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## EXTRANEOUS CARBON ASSESSMENTS IN RADIOCARBON MEASUREMENTS OF BLACK CARBON IN ENVIRONMENTAL MATRICES

Alysha I Coppola<sup>1,2</sup> • Lori A Ziolkowski<sup>3</sup> • Ellen R M Druffel<sup>1</sup>

**ABSTRACT.** Extraneous carbon ( $C_{ex}$ ) added during chemical processing and isolation of black carbon (BC) in environmental matrices was quantified to assess its impact on compound specific radiocarbon analysis (CSRA). Extraneous carbon is added during the multiple steps of BC extraction, such as incomplete removal of solvents, and carbon bleed from the gas chromatographic and cation columns. We use 2 methods to evaluate the size and  $\Delta^{14}C$  values of  $C_{ex}$  in BC in ocean sediments that require additional pretreatment using a cation column with the benzene polycarboxylic acid (BPCA) method. First, the direct method evaluates the size and  $\Delta^{14}C$  value of  $C_{ex}$  directly from the process blank, generated by processing initially empty vials through the entire method identically to the treatment of a sample. Second, the indirect method quantifies  $C_{ex}$  as the difference between processed and unprocessed (bulk)  $\Delta^{14}C$  values in a variety of modern and  $^{14}C$ -free or “dead” BC standards. Considering a suite of hypothetical marine sedimentary samples of various sizes and  $\Delta^{14}C$  values and BC Ring Trial standards, we compare both methods of corrections and find agreement between samples that are  $>50 \mu\text{g C}$ . Because  $C_{ex}$  can profoundly influence the measured  $\Delta^{14}C$  value of compound specific samples, we strongly advocate the use of multiple types of process standards that match the sample size to assess  $C_{ex}$  and investigate corrections throughout extensive sample processing.

### INTRODUCTION

Black carbon (BC) is produced from the incomplete combustion of fossil fuels and biomass, ubiquitous in the atmosphere, sediments, soils, and water, and influences a wide range of biogeochemical processes (Schmidt and Noack 2000; Watson et al. 2005). With the new technological developments and smaller accelerator mass spectrometry (AMS) sample size requirements (Santos et al. 2007), the ability to isolate individual compounds using compound specific radiocarbon analysis (CSRA) allows for better understanding of the timescales of individual compounds from a carbon pool (Eglinton et al. 1996; Ingalls and Pearson 2005). The turnover times of BC within these pools are determined by partially oxidizing aromatic BC in environmental matrices using the benzene polycarboxylic acid (BPCA) method to form marker compounds, benzene polycarboxylic acids (BPCAs). These environmental matrices contain non-BC organic matter, fine siliceous dust and heavy metals in a heterogeneous mixture, which can complicate the processing of a BC sample. In turn, for BC to be separated from the matrix, extensive treatment is needed to remove metals that interfere with BC extraction using the BPCA method (Brodowski et al. 2005; Ziolkowski and Druffel 2009). However, extensive processing adds extraneous ( $C_{ex}$ ) carbon, thereby influencing the size and  $\Delta^{14}C$  value of the BC sample (Santos et al. 2007; Ziolkowski and Druffel 2009). The  $C_{ex}$  originates from 2 major sources: (1) the chemical processing associated with extracting the BC from the sample (in this case, the BPCA method and pretreatment) and (2) the purification of BPCA marker compounds on a preparative capillary gas chromatograph (PCGC). After correction for graphitization and combustion (Santos et al. 2007), the mass of  $C_{ex}$  and the  $\Delta^{14}C$  value of the CSRA sample ( $C_{measured}$ ) originates from the contributions of 2 sources (Equation 1):

$$C_{measured} = C_{BPCA} + C_{chemistry} + C_{PCGC} = C_{BPCA} + C_{ex} \quad (1)$$

where  $C_{BPCA}$  is the mass of the BC isolated from the sample and  $C_{ex}$  is the mass of the extraneous C added due to processing ( $C_{chemistry}$ ) and PCGC collection ( $C_{PCGC}$ ). In previous studies,  $^{14}C$  analysis of standards of known chemical and isotopic composition have revealed deviations from consensus

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$\Delta^{14}\text{C}$  values, highlighting the need for correction of  $C_{\text{ex}}$  (Hwang and Druffel 2005; Santos et al. 2007; Ziolkowski and Druffel 2009).

