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Authors

Ziolkowski, Lori A

Druffel, Ellen RM

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Quantification of Extraneous Carbon during Compound Specific Radiocarbon Analysis of Black Carbon

Lori A. Ziolkowski* and Ellen R. M. Druffel

Department of Earth System Science, University of California Irvine, Irvine, California 92697

Radiocarbon (^{14}C) is a radioactive isotope that is useful for determining the age and cycling of carbon-based materials in the Earth system. Compound specific radiocarbon analysis (CSRA) provides powerful insight into the turnover of individual components that make up the carbon cycle. Extraneous or nonspecific background carbon (C_{ex}) is added during sample processing and subsequent isolation of CSRA samples. Here, we evaluate the quantity and radiocarbon signature of C_{ex} added from two sources: preparative capillary gas chromatography (PCGC, C_{PCGC}) and chemical preparation of CSRA of black carbon samples ($\text{C}_{\text{chemistry}}$). We evaluated the blank directly using process blanks and indirectly by quantifying the difference in the isotopic composition between processed and unprocessed samples for a range of sample sizes. The direct and indirect assessment of $\text{C}_{\text{chemistry+PCGC}}$ agree, both in magnitude and radiocarbon value ($1.1 \pm 0.5 \mu\text{g}$ of C, fraction modern = 0.2). Half of the C_{ex} is introduced before PCGC isolation, likely from coeluting compounds in solvents used in the extraction method. The magnitude of propagated uncertainties of CSRA samples are a function of sample size and collection duration. Small samples collected for a brief amount of time have a smaller propagated ^{14}C uncertainty than larger samples collected for a longer period of time. CSRA users are cautioned to consider the magnitude of uncertainty they require for their system of interest, to frequently evaluate the magnitude of C_{ex} added during sampling processing, and to avoid isolating samples $\leq 5 \mu\text{g}$ of carbon.

Radiocarbon dating of bulk organic and inorganic carbon reservoirs has allowed the average residence time of carbon in most carbon pools to be calculated. However, many of these reservoirs are comprised of complex, heterogeneous mixtures whose components have different residence times from bulk radiocarbon values. Initially, the heterogeneous mixtures were studied via compound class radiocarbon analysis (CCRA).¹ Introduction of compound specific radiocarbon analysis (CSRA) allowed

the ^{14}C measurement of a single compound.² CSRA usually involves a multiple-step purification procedure that culminates in the collection of a single compound (or group of compounds) of high purity. The applications of CCRA and CSRA range from source apportionment of atmospheric particles,^{3,4} biomarkers with paleoclimatic implications,^{5–7} microbial incorporation of fossil material,^{8,9} and compound class studies in marine sediments¹⁰ and marine dissolved organic carbon.^{11,12}

New developments in accelerator mass spectrometry (AMS) have decreased the sample size requirements for CSRA. Ultrasmall samples¹³ and online ^{14}C measurements¹⁴ enable CSRA as small as $2 \mu\text{g}$ of C. Preparation of CSRA samples requires two sets of laboratory protocols, sample isolation, and ^{14}C analysis, each of which introduce extraneous or nonspecific background carbon (C_{ex}). Thus a CSRA sample of $2 \mu\text{g}$ of C may have a large uncertainty associated with its isotopic composition. To date, few studies have quantified C_{ex} .¹⁵ Accounting for C_{ex} has largely been avoided by processing samples large enough so as to overwhelm the C_{ex} . However, not all environmental CSRA techniques allow for the preparation of large sample sizes because the compound of interest may be in low abundance.

Constraining the uncertainty of ^{14}C measurements is done by evaluating the mass and variability of C_{ex} added during sample preparation. Here we assess the mass and radiocarbon signatures of C_{ex} specific to the chemical oxidation of organic matter for quantifying black carbon using PCGC. We employed the benzene polycarboxylic acid method that

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* To whom correspondence should be addressed. E-mail: lorized@gmail.com.

