

Radiocarbon as a Tool To Apportion the Sources of Polycyclic Aromatic Hydrocarbons and Black Carbon in Environmental Samples

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To determine the relative inputs of polycyclic aromatic hydrocarbons (PAHs) and black carbon (BC) in environmental samples from the combustion of fossil fuels and biomass, we have developed two independent analytical methods for determining the ¹⁴C abundance of PAHs and BC. The 5730 yr half-life of ¹⁴C makes it an ideal tracer for identifying combustion products derived from fossil fuels (¹⁴C-free) versus those stemming from modern biomass (contemporary ¹⁴C). The ¹⁴C abundance of PAHs in several environmental Standard Reference Materials was measured by accelerator mass spectrometry after extraction and then purification by high-performance liquid chromatography and preparative capillary gas chromatography. This method yields pure compounds that allow for a high degree of confidence in the ¹⁴C results. The PAHs data were then used to compare and evaluate results from an operationally defined thermal oxidation method used to isolate a BC fraction. The ¹⁴C compositions of PAHs and BC were very similar and suggest that the thermal oxidation method employed for isolating BC is robust and free from interferences by non-BC components. In addition, these data indicate that both the PAHs and the BC species derive mostly from fossil fuels and/or their combustion products.

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Introduction

Black carbon (BC) and polycyclic aromatic hydrocarbons (PAHs) are products of the incomplete combustion of fossil fuels, biomass, and detrital organic matter (1–4). While fluxes and composition can vary with fuel type and burn conditions (5, 6), natural forest and grass fires as well as anthropogenic activities, such as burning of vegetation for energy and “slash and burn” methods of deforestation (biomass burning), are much more significant sources of BC (and presumably PAHs) than fossil fuels. For example, global emissions of BC have been estimated to be 7–24 Tg (Tg = 10¹² g) for fossil fuel and 40–600 Tg for biomass sources (2, 7, 8). These inputs of carbon are quite substantial and have been implicated in air visibility (9), climate (10), sorption of hydrophobic organic contaminants in aquatic systems (11), and as a significant component of the total organic carbon (TOC) in recent sediments (12–14).

Sediment and ice core records of BC and PAHs reveal that emissions of these species have dramatically increased during the past century (11, 15–20). The general trend in the Northern Hemisphere is a smooth increase beginning around 1880 to a maximum in the 1950s and 1960s (when coal usage was at its highest) and then a slow decrease until the present. However, one recent study of several sediment cores in the United States now shows that emissions of PAHs are increasing again (beginning in the 1990s) and are suggested to be due to urban sprawl (21). These century-long records generally parallel society’s increasing reliance on fossil fuels for energy and transportation during the industrial revolution but also correspond to rapid population expansion and urbanization. Biomass burning associated with agricultural practices, heating, and land clearance for urban expansion would be expected to increase concomitantly. These relationships also would be expected to vary locally and regionally. Therefore, it is not straightforward to establish which combustion sources have contributed to BC and PAHs through time. However, this information is necessary for developing temporal records so that current and future trends can be placed in the context of long-term variability and also to determine the success of source control measures.

Methods for determining and apportioning BC and PAHs have met with moderate degrees of success. Because BC represents a continuum of combustion products with a range in chemical and physical properties, a variety of operationally defined methods have been developed, including optical, chemical, thermal, or a combination of chemical and thermal techniques (1, 3). These techniques can yield very different results as evidenced in a recent intercalibration exercise where the measured BC content for an urban aerosol ranged from 12 to 92 mg g⁻¹ depending on the method and laboratory (22, 23). These results suggest that our ability to quantitatively measure and apportion BC is method-specific.

Sensitive methods have been used to apportion some sources of PAHs. These methods are commonly based on marker compounds presumed unique to a single source or the ratios of specific PAHs. In particular, the distribution of alkyl-substituted relative to parent PAHs has been successfully used to apportion petrogenic (petroleum) and pyrogenic (combustion) sources (18, 24, 25). Parent compound ratios such as phenanthrene:anthracene and fluoranthene:pyrene are also useful indicators of combustion processes (26). While such approaches provide a basis for differentiating petrogenic from pyrogenic sources, identification and quantification of pyrogenic PAHs derived from fossil fuel versus biomass combustion is more difficult. Two alkylphenanthrenes,

TABLE 1. Background Information and Bulk Properties of SRMs Investigated in This Study

sample id	source	physical size (μm)	date sampled or prepared	TOC (%) ^a	$\delta^{13}\text{C}$ of TOC (‰ vs VPDB)	f_M of TOC ^b	f_C of TOC ^c
SRM 1941a	Baltimore Harbor, Chesapeake Bay, 0–10 cm depth	150–250	sampled in 1991	4.8 ± 1.2^d	-25.14 ± 0.10^e	0.438 ± 0.005^e	0.350 ± 0.004^f
SRM 1944	combined from 6 locations in New York Bay and Newark Bay, 0–10 cm depths	61–250	sampled in 1994	4.4 ± 0.3^g	-25.51 ± 0.10^e	0.413 ± 0.004^e	0.344 ± 0.003^h
SRM 1597	extracted from medium crude coke oven tar with 10% methylene chloride in pentane	na ⁱ	prepared in 1986	na	na	na	na
SRM 1649a	parking lot in Washington, DC	<125	sampled in 1976–1977	17.68 ± 0.19^j	-25.327 ± 0.400^k	0.517 ± 0.007^l	0.383 ± 0.005^m