For the purpose of correcting BC  $\Delta^{14}\text{C}$  measurements, the size and isotopic composition of  $C_{\text{ex}}$  can be assessed using 2 different approaches. First, to implement direct method  $\Delta^{14}\text{C}$  assessments, we evaluate process blanks, which are initially empty vials that are processed through the entire method, identically to the treatment of a sample or standard. These process blanks serve as direct estimates of the size and isotopic signature of  $C_{\text{ex}}$ , and are evaluated periodically over time. The mass of  $C_{\text{ex}}$  added during sample preparation ( $C_{\text{chemistry}}$ ) and purification ( $C_{\text{PCGC}}$ ) can be evaluated by process blanks. To evaluate  $C_{\text{PCGC}}$ , we use a direct blank, generated by solvent injection onto the PCGC. The difference between the direct blank ( $C_{\text{PCGC}}$ ) and process blank ( $C_{\text{chemistry+PCGC}}$ ) is the  $C_{\text{chemistry}}$ . It is particularly important for new users to distinguish how much  $C_{\text{ex}}$  originates from both the chemical preparation of the sample ( $C_{\text{chemistry}}$ ) and PCGC ( $C_{\text{PCGC}}$ ) to determine the quality and total uncertainty of the BC  $\Delta^{14}\text{C}$  results.

The second method, the indirect method, assesses the  $C_{\text{ex}}$  assuming a 2-endmember approach. We assume  $C_{\text{ex}}$  has a dead ( $\Delta^{14}\text{C} = -1000\text{‰}$ ) component and a modern ( $\Delta^{14}\text{C} = 0\text{‰}$ ) component. Then, using process BC standards of known isotopic values (modern and dead), the size of  $C_{\text{ex}}$  is estimated by the deviation of the process standard from the consensus  $\Delta^{14}\text{C}$  value. After corrections for graphitization and combustion in AMS measurements are made, a carbon mass balance is applied using the mass and isotopic signature of  $C_{\text{ex}}$  determined by indirect and direct methods to correct samples and standards (Equation 1) (Ziolkowski and Druffel 2009).

The aim of this study is to determine  $C_{\text{ex}}$  added in the extraction of BPCA marker compounds in marine sediment throughout pretreatment, nitric acid oxidation, derivitization, and PCGC collection. Using direct and indirect assessments of  $C_{\text{ex}}$ , we evaluate the magnitude and  $^{14}\text{C}$  signature of  $C_{\text{ex}}$ , which allows us to calculate the true BC  $\Delta^{14}\text{C}$  value ( $C_{\text{BPCA}}$ ) of the sample. The sum of the different sources of  $C_{\text{ex}}$  can lead to significant contamination of samples, particularly for samples  $<50 \mu\text{g C}$ . This results in a size-related bias of the  $\Delta^{14}\text{C}$  values reported by AMS laboratories, which usually include corrections only for combustion and graphitization of samples. We compare both direct and indirect  $C_{\text{ex}}$  assessments by applying corrections of  $C_{\text{ex}}$  to a suite of hypothetical sedimentary organic carbon (SOC) samples. Based on these assessments, we demonstrate corrections for  $C_{\text{ex}}$  added during BC extraction in marine sediments with the routine use of processed standards and blanks.

## **METHODS**

### **Black Carbon Standards**

Black-carbon-rich standard reference materials were selected from the multilaboratory method and standard comparison called the BC Ring Trial (Hammes et al. 2007). Two types of dead and modern process standards were used to facilitate comparative analyses of BC: 1) laboratory-produced BC-rich and 2) BC-containing environmental matrices containing fine siliceous clays and heavy metals. Grass char (*Oryza sativa*) and wood char (*Castanea sativa*) BC standards were used as modern standards to estimate the  $^{14}\text{C}$ -depleted  $C_{\text{ex}}$  added during processing (Elmquist et al. 2004; Hammes et al. 2006). A  $^{14}\text{C}$ -depleted standard, hexane soot (Akhter et al. 1985; Goldberg 1985; Hammes et al. 2007) was also used to estimate modern  $C_{\text{ex}}$ . Environmental BC standards that contained a silicate and metal matrix, including urban dust aerosol NIST Standard Reference Material (SRM 1649a) (National Institute of Standards and Technology 2001; Masiello et al. 2002), NIST Standard Reference Material marine sediment (SRM 1941b), and US Geological Survey Green River Shale (Abbey 1983; Gladney and Roelandts 1988; Govindaraju 1994) were used to estimate modern  $C_{\text{ex}}$ . To

observe the matrix effect in marine sediments samples, wood char was added to SRM 1941b that had previously been baked in a muffle furnace for 2 hr at 550 °C to remove organic carbon. Duplicates of standards were processed to assess total uncertainty of  $\Delta^{14}\text{C}$  measurements.

