties to blank-corrected results. Although a measurement uncertainty is reported with the $\Delta^{14}C$ result by AMS laboratories, the total uncertainty is larger if sample preparation incorporates a significant amount of blank carbon. Total uncertainties should include the uncertainties of the mass and isotopic signature of the blank carbon.

In a previous study, we separated several organic compound classes from oceanic particulate organic matter (POM) and reported their carbon isotope ratios (Hwang and Druffel 2003). Because of extensive sample handling and chemical treatments, incorporation of blank carbon was inevitable. For example, extraneous carbon may have been introduced as a result of incomplete removal of organic solvents, presence of carbon-containing impurities in reagents, bleeding of organic carbon from ion-exchange resins, vaporization of vacuum grease, incorporation of dust, and leakage of CO_2 into the vacuum manifold. We studied the cumulative effect of these sources on the carbon isotope ratio measurements and compared different methods of blank correction. We report an example of blank correction based on our $\Delta^{14}C$ measurements of organic compound classes of oceanic POM. Hereafter, "samples" refer to the organic fraction samples in our previous work (Hwang and Druffel 2003).

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PROCESSING OF SAMPLES, BLANKS, AND STANDARDS

In previous work, we separated 3 organic compound classes: lipids, total hydrolyzable amino acids (THAA), total hydrolyzable neutral carbohydrates (TCHO), as well as the acid-insoluble fraction from sinking POM. These 4 organic fractions comprised about 82 (±5)% of the total organic matter, with the rest lost during processing. Carbon isotope ratios of the organic fractions as well as total organic matter were measured.

A detailed description of the isolation method can be found in Wang et al. (1998). Briefly, lipids were extracted first using a 2:1 volume:volume mixture of methylene chloride:methanol. One half of the remaining sample was hydrolyzed with 6N HCl for 19 hr at 100 °C under N_2 gas. The hydrolyzate was neutralized with 1.5N NH_4OH, then eluted through a cation-exchange resin column to isolate THAA. The other half of the sample was hydrolyzed for 2 hr in 72% H_2SO_4 at room temperature, then for 3 hr in 1.2N H_2SO_4 at 100 °C. The hydrolyzate was neutralized with $Ba(OH)_2$ powder and NH_4OH, then eluted through an anion and cation mixed-resin column to isolate TCHO. Any organic carbon that remained after HCl-hydrolysis was defined as the acid-insoluble fraction. Separated organic fractions were transferred to quartz tubes (Vycor™), acidified with 1 mL of 3% phosphoric acid overnight, dried, evacuated under vacuum with CuO and silver foil, and flame-sealed, then combusted at 850 °C for 2 hr. Volume of the cryogenically purified CO_2 gas was measured manometrically. The last digit of the pressure gauge reading (0.01) was equivalent to 2 μg C. A split of the resultant CO_2 was graphitized on a Co catalyst under H_2 gas at 580 °C for 8 hr. The $\Delta^{14}C$ and $\delta^{13}C$ values were measured at the National Ocean Sciences AMS Facility, Woods Hole Oceanographic Institution, USA (NOSAMS); the Center for AMS Research, Lawrence Livermore National Laboratory, USA (LLNL); and the Keck Carbon Cycle AMS Laboratory, University of California, Irvine, USA (KCCAMS). The internal precision for the $\Delta^{14}C$ and $\delta^{13}C$ measurements was 5‰ and 0.1‰, respectively.

For the purpose of blank correction, we ran zero-material blanks by processing initially empty reaction vessels in a manner identical to the processing of a sample. Therefore, "blank carbon" in this paper is extraneous carbon introduced during the processing for separation of each organic fraction and combustion of extracted samples to CO_2 gas, which are the main processes for contamination. Contaminant carbon introduced during further processing—including splitting CO_2 gas for $\Delta^{14}C$ and reducing it to graphite—is not counted in the blank correction in this paper.

We also analyzed cod liver oil (SQUIBB), an amino acid standard solution (SIGMA AA-S-18, 18 amino acids), and anhydrous D-glucose powder (Fisher, certified grade) as standards for lipid, THAA, and TCHO fractions, respectively, in a manner identical to the processing of a sample. Two sizes of each standard were processed. One size was close to the range of sizes typically obtained for organic fractions of sinking POM (0.5 to 0.9 mg C) and the other was larger (2 to 4 mg C). The presumed "true" $\Delta^{14}C$ and $\delta^{13}C$ values of the standards were obtained by combustion of large (2.8 to 11 mg C) unprocessed material to minimize the blank effect from the combustion process.

RESULTS AND DISCUSSION

Direct Measurements of Masses and Isotopic Signatures of Blank Carbon

The average masses of blank carbon were 0.025 ± 0.017, 0.042 ± 0.038, and 0.053 ± 0.029 mg C for lipids, THAA, and TCHO, respectively. These are 3, 6, and 7% of the average masses of the lipid, THAA, and TCHO samples that were previously obtained for POM, respectively. The blank carbon would cause significant differences in the $\Delta^{14}C$ results if the $\Delta^{14}C$ values of blank carbon were different from those of the samples. The mass of the blank carbon for the acid-insoluble fraction was

0.006 ± 0.002 mg C, or 0.4% of the average sample size. In the worst-case scenario, blank carbon ($\Delta^{14}C = -1000‰$) would change the $\Delta^{14}C$ value of a sample ($\Delta^{14}C = 0‰$) by 4‰ according to a simple mass balance calculation, which is small compared to the uncertainty of the $\Delta^{14}C$ measurement.