^a Total organic carbon (TOC) for SRMs 1941a and 1944 and defined as total, non-carbonate carbon for SRM 1649a (23). ^b Fraction modern (f_M) of total organic carbon. Uncertainties are calculated at the 95% confidence level. Each value is corrected for ^{14}C decay from time of sampling or calendar age of deposition into the sediments until time of analysis using a half-life of 5730 yr. Calendar ages of deposition for SRMs 1941a and 1944 were calculated using the mean sediment depth (5 cm) and an estimated sedimentation rate of 0.5 cm yr⁻¹. These dates are 1981 and 1984, respectively. ^c Fraction contemporary (f_C) of total organic carbon. Estimated by dividing the f_M of the sample by the f_M of the atmosphere at the time of sampling or calendar age of deposition. ^d Noncertified value in the Certificate of Analysis (37). ^e Determined as part of this study. ^f We used an f_M of the atmosphere of ~1.25 for 1981 (40, 41). ^g Noncertified value in the Certificate of Analysis (38). ^h We used an f_M of the atmosphere of ~1.20 in 1984 (40, 41). ⁱ na, not applicable. ^j Certified value in the Certificate of Analysis (23). ^k The mean and 95% uncertainty value of several noncertified values listed in the Certificate of Analysis (23). ^l Information value and 95% uncertainty listed in the Certificate of Analysis (23). ^m The f_M of the atmosphere was ~1.35 (40, 41) during the time of sampling, 1976–1977.

7-isopropyl-1-methyl phenanthrene (retene) and 1,7-dimethyl phenanthrene, have shown promise in distinguishing wood from fossil fuel combustion sources (27, 28). They have been proposed as tracers of soft (gymnosperm) wood combustion because these compounds are believed to derive primarily from abietic acid and pimaric acid, respectively, which are natural products in pine resin. However, these compounds are not exclusive to wood combustion. For example, certain organic-rich ancient (Jurassic) sediments have been found to contain enriched proportions of these same alkyl phenanthrenes (29), indicating that a petrogenic origin is possible. There also is no well-defined tracer of angiosperm wood combustion. Stable carbon isotope ratios of individual PAHs may provide some insight into sources due to natural variations in the isotopic composition of the precursor materials (30, 31). However, different combustion sources (e.g., fossil fuels vs biomass) may have identical isotopic signatures, and the extent to which secondary factors, especially combustion, lead to isotopic fractionation (i.e., modify the initial isotopic signatures) is presently unclear (32, 33).

The 5730 yr half-life of ^{14}C makes it ideal for discriminating combustion products derived from fossil fuels (^{14}C -free) versus those stemming from modern biomass (contemporary ^{14}C). Furthermore, in comparison to stable carbon isotope ratios, ^{14}C has well-defined end members, behaves conservatively upon introduction to the environment, and also has a large dynamic range (~500). The potential of using ^{14}C to distinguish PAH sources has been recognized by several groups; however, until recently, analytical constraints have limited this approach to the compound-class level (34, 35). Bulk ^{14}C measurements are susceptible to temperature (volatility) effects due to variations in particle and vapor phase PAH distributions and also do not allow for source apportionment of specific PAHs. Molecular level ^{14}C measurements (36) of PAHs offer the potential to quantify fossil fuel and biomass contributions to individual pyrogenic PAHs. Similar ^{14}C -based approaches for source apportioning BC in environmental matrices have been attempted, but the results vary as a function of the analytical methodology applied, implying methodological biases (22, 23).

Here we present and describe results from two independent analytical methods that determine the ^{14}C abundance of PAHs and BC. Four Standard Reference Materials (SRMs) provided by the National Institute of Standards and Tech-

nology (NIST) were used to evaluate our analytical methods and to examine potential variability of ^{14}C abundance in BC and PAHs. These samples were chosen because they are well-studied, homogeneous, and commercially available. The goals of this manuscript are 2-fold. First, we will introduce the concept of molecular level ^{14}C abundance measurements of PAHs for source apportionment. Second, we will use these ^{14}C measurements of the PAHs to provide a check on the validity of the BC method.

Experimental Methods

Samples. Background and bulk properties of the SRMs investigated in this study are presented in Table 1. Additional information is listed in the Certificate of Analysis of each SRM (23, 37–39). Three of the SRMs are environmental samples: SRM 1941a (Organics in Marine Sediment), SRM 1944 (New York/New Jersey Waterway Sediment), and SRM 1649a (Urban Dust). The fourth sample, SRM 1597 (Complex Mixture of PAHs from Coal Tar), is a solvent extract of coal tar that was purified on a chromatographic column packed with clay (to remove highly polar compounds). No extraction or purification of SRM 1597 was performed prior to single-compound isolation (see below).

Extraction and Purification. Approximately 20–200 g of SRMs 1941a, 1944, and 1649a was extracted with a mixture of dichloromethane (DCM)/methanol (93/7, volume fraction) in a Soxhlet apparatus for 48 h or by pressurized fluid extraction (Dionex ASE-200) using DCM at 7 000 kPa at 100 °C. The extract was reduced in volume and dried onto 10 g of precombusted quartz sand. This mixture was added to the top of a glass-column pressurized flash chromatography system (5 cm × 45.7 cm) packed with silica gel (20–45 μm particle size). Three fractions (each 375 mL) were collected under constant pressure of nitrogen. The first fraction was eluted with 100% hexane and contained only aliphatic hydrocarbons. The second fraction was eluted with 50:50 hexane/toluene and contained the aromatic fraction, including PAHs and an unresolved complex mixture (UCM). The remaining polar material was collected using 100% methanol and saved for further studies. To separate the PAHs from the aromatic UCM in the second fraction, each sample was injected into a Hitachi L-6200 high-performance liquid chromatograph (HPLC) with an ultraviolet detector (254 nm) and separated into ring-size classes on a 30 cm × 7.8 mm Waters $\mu\text{Bondapak NH}_2$ column (42). The mobile phase was

a mixture of hexane/DCM (98/2, volume fraction) at a flow rate of 2 mL min⁻¹. Three fractions were collected at 12–24, 24–41, and 41–60 min. The 12–24 min fraction contained the aromatic UCM and 2-ring PAHs (naphthalene and alkyl naphthalenes) and was not processed further. The latter two fractions contained PAHs with 3–6 rings and were retained for isotope ratio monitoring gas chromatography–mass spectrometry (irmGC–MS) and single-compound isolation.