#### **Elimination of Polyvalent Metals, BPCA Oxidation, and Purification**

Standards that contained polyvalent metals were treated with trifluoroacetic acid (TFA) to remove metals that interfere with BPCA analysis (Brodowski et al. 2005; Hammes et al. 2007; Ziolkowski and Druffel 2009). First, metals in the environmental matrices standards were removed by high-temperature (104 °C) and high-pressure digestion in TFA for 4 hr (Brodowski et al. 2005). The solution was passed through a 0.8- $\mu\text{m}$  quartz filter into a vacuum filtration flask, and the filter was rinsed with Milli-Q<sup>TM</sup> water. Sample retained on the quartz filter was dried at 30–40 °C for at least 3 hr before high-temperature, high-pressure digestion in 65% nitric acid, at 170 °C for 8 hr for the BPCA method (Brodowski et al. 2005; Ziolkowski and Druffel 2009). The BPCA method partially oxidizes aromatic BC, converting it to BPCA marker compounds (Glaser et al. 1998; Brodowski et al. 2005; Hammes et al. 2007; Ziolkowski and Druffel 2009). The solution was filtered and the filtrate was passed through a cation exchange column (Brodowski et al. 2005) and eluted into Erlenmeyer flasks. Briefly, following the method of Ziolkowski et al. (2011), dehydrated BPCAs were dissolved in methanol that contained biphenyl-2,2'-dicarboxylic acid (internal standard) and titrated with (trimethylsilyl)diazomethane (Sigma Aldrich) in 2.0M ethyl ether to derivatize the carboxylic acids to methyl esters. Methanol was evaporated by a stream of nitrogen gas and dichloromethane was used to transfer the samples into freshly baked vial inserts (0.3 mL) for PCGC analysis and separation.

Methylated BPCAs were quantified for BPCA distributions and isolated for <sup>14</sup>C analysis using a Hewlett Packard 6890 Preparative Column Gas Chromograph (PCGC) with an HP 7683B auto-injector, and Gerstel cooled injection system (CIS-4) with a split/splitless inlet. The CIS injector was operated in “solvent vent” mode, with a vent flow adjusted to 60 mL/min and 20 psi. The solvent venting time was 0.3 min, and the split vent time was 1 min. The injection volume was 4  $\mu\text{L}$  for all collections. The temperature of the inlet was 40 °C, then increased to 300 °C at a rate of 10 °C/s, then kept isothermal for 3 min. A megabore fused-silica capillary column (50 m length) coated with 1  $\mu\text{m}$  of DB-XLB was used for all samples in this study. Ultra high-purity hydrogen gas was used as the carrier gas at a flow rate of 8.7 mL/min. The temperature program on the PCGC for separating BPCAs started at 100 °C, 10 °C/min to 250 °C (isothermal for 15 min), 5 °C/min to 280 °C (isothermal for 5 min), then 25 °C/min to 320 °C (isothermal for 3 min). Approximately 1% of the flow was diverted to the FID, while the other 99% was sent to the fraction collector. The fraction collector was computer controlled to collect samples at specific retention times. The fraction collector switch temperature and transfer line was kept at 320 °C, and the traps were chilled at –10 °C. To standardize  $C_{\text{ex}}$  to samples that have different numbers of injections, time windows of collection, and injection volumes, we normalized the  $C_{\text{ex}}$  mass determined by a manometer measurement of pressure in a known volume to units of  $\mu\text{g C}$  per min collection per 50 1- $\mu\text{L}$  injections, after Ziolkowski and Druffel (2009). In all direct evaluations of  $C_{\text{PCGC}}$ , the 4-min collection window set for each blank injection reflected the same time window in which BPCAs were collected in a sample run.

Briefly, following the method of Ziolkowski et al. (2011), BPCA marker compounds were identified using commercially available BPCAs (Sigma Aldrich; 1,2,3 benzene tricarboxylic acid, pyromellitic acid, benzene pentacarboxylic acid, mellitic acid) and mass fragmentation patterns when run on a Finnigan Trace MS and GC/MS ESI at UC Irvine. The preparative fraction collector on the PCGC captured BPCA marker compounds with 3 to 6 substituted carboxylic acid groups from the partial oxidation of aromatic BC, including the nitrated BPCAs (about half of the BPCAs were nitrated). The collection windows were set to capture the eluting peaks of interest, for a total of 4 min. The

BPCA marker compounds with only 2-substituted carboxylic acid groups were not collected because they can be derived from recalcitrant lignin or other non-BC material that may survive oxidation (Brodowski et al. 2005). Between sample collections (30 injections), the GC column was baked out twice at 320 °C for 10 min, the injection needle was cleaned with dichloromethane, and a freshly baked (550 °C for 2 hr) injection liner was installed. Also, to remove any contamination or memory from the previous sample, the first 10 injections were discarded for  $^{14}\text{C}$  measurements as per Ziolkowski et al. (2011). After combustion, graphitization, and  $\text{C}_{\text{ex}}$  assessments, standards were corrected for the  $^{14}\text{C}$ -free derivative C added during the derivitization (Ziolkowski and Druffel 2009).

