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Quantification of black carbon in marine systems using the benzene polycarboxylic acid method: a mechanistic and yield study

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Abstract

Quantification of black carbon (BC), carbonaceous material of pyrogenic origin, has typically required either chemical or thermal oxidation methods for isolation from heterogeneous matrices, such as sediment or soil. The benzene polycarboxylic acid (BPCA) method involves chemical oxidation of aromatic structures, such as those in BC, into BPCAs. We revised the BPCA method with the intent to quantify BC in marine dissolved organic carbon (DOC). As part of this work, we evaluated the mechanism and yield of the method using nine polycyclic aromatic hydrocarbons (PAHs) and six BC reference materials. After 8 h of oxidation at 180°C, the average carbon yield was $26 \pm 7\%$ C and was not correlated to the molecular weight of the PAH oxidized. The majority of observed BPCAs were nitrated, which has serious implications for the quantification of BC. Smaller PAHs favor the formation of less substituted BPCAs, whereas larger PAHs, such as coronene, favor the formation of more fully substituted BPCAs. Time-course experiments revealed variations of BPCA distributions over time, favoring less substituted BPCAs with longer oxidation times, whereas the carbon yield exhibited little variation. No decarboxylation of fully substituted mellitic acid (B6CA) was observed during time course experiments. Using the model compound anthracene, a potential internal standard, we propose a mechanism for the oxidation reaction based on time-course experiment data. Quantification of BC in reference materials revealed that this revision of the BPCA method is significantly more efficient than previous versions and is effective for quantifying both char and soot BC.

Black carbon (BC) particles are byproducts of combustion processes that can be defined by a broad range of characteristics. Sizes range from nanometer soot particles to millimeter pieces of charcoal. Chemically, BC has a condensed, highly aromatic structure (Fig. 1). Environmental scientists are interested in isolating BC from organic matrices, such as soils and sediments, to address questions regarding the time scales of carbon storage in the Earth system. The wide ranges of physical and chemical characteristics of both BC and heterogeneous matrices in which it is found pose challenges when isolating

and quantifying BC (Masiello 2004). Various techniques are used to quantify BC isolated from environmental matrices including thermal oxidation (Gustafsson et al. 1997), chemical oxidation (nitric acid: Glaser et al. 1998; Brodowski et al. 2005; and acid dichromate: Wolbach and Anders 1989) and mild chemical or photo-oxidation (NaClO, Simpson and Hatcher 2004; and ultra-violet radiation, Skjemstad et al. 1996) followed by NMR.

The benzene polycarboxylic acid (BPCA) method (Glaser et al. 1998; Brodowski et al. 2005) converts BC to benzene rings that are substituted with various numbers (2-6) of carboxylic acid groups. Assuming that the aromatic carbon within the sample is BC and additional carbon is neither added nor exchanged, this method provides both yield and general structural information about the BC. Nitric acid oxidizes the BC structure to BPCAs in which a single aromatic ring from the BC is preserved and is substituted with carboxylic acids derived from adjacent rings or side chains. This method retains the carbon from the molecular structure, which is essential for subsequent isotopic abundance assays such as

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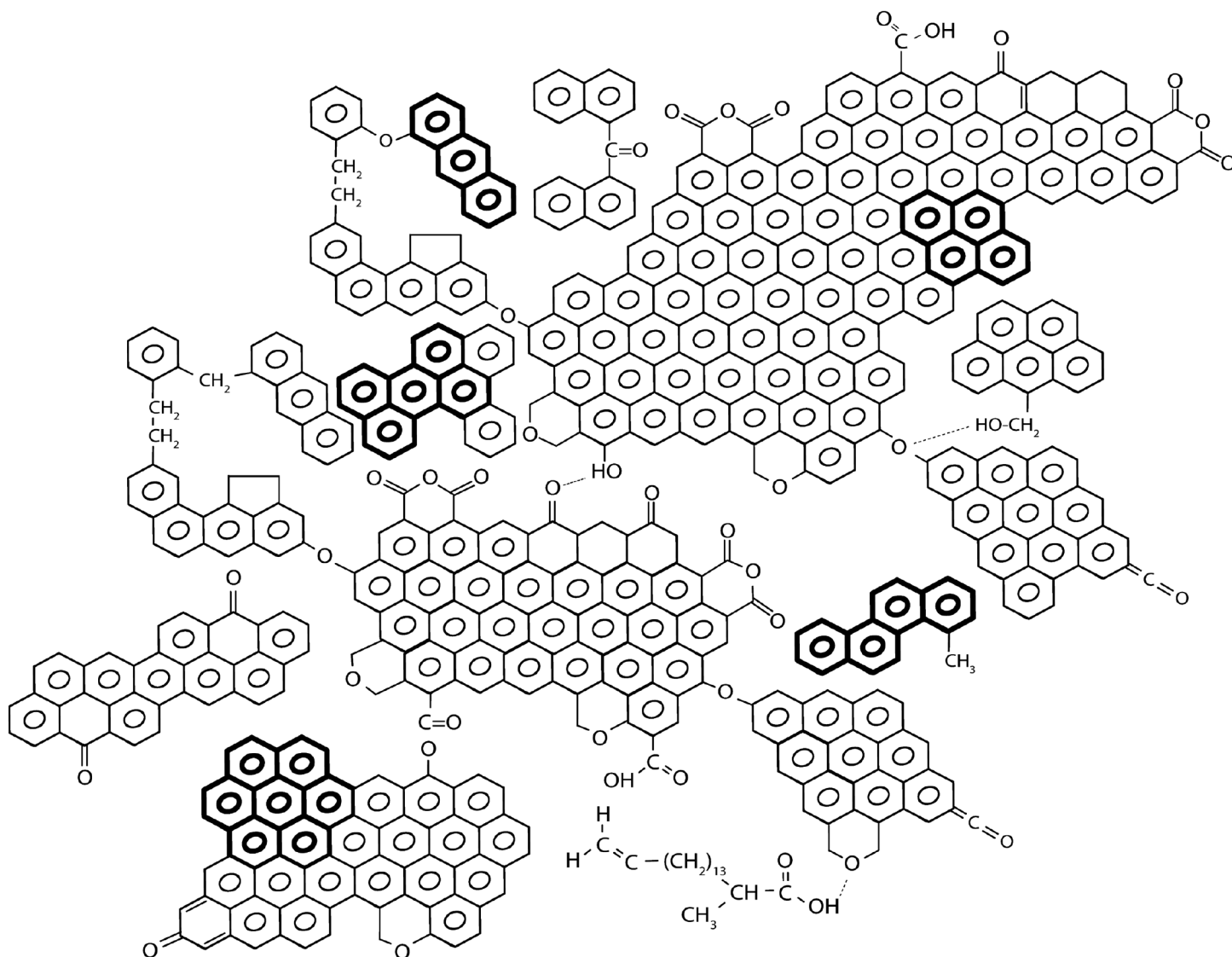