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Table 1. Materials Processed and Associated Solvents Used for CSRA of Black Carbon^a

material	use	source	bulk ¹⁴ C (FM)
Materials Processed			
modern vanillin	GC process standard	Sigma Aldrich	1.052 ± 0.002
synthetic vanillin	GC process standard	Sigma Aldrich	0.002 ± 0.001
grass char	method process standard	University of Zurich	1.056 ± 0.002
hexane soot	method process standard	University of Denver	0.005 ± 0.001
Solvents and Materials			
methanol	solvent	Burdick and Jackson ^b	0.000 ^c
dichloromethane	solvent	Omni Solvent ^b	0.000 ^c
biphenyl-2,2'-dicarboxylic acid	internal standard	Sigma Aldrich	0.000 ± 0.001
TMS-diazomethane	derivatization agent	Sigma Aldrich	0.000 ^c
DB-XLB	GC column	Agilent	0.000 ± 0.001

^a The bulk ¹⁴C was measured in duplicate. ^b High-purity solvent. ^c Assumed radiocarbon values.

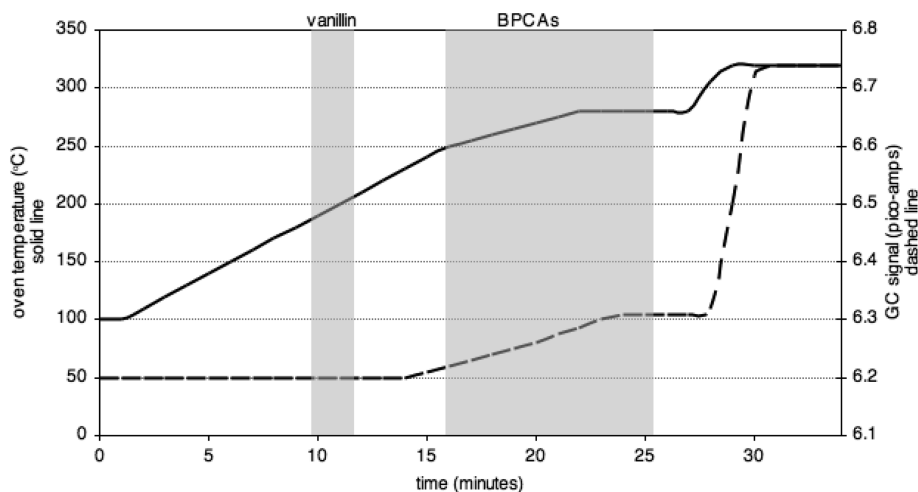


Figure 1. The magnitude of column bleed (indicated by the magnitude of the baseline signal) and oven temperature as a function of retention time. The retention time windows for the isolation of vanillin and BPCAs are marked.

chemically oxidizes black carbon to benzene rings substituted with three to six carboxylic acid groups.

METHODS

Natural and synthetic vanillin (4-hydroxy-3-methoxybenzaldehyde, Table 1) were used as standards to assess the extraneous carbon added during PCGC isolation. Black carbon (BC) reference materials were used as process standards to quantify C_{ex} added throughout the entire isolation procedure (Table 1).^{16,17}

Chemical Oxidation. To minimize carbon contamination, all glassware and quartz filters that came in contact with the samples and standards were baked at 550 °C for 2 h prior to use. Samples were processed using a modification of the benzene polycarboxylic acid (BPCA) method.^{18,19} Process materials, wood char, and hexane soot (Table 1) were oxidized in 2 mL of concentrated nitric acid (grade ACS, Fisher Scientific) in quartz tubes inside a high-

pressure digestion apparatus at 180 °C for 8 h. Postdigestion, the samples were filtered through quartz fiber filters (27 mm diameter, 0.8 μm pore diameter), and 15 mL of Milli-Q water was used to rinse any remaining BPCAs from the filter. The filtrate was collected and freeze-dried overnight.

Dried samples were redissolved in 5 mL of methanol, and the internal standard, biphenyl-2,2'-dicarboxylic acid (1 mg mL⁻¹ in methanol), was added. Samples were derivatized by titration with 2.0 M trimethylsilyl diazomethane in ethyl ether (Sigma Aldrich). Derivatization was considered complete when the solution retained the yellow color of the trimethylsilyl-diazomethane. Methanol was dried with in stream of ultrahigh-purity nitrogen. A fixed volume of dichloromethane was added.