### **Radiocarbon Measurements**

In preparation for  $^{14}\text{C}$  analysis, BPCA marker compound isolates from the PCGC were transferred using dichloromethane to clean quartz tubes, dried, and combusted to  $\text{CO}_2$  at 850 °C with cupric oxide and silver. The volume of the  $\text{CO}_2$  gas produced from combustion was cryogenically purified, then quantified manometrically and reduced to graphite for  $^{14}\text{C}$  analysis (Santos et al. 2007). Measurements were made at UC Irvine in the Keck Carbon Cycle Acceleration Mass Spectrometry Facility and normalized to the AMS  $\delta^{13}\text{C}$ .  $^{14}\text{C}$  results were reported as  $\Delta^{14}\text{C}$  without known-age correction (Stuiver and Polach 1977).

### **Preparation of Standards for Bulk Measurements**

In order to facilitate the indirect assessment of  $\text{C}_{\text{ex}}$ , the  $\Delta^{14}\text{C}$  values of the unprocessed standards were measured. Inorganic carbon was removed by acidification with 3% phosphoric acid (Hwang et al. 2005). Standards were prepared in small and large sizes to bracket the sizes of the BC samples.

## **RESULTS AND DISCUSSION**

### **Direct Blank Evaluation of Mass and $\Delta^{14}\text{C}$ Value of $\text{C}_{\text{ex}}$**

We directly evaluated the  $\text{C}_{\text{ex}}$  mass and  $\Delta^{14}\text{C}$  value using 1) process blanks and 2) direct blanks on the PCGC. The process blank contained no sample but was subjected to the same preparatory steps as samples, so it includes both  $\text{C}_{\text{PCGC}}$  and  $\text{C}_{\text{chemistry}}$  (Equation 1). The direct blank from the PCGC only is determined by injecting solvent onto the PCGC ( $\text{C}_{\text{PCGC}}$ ).

We found the process blank ( $\text{C}_{\text{chemistry+PCGC}}$ ) was  $1.4 \pm 0.7 \mu\text{g C min}^{-1}$  per 50 1- $\mu\text{L}$  injections in 2012 and  $0.3 \pm 0.2 \mu\text{g C min}^{-1}$  per 50 1- $\mu\text{L}$  injections in 2011 and the  $\Delta^{14}\text{C}$  values were  $-957 \pm 46\text{‰}$  and  $-963 \pm 54\text{‰}$ , respectively. The difference in the magnitude of  $\text{C}_{\text{ex}}$  between these 2 time periods highlights the imperative need for routine blank assessments.

In order to deduce the relative sizes of  $\text{C}_{\text{chemistry}}$  and  $\text{C}_{\text{PCGC}}$ , we evaluated  $\text{C}_{\text{PCGC}}$  alone from the injections of clean solvent directly onto the PCGC. We made 230 injections to obtain enough C for an AMS analysis. We report a direct blank  $\text{C}_{\text{PCGC}}$  of  $0.1 \pm 0.1 \mu\text{g C min}^{-1}$  per 50 1- $\mu\text{L}$  injections with a  $\Delta^{14}\text{C}$  value  $-982 \pm 15\text{‰}$  (Table 1). Using a mass balance approach from the difference between the total  $\text{C}_{\text{chemistry+PCGC}}$  determined from the process blank and  $\text{C}_{\text{PCGC}}$  using the direct blank, we calculate that the  $\text{C}_{\text{chemistry}}$  in 2012 was  $1.3 \pm 0.8 \mu\text{g C min}^{-1}$  per 50 1- $\mu\text{L}$  injections. In 2012, we find that  $\sim 10\%$  of  $\text{C}_{\text{ex}}$  is  $\text{C}_{\text{PCGC}}$  ( $0.1 \pm 0.1 \mu\text{g C min}^{-1}$  per 50 1- $\mu\text{L}$  injections) and  $\sim 90\%$  is  $\text{C}_{\text{chemistry}}$  ( $1.3 \pm 0.7 \mu\text{g C min}^{-1}$  per 50 1- $\mu\text{L}$  injections). Additional  $\text{C}_{\text{chemistry}}$  may originate from the treatment of samples in the cation exchange column following the BPCA method. Interpretations of the  $\text{C}_{\text{chemistry}}$  suggests that these extra steps add twice the amount of  $\text{C}_{\text{chemistry}}$  as that found by Ziolkowski and Druffel (2009), who did not use the cation column and pretreatment steps.