Fig. 1. Theoretical black carbon type of molecule (adapted from Goldberg 1985). Highlighted are a number of PAHs used in this study to mimic edge functionalities of the theoretical BC structure.

compound specific radiocarbon analysis (Eglinton et al. 1996; Ziolkowski and Druffel 2009a). While nitric acid oxidation of BC results in a significant loss of carbon (roughly 25% is retained), this method provides both qualitative and quantitative information about the original BC with negligible methodological artifacts.

A recent intercomparison of BC analysis methods (Hammes et al. 2007) revealed that the previous version of the BPCA method (Glaser et al. 1998; Brodowski et al. 2005), which silylated rather than methylated the BPCAs, was more efficient for the analysis of char-like BC than soot-like BC. Char-like BC is less condensed, contains more functional side chains and forms BPCAs that are less substituted. Soot-like BC is highly condensed with few additional side chains and forms BPCAs with a higher degree of substitution. Generally, the chemical

structure of BC is unknown in environmental matrices, such as marine sediment. Therefore, a method that provides both quantitative and general qualitative data from both char-like and soot-like BC would be ideal.

Before this method was employed to quantify the radiocarbon of BC in marine dissolved organic carbon (DOC) (Ziolkowski and Druffel 2010), we evaluated the mechanism and yield information of known materials. To understand the distribution and yield of BPCA oxidation products, we studied the oxidation of PAHs to model edge functionalities of BC (Fig. 1). This is the first study to systematically examine the oxidation products of the BPCA method and suggest an oxidation mechanism. Polycyclic aromatic hydrocarbons (PAHs) of various sizes and structures were digested and the resulting products were quantified. Previous versions of this method

did not quantify nitrated BPCAs. Here we present results of experiments that quantified the BPCAs and nitrated-BPCAs as methyl esters. We examined the reaction kinetics by evaluating the reaction products as a function of time. Using mellitic acid, we also address the possibility of decarboxylation of BPCAs during the oxidation and subsequent steps. Furthermore, we suggest a mechanism of oxidation for the PAH anthracene. Finally, using this revised method the BC in reference materials was quantified. Compared with the previous version of the BPCA method, this method produces higher estimates of BC content and is able to quantify soot BC.

Materials and procedures

All glassware and quartz filters that came in contact with the samples and standards were baked at 550°C for 2 h before

use to minimize carbon contamination. Individual PAHs (Fig. 2), varying in amounts from 2 to 10 mg C were weighed into 12 mL quartz digestion tubes. Two milliliters concentrated nitric acid (grade ACS) were added to each tube. These tubes were subsequently capped and heated to 180°C in a high-pressure digestion apparatus (Schramel et al. 1980). Briefly, the digestion apparatus consisted of a custom-made aluminum block with holes to fit up to six Teflon sleeves and quartz digestion tubes and caps. The block was mechanically clamped closed to secure the quartz tubes within the Teflon sleeves and then placed into an oven at 180°C for 0.5 to 16 h. Post-digestion, the samples were filtered through quartz fiber filters (27 mm diameter, 0.8 µm pore diameter) and rinsed with 15 mL Milli-Q water that was generated immediately before use. The filtrate was then freeze-dried.