Masses of blank carbon for each organic fraction do not show a statistical distribution around a mean, likely because of the small number of repetitions. Therefore, we assigned 1 standard deviation for each sample type as the uncertainty in the mass of the blank. However, it should be noted that 1 standard deviation in this case provides a smaller confidence level than in the case of a normal distribution (68%).

For the $\Delta^{14}C$ measurements, material from 5 to 6 runs was combined to obtain enough CO_2. Because of this pooling, information regarding the variability of the individual isotope ratios of blank carbon was lost. The $\Delta^{14}C$ values of blank carbon measured from the combined blanks were –800, –313, and –171‰ for lipids, THAA, and TCHO, respectively (Table 1).

Table 1 Measured and estimated values of masses and isotopic signatures of the blank for each organic fraction.

Type	Blank mass (m_b) measured[1] (mg C ± 1 SD)	Blank mass (m_b) estimated[2] (mg C)	$\Delta^{14}C$ (Δ_b) measured[3] (‰)	$\Delta^{14}C$ (Δ_b) estimated[4] (‰)	$\Delta^{14}C$ (Δ_b) estimated[2] (‰)
Lipids	0.025 ± 0.017 (6)	—	–800 ± 5	–600 ± 470	—
THAA	0.042 ± 0.038 (6)	0.023 ± 0.028	–313 ± 5	–630 ± 420	–950 ± 1300
TCHO	0.053 ± 0.029 (6)	—	–171 ± 5	–400 ± 300	—
Acid insoluble	0.006 ± 0.002 (5)	—	—	—	—

[1]Measured mass of blank carbon (m_b). The uncertainties are 1 standard deviations of the masses of blank of individual processing. In parentheses is the number of analyses.

[2]Estimated mass and the $\Delta^{14}C$ value of blank carbon for THAA using 2 standards: an AA standard solution and glutamic acid. The standard dilution method was used for calculation (see text). The uncertainties are propagated errors of the standard errors for slopes of the linear regression lines.

[3]Measured $\Delta^{14}C$ values of the accumulated blanks. The uncertainty reported by CAMS, LLNL is reported.

[4]The $\Delta^{14}C$ values calculated from the measured m_b and the results of the processed and the unprocessed standards. Each set (m_{s+b}, Δ_{s+b}) of standards was used with average Δ_s and m_b to calculate Δ_b using equation (1). The average of the calculated Δ_b values for each type is reported here. The uncertainties are the largest value among the calculated uncertainties using each set (m_{s+b}, Δ_{s+b}) of standards, and the standard deviation of calculated Δ_b values.

Estimation of Isotopic Signatures of Blank Carbon Using Standards

If incorporation of blank carbon has a significant effect on the $\Delta^{14}C$ measurement of samples, an effect will be observed when chemical standards are processed in the same way as the sample. Therefore, the change in $\Delta^{14}C$ of a standard by processing can be used to estimate the mass and $\Delta^{14}C$ value of the blank carbon (Pearson et al. 1998; McNichol et al. 2000).

The $\Delta^{14}C$ and $\delta^{13}C$ values and the sizes of the processed standards are listed in Table 2. The $\Delta^{14}C$ values of the smaller-sized standards after processing were lower than the true values by 17‰, 38‰, and 49‰ for lipids, THAA, and TCHO standards, respectively (Table 2). These changes are larger than measurement uncertainties reported by AMS laboratories (3–8‰), clearly showing the need for blank corrections.

The variability of $\Delta^{14}C$ values for the processed standards provides an estimate of the uncertainty expected for real samples, provided their sizes and $\Delta^{14}C$ values are similar to the samples. The standard deviations for $\Delta^{14}C$ values of standards of similar size (0.5–0.9 mg C) to our samples were ±14, ±10, and ±15‰ for lipids, THAA, and TCHO standards, respectively (Table 2).

Table 2 The masses, $\Delta^{14}C$, $\delta^{13}C$ values and the average values (±SD) of the unprocessed and processed standards.

Standard		Size (mg C)	$\Delta^{14}C$ (‰)	Average	$\delta^{13}C$ (‰)	Average
Cod liver oil	unprocessed (Δ_{std})	2.98	47		–25.5	
		11.69	44		–25.5	
		9.83	46		–25.4	
		11.31	37		–25.4	
		0.58	38	43 ± 5	–25.4	–25.4 ± 0.1
		1.48	45		–25.4	
		2.22	44		–25.3	
		7.21	43		–25.4	
	processed (Δ_{std+b})	3.32	39	36 ± 5	–25.4	–25.4 ± 0.1
		3.53	37		–25.4	
		0.85	11		–25.7	
		0.92	34	26 ± 14	–25.5	–25.6 ± 0.1
		0.67	34		–25.5	
AA standard solution	unprocessed (Δ_{std})	3.60	–166		–19.9	
		3.19	–189	–176 ± 12	–19.9	–19.9 ± 0.1
		1.69	–173			
	processed (Δ_{std+b})	2.49	–192		–20.2	
		0.74	–226		–20.9	
		0.77	–222		–20.7	
		0.74	–211	–214 ± 10	–20.7	–20.7 ± 0.1
		0.73	–211		–20.6	
		0.65	–200		–20.7	
D-glucose	unprocessed (Δ_{std})	8.08	107		–10.2	
		8.63	88		–10.2	
		7.65	96		–10.0	
		8.20	101		–10.0	
		7.14	95	98 ± 6	–9.9	–10.0 ± 0.1
		0.67	106		–10.0	
		0.93	94		–10.0	
		1.81			–10.0	
		5.10	95		–10.0	
	processed (Δ_{std+b})	1.823	89	84 ± 5	–10.5	–10.6 ± 0.1
		1.810	80		–10.8	
		0.578	45		–10.5	
		0.558	67	49 ± 15	–10.7	–10.6 ± 0.1
		0.520	54			
		0.560	32		–10.7	