The derivatized oxidation products were separated and quantified on a Hewlett-Packard 6890N outfitted with a Gerstel cooled injection system, a DB-XLB capillary column (30 m × 0.53 mm i.d., 1.5 μm film thickness), and a flame ionization detector (FID), and a Gerstel preparative fraction collector (PFC). After injection, the column temperature was maintained at 100 °C for 1 min, then raised at 25 °C min⁻¹ to 250 °C followed by a 5 °C min⁻¹ ramp to 280 °C for 10 min, and then raised to 320 °C for 5 min of bake out (Figure 1). The FID temperature was 300 °C. The splitless injection volume was 1 μL for all samples in this study.

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Approximately 1% of the flow eluting from the capillary column was diverted to the FID, and 99% was sent to the PFC, which consists of a zero-dead-volume valve in a heated interface (320 °C) and seven 200 μL glass U-tube traps (six sample traps and a waste trap). The PFC transfer was kept constant at 320 °C for all samples processed. U-tubes were supported in isopropyl alcohol cooled units (-10 °C). The autoinjector, CIS, and trapping device are programmable and computer controlled, and FID data was acquired using Chemstation software.

BPCAs were identified by comparison of their retention times with those obtained for a commercially available mixture, and they were also verified using gas chromatography/mass spectrometry (GC/MS). All methylated BPCAs were quantified relative to the biphenyl-2,2'-dicarboxylic acid internal standard.

Radiocarbon Analysis of Isolated Samples. To avoid cross contamination from previously injected samples (e.g., memory), the U-tubes (and the material collected within) for the first 10 injections were replaced with clean, baked U-tubes. Unless otherwise noted, trapped samples were collected from 50 injections of each sample. To avoid possible isotope fractionation of isolates,²⁰ care was taken to trap the entire peak.

After PCGC isolation, the U-tubes containing trapped samples were rinsed with 700 μL of dichloromethane into prebaked GC autosampler vials. Samples were evaluated by GC-FID for purity and yield. Samples were then transferred to 6 mm quartz tubes using an additional 700 μL of dichloromethane, and the solvent was removed in a stream of UHP nitrogen. CuO and silver wire were added, and the sample tube was evacuated to 10^{-6} Torr and flame-sealed under vacuum. Tubes were then heated to 850 °C for 2 h. The resulting CO_2 was purified, quantified, and reduced to graphite according to standard procedures.²¹ Measurements of ^{14}C were made at the Keck Carbon Cycle Accelerator Mass Spectrometry Laboratory at University of California Irvine. In all cases, radiocarbon analysis are reported as fraction modern, which is the deviation of a sample from 95% of the activity in 1950 A.D., of National Bureau of Standards (NBS) oxalic acid 1 normalized to $\delta^{13}\text{C} = -25$ with respect to Pee Dee Belemnite.^{22,23} All fraction modern values reported within this article have been corrected for combustion and graphitization^{13,21} and mass dependent isotope fractionation by reporting all data to a common $\delta^{13}\text{C}$ value of -25 .²³

RESULTS

Carbon Mass Balance and Corrections. Once corrected for graphitization and combustion, the mass of carbon graphitized in CSRA samples (C_{reported}) originate from four sources:

$$C_{\text{reported}} = C_{\text{sample}} + C_{\text{derivative}} + C_{\text{chemistry}} + C_{\text{PCGC}} \quad (1)$$

the mass of carbon in the compound of interest isolated from the sample (C_{sample}), the mass of derivative carbon ($C_{\text{derivative}}$), the

mass of extraneous carbon added during chemical extraction ($C_{\text{chemistry}}$), and subsequent isolation via PCGC (C_{PCGC}).

The compounds of interest in this study, BPCAs, contain functional groups that require derivatization to adjust their polarity and volatility to enable separation by PCGC. The derivatization adds a methyl group ($-\text{CH}_3$) to each carboxylic acid group, and this additional carbon alters the ^{14}C signature of the sample. Since the isotopic composition of the derivative carbon is assumed to be ^{14}C -free ($\text{FM}_{\text{derivative}} = 0$), the reported isotopic signature is known, and the amount of added derivative carbon is known, the radiocarbon composition of the parent BPCA compound can be calculated via mass balance.