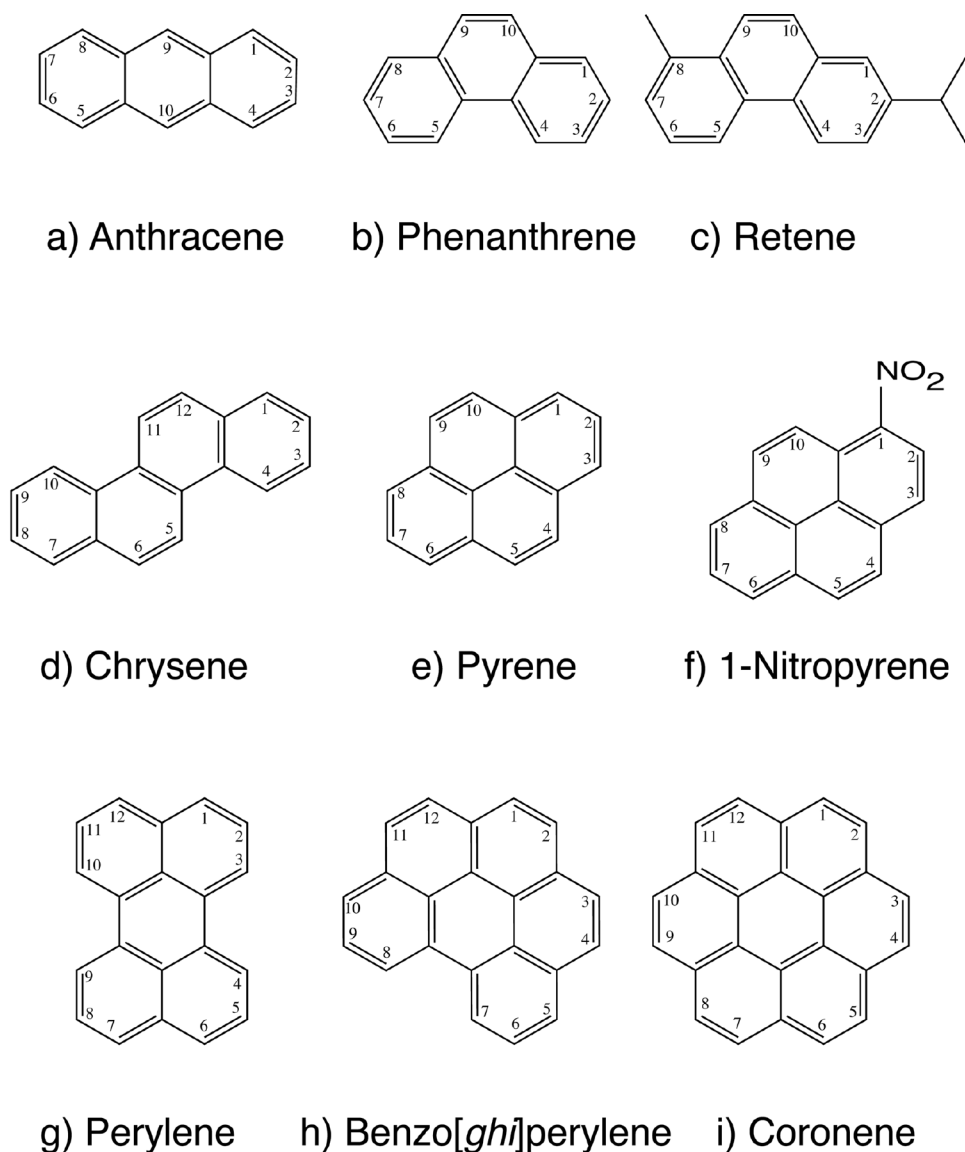


Fig. 2. PAHs used in this study.

Dried samples were redissolved in 5 mL 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 a faint yellow color of the excess trimethylsilyl-diazomethane. Extreme care should be taken when working with trimethylsilyl-diazomethane, as it is a health risk.

The derivatized oxidation products were blown dry under ultra-high purity nitrogen, re-dissolved in methylene chloride, and subsequently separated and quantified on a Hewlett Packard 6890 gas chromatograph outfitted with a Gerstel cooled injection system and a DB-XLB capillary column (30 m × 0.53 mm ID, 1.5 μm film thickness) and a flame ionization detector (FID). After injection, the column temperature was maintained at 100°C for 1 minute, then raised at 25°C min⁻¹ to 250°C followed by a 5°C min⁻¹ ramp to a final temperature of 280°C. The column was held at the final temperature for 10 minutes. The detector temperature was 300°C. The splitless injection volume was between 1 and 3 μL. BPCAs collected for radiocarbon analysis were collected using a preparative fraction collector as outlined in Ziolkowski and Druffel (2009a). ¹⁴C measurements were made at the Keck Carbon Cycle Accelerator Mass Spectrometry Laboratory at University of California Irvine. All radiocarbon values reported in this article have been corrected for combustion, graphitization and mass dependent isotope fractionation by reporting all data to a δ¹³C value of -25.

Compound verification was performed using a Finnigan Trace MS + GC/MS system operating in electron ionization (EI) mode. The GC was equipped with a J&W Scientific DB-5 capillary column (30 m × 0.32 mm ID, 0.25 μm film thickness). Helium was used as the carrier gas. The temperature program used was 50°C ramping at 10°C min⁻¹ to a final temperature of 290°C. The injector temperature was 250°C. BPCAs were identified by comparison of their retention times with those obtained for a commercially available mixture and were verified using the GC/MS. All methylated BPCAs were quantified relative to the biphenyl-2,2'-dicarboxylic acid internal standard. BPCA calibration curves were calculated relative to the internal standard peak area. Except where otherwise noted, samples were processed and analyzed in triplicate. On column detection of BPCAs was 10 ng BPCA per injection. When analyzing environmental samples, only BPCAs with three or more acids are quantified as BC to avoid potential non-BC artifacts. Whereas it is not recommended for natural samples, in this study we quantified BPCAs with two acids because we were using pure chemicals.