As a test for consistency of blanks (i.e. constant mass and isotopic signatures of blank carbon from run to run), the true isotopic signatures of the standards were estimated from those of the processed standards using the standard dilution method. If isotope ratios of at least 2 different-sized standards are measured, the true value of the standard can be estimated from a mass balance equation (Hayes 2002):

$$\Delta_{s+b} m_{s+b} = \Delta_b m_b + \Delta_s m_s = \Delta_b m_b + \Delta_s (m_{s+b} - m_b) \quad (1)$$

where Δ is $\Delta^{14}C$, m is mass of carbon, and subscripts $_b$ and $_s$ are blank and standard, respectively. Fractional abundance of ^{14}C must be rigorously used for the mass balance calculation. For environmental samples, however, using $\Delta^{14}C$ instead of fractional abundance will cause a negligible error compared to the measurement uncertainty of $\Delta^{14}C$ (see John Hayes' excellent lecture notes: Hayes 2002). Assuming that Δ_b and m_b are constant, equation (1) can be expressed as a linear equation with $1/m_{s+b}$ as the x variable and Δ_{s+b} as the y variable:

$$\Delta_{s+b} = \Delta_s + (\Delta_b - \Delta_s)m_b \times \frac{1}{m_{s+b}} \quad (2)$$

The true $\Delta^{14}C$ (or $\delta^{13}C$) of the standard (Δ_s) is the y intercept of the linear regression line. The $\Delta^{14}C$ values of the standards for several different sizes that have undergone the same separation processes as the samples were used to calculate Δ_s (Figure 1a–c). The y intercepts (Δ_s) calculated by linear regression of the data were 40 ± 11‰, –190 ± 16‰, and 99 ± 14‰ (the uncertainties are standard errors) for cod liver oil, AA standard solution, and D-glucose, respectively. These were within the uncertainties of the true $\Delta^{14}C$ values of the unprocessed standards (thick lines on the y axes of each graph: 43 ± 5, –176 ± 12, and 98 ± 6 for cod liver oil, AA standard solution, and D-glucose, respectively). Since the true $\Delta^{14}C$ values of the standards could indeed be estimated from those of the processed standards, this indicates that the masses and the isotopic signatures of blank carbon were consistent from run to run within the error range of our true values (Figure 1).

Theoretically, both the mass and isotopic signature of the blank carbon can be calculated using the standard dilution method if two or more kinds of standards are used. Two different values for the slope in equation (2), $(\Delta_b - \Delta_s)m_b$, from 2 different standards, enable calculation of both Δ_b and m_b, when Δ_s is known. However, only 1 standard was used for each organic fraction in previously reported work. Therefore, only 1 mass balance equation was available for 2 variables, requiring one of them to be determined by an independent method. Once m_b or Δ_b is determined, the other can be calculated using the mass balance equation (1). For example, $\Delta^{14}C$ of blank carbon (Δ_b) for a lipid standard (measured mass of the standard, m_{s+b} = 0.92 mg C; Δ_{s+b} = 34‰) can be calculated from the $\Delta^{14}C$ value of the unprocessed standard (Δ_s = 43‰) and mass of blank carbon (m_b = 0.025 mg C) using equation (1); $34‰ \times 0.92 = \Delta_b \times 0.025 + 43‰ \times (0.92–0.025)$, Δ_b = –288‰. Averages of the estimated Δ_b values from results of the processed standard for each organic fraction in this way are –600 ± 470‰, –630 ± 420‰, and –400 ± 300‰ for lipids, THAA, and TCHO fractions, respectively (Table 1). The estimated $\Delta^{14}C$ values have large uncertainties; therefore, they are not different from the measured values. The large uncertainties are mainly caused by the uncertainties in m_b measurements.

For the THAA fraction, glutamic acid was also used as a standard later in the laboratory. We used the results of glutamic acid, in addition to those of the AA standard solution, to calculate Δ_b and m_b using the standard dilution method. Both Δ_b and m_b were calculated using the values of the 2 linear regression lines (Figure 2 and Table 1). Unfortunately, the uncertainties for Δ_b and m_b were large, mainly because the slopes were similar to each other (–17.6 and –24.4). Subtraction of 2 similar values with large uncertainties resulted in a large total uncertainty. Therefore, for the effective use of the standard dilution method, it is crucial to choose standards that have considerably different $\Delta^{14}C$ values to obtain a small total uncertainty.