When samples are corrected for $C_{\text{derivative}}$, eq 1 is simplified to

$$C_{\text{sample+chemistry+PCGC}} = C_{\text{sample}} + C_{\text{chemistry+PCGC}} = C_{\text{sample}} + C_{\text{ex}} \quad (2)$$

To provide accurate isotopic values of $C_{\text{sample+chemistry+PCGC}}$, the mass and isotopic composition (FM) of C_{ex} must be determined. Here we evaluated two sources of C_{ex} : added during chemical extraction ($C_{\text{chemistry}}$) and during PCGC isolation (C_{PCGC}). Reported values of CSRA samples (C_{reported}) need to be corrected for C_{ex} . For the purposes of estimating the C_{ex} via process materials, samples had to be corrected for derivative carbon before estimating C_{ex} , which assumes that all C_{ex} has been derivatized.

Extraneous Carbon Added during PCGC Isolation (C_{PCGC}). Two methods were used to evaluate the mass and FM of C_{ex} from PCGC isolation. First, the direct approach was used to collect a process blank over a 7 min retention time window (from 18 to 25 min, Figure 1) from 400 dry injections (direct C_{PCGC}). No solvent was injected during the dry injections, that is, there was no needle in the autosampler, and all other GC parameters (i.e., carrier gas, oven temperature) were maintained. This sample yielded 7.6 ± 0.4 μg of C and had a FM_{PCGC} of 0.125 ± 0.034 . Because the sample collection window varied with sample type (Figure 1), we normalized the amount of C_{ex} (μg of C) to collection duration (in minutes) and 50 injections. Normalizing the C_{ex} to time assumes the majority of C_{ex} is due to column bleed (sample history and/or breakdown of the GC-column stationary phase) and that the bleed does not change over time or temperature. To standardize this nonspecific background correction, all subsequent collections maintained the same injection volume and number of injections; only the collection time and injected materials varied for the samples reported here. We normalized all samples that evaluated C_{ex} , even samples that included the $C_{\text{chemistry}}$. Thus evaluated directly, the C_{PCGC} added in the dry injections was 0.1 ± 0.05 μg of C min^{-1} per 50 injections.

The second method of evaluating the mass and FM of C_{PCGC} used various sizes of isolated process standards of known FM values. It was assumed that the sample was diluted with a constant mass and isotopic signature of C_{ex} , and the presence of C_{ex} would cause a deviation in the consensus ^{14}C value. The FM values of samples were expressed by the following equation:

$$\text{FM}_{\text{sample}} = \frac{\text{FM}_{\text{reported}} C_{\text{reported}} - \text{FM}_{\text{PCGC}} C_{\text{PCGC}}}{C_{\text{sample}}} \quad (3)$$

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where FM_{sample} is the radiocarbon value of the sample corrected for C_{PCGC} , FM_{reported} is the measured radiocarbon value of the sample uncorrected for C_{PCGC} , and FM_{PCGC} is the radiocarbon value of the extraneous carbon added during PCGC isolation. Because C_{ex} was assessed as a combination of both dead and modern material, FM_{ex} fell between 0.0 and 1.0. Therefore, small samples of modern isotopic composition were lower and samples of ^{14}C -depleted composition were higher in radiocarbon (e.g., Figure 2).

With the use of the above approach, the PCGC isolation size-series of modern vanillin ($FM_{\text{sample}} = 1.052$, Table 1) samples revealed that C_{PCGC} ($FM_{\text{PCGC}} = 0.0$) was $0.4 \pm 0.2 \mu\text{g}$ of C min^{-1} per 50 injections. The PCGC isolation of a series of different sized samples of ^{14}C -free vanillin ($FM_{\text{sample}} = 0.002$) revealed an additional $0.2 \pm 0.1 \mu\text{g}$ of C min^{-1} per 50 injections was added with an assumed $FM_{\text{PCGC}} = 1.0$. Combined, these two blanks revealed the total indirect C_{PCGC} of $0.6 \pm 0.3 \mu\text{g}$ of C with an average $FM_{\text{PCGC}} = 0.3$ (Table 2).