irmGC–MS of PAHs. Stable carbon isotope analyses were performed on a Hewlett-Packard 6890 GC interfaced to a modified Finnigan GC Combustion III unit followed by a Finnigan Delta Plus isotope ratio mass spectrometer. Compounds were separated on a J&W DB-5 fused silica capillary column (60 m length; 0.32 mm diameter; 0.25 μm film thickness). During each analysis, pulses of reference CO₂ were bled into the mass spectrometer and were used to calibrate it relative to the Vienna Pee Dee belemnite standard (VPDB). Each sample was injected three times, and the data reported are mean values. The repeatability (expressed as the standard deviation of the three injections) was better than ±0.9‰ and usually within ±0.3‰. The δ¹³C values for co-injected perdeuterated *n*-C₃₈ alkane were within 0.25‰ of the actual value (as determined with standard off-line techniques).

Preparative Capillary Gas Chromatography (PCGC).

Details on isolating individual organic compounds by PCGC are described in detail by Eglinton et al. (36). Briefly, individual PAHs were isolated from SRM 1597 and from the 3–6-ring fractions of SRMs 1941a, 1944, and 1649a with repeated injections (~100) on a PCGC system until 25–250 μg of each individual PAH was obtained. PAHs were separated with a 60 m SGE BPX-5 fused silica column (60 m length; 0.53 mm diameter; 0.5 μm film thickness) and collected in cryogenically cooled glass u-tubes (0 °C). Six different compounds can be trapped per injection. The isolated compounds were rinsed from the u-tubes with DCM and ~5% was saved to test for purity by injection on a GC employing a single inlet with dual capillary columns and dual flame ionization detectors (FIDs). The remaining material was transferred to precombusted quartz tubes (12 mm × 20 cm), where the solvent was evaporated under a stream of nitrogen, and ~100 mg of copper oxide was added to each tube. The tubes were evacuated on a vacuum line and then combusted at 850 °C for 5 h. The resulting carbon dioxide was isolated through a series of cold traps, quantified by manometry, and then reduced to graphite (43). Targets of the graphite were pressed and mounted on target wheels for ¹⁴C analysis by acceleratory mass spectrometry (AMS).

BC Analysis. BC was isolated for ¹⁴C analysis using a modified version of the method described by Gustafsson et al. (11, 44). This method operationally defines BC in environmental samples as the fraction of carbon remaining after thermal oxidation at 375 °C for 24 h (to remove labile organic carbon) and acidification (to remove inorganic carbon). Briefly, ~200 mg of material was thinly spread onto 3–4 glass Petri dishes (10 cm diameter) and heated at 375 °C for 24 h in a programmable muffle furnace. The residue in each Petri dish was combined and then analyzed for ¹⁴C analysis in a similar manner for that of sedimentary TOC (45). Briefly, residues were treated with 10% hydrochloric acid and centrifuged. The supernatant was removed by pipet, and the residue was rinsed with deionized water and filtered on a precombusted quartz filter (Whatman QMA, pore size 0.45 μm). After several rinses with deionized water, the filter was removed, placed in a desiccator until dry, rolled, and then packed into 12 mm × 20 cm quartz tubes containing copper oxide (100 mg) and elemental silver wires. The tubes were then attached to a vacuum line, evacuated, flame-sealed, and combusted at 850 °C for 5 h. The carbon dioxide was

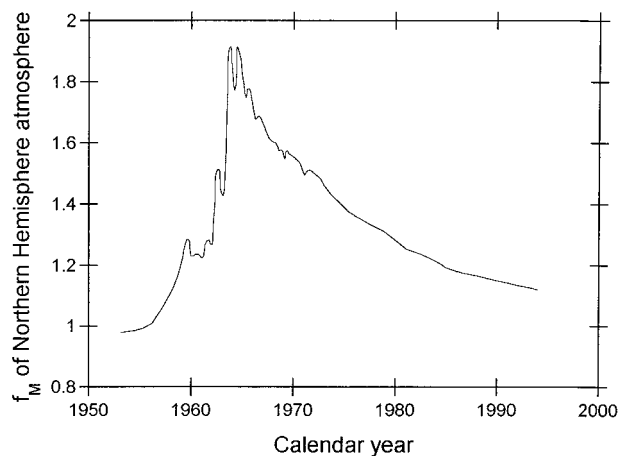


FIGURE 1. ¹⁴C abundance of the Northern Hemisphere atmosphere (40, 47).

isolated through a series of cold traps and quantified by manometry. Approximately, 10% of the carbon dioxide was analyzed for δ¹³C analysis, and the remainder was reduced to graphite for ¹⁴C analysis by AMS.

Reporting Radiocarbon Results. In this study, all ¹⁴C measurements are expressed as fraction modern (*f_M*). This term is defined by reference to the international standard for ¹⁴C dating and is derived from the ¹⁴C/¹²C ratio observed, relative to 0.95 times that of the contemporary standard for ¹⁴C dating, SRM 4990B (46). Each result is corrected for δ¹³C fractionation and for ¹⁴C decay from the approximate date of sampling (or deposition) to the date of AMS analysis. Relative estimates of fossil versus biomass inputs during the late 20th century cannot be simply derived from values of *f_M* because above ground nuclear weapon testing almost doubled the ¹⁴C content of the atmosphere in the 1950s and 1960s; a gradual decline in the atmospheric inventory of ¹⁴C has occurred in subsequent decades (Figure 1; 40, 41). This ¹⁴C “bomb spike” propagated into the biosphere via photosynthetic carbon fixation and is reflected in combustion products of recently synthesized biomass. To compensate for any bomb-derived ¹⁴C in BC and PAHs from living biomass, the fraction of contemporary carbon (*f_C*) is calculated using the time-dependent ¹⁴C content of the living biosphere with the following equation:

$$f_{C(\text{sample})} = f_{M(\text{sample})} / f_{M(\text{atm})} \quad (1)$$

where *f_{C(sample)}* and *f_{M(sample)}* are the *f_C* and *f_M* of the sample, respectively, and *f_{M(atm)}* is the *f_M* of the atmosphere at the time of PAHs formation (in this study, we are using the date of sampling or deposition) (47). The fraction of fossil carbon is then 1 – *f_C*. Caution must be exercised when interpreting *f_C* since this approach assumes that the combusted biomass has the same ¹⁴C content as the atmosphere at the time of formation. While this assumption is valid for combustion of freshly grown material (e.g., grass), it may lead to errors for products derived from burning of vegetation with multi-year life-cycles (e.g., trees) that continuously integrate the *f_M* of the atmosphere into their biomass (48).