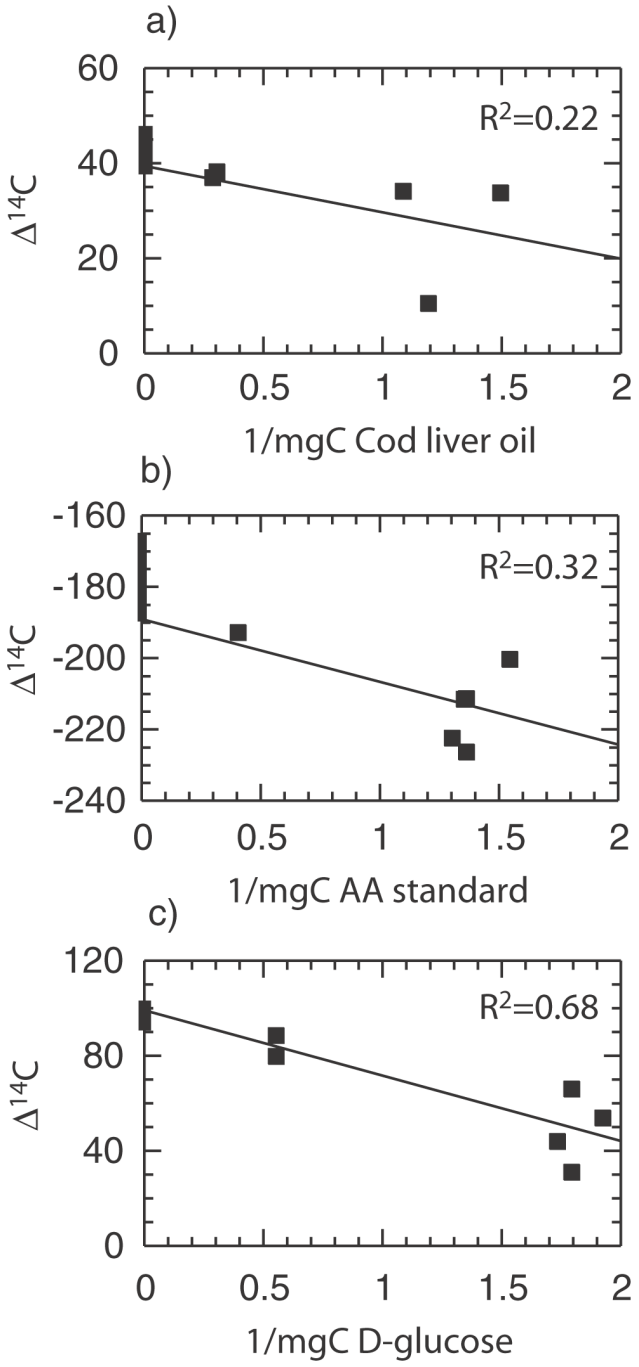

Figure 1 Estimation of true $\Delta^{14}C$ values of the standards from those of the processed standards for a) cod liver oil, b) AA standard solution, and c) D-glucose by the standard addition method. The thick line on the left *y* axis of each graph indicates the true values determined by combustion of large unprocessed standards, with 1 standard deviation of individual standards (Table 2).

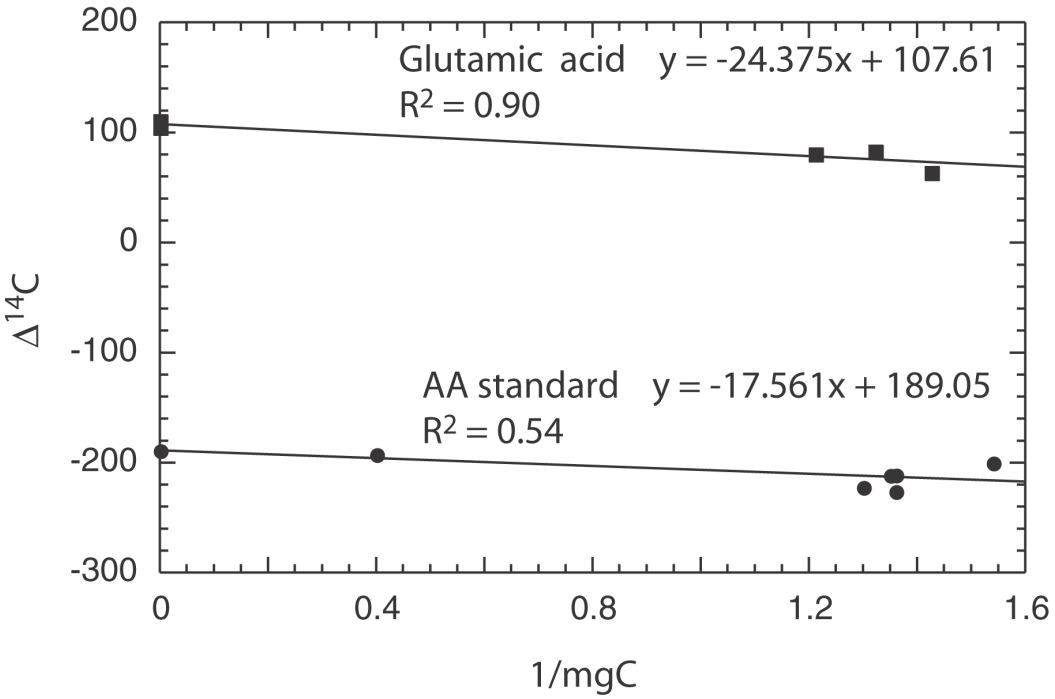

Figure 2 The standard dilution method was used to calculate the mass and $\Delta^{14}C$ value of blank carbon for the THAA fraction from the results of an AA standard solution and glutamic acid (see text).