Assessment and discussion

Nitration of BPCAs

Previous BPCA method development studies (Glaser et al. 1998; Brodowski et al. 2005) quantified only the nonnitrated BPCAs produced during oxidation and did not consider

whether the oxidation products of the BC also included significant amounts of nitrated BPCAs. Early studies of the organic chemistry of electrophilic substitution illustrated that nitration of PAHs was important (Dewar and Mole 1956; Watts 1873). We have found that the majority of the BPCAs produced from all PAHs studied were substituted with at least one nitro-group (-NO₂). The reported BPCAs in this study are a sum of the BPCAs for a given number of acids, including the nitrated BPCAs (e.g., B2CA = phthalic acid + mononitrophthalic acid + dinitrophthalic acid). Phthalic acid was observed as both mono- and di-nitrated. All other BPCAs (B3CA, B4CA, and B5CA) were mononitrated. Both 3-nitrophthalic and 4-nitrophthalic acid are commercially available and were used for calibration of the nitrated phthalic acid (including dinitrophthalic acid). Larger nitrated BPCAs were not commercially available. However, because the calibration curves for 3-nitrophthalic and 4-nitrophthalic acid were the same as that for phthalic acid, we applied the nonnitrated calibration curves to the larger BPCAs (e.g., the calibration curve for B3CA was applied to all nitrated B3CA isomers). The BPCA distributions and carbon yields discussed below include nitrated BPCAs.

Carbon yields

For each oxidized and derivatized PAH, the BPCAs were quantified, and a carbon yield was calculated by comparing the sum of BPCA carbon to the initial carbon (see Table 1 for an example). For all nine PAHs analyzed in this study, the average carbon yield was 25.7 ± 6.8% C, with values for individual PAHs ranging from 19.5 ± 2.2 to 37.0 ± 7.2% C (Table 2). There was no significant correlation between the molecular weight of the PAH and the carbon yield ($r^2 = 0.022$, $n = 9$). The two smallest PAHs studied, anthracene and phenanthrene, exhibited carbon yields of 24.2 ± 1.6% and 23.7% ($n = 1$), respectively. Retene, a three-ring PAH with two small side chains, exhibited a significantly higher carbon yield (29.3 ± 1.4%). Chrysene, a four-ring PAH with a structure similar to phenanthrene, had a carbon yield of 21.5 ± 2.3%. Four-ring pyrene and 1-nitropyrene had the highest measured carbon yields, 37.0 ± 7.2% and 36.1 ± 9.3%, respectively. The five-ring perylene and six-ring benzo[ghi]perylene had the same carbon yield (22.5 ± 1.3% and 22.5 ± 3.9%, respectively). The largest PAH studied, seven-ring coronene, had the lowest carbon yield of 19.5 ± 2.2%. No significant correlations were found between the carbon yield and the number of aromatic rings or the percentage of carbon in the PAH; thus we are not able to draw any conclusions as to how the type or size of PAH oxidized is related to the carbon yield.

The BPCA method requires the use of a conversion factor to convert the BPCAs formed into an estimate of BC mass. Previously activated charcoal was used to determine the conversion factor (Glaser et al. 1998; Brodowski et al. 2005). Because the composition and character of this material may vary between production lots of activated charcoal, the distribution and yield of BPCAs from this material may vary. We recommend

Table 1. Example calculation of BPCAs in PAHs using anthracene. Peak areas are reported relative to the biphenyl-2,2'-dicarboxylic acid internal standard. The calibration curve for nitrophthalic acid was generated using 3-nitrophthalic acid relative to biphenyl-2,2'-dicarboxylic acid internal standard. Nitrophthalic acid was converted from normalized peak area (nPA) to mg C using the equation: $\text{mg C} = 0.451 \times (\text{nPA} - 0.01495)/1.0672$. Nitrophthalic acid is 45.1% carbon. The same calibration curve was applied to dinitrophthalic acid, adjusting the carbon percentage to 36.9%. UCIZ number is an in-house sample identifier.

UCIZ	Anthracene mg C	B2CA normalized peak area		mg C B2CA			% C yield
		nitrophthalic acid	dinitrophthalic acid	nitrophthalic acid	dinitrophthalic acid	sum	
94	4.70	2.46	0.42	1.03	0.14	1.17	24.9
95	5.96	3.10	0.52	1.30	0.18	1.48	24.8
107	3.09	1.70	0.31	0.71	0.10	0.81	26.2
108	2.35	1.07	0.19	0.45	0.06	0.51	21.7
109	4.81	2.44	0.19	1.03	0.06	1.09	22.7
110	5.01	2.61	0.35	1.09	0.12	1.21	24.2
112	5.28	2.70	0.34	1.13	0.11	1.24	23.5
113	7.90	3.27	0.26	1.81	0.09	2.00	25.3
						average	24.2 ± 1.6

Table 2. Carbon yield and percent BPCA distribution of the nine PAHs oxidized in this study. All samples were oxidized for 8 h. The standard deviation of three replicates is given. – indicates no BPCAs were detected. The average % C recovered and standard deviation is of 40 analyses.