For individual PAHs and BC, analytical repeatability for small-sample ¹⁴C-AMS (25–300 μg of carbon) targets typically ranges between ±1% and 2% of the *f_M*, when determined for identical replicate samples and standards (determined on “modern” samples). In the case of small *f_M* values reported for largely “fossil” samples, other factors such as counting statistics and internal AMS error figure more strongly into the reported 95% confidence level errors (typically ±10–30% of the *f_M*).

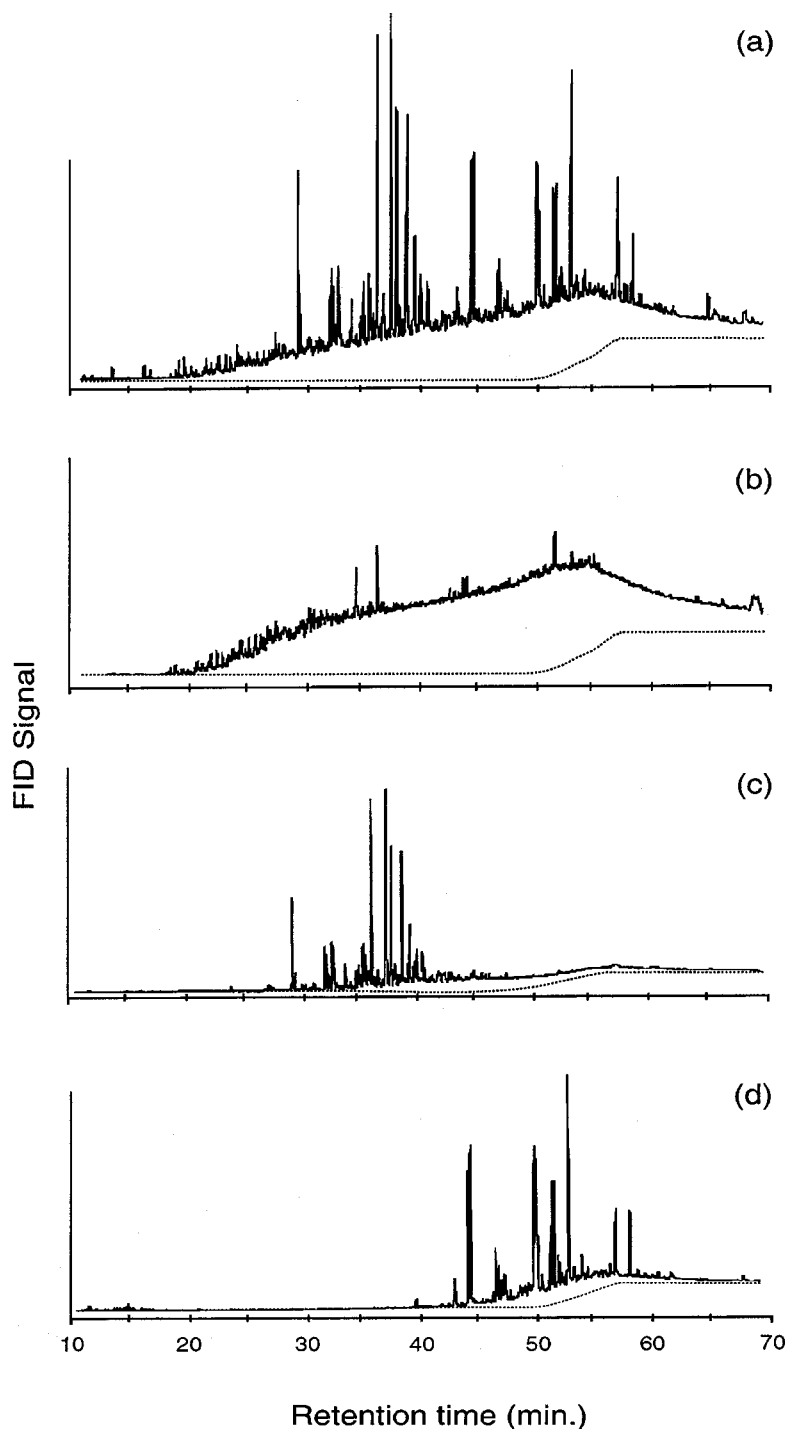


FIGURE 2. High-resolution gas chromatographic traces of different organic fractions: (a) crude aromatic fraction of SRM 1944. Panels b, c, and d contain the normal phase aminopropyl HPLC fractions 1, 2, and 3, respectively, of the crude aromatic fraction of SRM 1944 (shown in panel a). The dashed line is the GC baseline.