Blank Correction and Associated Uncertainties

Blank correction can be performed using the mass balance equation:

$$\Delta_{smp} = \frac{\Delta_{smp+b} \times m_{smp+b} - \Delta_b \times m_b}{m_{smp+b} - m_b} \quad (3)$$

where subscript $_{smp}$ is sample, and $_b$ is blank. Equation 3 can be used when Δ_b, m_b, and their uncertainties can be directly determined. However, the uncertainty of Δ_b could not be determined because the mass of blank carbon from individual processing was too small for $\Delta^{14}C$ measurement.

However, mathematically more robust calculations for both blank correction and uncertainty determination can be used when one or more of these numbers is not measured directly. Equation (3) is modified in equation (4), so that $\Delta_b \times m_b$ can be determined indirectly from the processed (Δ_{std+b}) and unprocessed (Δ_{std}) standards:

$$\Delta_{smp} = \frac{\Delta_{smp+b} \times m_{smp+b} - [\Delta_{std+b} \times m_{std+b} - \Delta_{std} \times (m_{std+b} - m_b)]}{m_{smp+b} - m_b} \quad (4)$$

where subscript $_{std}$ is standard.

The total uncertainties can be determined mathematically in equation (4) because the uncertainties for all variables are available. (Detailed equations for the total uncertainty calculation appear in the Appendix.) The blank-corrected $\Delta^{14}C$ value of a sample (Δ_{smp}) is calculated from one sample result (Δ_{smp+b}, m_{smp+b}) using the results of a processed standard (Δ_{std+b}, m_{std+b}). Table 3 shows an example

of blank correction for a lipid $\Delta^{14}C$ measurement (Δ_{smp+b} = –36‰, m_{smp+b} = 0.79) using 3 sets of standard results (Δ_{std+b} = 34‰, 34‰, 11‰ when m_{std+b} = 0.92, 0.67, and 0.85 mg C, respectively). The average value (–21‰) of the 3 results of Δ_{smp} is reported as the blank-corrected $\Delta^{14}C$ value. The total uncertainty for each standard result ($\sigma\Delta_{smp}$ in each row in Table 3) is calculated using equation (A1). The larger of the average of the total uncertainties ($\sigma\Delta_{smp}$) and the standard deviation of the 3 blank-corrected $\Delta^{14}C$ values (Δ_{smp}) is reported as the final uncertainty (in this case, 15‰).

Table 3 An example of blank correction. A measured $\Delta^{14}C$ value (Δ_{smp+b}) is blank corrected using equation (4). The total uncertainties are calculated using equation (A1). Three sets of standard results (Δ_{std+b}, m_{std+b}) are used to correct the sample result. The average value (–21‰) of the calculated Δ_{smp} (–27.8, –30.7, and –3.0‰) is taken as the blank-corrected value. The larger of the average (9.5‰) of the total uncertainties ($\sigma\Delta_{smp}$, 10.0, 8.2, and 10.2‰) and the standard deviation (15‰) of the blank-corrected values (Δ_{smp}, –27.8, –30.7, and –3.0‰) is taken as the final uncertainty. Therefore, the blank-corrected result in this example is –21 ± 15‰. (The lower set of rows is a continuation of the upper set.)

Standards	Δ_{smp+b}[1] ‰	$\sigma\Delta_{smp+b}$[2] ‰	Δ_{std+b}[3] ‰	$\sigma\Delta_{std+b}$[2] ‰	Δ_{std}[4] ‰	$\sigma\Delta_{std}$[4] ‰	m_{smp+b}[5] mg	σm_{smp+b}[6] mg	m_{std+b}[3] mg	σm_{std+b}[6] mg
Lipids	–36	5	34	5	43	5	0.79	0.04	0.92	0.092
	–36	5	34	5	43	5	0.79	0.04	0.67	0.067
	–36	5	11	5	43	5	0.79	0.04	0.85	0.085

m_b[7] mg	σm_b[7] mg	$\frac{\partial\Delta_{smp}}{\partial\Delta_{smp+b}}$	$\frac{\partial\Delta_{smp}}{\partial\Delta_{std+b}}$	$\frac{\partial\Delta_{smp}}{\partial\Delta_{std}}$	$\frac{\partial\Delta_{smp}}{\partial m_{smp+b}}$	$\frac{\partial\Delta_{smp}}{\partial m_{std+b}}$	$\frac{\partial\Delta_{smp}}{\partial m_b}$	Δ_{smp}[8] ‰	$(\sigma\Delta_{smp})^2$	$\sigma\Delta_{smp}$[9] ‰
0.025	0.017	1.0	–1.2	1.2	–10.8	11.8	–92.5	–27.8	100.9	10.0
0.025	0.017	1.0	–0.9	0.8	–6.9	11.8	–96.3	–30.7	67.0	8.2
0.025	0.017	1.0	–1.1	1.1	–43.1	41.8	–60.2	–3.0 Avg = –21 SD = 15	103.2	10.2

[1]Measured $\Delta^{14}C$ value of a lipid fraction.
[2]The internal precision (the measurement uncertainty only) is given as the uncertainty of any measured $\Delta^{14}C$ values.
[3]$\Delta^{14}C$ values and mass of the processed standards. Three sets of $\Delta^{14}C$ value and mass of the processed cod liver oil were used for blank correction of 1 sample $\Delta^{14}C$ value.
[4]Average $\Delta^{14}C$ value of the unprocessed cod liver oil and 1 standard deviation as the uncertainty.
[5]Mass of lipid fraction measured manometrically.
[6]5% of the measured value was assigned as an uncertainty for any measured mass.
[7]Measured mass of blank carbon. One standard deviation was assigned as the uncertainty.
[8]Blank-corrected values.
[9]The total uncertainties of the blank-corrected result.