The difference of $0.5 \mu\text{g}$ of C min^{-1} per 50 injections of C_{ex} added to isolated vanillin samples calculated using standard materials ($0.6 \pm 0.3 \mu\text{g}$ of C min^{-1} per 50 injections) as compared to the dry injections ($0.1 \mu\text{g}$ of C min^{-1} per 50 injections) may be due to several factors. First, no solvent was injected into the GC column during dry injections. It is likely that when solvent is present in the GC column, more C_{ex} is mobilized than during the absence of solvent. The FM_{ex} values for vanillin ($FM_{\text{ex}} = 0.3 \pm 0.1$) and that for the dry injections ($FM_{\text{ex}} = 0.125 \pm 0.034$) were similar suggesting the same source of C_{ex} . Other possible explanations are that C_{PCGC} and its isotopic signature vary with time and the presence of sample memory and/or contamination of the injector port. Therefore, we estimate that for each minute of collection on the PCGC,

at least $0.6 \mu\text{g}$ of C with a $FM = 0.3$ was being added to samples from PCGC. Possible sources of C_{PCGC} are column bleed, break down of non-GC column tubing, post-PCGC sample handling, and residual solvent in the programmable fraction collector trap.

Extraneous Carbon Added during Chemical Oxidation and PCGC Isolation ($C_{\text{chemistry+PCGC}}$). CSRA samples are typically subjected to extensive chemical extraction procedures prior to isolation by PCGC and consequently it is likely that extraneous carbon is added during these procedures. In theory, isolation of compounds by PCGC should removed any extraneous carbon added during sample preparation. Similar to the evaluation of C_{ex} added during PCGC isolation, we evaluated the mass and FM of C_{ex} added during the chemical methods and PCGC isolation ($C_{\text{chemistry+PCGC}}$) using both an indirect and direct approach. To evaluate C_{ex} directly, the chemical oxidation, derivatization, and PCGC isolation steps were carried out with no sample added. In this way, direct analysis of the C_{ex} was $1.1 \pm 0.2 \mu\text{g}$ of C min^{-1} per 50 injections and $FM = 0.200 \pm 0.054$ (Table 2).

The C_{ex} was evaluated indirectly by quantifying the deviation in $FM_{\text{sample+ex}}$ from the unprocessed material for radiocarbon dead (hexane soot) and modern (grass char) of different sizes. Samples of modern grass char (2–16 μg of C) were chemically oxidized, derivatized, and isolated by PCGC. We found that $0.80 \pm 0.40 \mu\text{g}$ of C min^{-1} per 50 injections of an assumed $FM_{\text{ex}} = 0.0$ was added in chemical oxidation and PCGC isolation. Fossil hexane soot revealed $0.15 \pm 0.08 \mu\text{g}$ of C min^{-1} per 50 injections of an assumed $FM_{\text{ex}} = 1.0$ was added in sample processing. The total indirect method C_{ex} was then calculated to be $1.0 \pm 0.5 \mu\text{g}$ of C min^{-1} per 50 injections and with $FM_{\text{ex}} = 0.15$.

When evaluated directly and indirectly the mass and isotopic composition of the time normalized C_{ex} added during sample processing and isolation was the same even though the collection window varied from 0.4 to 7 min. This suggests that $C_{\text{chemistry}}$ can be scaled with time. If the C_{ex} for indirect assessment was much larger than the direct method, the source of the C_{ex} may be a matrix effect of the oxidation process. The agreement of the two methods suggests that the C_{ex} is not associated with matrix effects during the processing of a sample.