Results and Discussion

Isolation of PAHs for ^{14}C Analysis. Obtaining clean fractions that yield baseline-resolved components upon PCGC is important for accurate ^{14}C measurements of individual compounds (36). Previous attempts at isolating individual PAHs were hindered by trapping large amounts of UCM when sample preparation only involved silica gel chromatography (49). This is shown in the crude PAHs fraction of SRM 1944 following silica gel chromatography (Figure 2a) in which the UCM dominates the gas chromatogram. Additional separation of the crude PAHs fraction by normal phase aminopropyl HPLC provided a means to remove most of the UCM by

elution according to the number of aromatic rings (Figure 3) (42, 50). The aromatic UCM and 2-ring PAHs, 3–4-ring PAHs, and 5–6-ring PAHs were collected in fractions 1, 2 and 3, respectively (Figure 2b–d). (Similar chromatograms were observed for SRMs 1941a and 1649a.) Since the additional HPLC step did not remove all of the aromatic UCM, especially for SRM 1944, subsequent PCGC isolation of some compounds from these fractions contained small quantities of aromatic UCM. Gas chromatograms of PCGC traps from SRM 1597 are shown in Figure 4 and indicate that trapping of individual PAHs was highly effective. Significant amounts of material (up to 25%) were often lost during PCGC.

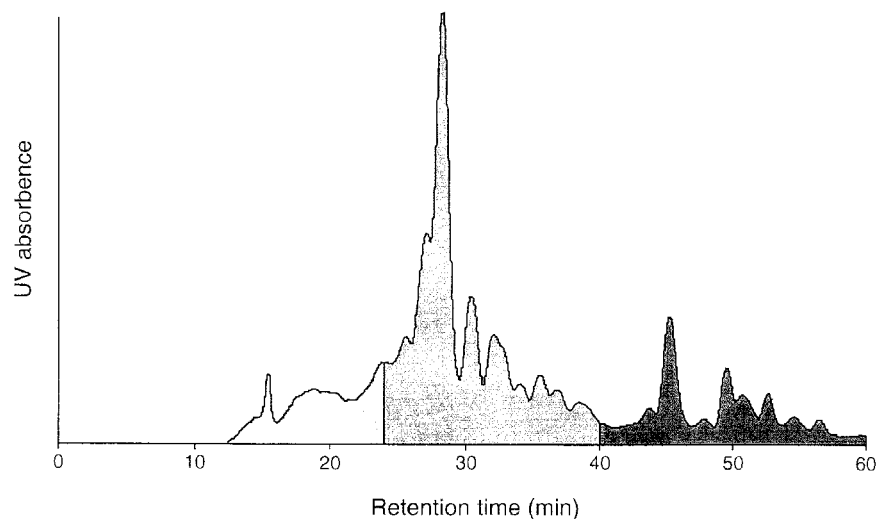


FIGURE 3. Normal phase aminopropyl HPLC chromatogram of the crude aromatic fraction of SRM 1944. The aromatic UCM and 2-ring PAHs, 3–4-ring PAHs, and 5–6-ring PAHs were collected from 12 to 24 min (fraction 1), from 24 to 41 min (fraction 2), and from 41 to 60 min (fraction 3), respectively.

Efforts to identify these losses have been unsuccessful but must be considered in future studies when sample sizes are very small.

^{14}C and ^{13}C in PAHs. The ^{14}C abundance in PAHs from each SRM is listed in Table 2. PAHs isolated from SRM 1597 contained very little or no ^{14}C ($f_M < 0.0085$). These measurements are consistent with the fossil fuel origin (coal tar) of this SRM and indicate that modern carbon contamination is not significant in this method. SRM 1597 will not be discussed further in this paper. Values of f_M in PAHs for SRMs 1941a, 1944, and 1649a ranged from 0.01 to 0.29 and reveal that these samples contain PAHs that derive mainly from fossil fuels and/or the combustion of fossil fuels. The latter appears to be the more dominant source based on the (methyl phenanthrenes and anthracenes):phenanthrene ratios, which were 1, 1.5, and 0.5 in SRMs 1941a, 1944, and 1649a, respectively. [For comparison, Gustafsson and Gschwend (51) compiled the results from 20 studies and found that the approximate values for this ratio were 0.5 and 5 for pyrogenic and petrogenic sources, respectively.] While difficult to actually quantify, the impact of small quantities of UCM trapped with individual PAHs in this study is likely to be minimal since we have found that the UCM in these SRMs and other environmental samples is largely fossil in origin (52). For example, the f_M of the UCM in SRM 1944 is 0.011.

Excluding perylene, which will be discussed in the next paragraph, PAHs in SRMs 1941a and 1649a had similar ^{14}C contents with f_M values from 0.0347 to 0.0864. SRM 1944 had PAHs with the lowest and highest ^{14}C content ($f_M = 0.0144$ –0.143). These molecular data reveal the existence of isotopic heterogeneity both between samples and for individual PAHs within a single sample. Surprisingly, benzo[ghi]perylene had the largest contribution from modern carbon in all three SRMs. This finding conflicts with previous studies that have suggested that this PAH may be a marker for automobile emissions (53). Prior laboratory studies, however, comparing PAHs patterns from flaming combustion of oak, pine, and paraffin fuels support the observations here, demonstrating significant emissions of benzo[ghi]perylene from biomass burning (pine but not oak) (32). Individual PAHs exhibiting consistently lower radiocarbon contents are likely the best tracers of fossil fuel inputs. Chrysene yielded the lowest f_M values in SRMs 1941a and 1944, while pyrene had the lowest ^{14}C content in SRM 1649a. The latter is consistent with field studies of aerosols from Albuquerque, NM, where the concentration of pyrene (out of 20 PAHs) was the most highly

correlated to estimates of fossil fuel-derived carbon inputs from bulk ^{14}C analysis (54).

The ^{14}C abundances of perylene in SRMs 1941a and 1944 reflect the multiple sources of this PAH to sediments. These include fallout or runoff from the combustion of organic matter, petroleum spills or seeps, and in situ diagenetic formation from aquatic and/or terrestrial precursors (55). Perylene in SRM 1944 appears to be predominantly fossil fuel-derived as it has a ^{14}C abundance similar to the other PAHs. A natural in situ source of perylene, however, is apparent in SRM 1941a, where its ^{14}C abundance is quite distinct from the other PAHs and closer to the bulk TOC (Table 1, Figure 5). In the absence of ancillary information, it is difficult to accurately constrain the importance of each precursor because of the contrasting ^{14}C contents of aquatic and terrestrial organic matter (56).