	# of C	% C	% C recovered	B2CA	B3CA	B4CA	B5CA	B6CA
Anthracene	14	94.4	24.2 ± 1.6	100.0 ± 0.0	–	–	–	–
Phenanthrene	14	94.4	23.7 ± n.a.	72.1 ± 2.1	–	27.9 ± 2.1	–	–
Retene	18	92.3	29.3 ± 1.4	1.3 ± 2.2	62.4 ± 0.8	36.4 ± 1.7	–	–
Chrysene	18	94.7	21.5 ± 2.3	64.4 ± 2.5	–	35.6 ± 1.7	–	–
Pyrene	16	95	37.0 ± 7.2	–	18.8 ± 3.5	79.3 ± 5.2	–	–
1-Nitropyrene	16	77.4	36.1 ± 9.3	4.0 ± 3.5	17.9 ± 3.5	78.1 ± 5.4	–	–
Perylene	20	95.2	22.5 ± 1.3	–	80.3 ± 1.7	–	–	19.7 ± 1.7
Benzo[ghi]perylene	22	95.5	22.5 ± 3.9	–	6.9 ± 0.4	53.1 ± 1.2	–	40.0 ± 1.5
Coronene	24	96	19.5 ± 2.2	–	–	67.4 ± 2.4	–	32.6 ± 2.4
		average	25.7 ± 6.8					

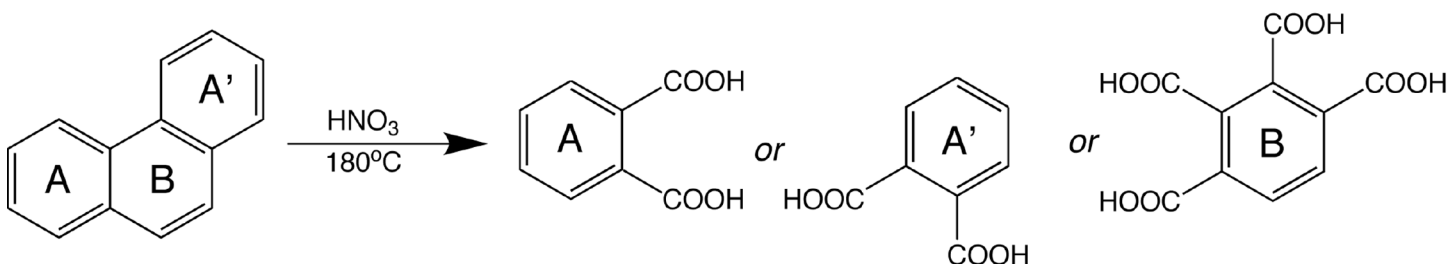


Fig. 3. Schematic of the oxidation products of phenanthrene using the BPCA method. One molecule of phenanthrene theoretically could produce either one molecule of B2CA (A or A') or one molecule of B4CA (B).

using materials of known chemical formulas, such as PAHs, to calibrate the BPCA method. Our results from the oxidation of PAHs suggest using the average carbon yield of $26 \pm 7\%$ C to calculate the BC mass in samples.

BPCA products

The BPCA method oxidizes condensed aromatic compounds to produce single benzene rings with carboxylic acid functional groups derived from adjacent aromatic rings or side

chains. For example, when phenanthrene is oxidized (Fig. 3) only two BPCAs can be produced: phthalic acid (B2CA) and benzene-1,2,3,4-tetracarboxylic acid (B4CA). If the method oxidized the aromatic structure according to its stoichiometry, we would expect two molecules of B2CA to form for every one molecule of B4CA, based on the fact that one phenanthrene consists of two outer rings suited to become B2CAs and one central ring suited to become B4CA. Indeed, oxidized phenan-

threne preferentially formed B2CA ($72.1 \pm 2.1\%$ of the carbon recovered) and the remainder was B4CAs ($27.9 \pm 2.1\%$). Oxidized anthracene also is expected to yield 66.7% B2CA and 33.3% B4CA, however, it produced exclusively B2CAs. The four-ring PAH chrysene is expected to yield equal proportions of B2CA and B4CA, however it yielded $64.4 \pm 2.5\%$ B2CA and $35.6 \pm 1.7\%$ B4CA. Anthracene and chrysene preferentially formed smaller BPCAs than expected.

If the aliphatic side chains are incorporated into the BPCA, the oxidation of retene yielded the expected distribution of BPCAs (2 B3CAs: 1 B4CA, Table 2). Carbon on each side chain was oxidized to a carboxylic acid. This result suggests that aliphatic side chains of BC could be oxidized to carboxylic acids. Theoretically, perylene would yield four B3CAs for every one B6CA, and indeed, we found $80.3 \pm 1.7\%$ B3CAs and $19.7 \pm 1.7\%$ B6CA formed. Previously, perylene oxidation was reported (Glaser et al. 1998) to yield 75% B3CAs and 25% B6CAs, similar to our finding. In contrast, oxidized perylene by microwave-assisted oxidation and HPLC quantification resulted in 19% B3CA and 81% B6CA (Dittmar 2008). Our study did not use microwave-assisted oxidation and BPCAs were quantified as methyl-esters by GC, not as carboxylic acids via HPLC. Thus, it is not clear if the difference in these results is due to the different oxidation and/or quantification methods.