The magnitude of the C_{ex} added during chemical oxidation ($C_{\text{chemistry}} = 0.5 \mu\text{g}$ of C min^{-1} per 50 injections) is approximately equal to that added during PCGC isolation ($C_{\text{PCGC}} = 0.6 \mu\text{g}$ of C min^{-1} per 50 injections). This was determined by the difference between $C_{\text{chemistry+PCGC}}$ and C_{PCGC} . Since all samples were treated to the same post-PCGC handling, our data suggests that only half of the nonspecific background (C_{ex}) is originating from PCGC isolation (e.g., column bleed) and post-PCGC sample handling. The dry injection blank was very small ($0.1 \mu\text{g}$ of C) suggesting that post PCGC handling is likely a small part of C_{PCGC} . The remainder, $C_{\text{chemistry}}$, is likely from coeluting compounds in the reagents and solvents used in the oxidation and derivatization processes. Reagents and solvents can become contaminated over time and with use. Therefore, if the source of this additional carbon is coeluting compounds, it is essential to frequently evaluate the C_{ex} (e.g., every 2 to 5 samples) to ensure reagent and solvent purity.

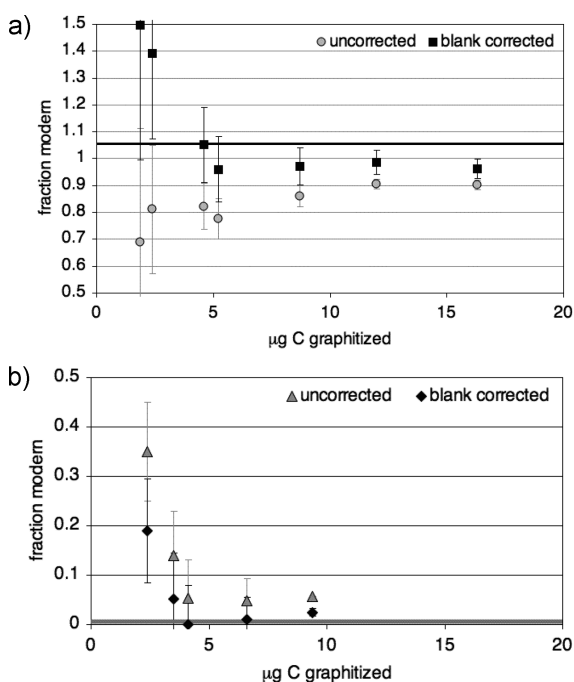


Figure 2. (a) Grass char and (b) hexane soot before (open symbols) and after (filled symbols) C_{ex} correction. The radiocarbon value of the unprocessed material is indicated by the bold line: grass char, $FM = 1.056 \pm 0.002$, and hexane soot, $FM = 0.005 \pm 0.001$.

Table 2. Type, Number (n), and Treatment of Materials (Indicated by Yes or No) Used to Quantify the C_{ex} and FM_{ex} Added during Chemical Oxidation and PCGC Isolation^a

evaluation	material	n	BPCA ^b	dichloromethane	PCGC ^c	extraneous carbon, C _{ex}	
						μg C ^d	FM
direct	dry injection	1	No	No	Yes	0.1	0.125 ± 0.034
indirect	modern vanillin	6	No	Yes	Yes	0.4 ± 0.2	0.0
indirect	dead vanillin	5	No	Yes	Yes	0.2 ± 0.1	1.0
	total indirect PCGC					0.6 ± 0.3	0.3 ± 0.1
direct	process blank	6	Yes	Yes	Yes	1.1 ± 0.2	0.200 ± 0.054
indirect	grass char	7	Yes	Yes	Yes	0.80 ± 0.40	0.0
indirect	hexane soot	5	Yes	Yes	Yes	0.15 ± 0.08	1.0
	total indirect chemistry + PCGC					1.0 ± 0.5	0.15 ± 0.08

^a Materials were subjected to varying treatments to determine the mass and source of C_{ex}. The uncertainty of the mass of extraneous carbon was estimated at 50% of the sample mass. The uncertainty of FM_{ex} determined by the indirect approach was estimated at 50% of the FM value. All estimates of C_{ex} are scaled to the width of the collection window per 50 injections to facilitate comparison between direct and indirect estimations of C_{ex}. ^b BPCA includes the chemical oxidation of BC into BPCAs and their subsequent derivatization, see text for details. ^c All samples processed through the PCGC were subjected to the same post-PCGC handling procedures. ^d The mass of C_{ex} is normalized to per minute per 50 injections.