### **Indirect Blank Evaluation of Mass and $\Delta^{14}\text{C}$ Value of $C_{\text{ex}}$**

The second method of evaluating  $C_{\text{ex}}$ , the indirect method, involves processing standards of known consensus  $\Delta^{14}\text{C}$  value and measuring the deviation from the unprocessed consensus  $\Delta^{14}\text{C}$  value. Differences between the  $\Delta^{14}\text{C}$  values of processed and unprocessed standards are used to measure the mass and  $\Delta^{14}\text{C}$  value of the  $C_{\text{ex}}$  to thereby correct sample  $\Delta^{14}\text{C}$  values of samples (Hwang and Druffel 2005; Ziolkowski and Druffel 2009; Santos et al. 2010). Incorporation of  $C_{\text{ex}}$  in standards is assumed to be the same as that in samples that are processed identically. In this study, modern and dead standards were processed throughout the entire pretreatment, chemical extraction, cation exchange column, and PCGC isolation. When using the indirect method,  $C_{\text{ex}}$  is assessed as 2 end-members, 1 modern ( $\Delta^{14}\text{C} = 0\text{‰}$ ) and 1 dead ( $\Delta^{14}\text{C} = -1000\text{‰}$ ), the mass-weighted sum of which equals  $C_{\text{ex}}$ .

Modern process standards are used to assess the dead component of  $C_{\text{ex}}$ , while dead standards are used to assess the modern component of  $C_{\text{ex}}$ . After standards are corrected for graphitization and combustion, dead  $C_{\text{ex}}$  is evaluated using a simple mass balance approach (Equation 1) (Ziolkowski and Druffel 2009; Santos et al. 2010). The measured AMS  $\Delta^{14}\text{C}$  values of BPCAs produced from wood and grass char were lower than the consensus values due to the presence of low- $^{14}\text{C}$   $C_{\text{ex}}$ . The mass of dead C in grass char and wood char standards were  $1.8 \pm 0.9 \mu\text{g C min}^{-1}$  per 50 1- $\mu\text{L}$  injections and  $1.5 \pm 0.8 \mu\text{g C min}^{-1}$  per 50 1- $\mu\text{L}$  injections, in 2011 and 2012, respectively. Low- $^{14}\text{C}$  standards are used to assess the modern component of  $C_{\text{ex}}$  (e.g. hexane soot) and samples that contain a silicate matrix (e.g. SRM 1649a aerosol dust and Green River Shale). The masses of modern  $C_{\text{ex}}$  in these standards were  $0.2 \pm 0.1 \mu\text{g C min}^{-1}$  per 50 1- $\mu\text{L}$  injections and  $0.1 \pm 0.1 \mu\text{g C min}^{-1}$  per 50 1- $\mu\text{L}$  injections, in 2011 and 2012, respectively.

From these modern and dead components of  $C_{\text{ex}}$ , the calculated  $\Delta^{14}\text{C}$  values of  $C_{\text{ex}}$  are  $-842 \pm 26\text{‰}$  and  $-933 \pm 25\text{‰}$  in 2011 and 2012, respectively (Table 1). Variables such as different users and GC column degradation change with time, making it imperative that standards are routinely processed to document the inevitable variability of  $C_{\text{ex}}$ . To maintain consistency with these  $C_{\text{ex}}$  variations, standards processed with the same suite of BC samples should be used to correct the  $\Delta^{14}\text{C}$  data. In other words,  $C_{\text{ex}}$  evaluations using the indirect method should be performed with every suite of BC measurements to adequately correct BC sample  $\Delta^{14}\text{C}$  values.

### **Correction of Standards Using $C_{\text{ex}}$ Assessments**

We report corrected  $\Delta^{14}\text{C}$  values for standards using the mass and  $\Delta^{14}\text{C}$  value of  $C_{\text{ex}}$  determined by both methods. More than half of the standard  $\Delta^{14}\text{C}$  values corrected using the direct method were outside  $2\sigma$  from the consensus values (Table 2 and Appendix). In contrast, all but 2 of the standards corrected using the indirect method agreed within  $2\sigma$  of the consensus values (Table 2). There were greater deviations in corrected  $\Delta^{14}\text{C}$  values of modern standards because the majority of  $C_{\text{ex}}$  is  $^{14}\text{C}$ -depleted, thereby affecting the modern  $\Delta^{14}\text{C}$  values more substantially. The low- $^{14}\text{C}$  standards (SRM 1649a aerosol dust, hexane soot, and Green River Shale) had corrected  $\Delta^{14}\text{C}$  values that were closer to their consensus values (Table 2).