Other PAHs used in this study formed a higher proportion of larger BPCAs than expected from PAH stoichiometry. Pyrene formed $18.8 \pm 3.5\%$ B3CA and $79.3 \pm 5.2\%$ B4CA instead of the expected equal distribution. The oxidation products of the nitrated pyrene, 1-nitropyrene, were not significantly different from the nonnitrated compound, except that a small percentage ($4.0 \pm 3.5\%$) of B2CA was also produced. The observed B2CA was a mixture of two isomers of dinitrophthalic acid. Benzo[ghi]perylene was expected to form 33% B3CA, 50% B4CA, and 17% B6CA; instead it formed $6.9 \pm 0.4\%$ B3CA, $53.1 \pm 1.2\%$ B4CA and $40.0 \pm 1.5\%$ B6CA. The proportion of B4CAs formed was as expected, however more B6CAs and less B3CAs were measured than expected. The largest PAH studied, coronene, was expected to form 86% B4CA and 14% B6CA. Instead, coronene produced $67.4 \pm 2.4\%$ B4CA and $32.6 \pm 2.4\%$ B6CA, again more B6CAs than expected. A linear regression of the difference between the expected and observed smaller BPCA percentage against the number of carbons in the PAH for all the non-pyrene PAHs had a positive slope with an $r^2 = 0.69$. These results demonstrate that larger PAHs generally formed larger BPCAs than predicted from their stoichiometry.

This BPCA distribution data illustrates the complexity of the oxidation reaction. Because there seems to be no systematic pattern of oxidation, we cannot accurately model the oxidation products. Nor can we, without additional data, reconstruct the original structure of the BC using the BPCA distribution. However, these distribution data are useful when drawing qualitative distinctions between different types of BC

(Ziolkowski and Druffel 2009b). In general, it is possible to distinguish between material with aliphatic side-chains and fully condensed BC material.

Time-course and mechanistic experiments

To evaluate the optimal time of the high pressure and high temperature oxidation of PAHs to BPCAs, we conducted time-course experiments. Anthracene was chosen as a model compound for time course and mechanistic experiments because it was being evaluated for use as an internal standard. First, we evaluated the evolution of BPCAs from anthracene by conducting the high temperature nitric acid oxidation from 0.5 to 16 h. The carbon yield of BPCAs increased from 1 to 8 h (Table 3). While the difference between anthracene yield for the 4-h and 16-h oxidation are different (unpaired t test, P value = 0.012), the differences in yield between the time points (4-h to 8-h and 8-h to 16-h) are not significantly different (unpaired t tests, P value₄₋₈ = 0.446, P value₈₋₁₆ = 0.140). Regardless of oxidation duration, B2CAs were always the sole product. Therefore oxidation of at least 8 h was optimal, as shorter oxidations gave lower carbon yields and longer oxidations a greater variability of carbon yield. We also examined the degree of nitration of the B2CAs formed from anthracene as a function of time (Fig. 4). With oxidations of 0.5 and 1.0

Table 3. Carbon yields for time course experiments of two PAHs (anthracene and perylene) and mellitic acid (B6CA). All samples were oxidized at 180°C. The standard deviation of three replicates is given. – indicates time points that were not studied. n.a. indicates not available.

Oxidation time (h)	% C recovered		
	Anthracene	Perylene	Mellitic acid
0.5	16.5 ± 8.5	–	–
1	11.7 ± 3.4	–	95.9 ± 7.7
2	18.6 ± 1.7	20.4 ± 0.1	97.4 ± 13
4	20.5 ± 0.7	24.0 ± 1.1	97.3 ± 5.7
8	24.2 ± 1.6	22.6 ± 1.3	104.7 ± 1.0
16	23.6 ± 3.1	19.9 ± 3.4	95.2 ± n.a.

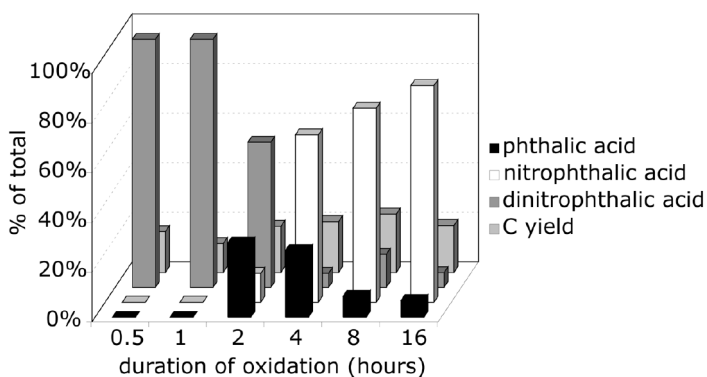


Fig. 4. Distribution of nonnitrated, nitrated, and dinitrated dicarboxylic acid formed and carbon yield from oxidation of anthracene as a function of oxidation time.