An example of a lipid $\Delta^{14}C$ measurement (first row in Table 3, Δ_{smp+b} = –36‰, Δ_{std+b} = 34‰, Δ_{std} = 43‰, m_{smp+b} = 0.79, m_{std+b} = 0.92; second row, m_b = 0.025) was used as a model case to study the dependence of the total uncertainty on m_b and m_{std+b} in the following discussion. Equation (4) is especially useful when direct measurements of m_b and Δ_b are subject to large uncertainties. The uncertainty ($\sigma\Delta_{smp}$) of the blank-corrected result is not heavily dependent on m_b, as explained by the small values of $\partial\Delta_{smp}/\partial m_b$ ($\partial\Delta_{smp}/\partial m_b$ = –93, meaning a –93‰ change in Δ_{smp} per 1 mg error in determination of the mass of the blank. See the first row of Table 3 and the Appendix for the calculation of $\partial\Delta_{smp}/\partial m_b$. An error of ±0.017 mg C (σm_b), associated with determination of m_b, is equivalent to ±1.6‰ in the final result. Figure 3 shows that when equation (4) is used (solid line),

the blank-corrected $\Delta^{14}C$ value does not change much depending on m_b. However, if the directly measured values (Equation 3) are used, the blank-corrected $\Delta^{14}C$ value changes much more than the $\Delta^{14}C$ value determined by the standard dilution method (Equation 4). For example, $\partial\Delta_{smp}/\partial\, m_b = [m_{smp+b} \times (\Delta_{smp+b}-\Delta_b)]/(m_{smp+b}-m_b)^2 = 789‰/\text{mg C}$ when the same values are used.

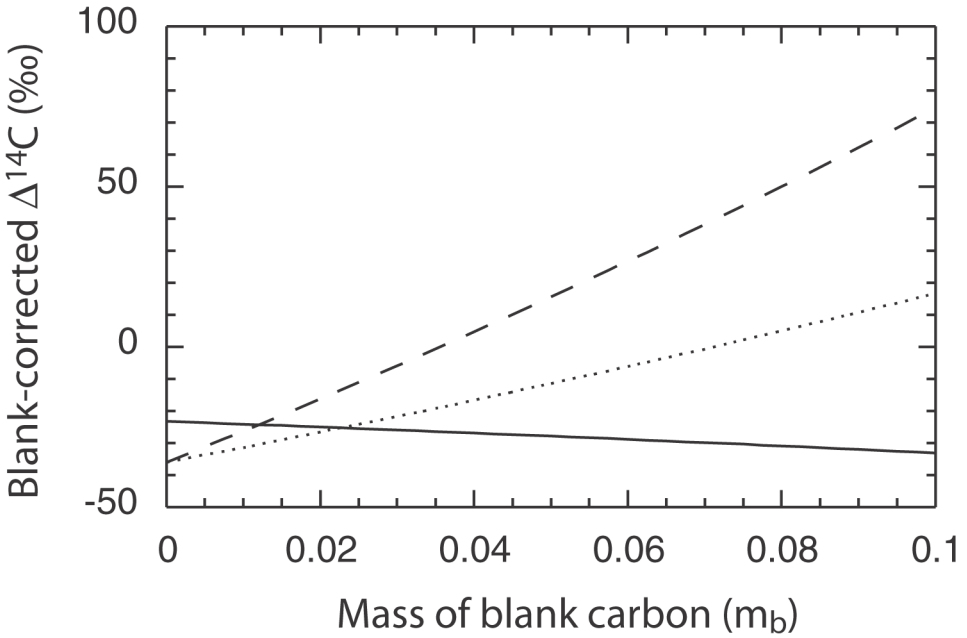

Figure 3 A model case showing the dependence of blank-corrected $\Delta^{14}C$ results on the mass of blank carbon (m_b). All other parameters were fixed in the model case and m_b was varied to simulate an error in its determination. Blank-corrected results were much less sensitive when equation (4) was used (standard dilution method, solid line) than when equation (3) was used (direct measurements). The dotted and dashed are when the blank $\Delta^{14}C$ value was –400‰ and –800‰, respectively.

Low sensitivity to the uncertainty in m_b is important because the direct measurements of m_b can be erroneous. The incorporation of blank carbon during the simulated processing of a sample may not adequately mimic the incorporation of extraneous carbon when a sample is present. This may be caused by differences in the physical environment, such as the surface of the sample, existence of mineral in the real sample to enhance the sorption of blank carbon, or other factors. Manometric determination of CO_2 also can be erroneous. During the cryogenic purification of CO_2, other vapors (such as N_2O, NO, HCl, and H_2O) can escape a dry ice/isopropyl alcohol trap and be collected in the liquid nitrogen trap with the CO_2 gas (Pearson et al. 1998; Currie at al. 2000). For the absolute determination of CO_2 gas, other analytical methods (such as gas chromatography and mass spectrometry) are necessary (Pearson et al. 1998).

It is important to use a small standard when employing the standard dilution method for blank correction because the total uncertainty of the blank-corrected value increases as m_{std+b} increases (Figure 4). This is because the effect of blank becomes less significant as the size of a standard increases. The total uncertainty was calculated as a function of the size of a standard, using our model case in Table 3 to demonstrate this. When the size of the standard exceeds 1 mg C, total uncertainty exceeds 10‰. Although 2 sizes of standards were processed, the larger standards resulted in over ±20‰ total uncertainties.