The $\delta^{13}\text{C}$ values for each PAH are shown in Table 2 and reveal a narrow range in isotopic composition (–25.8 to –22.4‰). Similar values for PAHs have been observed in harbor sediments (31) and atmospheric particles (57). Very little isotopic heterogeneity (–24.9 to –24.3‰) exists in the coal tar extract, SRM 1597, which is not surprising since each PAH is derived from the same source of organic matter. The $\delta^{13}\text{C}$ values in the two sediment SRMs, 1941a and 1944, were more ^{13}C -depleted than those for the urban dust, SRM 1649a.

BC Results. The bulk content, $\delta^{13}\text{C}$ values, and ^{14}C abundance of BC in SRMs 1941a, 1944, and 1649a are listed in Table 3. Repeatability was also good for the bulk BC measurements (<4% relative standard deviation), $\delta^{13}\text{C}$ values (<0.1‰; standard deviation) and ^{14}C measurements (<0.02 f_M units; 13–30% of the reported value). The ^{14}C abundance of each SRM reveals that >90% of the BC is derived from the combustion of fossil fuels. These ^{14}C results are consistent with the urban settings of each SRM where fossil inputs, especially vehicular and industrial emissions, dominate. Such information will also be useful to parties interested in the different sorptive capabilities of BC (fossil vs biomass derived) for planar, hydrophobic organic contaminants in marine sediments (11, 51).

In this study, BC was isolated with an operationally defined thermal method. As mentioned earlier, a recent international intercomparison exercise (using SRM 1649a) compared results from many different techniques. Two other groups also used a 24-h 375 °C oxidation step that was similar to the one employed here, and agreement for bulk BC content of SRM 1649a was better than 10%. In terms of the ratio of black

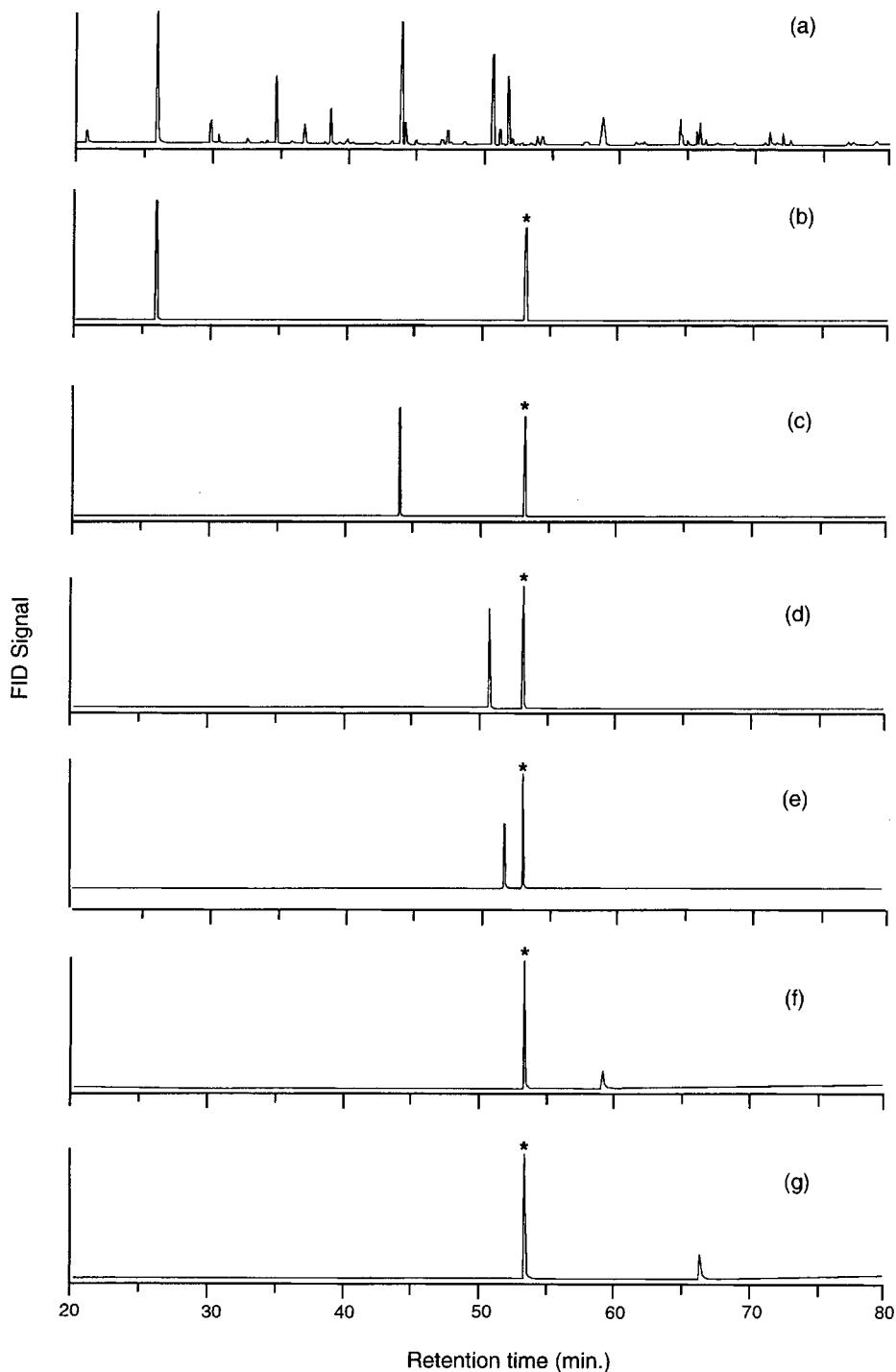


FIGURE 4. High-resolution gas chromatographic traces of (a) total SRM 1597 and (b–g) corresponding fractions isolated by PCGC. Individual compound traps are (b) naphthalene, (c) phenanthrene, (d) fluoranthene, (e) pyrene, (f) chrysene, and (g) benzo[a]pyrene. The asterisk denotes an internal standard (terphenyl-*d*₁₄) added for quantitation purposes.