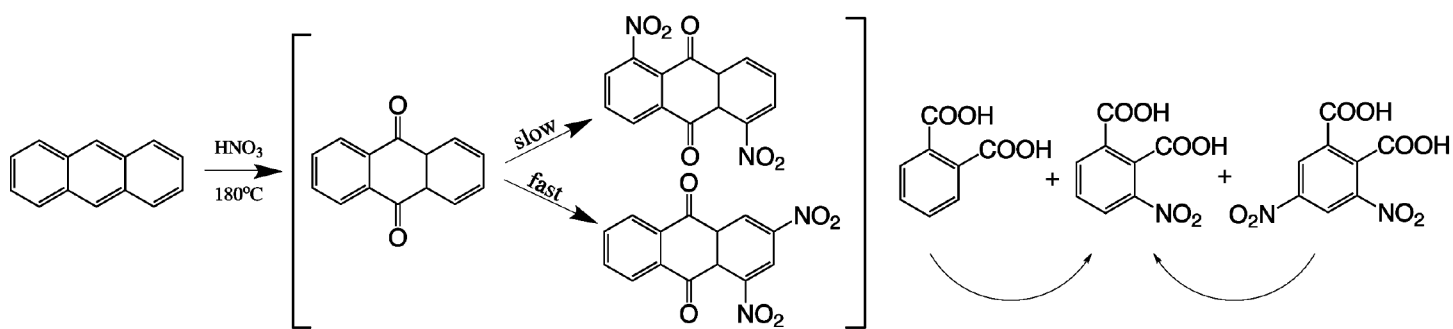


Fig. 5. A proposed reaction schematic for the high pressure, high temperature oxidation of anthracene to B2CA. The products initially formed reach thermodynamic equilibrium as nitrophthalic acid (see Fig. 6).

h, the B2CA formed were exclusively dinitrophthalic acid. Between the 1 and 2 h oxidations, the carbon yield increased and the quantity of dinitrophthalic acid produced decreased significantly and was replaced by phthalic acid and nitrophthalic acid (Fig. 4).

These results suggest that the oxidation mechanism of anthracene is a multi-step process with dinitrophthalic acid as the initial product (≤ 1 hour). With increased oxidation time (8 h) the dominant product was nitrophthalic acid. When the shortest oxidations of anthracene were filtered, a solid remained, and was identified by GC/MS and NMR as 100% anthraquinone. Oxidation of anthracene in nitric acid, under milder conditions, has been found to produce anthraquinone (Cho 1995). We hypothesize that the anthraquinone generated was then nitrated to dinitroanthraquinone before being oxidized to dinitrophthalic acid (Fig. 5), which was then denitrated to mononitrophthalic acid, the thermodynamically favored product under these conditions.

We tested this hypothesis by oxidizing four forms of B2CA: phthalic acid, 3-nitrophthalic acid, 4-nitrophthalic acid, and 3,5-dinitrophthalic acid for 16 h. With the exception of 4-nitrophthalic acid, we found that regardless of the form of phthalic acid we oxidized, the primary product was 3-nitrophthalic acid (Fig. 6), supporting our hypothesis. Furthermore, after 16 h of oxidation 4-nitrophthalic acid yielded 85% mononitrophthalic acid and 15% dinitrophthalic acid and more than half of the mononitrophthalic acid was 3-nitrophthalic acid. This demonstrated the conversion of 4-nitrophthalic acid to the more stable 3-nitrophthalic acid. These results confirm the importance of quantifying nitrated BPCAs, because nitration occurs before the formation of BPCAs and can comprise a significant portion of the oxidation products.

Perylene was also studied in a time course experiment. Although the average carbon yield was relatively constant over the course of these experiments at $21.7 \pm 1.9\%$ (Table 3), the distribution of BPCAs changed significantly as a function of oxidation time (Fig. 7). A ratio of observed B3CA to B6CA plotted as a function of oxidation time had an $r^2 = 0.77$ (least squares fit of data $n = 12$). The shortest perylene oxidation (2

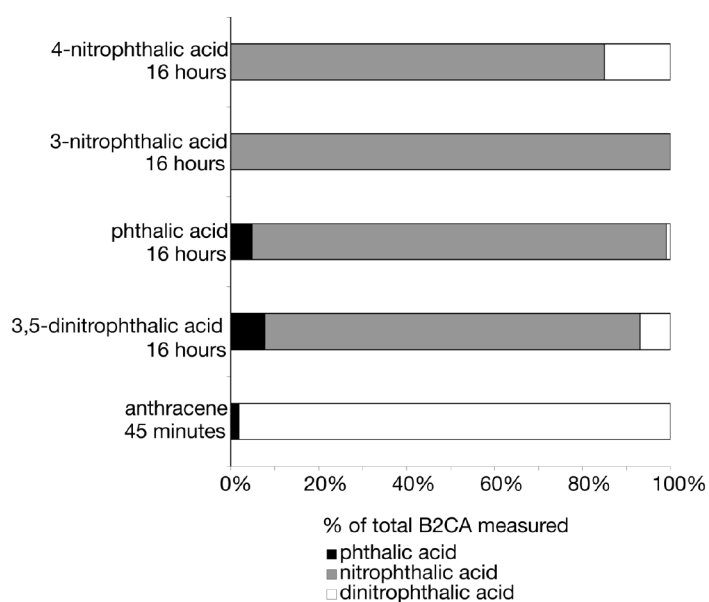


Fig. 6. Distribution of phthalic acid, nitrophthalic acid, and dinitrophthalic acid as a function of reactants and oxidation durations. Anthracene was oxidized for 45 min and four forms of phthalic acid were oxidized for 16 h: phthalic acid, 3-nitrophthalic acid, 4-nitrophthalic acid and 3,5-dinitrophthalic acid. Regardless of the starting materials, 3-nitrophthalic acid is the most abundant product after 16 h (see Table 1). This experiment was conducted in duplicate and the associated error is 5%.