The direct correction applies 1 mass and 1  $\Delta^{14}\text{C}$  value from the process blank, whereas the indirect correction is determined using the average value of dead and modern  $C_{\text{ex}}$  for a large range of standard types. The indirect method includes the variability of sample processing with multiple standards that mirrors the variability of  $C_{\text{ex}}$ . The ability of indirect evaluations to correct standards illustrates why we recommend using the indirect method for correcting BC  $\Delta^{14}\text{C}$  measurements.

Table 1 Standards subjected to various treatments to evaluate the  $C_{ex}$  in the determination of BC in marine sediment. The uncertainty of the mass of  $C_{ex}$  was estimated as 50% of the sample mass (but no lower than 0.1  $\mu\text{g}$  of C/min per 50 1- $\mu\text{L}$  injections). The uncertainty of the  $C_{ex}$  mass using the indirect method correction was estimated at 50% of the mass value.

Type of standard	Evaluates for	Process standard	<i>n</i>	Cation column and pretreatment	BPCA	PCGC	Extraneous carbon, $C_{ex}$	
							Average $\mu\text{g C/min}$ per fifty 1- $\mu\text{L}$ injections <sup>a</sup>	$\Delta^{14}\text{C}$ (‰)
<b>Indirect blank</b>								
Dead	Modern $C_{ex}$	SRM 1649a Hexane soot Green River Shale	4 2 2	Yes Yes Yes	Yes Yes Yes	Yes Yes Yes	0.1 $\pm$ 0.1 (2012) 0.2 $\pm$ 0.1 (2011)	0
Modern	Dead $C_{ex}$	Grass char Wood char Wood char in muffled SRM1941b	3 4 2	No No Yes	Yes Yes Yes	Yes Yes Yes	1.5 $\pm$ 0.8 (2012) 1.8 $\pm$ 0.9 (2011)	-1000
<b>Total indirect</b>								
							1.6 $\pm$ 0.9 2.0 $\pm$ 1.0	-933 $\pm$ 25 (2012) -842 $\pm$ 26 (2011)
<b>Direct blank</b>								
Process blank (collected in 2012)	Dead and Modern	—	1	Yes	Yes	Yes	1.4 $\pm$ 0.7	-957 $\pm$ 46
Process blank (collected in 2011)	Dead and Modern	—	1	Yes	Yes	Yes	0.3 $\pm$ 0.2	-963 $\pm$ 54
<b>Assessment of <math>C_{PCGC}</math></b>								
Solvent injection into PCGC (2012)	Dead and Modern	—	1	No	No	Yes	0.1 $\pm$ 0.1	-982 $\pm$ 15

<sup>a</sup>The masses of  $C_{ex}$  were normalized to  $\mu\text{g C min}^{-1}$  per fifty 1- $\mu\text{L}$  injections.

*Extraneous C in <sup>14</sup>C Measurements of Black Carbon*

Table 2 Mass and  $\Delta^{14}\text{C}$  of the unprocessed and isolated BPCAs in processed standard before and after corrections for  $C_{\text{ex}}$ .

Standard type (lab code UCID-)	Consensus BC $\Delta^{14}\text{C}$ values (‰)	BPCA compound class		
		$\mu\text{g C}$	Direct method corrected $\Delta^{14}\text{C}$ (‰)	Indirect method corrected $\Delta^{14}\text{C}$ (‰)
Grass char (13206) (13103)	$53 \pm 5^{\text{a}}$ ( $n = 4$ )	52	$-69 \pm 19$	$+27 \pm 25$
		85	$+53 \pm 11$	$+89 \pm 49$
Wood char (13180) (13179) (16519) (16520)	$165 \pm 5^{\text{a}}$ ( $n = 4$ )	108	$+149 \pm 14$	$+186 \pm 33$
		178	$+106 \pm 27$	$+139 \pm 34$
		108	$+138 \pm 31$	$+143 \pm 28$
		60	$+147 \pm 21$	$+144 \pm 53$
Wood char in a matrix SRM 1941b (16509) (16510)	$165 \pm 5^{\text{a}}$ ( $n = 2$ )	40	$+299 \pm 25$	$+129 \pm 28$
		50	$+175 \pm 23$	$+130 \pm 43$
Aerosol SRM 1649a (13183) (13101) (13102) (13184)	$-885 \pm 50^{\text{b}}$	21	$-653 \pm 28$	$-884 \pm 50$
		37	$-899 \pm 10$	$-963 \pm 29$
		25	$-742 \pm 24$	$-859 \pm 40$
		77	$-906 \pm 8$	$-924 \pm 47$
Hexane soot (16511) (16512)	$-982 \pm 8$ ( $n = 3$ )	102	$-986 \pm 3$	$-992 \pm 4$
		35	$-998 \pm 2$	$-992 \pm 4$
Green River Shale (13207) (13182)	$<-976$ ( $n = 3$ )	42	$-823 \pm 32$	$-894 \pm 38$
		73	$-796 \pm 15$	$-834 \pm 18$