(or elemental carbon) to total organic carbon in SRM 1649a, values ranged from 0.069 to 0.520 across all methods (22, 23). The 24-h 375 °C thermal oxidation method generally gave the lowest ratios, which suggests that it quantifies a highly resistant fraction of organic matter. Only a few ¹⁴C measurements were performed on SRM 1649a during the laboratory intercomparison. Besides our value, there was one datum from another thermal method and one from a chemical method. The other thermal method involved a kinetic approach based on combustion of the sample at 560 °C in a helium/oxygen atmosphere (95/5). The chemical method involved treatment of the sample with 0.1 mol L⁻¹

Cr₂O₇²⁻ in 2 mol L⁻¹ H₂SO₄ at 50 °C for periods up to 406 h. The *f*_M of BC isolated from SRM 1649a for the former method was 0.038 ± 0.012 while that for the latter method was 0.153 ± 0.002. The similarity in the *f*_M values for the two thermal methods and the significantly higher ¹⁴C content of BC isolated by chemical oxidation may mean that thermal methods not only quantify a highly resistant fraction but also one that is more enriched in pyrogenic inputs. However, we do not believe that the thermal method is biased toward fossil fuel-derived BC as we have observed more contemporary levels of ¹⁴C (*f*_M = 0.77) in the BC fraction of Saharan Dust depositing in the Atlantic Ocean, presumably from

TABLE 2. Stable Carbon Isotope Values and Radiocarbon Content^a of PAHs in Environmental Matrix SRMs

sample id	AMS accession no. ^b	$\delta^{13}\text{C}$ (‰ vs VPDB) ^c	f_M ^d	f_C ^e
SRM 1941a				
benz[<i>a</i>]anthracene (BAA)	OS-11302	-23.0 ± 0.8	0.0520 ± 0.0100	0.0420 ± 0.0080
chrysene (CHR)	OS-11295	nm ^f	0.0347 ± 0.0053	0.0278 ± 0.0042
perylene (PER)	OS-11293	-25.8 ± 0.2	0.290 ± 0.022	0.232 ± 0.018
benzo[<i>ghi</i>]perylene (BGP)	OS-11301	-25.0 ± 0.2	0.0800 ± 0.0210	0.0637 ± 0.0170
SRM 1944				
benz[<i>a</i>]anthracene (BAA)	OS-11287	-24.7 ± 0.1	0.0400 ± 0.0240	0.0333 ± 0.0200
chrysene (CHR)	OS-11282	nm	0.0144 ± 0.003	0.0120 ± 0.0025
benzo[<i>a</i>]pyrene (BAP)	OS-11284	-25.7 ± 0.2	0.0290 ± 0.0045	0.0238 ± 0.0038
perylene (PER)	OS-11293	-24.8 ± 0.9	0.0700 ± 0.0160	0.0579 ± 0.0130
benzo[<i>ghi</i>]perylene (BGP)	OS-11286	-24.9 ± 0.1	0.143 ± 0.011	0.119 ± 0.009
SRM 1597				
naphthalene (NAP)	OS-8738	nm	0.0001 ± 0.0022	nc ^g
phenanthrene (PHE)	OS-8736	-24.3 ± 0.1	0.0023 ± 0.0050	nc
fluoranthene (FLU)	OS-8740	-24.8 ± 0.1	0.0034 ± 0.0017	nc
pyrene (PYR)	OS-8745	-24.9 ± 0.1	-0.0029 ± 0.0016	nc
chrysene (CHR)	OS-8760	nm	-0.0133 ± 0.0039	nc
benzo[<i>a</i>]pyrene (BAP)	OS-8758	-24.7 ± 0.4	0.0085 ± 0.0049	nc
SRM 1649a				
phenanthrene (PHE)	OS-17335	nm	0.0406 ± 0.0096	0.0301 ± 0.0071
fluoranthene (FLU)	OS-17311	-24.3 ± 0.3	0.0637 ± 0.0051	0.0471 ± 0.0038
pyrene (PYR)	OS-17305	-23.7 ± 0.3	0.0372 ± 0.0043	0.0276 ± 0.0032
benz[<i>a</i>]anthracene (BAA)	OS-17333	-22.4 ± 0.1	0.0413 ± 0.0073	0.0306 ± 0.0054
chrysene/triphenylene (CHR/TRI)	OS-17312	nm	0.0553 ± 0.0059	0.0410 ± 0.0043
benzofluoranthenes [<i>b,j,k</i> isomers] (BF)	OS-17302	-23.9 ± 0.2	0.0842 ± 0.0053	0.0624 ± 0.0039
benzo[<i>ghi</i>]perylene (BGP)	OS-17314	-22.9 ± 0.1	0.0864 ± 0.0090	0.0640 ± 0.0067

^a Corrections for ¹⁴C decay and bomb effects are the same as discussed in Table 1. ^b AMS accession numbers for each ¹⁴C analysis. ^c Uncertainty for $\delta^{13}\text{C}$ values are the standard deviation from triplicate analysis. ^d f_M is the fraction modern of each PAH listed with 95% confidence intervals. ^e f_C is the fraction contemporary of each PAH listed with 95% confidence intervals. ^f nm, not measured. ^g nc, not calculated.