Table 3. Radiocarbon Values (Fraction Modern) and Associated Uncertainty of Black Carbon Reference Materials before and after Correction for C_{ex}^a

type	UCID	duration (min)	C _{reported} (μg of C)	FM _{reported} ^b	C _{ex} (μg of C)	FM _{sample} ^c
grass char	11782	1.2	16.3	0.90 ± 0.02	1.32 ± 0.36	0.96 ± 0.03
	11801	3.7	12.0	0.91 ± 0.02	4.07 ± 1.11	1.27 ± 0.15
	11779	1.2	8.7	0.86 ± 0.04	1.32 ± 0.36	0.98 ± 0.06
	11777	2.1	5.2	0.78 ± 0.07	2.31 ± 0.53	1.24 ± 0.27
	11780	2.1	4.6	0.82 ± 0.09	2.31 ± 0.63	1.45 ± 0.39
	11778	0.4	2.4	0.81 ± 0.24	0.44 ± 0.12	0.95 ± 0.30
	11781	0.4	1.9	0.69 ± 0.43	0.44 ± 0.12	0.84 ± 0.56
	isolate average ± std deviation				0.824 ± 0.128	
bulk value						1.056 ± 0.002
hexane soot	11711	0.6	9.4	0.004 ± 0.010	0.660 ± 0.180	0.000 ± 0.012
	11723	0.6	6.6	0.049 ± 0.044	0.660 ± 0.180	0.032 ± 0.049
	11713	0.9	4.1	0.054 ± 0.077	0.990 ± 0.270	0.007 ± 0.103
	11710	0.9	3.5	0.139 ± 0.090	0.990 ± 0.270	0.115 ± 0.125
	11712	0.9	2.4	0.349 ± 0.100	0.990 ± 0.270	0.454 ± 0.178
isolate average ± std deviation				0.061 ± 0.055		0.036 ± 0.056
bulk value						0.005 ± 0.001

^a Duration (minutes) is the time the collection window is left open. The C_{ex} (C_{chemistry+PCGC}) is assumed to be 1.1 ± 0.2 μg of C per minute of collection for a 50 injection run with a FM = 0.2 ± 0.054 (see Table 2). The uncertainty associated with the FM_{reported} is the AMS machine uncertainty, and the uncertainty associated with FM_{sample} is the propagated uncertainty. The collection window duration was varied to collect individual BPCAs or ΣBPCAs. ^b After diazomethane correction. ^c Determined using eq 3.

Correcting for Extraneous Carbon and Associated Uncertainties. Radiocarbon measurements are typically reported with an uncertainty of the AMS measurement alone. As we have shown above, the corrected radiocarbon value of a CSRA sample is dependent on the mass and FM of the C_{ex}. In our work, if the sample was ≥ 50 μg of C, the C_{ex} was insignificant. However most of samples were small so the FM of small CSRA samples required a correction for the presence of C_{ex}. The uncertainties of all terms needed to be considered when reporting the uncertainty of the CSRA FM value. To determine the propagated total mathematical uncertainty of FM_{sample} (e.g., eq 3), we applied the following equation:

$$\sigma_{FM_{sample}}^2 = \left(\frac{\partial FM_{sample}}{\partial FM_{reported}}\right)^2 \sigma_{FM_{reported}}^2 + \left(\frac{\partial FM_{sample}}{\partial FM_{ex}}\right)^2 \sigma_{FM_{ex}}^2 + \left(\frac{\partial FM_{sample}}{\partial m_{reported}}\right)^2 \sigma_{m_{reported}}^2 + \left(\frac{\partial FM_{sample}}{\partial m_{ex}}\right)^2 \sigma_{m_{ex}}^2 \quad (4)$$

where $\sigma_{FM_{reported}}$ is the AMS uncertainty of FM_{reported} (machine uncertainty), $\sigma_{FM_{ex}}$ is the uncertainty for FM_{ex}, $\sigma_{m_{reported}}$ is the uncertainty for C_{reported} (uncertainty in graphitization), and $\sigma_{m_{ex}}$ is the uncertainty for C_{ex}. The total uncertainty of the direct process blank (C_{chemistry+PCGC} in Table 2) was used for FM_{ex} and C_{ex}.