<sup>a</sup>Determined by the combustion of unprocessed samples.

<sup>b</sup>Aerosol 1649a is a mixture of BC and other aerosols containing organic carbon. The unprocessed BC  $\Delta^{14}\text{C}$  values are from Ziolkowski and Druffel (2009) and Currie et al. (2002) ( $-620 \pm 50\%$ ;  $n = 5$ ).

### Evaluation of the Sediment Matrix on Corrected $\Delta^{14}\text{C}$ Values

We needed to verify the presence or absence of a matrix effect associated with the metals contained in our sediment samples. The effect on  $C_{\text{ex}}$  of a sediment matrix was evaluated by comparing corrected  $\Delta^{14}\text{C}$  values of wood char run with and without a sediment (SRM 1941b) matrix. We processed 2 wood char standards that had added SRM 1941b marine sediment. Results showed that both standards had the same mass of  $C_{\text{ex}}$  ( $1.5 \pm 0.8 \mu\text{g C min}^{-1}$  per 50 1- $\mu\text{L}$  injections), indicating that  $C_{\text{ex}}$  is unaffected by the presence of a sediment matrix. When the indirect corrections were applied to wood char standards containing a sediment matrix, the corrected  $\Delta^{14}\text{C}$  values were  $129 \pm 28\%$  and  $130 \pm 43\%$  (Table 2), within  $2\sigma$  of the consensus value ( $165 \pm 5\%$ ). The corrected  $\Delta^{14}\text{C}$  values of the wood char standards without a matrix ( $n = 4$ ) were also equal to the consensus value (average  $\Delta^{14}\text{C} = 153 \pm 10\%$ ).



### Hypothetical Marine Sediment BC $\Delta^{14}\text{C}$

To test how the addition of  $C_{\text{ex}}$  impacts the  $\Delta^{14}\text{C}$  values of BC in sediment samples of various sizes, we applied these corrections to a suite of hypothetical samples of different sizes (25 to 150  $\mu\text{g C}$ ) and  $\Delta^{14}\text{C}$  values ( $\Delta^{14}\text{C} = -250\text{‰}$  to  $-750\text{‰}$ ). We assumed that the  $C_{\text{ex}}$  associated with these hypothetical samples was the same as those obtained in 2012 (Table 1). Corrected  $\Delta^{14}\text{C}$  values associated with both indirect and direct method corrections are within  $2\sigma$  of the consensus values (Figure 1). The differences between indirect and direct corrections diverge for samples that are  $\leq 25 \mu\text{g C}$ , where the “true”  $\Delta^{14}\text{C}$  values ( $C_{\text{BPCA}}$ ) (Equation 1) of samples are close to modern ( $> -250\text{‰}$ ) (Figure 1). Deviations in the corrected  $\Delta^{14}\text{C}$  values for samples  $< 25 \mu\text{g C}$  illustrate the difficulty of assessments of both the mass and  $\Delta^{14}\text{C}$  variability of  $C_{\text{ex}}$  within sample suites. Gaining insights with the use of multiple standards and duplicate samples is necessary to constrain  $C_{\text{ex}}$ .