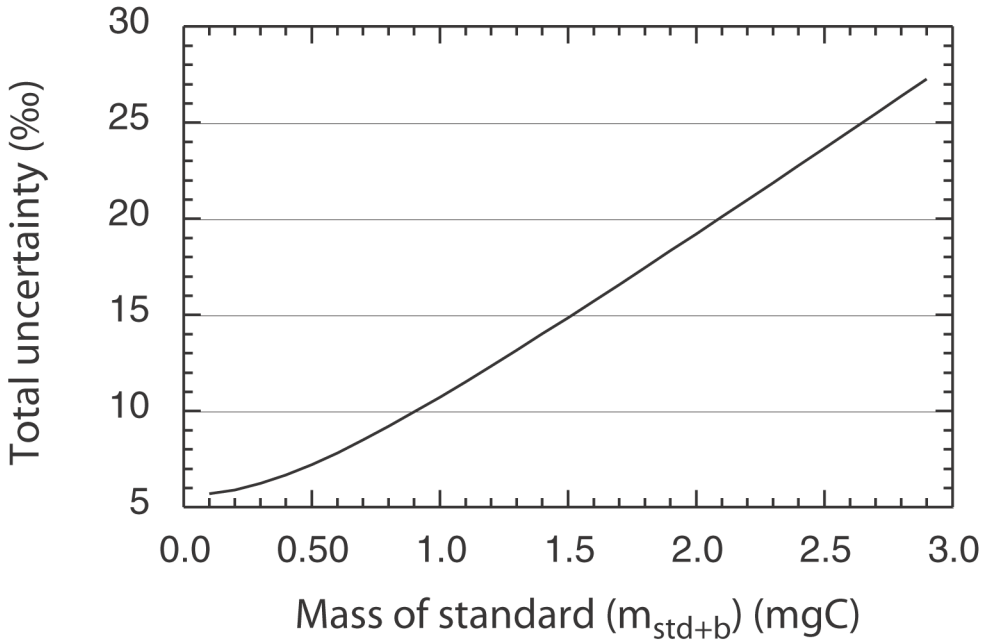

Figure 4 A model case showing the dependence of total uncertainty of a blank-corrected $\Delta^{14}C$ value of a sample on the mass of standard when the standard dilution method was used. The total uncertainty was calculated using equation (A1), varying m_{std+b} and consequently Δ_{std+b}, but with the other parameters fixed. As the mass of a standard increases, total uncertainty increases as well. The plot shows that the mass of the standard should be smaller than 1 mg C to obtain a total uncertainty smaller than 10‰.

The total uncertainties of $\Delta^{14}C$, when equation (4) was used for blank correction of samples in previous work, were 15‰ for lipids (Table 3) and 13 and 21‰ for THAA, and TCHO, respectively (not shown). These values are comparable to the standard deviations of the processed standards of similar size discussed previously in the section "Estimation of Isotopic Signatures of Blank Carbon Using Standards" (Table 2). The fact that the uncertainties determined by the 2 methods are comparable makes the assigned total uncertainties meaningful. Furthermore, it implies that if a proper standard is used, the uncertainty obtained from the processed standard can be justifiably assigned for a sample.

Verification of Blank-Corrected Values

The $\Delta^{14}C$ value of a total organic matter sample can be calculated using a mass balance equation from the percentages of the 4 organic fractions extracted from the sample and their $\Delta^{14}C$ values. Although not perfect (because the recovered fractions comprise only about 82% of the bulk samples), the $\Delta^{14}C$ values calculated in this way can be compared to those measured independently by combustion of total organic matter samples. When the initial results of the organic fractions were used without blank correction, the calculated $\Delta^{14}C$ values of the total organic matter samples (open squares in Figure 5) were lower than the measured values by an average of 16 (±10)‰. This is consistent with the existence of a blank carbon with a $\Delta^{14}C$ value lower than that of the sample. After blank correction using the standard dilution method (solid squares in Figure 5), the average difference between the calculated and measured $\Delta^{14}C$ values was 1 ± 10‰.

