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

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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 \((C_{chemistry})\). We evaluated the blank uncertainty of propagated uncertainties of CSRA samples. 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 are a function of sample size and collection duration. The magnitudes 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 \(\leq 5 \mu g\) 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 sediments\(^10\) and marine dissolved organic carbon.\(^11,12\)

New developments in accelerator mass spectrometry (AMS) have decreased the sample size requirements for CSRA. Ultrasound samples\(^13\) and online \(^{14}C\) measurements\(^14\) enable CSRA as small as \(2 \mu g\) 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 \(2 \mu g\) 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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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 trimethylsil-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.

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.

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

| Material Processed | Use | Source | Bulk $^{14}$C (FM) |
|--------------------|-----|--------|-------------------|
| 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 |
| methanol           | solvent | Burdick and Jackson$^{a}$ | 0.000$^{c}$ |
| dichloromethane    | solvent | Omni Solvent | 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 $^{14}$C was measured in duplicate. $^{b}$ High-purity solvent. $^{c}$ Assumed radiocarbon values.
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 isopropryl 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 CO2 was purified, quantified, and reduced to graphite according to standard procedures.21 Measurements of 14C were made at the Keck Carbon Cycle Accelerator Mass Spectrometry Laboratory at University of California Irvine. In all cases, radiocarbon analysis is 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 95% of the activity in 1950 A.D., of National Bureau of Standards California Irvine. In all cases, radiocarbon analysis are reported °

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 (−CH3) to each carboxylic acid group, and this additional carbon alters the 13C signature of the sample. Since the isotopic composition of the derivative carbon is assumed to be 14C-free (FMderivative = 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 Cderivative, eq 1 is simplified to

\[
C_{\text{sample+chemistry+PCGC}} = C_{\text{sample}} + C_{\text{chemistry}} + C_{\text{PCGC}} = C_{\text{sample}} + C_{\text{ex}}
\]

(2)

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

**Extraneous Carbon Added during PCGC Isolation**

Two methods were used to evaluate the mass and FM of Cex 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 CPCGC). 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 FMPCGC of 0.125 ± 0.034. Because the sample collection window varied with sample type (Figure 1), we normalized the amount of Cex (µg of C) to collection duration (in minutes) and 50 injections. Normalizing the Cex to time assumes the majority of Cex 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 Cex, even samples that included the Cchemistry. Thus evaluated directly, the CPCGC 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 CPCGC 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 Cex, and the presence of Cex would cause a deviation in the consensus 13C value. The FM values of samples were expressed by the following equation:

\[
FM_{\text{sample}} = \frac{FM_{\text{reported}}C_{\text{reported}} - FM_{\text{PCGC}}C_{\text{PCGC}}}{C_{\text{sample}}}
\]

(3)
where \( \text{FM}_{\text{sample}} \) is the radiocarbon value of the sample corrected for \( \text{C}_{\text{PCGC}} \). \( \text{FM}_{\text{reported}} \) is the measured radiocarbon value of the sample uncorrected for \( \text{C}_{\text{PCGC}} \) and \( \text{FM}_{\text{PCGC}} \) is the radiocarbon value of the extraneous carbon added during PCGC isolation. Because \( \text{C}_{\text{ex}} \) was assessed as a combination of both dead and modern material, \( \text{FM}_{\text{ex}} \) fell between 0.0 and 1.0. Therefore, small samples of modern isotopic composition were lower and samples of \(^{14}\text{C}\)-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 (\( \text{FM}_{\text{sample}} = 1.052 \), Table 1) samples revealed that \( \text{C}_{\text{PCGC}} \) (\( \text{FM}_{\text{PCGC}} = 0.0 \)) was 0.4 ± 0.2 \( \mu \text{g} \) of \( \text{C} \) min\(^{-1} \) per 50 injections. The PCGC isolation of a series of different sized samples of \(^{14}\text{C}\)-free vanillin (\( \text{FM}_{\text{sample}} = 0.002 \)) revealed an additional 0.2 ± 0.1 \( \mu \text{g} \) of \( \text{C} \) min\(^{-1} \) per 50 injections was added with an assumed \( \text{FM}_{\text{PCGC}} = 1.0 \). Combined, these two blanks revealed the total indirect \( \text{C}_{\text{PCGC}} \) of 0.6 ± 0.3 \( \mu \text{g} \) of \( \text{C} \) with an average \( \text{FM}_{\text{PCGC}} = 0.3 \) (Table 2).

The difference of 0.5 \( \mu \text{g} \) of \( \text{C} \) min\(^{-1} \) per 50 injections of \( \text{C}_{\text{ex}} \) added to isolated vanillin samples calculated using standard materials (0.6 ± 0.3 \( \mu \text{g} \) of \( \text{C} \) min\(^{-1} \) per 50 injections) as compared to the dry injections (0.1 \( \mu \text{g} \) of \( \text{C} \) 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 \( \text{C}_{\text{ex}} \) is mobilized than during the absence of solvent. The \( \text{FM}_{\text{ex}} \) values for vanillin (\( \text{FM}_{\text{ex}} = 0.3 ± 0.1 \)) and that for the dry injections (\( \text{FM}_{\text{ex}} = 0.125 ± 0.034 \)) were similar suggesting the same source of \( \text{C}_{\text{ex}} \). Other possible explanations are that \( \text{C}_{\text{PCGC}} \) 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 \( \text{C} \) with a \( \text{FM} = 0.3 \) was being added to samples from PCGC. Possible sources of \( \text{C}_{\text{PCGC}} \) 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 (\( \text{C}_{\text{chemistry}}+\text{PCGC} \)).** 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 remove any extraneous carbon added during sample preparation. Similar to the evaluation of \( \text{C}_{\text{ex}} \) added during PCGC isolation, we evaluated the mass and FM of \( \text{C}_{\text{ex}} \) added during the chemical methods and PCGC isolation (\( \text{C}_{\text{chemistry}}+\text{PCGC} \)) using both an indirect and direct approach. To evaluate \( \text{C}_{\text{ex}} \) directly, the chemical oxidation, derivatization, and PCGC isolation steps were carried out with no sample added. In this way, direct analysis of the \( \text{C}_{\text{ex}} \) was 1.1 ± 0.2 \( \mu \text{g} \) of \( \text{C} \) min\(^{-1} \) per 50 injections and \( \text{FM} = 0.200 ± 0.054 \) (Table 2).