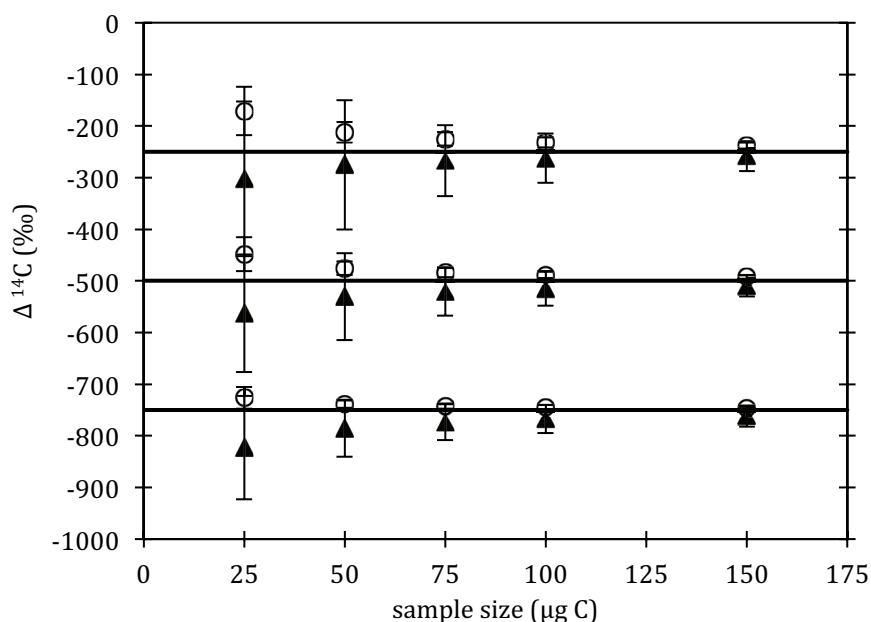


Figure 1 Masses of hypothetical BC in sediment samples plotted versus corrected  $\Delta^{14}\text{C}$  values to illustrate the difference between direct (open circles) and indirect (black triangles) corrections. Solid black lines represent the consensus  $\Delta^{14}\text{C}$  values for each hypothetical sample.

### CONCLUSION

The main challenge for reporting meaningful BC  $\Delta^{14}\text{C}$  values in sedimentary matrices involves multiple evaluations of  $C_{\text{ex}}$  added during extensive chemical processing and PCGC separation. The mass of  $C_{\text{ex}}$  is significant and variable, thus requiring a correction beyond that made for graphitization and combustion. Correction for  $C_{\text{ex}}$  is critical, especially for samples  $< 25 \mu\text{g C}$ .

We were unable to reliably correct standards to their consensus  $\Delta^{14}\text{C}$  values using the direct method. We recommend use of the indirect method to capture the variability of sample processing by the use of multiple standards. Standard sizes should match the sample sizes and approximate  $\Delta^{14}\text{C}$  values. Although processing dead and modern BC standards is time consuming, it is crucial because  $C_{\text{ex}}$  is variable over time. To gain the most information about the mass and isotopic signatures of  $C_{\text{ex}}$ , the indirect method is recommended.

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## APPENDIX

### Calculation of Uncertainties in $\Delta^{14}\text{C}$ Corrected Values

To determine the propagated total uncertainty of  $\Delta^{14}\text{C}_{BPCA}$  (Equation 2), we applied the following equation:

$$\begin{aligned} \sigma \Delta^{14}\text{C}_{BPCA}^2 = & \left( \frac{\partial \Delta^{14}\text{C}_{BPCA}}{\partial \Delta^{14}\text{C}_{reported}} \right)^2 \sigma \Delta^{14}\text{C}_{reported}^2 + \left( \frac{\partial \Delta^{14}\text{C}_{BPCA}}{\partial \Delta^{14}\text{C}_{ex}} \right)^2 \sigma \Delta^{14}\text{C}_{ex}^2 + \\ & \left( \frac{\partial \Delta^{14}\text{C}_{BPCA}}{\partial C_{reported}} \right)^2 \sigma C_{reported}^2 + \left( \frac{\partial \Delta^{14}\text{C}_{BPCA}}{\partial C_{ex}} \right)^2 \sigma C_{ex}^2 \end{aligned} \quad (2)$$

where  $\sigma \Delta^{14}\text{C}_{BPCA}$  is the propagated error of the corrected  $\Delta^{14}\text{C}$  value,  $\sigma \Delta^{14}\text{C}_{reported}$  is the AMS uncertainty of  $\Delta^{14}\text{C}_{reported}$  (machine uncertainty),  $\sigma \Delta^{14}\text{C}_{ex}$  is the uncertainty for  $\Delta^{14}\text{C}_{ex}$ ,  $\sigma C_{reported}$  is the uncertainty for  $C_{reported}$  (uncertainty in graphitization), and  $\sigma C_{ex}$  is the uncertainty in  $C_{ex}$  (assigned as 50%). The total uncertainty for  $\Delta^{14}\text{C}_{ex}$  and  $C_{ex}$  was used as the direct process blank.