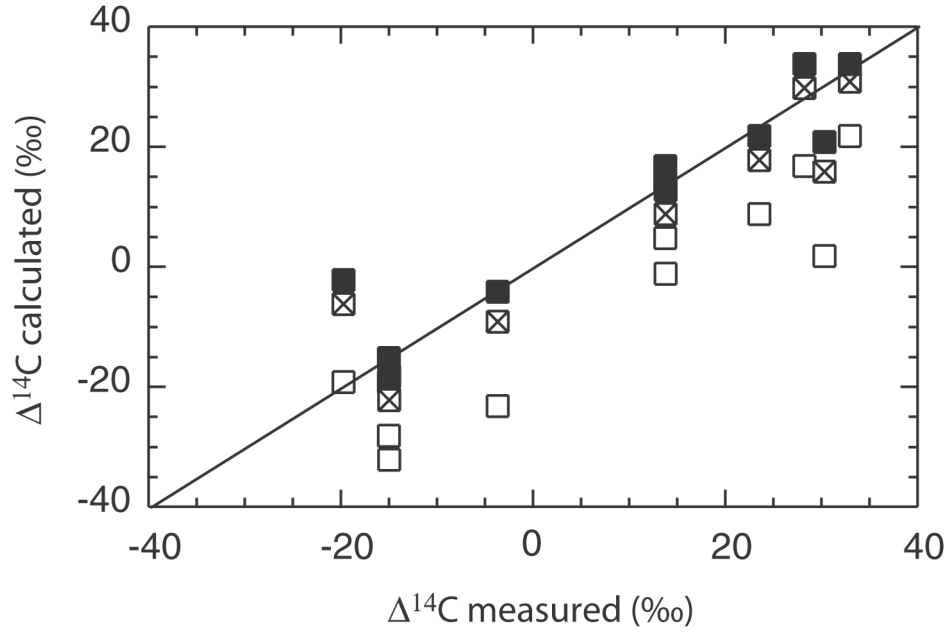

Figure 5 Independently measured $\Delta^{14}C$ values of the total organic matter were compared to the calculated values from the 4 organic fractions using a mass balance equation. Open squares are the results when raw $\Delta^{14}C$ values of the organic fractions were used for a mass balance calculation. Solid squares and open squares with diagonal crosses are the results when $\Delta^{14}C$ values of the organic fractions were blank-corrected using measured m_b and estimated Δ_b (standard dilution method) and measured m_b and Δ_b (direct measurements), respectively. The calculated $\Delta^{14}C$ values using blank-corrected values of the organic fractions were close to the $\Delta^{14}C$ values of total organic matter.

CONCLUSION

It has been shown that the incorporation of contaminant carbon during processing can change the $\Delta^{14}C$ values of small organic samples beyond the uncertainties inherent in the $\Delta^{14}C$ measurements themselves. Two methods of blank correction were compared. For direct measurements, repetition of processing is necessary to obtain enough CO_2 for the $\Delta^{14}C$ measurements. The uncertainty in the $\Delta^{14}C$ determination of individual blanks cannot be obtained by this method. The total uncertainty by this method heavily depends on the uncertainty in determination of the mass of blank carbon, the measurement of which may be erroneous (i.e. contaminating gases). Furthermore, handling of small-volume samples on a vacuum line to combine the individual blanks is subject to more contamination.

The standard dilution method is recommended for blank correction, though it is time consuming and requires numerous $\Delta^{14}C$ measurements of standards. Processing of two or more types of standards is the best method to obtain both the mass and $\Delta^{14}C$ values of blank carbon. However, it must be noted that the standards should have a wide range of $\Delta^{14}C$ values in order to obtain small total uncertainties.

When only one kind of standard is used, the mass of blank carbon needs to be determined by an independent method. However, blank correction using this method is not very sensitive to the error in determination of the mass of blank carbon. Another advantage of the standard dilution method is that the standard can be chosen or made to simulate samples closely. For example, an amino acid

mixed with carbon-free minerals can be used as a standard for THAA of POM or sediment. The results of standards can provide a realistic estimate of the actual total uncertainty for isotopic measurements of samples. This is useful especially when multiple analyses of one sample are not possible due to size limitations.

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APPENDIX

Error Analysis

The total uncertainty of the blank-corrected values using equation (4) can be calculated by the following equation:

$$(\partial\Delta_{smp})^2 = \left(\frac{\partial\Delta_{smp}}{\partial\Delta_{smp+b}}\right)^2(\partial\Delta_{smp+b})^2 + \left(\frac{\partial\Delta_{smp}}{\partial\Delta_{std+b}}\right)^2(\partial\Delta_{std+b})^2 + \left(\frac{\partial\Delta_{smp}}{\partial\Delta_{std}}\right)^2(\partial\Delta_{std})^2 \quad \text{(A1)}$$

$$+ \left(\frac{\partial\Delta_{smp}}{\partial m_{smp+b}}\right)^2(\partial m_{smp+b})^2 + \left(\frac{\partial\Delta_{smp}}{\partial m_{std+b}}\right)^2(\partial m_{std+b})^2 + \left(\frac{\partial\Delta_{smp}}{\partial m_b}\right)(\partial m_b)^2$$

where Δ and m are $\Delta^{14}C$ (or $\delta^{13}C$) and mass of blank carbon, respectively, and subscripts $_{smp}$, $_{std}$, and $_b$ are sample, standard, and blank, respectively;

$$\frac{\partial\Delta_{smp}}{\partial\Delta_{smp+b}} = \frac{m_{smp+b}}{m_{smp+b} - m_b}$$

$$\frac{\partial \Delta_{smp}}{\partial \Delta_{std+b}} = \frac{-m_{std+b}}{m_{smp+b} - m_b}$$

$$\frac{\partial \Delta_{smp}}{\partial \Delta_{std}} = \frac{m_{std+b} - m_b}{m_{smp+b} - m_b}$$

$$\frac{\partial \Delta_{smp}}{\partial m_{smp+b}} = \frac{-m_b \times (\Delta_{smp+b} - \Delta_{std}) + m_{std+b} \times (\Delta_{std+b} - \Delta_{std})}{(m_{smp+b} - m_b)^2}$$

$$\frac{\partial \Delta_{smp}}{\partial m_{std+b}} = \frac{-\Delta_{std+b} + \Delta_{std}}{m_{smp+b} - m_b}$$

$$\frac{\partial \Delta_{smp}}{\partial m_b} = \frac{m_{smp+b} \times (\Delta_{smp+b} - \Delta_{std}) - m_{std+b} \times (\Delta_{std+b} - \Delta_{std})}{(m_{smp+b} - m_b)^2} .$$