To illustrate how correcting CSRA samples for C_{ex} affects the isotopic values and associated uncertainties,¹⁰ we corrected modern grass char and fossil hexane soot samples using the direct process blank determined in Table 2. For grass char, a modern BC standard,¹⁶ the measured FM_{reported} values for 7 small samples without C_{ex} correction (average FM_{reported} = 0.824 ± 0.128, Table 3) were all significantly lower than the FM value of the unprocessed material (FM = 1.056 ± 0.002, Figure 2). After correction for C_{chemistry+PCGC}, the FM_{sample} (average 1.098 ± 0.221) agreed with that of the unprocessed material. For hexane soot, a dead BC standard, the measured FM values without correc-

tion for C_{ex} (average $FM_{\text{reported}} = 0.061 \pm 0.55$, Table 3) were significantly higher than the unprocessed material ($FM = 0.005 \pm 0.001$). After correction for $C_{\text{chemistry+PCGC}}$, the FM_{reported} (average 0.036 ± 0.056) was within error of the FM of the unprocessed material. The deviation of low mass corrected hexane soot samples from the consensus value indicated that the mass or FM signature of $C_{\text{chemistry+PCGC}}$ was different for samples smaller than $5 \mu\text{g}$ of C. Because this phenomenon was not observed for low mass grass char samples, it appeared that the FM_{ex} value of ultrasmall samples ($5 \mu\text{g}$ of C) contained additional modern carbon. To avoid this complication, we avoided processing samples smaller than $5 \mu\text{g}$ of C.

These results demonstrate that the uncertainties of FM_{sample} associated with the preparation and isolation of samples by CSRA are significantly larger than the machine error. Propagated total uncertainty of modern process materials is much higher than ^{14}C depleted process materials due to (1) the logarithmic nature of radioactive decay and (2) the FM_{ex} was more ^{14}C depleted than modern. Each system will be distinct, therefore each user needs to evaluate the C_{ex} and FM_{ex} values specific for their system.

Thus, when considering CSRA applications, one must consider the magnitude of uncertainty required to provide useful information about the system being studied. For example, our interest in CSRA of BPCAs is to examine the BC in marine dissolved organic carbon (DOC).¹⁹ Bulk DOC, which is comprised of a wide range of organic molecules of varying ^{14}C ages, typically ranges from $FM = 0.8$ to 0.5 .¹² The BC in marine DOC has been postulated to be more depleted in radiocarbon. Provided that BC extracted from marine DOC has a propagated total uncertainty for FM less than 0.10 , the results should provide valuable information about this pool of recalcitrant carbon. However, if one was interested in studying the removal of BC from soils over a few centuries, much larger samples than those presented here are required in order to ensure that the contribution of C_{ex} to the FM_{reported} is insignificant. Regardless of the application, it is

equally important that CSRA users assess their ability to duplicate CSRA measurements. In some cases, the variation of duplicate analyses of CSRA samples may be larger than the propagated uncertainty, which may not be precise enough for certain applications. The mass and isotopic composition of C_{ex} should ideally be evaluated with each batch of samples, as we found that the mass of C_{ex} varied by over 50% over the course of 6 months.¹⁹

CONCLUSIONS

Half of the C_{ex} was added during PCGC isolation and half was added during the chemical oxidation and derivatization. Extraneous carbon added during PCGC isolation of CSRA samples was found to be a function of collection duration on the GC. The estimates of extraneous or nonspecific background carbon presented here are specific to the BPCA chemical isolation technique. After background correction, CSRA samples $5 \mu\text{g}$ of C were unreliable with respect to accuracy and precision. Another facility using the same chemical extraction technique would need to determine the extraneous carbon (C_{ex}) introduced to samples that they process. Different GC columns, solvents, and users will likely produce more or less C_{ex} carbon, with unique FM_{ex} signatures.

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