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

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

The magnitude of the \( \text{C}_{\text{ex}} \) added during chemical oxidation (\( \text{C}_{\text{chemistry}} = 0.5 \mu \text{g} \) of \( \text{C} \) min\(^{-1} \) per 50 injections) is approximately equal to that added during PCGC isolation (\( \text{C}_{\text{PCGC}} = 0.6 \mu \text{g} \) of \( \text{C} \) min\(^{-1} \) per 50 injections). This was determined by the difference between \( \text{C}_{\text{chemistry}}+\text{PCGC} \) and \( \text{C}_{\text{PCGC}} \). Since all samples were treated to the same post-PCGC handling, our data suggests that only half of the nonspecific background (\( \text{C}_{\text{ex}} \)) 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 \( \text{C} \)) suggesting that post PCGC handling is likely a small part of \( \text{C}_{\text{PCGC}} \). The remainder, \( \text{C}_{\text{chemistry}} \), 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 \( \text{C}_{\text{ex}} \) (e.g., every 2 to 5 samples) to ensure reagent and solvent purity.

![Figure 2](image-url)

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

| Material       | Type       | Number (n) | BPCA | dichloromethane | PCGC | Treatment of Materials (Indicated by Yes or No) Used to Quantify the C_{ex} and FM_{ex} | Extraneous carbon, C_{ex} (µg C) | FM,
|----------------|------------|------------|------|----------------|------|-------------------------------------------------------------------------------------------------|----------------------------------|------|
| process blank  | direct     | 6          | Yes  | Yes            | Yes  | FM_{sample} (average 1.098 ± 0.002)                                                                | 0.90 ± 0.02, 1.32 ± 0.36          | 0.96 ± 0.03 |
| grass char     | direct     | 7          | Yes  | Yes            | Yes  | FM_{sample} (average 1.098 ± 0.002)                                                                | 0.90 ± 0.02, 1.32 ± 0.36          | 0.96 ± 0.03 |
| hexane soot    | indirect   | 5          | Yes  | Yes            | Yes  | FM_{sample} (average 1.098 ± 0.002)                                                                | 0.90 ± 0.02, 1.32 ± 0.36          | 0.96 ± 0.03 |

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

| Type of Treatment | UCID | Duration (min) | C_{reported} (µg of C) | FM_{reported} | C_{ex} (µg of C) | FM_{sample} | C_{ex} (µg of C) | FM_{sample} | C_{ex} (µg of C) | FM_{sample} | C_{ex} (µg of C) | FM_{sample} |
|------------------|------|----------------|------------------------|---------------|-----------------|--------------|-----------------|--------------|----------------|--------------|----------------|--------------|
| isolating        | 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 ± 0.53     | 1.24 ± 0.27  |                |              |                |              |                |              |
|                  | 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  |                |              |                |              |                |              |

**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:

\[
\sigma_{FM_{sample}}^2 = \left( \frac{\sigma_{FM_{sample}}}{\sigma_{FM_{reported}}} \right)^2 \sigma_{FM_{reported}}^2 + \left( \frac{\sigma_{FM_{sample}}}{\sigma_{FM_{ex}}} \right)^2 \sigma_{FM_{ex}}^2 + \left( \frac{\sigma_{FM_{sample}}}{\sigma_{mex}} \right)^2 \sigma_{mex}^2
\]

where \(\sigma_{FM_{reported}}\) is the AMS uncertainty of FM_{reported} (machine uncertainty), \(\sigma_{FM_{ex}}\) is the uncertainty for FM_{ex}, \(\sigma_{mex}\) is the uncertainty for C_{ex} reported (uncertainty in graphitization), and \(\sigma_{mex}\) 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, 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, the measured FM_{sample} 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 ± 0.021) 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 \( C_{\text{chemistry}} + \text{PCGC} \), the \( FM_{\text{reported}} \) (average \( 0.036 \pm 0.056 \)) 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 \( C_{\text{chemistry}} + \text{PCGC} \) was different for samples smaller than 5 \( \mu g \) 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 \( \mu g \) of \( C \)) contained additional modern carbon. To avoid this complication, we avoided processing samples smaller than 5 \( \mu g \) of \( C \).

These results demonstrate that the uncertainties of \( FM_{\text{sample}} \) 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, the interest in CSRA of BPCAs is to examine the BC in marine dissolved organic carbon (DOC). \(^{12}\) 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 \( FM_{\text{reported}} \) 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. Extrinsic 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 \( \mu g \) 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.

**ACKNOWLEDGMENT**

The authors would like to thank John Southon, Guacaria dos Santos, Sheila Griffin, Dachun Zhang, and Xiaomei Xu for their technical assistance and comments. We would also like to thank two anonymous reviewers and the editor, Reinhard Niessner, for their comments and suggestions on the manuscript. This work was funded by the National Science Foundation Chemical Oceanography Program.

Received for review August 25, 2009. Accepted November 2, 2009.

AC901922S