TABLE 3. BC Properties of SRMs 1941a, 1944, and 1649a^a

sample id	no. of measurements	BC content (mg g ⁻¹)	BC/TOC	$\delta^{13}\text{C}$ (‰ vs VPDB)	AMS accession no. ^b	f_M	f_C
SRM 1941a	3	14.2 ± 0.5	0.29 ± 0.07	-25.15 ± 0.06	OS-20899 OS-21246 OS-21248	0.0150 ± 0.002	0.0120 ± 0.002
SRM 1944	2	8.0 ± 0.2	0.18 ± 0.01	-24.10 ± 0.08	OS-21686 OS-21687	0.0623 ± 0.018	0.0519 ± 0.015
SRM 1649a	3	14.0 ± 0.1	0.08 ± 0.01	-26.55 ± 0.04	OS-20898 OS-21247 OS-21495	0.0650 ± 0.014	0.048 ± 0.010

^a Corrections for ¹⁴C decay and bomb effects are the same as discussed in Table 1. ^b AMS accession numbers for each ¹⁴C analysis.

biomass burning and the combustion of recent detrital organic matter (58).

The comparison between data for the individual PAHs and BC isolated from the same suite of SRMs provides a unique opportunity to assess BC isolation methods and genetic relationships between these combustion products. Because the PAHs are isolated on a molecular basis, corresponding ¹⁴C data for these species can be interpreted with a high degree of confidence. In contrast, much controversy persists concerning BC isolation methods that largely employ operationally defined methods, which are prone to greater uncertainty. For example, the extent to which non-BC components in an environmental matrix interfere with a given isolation method has been subject to considerable debate. With respect to the thermal method, "charring" reactions may potentially contribute to the residue during the isolation procedure (59). In addition, some refractory biopolymeric materials (e.g., pollen) may survive the thermal treatment (11, 44). Both of these artifacts would manifest themselves in the ¹⁴C measurements described here as artificially "modern" BC because of contributions from biomolecule-derived carbon to the BC residues. This in turn

would lead to an apparent discrepancy between the f_M values for the pyrogenic PAHs and BC. In each of the environmental SRMs studied, we find that the f_M values for PAHs and BC are (a) similar and (b) significantly lower than that of the TOC (which is composed to a large extent of recent biological detritus), implying that BC isolated and measured using the method described is not subject to these interferences (Figure 5). It is worth noting that the $\delta^{13}\text{C}$ data alone in these samples are insufficient to resolve these similar arguments concerning artifacts (Tables 1 and 3). Overall, we believe these results validate the thermal oxidation approach as a means to accurately quantify and isotopically characterize BC in environmental matrices that have been moderately to severely impacted by combustion inputs. Its applicability to samples receiving minimum inputs is yet to be determined.

In summary, analytical methods for determining the ¹⁴C and ¹³C abundance of PAHs and BC have been presented. The similarity in ¹⁴C compositions of PAHs and BC in the samples analyzed indicate that the thermal oxidation approach for isolating BC appears to be free from interferences by non-BC components. Radiocarbon measurements of PAHs and BC in these samples, which are proximal to urban/

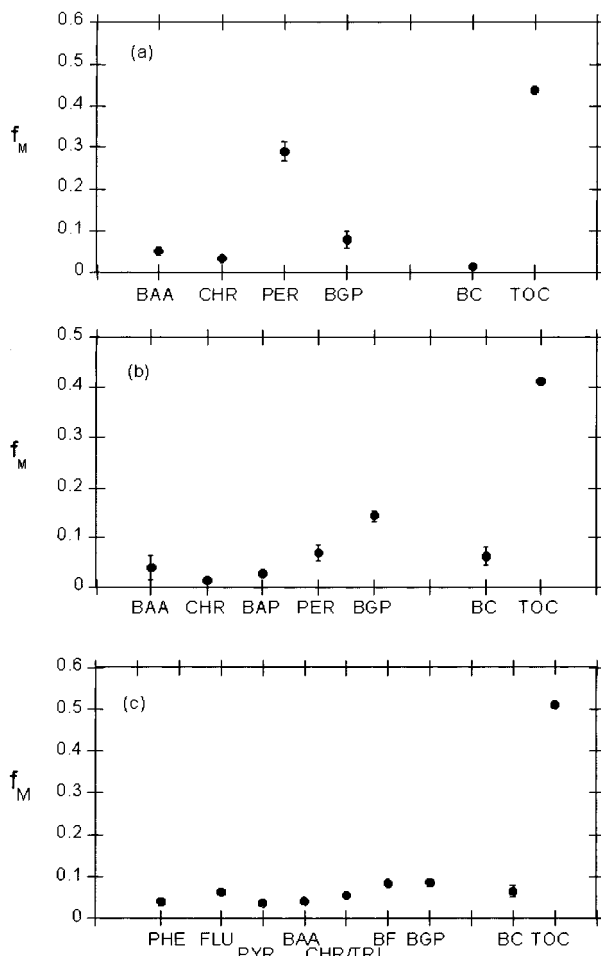


FIGURE 5. ^{14}C abundance of PAHs, BC, and TOC in (a) SRM 1941a, (b) SRM 1944, and (c) SRM 1649a. See Table 2 for listing of PAHs abbreviations.

industrial centers, show that they derive mostly from fossil fuels or their combustion products. While these results are not unexpected (i.e., mainly fossil-derived PAHs and BC in industrial regions), other locations (e.g., Southern Hemisphere) may have vastly different inputs of fossil and biomass carbon. Since there is a growing need for global coverage of sources, transport, and deposition of combustion products, this isotopic distinction between fossil fuels and biomass may prove particularly valuable in future studies. Because of the large amounts of material necessary for ^{14}C measurements of individual PAHs, we do not foresee this technique to be part of any routine investigations but rather used in selected cases to constrain inputs for key geographic regions. In contrast, ^{14}C of BC can be measured on much smaller samples and with greater ease.

On the basis of the preliminary molecular isotopic data, chrysene and pyrene were the most fossil fuel-derived, and the ^{14}C content of benzo[ghi]perylene was surprisingly more modern than other PAHs. Both natural (diagenetic) and anthropogenic sources of perylene were evident in two marine sediments (SRMs 1941a and 1944).

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Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the NIST, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

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