h) yielded more B6CA than the 16 h oxidation ($23.3 \pm 0.5\%$ B6CA versus $14.4 \pm 0.3\%$). The mononitrobenzenetricarboxylic acid was predominantly 4-nitro-1,2,3-benzenetricarboxylic acid and a small proportion was 5-nitro-1,2,3-benzenetricarboxylic acid ($\leq 10\%$). Relative distributions of these two acids did not vary with increased oxidation time (up to 16 h). Perylene nitrates at the #3 position (Dewar and Mole 1956), which is consistent with our observation that 4-nitro-1,2,3-benzenetricarboxylic acid is the dominant B3CA formed. This provides further evidence that nitration occurs before the break-up of the PAHs. The decrease in B6CA with oxidation time may indicate that decarboxylation may take place with longer oxidation times. The ratio of B3CA to B6CA doubled

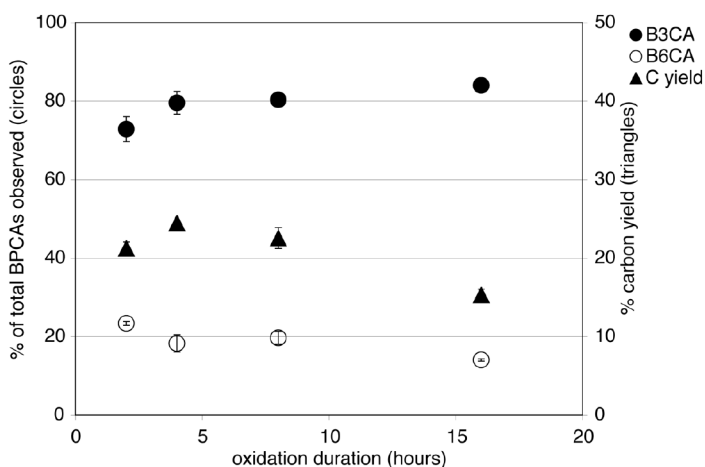


Fig. 7. Change in B3CA (filled circles) and B6CA (open circles) oxidation products (% of total BPCAs observed) and carbon yield (filled triangles) from perylene over time (% carbon yield). Error bars represent the standard deviation of three replicates.

between 2 and 16 h and was positively correlated to the duration of the oxidation ($r^2 = 0.77$, data not shown). However, the change in carbon yield between 4 and 16 h was not significantly different (P value = 0.116). Thus, if decarboxylation is occurring with prolonged oxidation durations, it did not change the carbon yield. At no point during the perylene time course experiments did we observe more B6CA than B3CA, as reported when microwave-assisted oxidation was employed (Dittmar 2008). In the future, it is important for users of the BPCA method to quantify nitrated BPCAs and calibrate the oxidation performed in each laboratory. Comparing the ratio of smaller to larger BPCAs (including nitrated molecules) of a known compound, such as a PAH, should be used to calibrate the method for inter-laboratory comparisons of BPCA distributions.

To test for decarboxylation, we oxidized commercially available mellitic acid (B6CA) at 180°C for 1 to 16 h (Table 3). The average recovery of mellitic acid for all time points was $98.1 \pm 3.8\%$. For all time points except 8 h, the amount of mellitic acid remaining after oxidation was between 95% and 97%. The 8-h oxidation yielded $104.7 \pm 1.0\%$ of the initial carbon. The mellitic acid carbon yield did not change between 4 and 16 h (P value = 0.675). These results demonstrate that mellitic acid is not decarboxylated over the course of the oxidation.

The time course results demonstrate that oxidations conducted for 4 to 16 h show little variation in the carbon yield, whereas the relative distribution of BPCAs changes as a function of oxidation time. Since the anthracene carbon yield (Table 2) and nitration (Fig. 4) continued to evolve from 4 to 8 h of oxidation time, we elected to conduct all further oxidations at 8 h.

Analysis of black carbon ring trial materials

An analytical challenge in the analysis of black carbon is its wide variety of chemical and physical characteristics. Many methods of BC quantification focus on particular components

of BC (i.e., soot or char). Recently, an intercomparison of BC quantification methods for BC-rich materials (Hammes et al. 2007) revealed that the previous version of the BPCA method was better suited for the analysis of char than for soot BC. Additionally, the intercomparison revealed that the conversion factor of BPCAs to BC was not easily reproducible.

Because many modifications of the original BPCA method were made in this work, we re-analyzed a suite of BC rich materials to contextualize this version of the BPCA method (Table 4, Ziolkowski and Druffel 2010). The PAH carbon yield data reported here was combined with additional carbon yield data of soot-like BC materials in another study (Ziolkowski and Druffel 2009b) to generate a more robust conversion factor, for converting BPCAs to BC, of 4 ± 1 or the inverse of $25 \pm 6\%$. A wide range of BC materials (e.g., carbon nanotubes, soot, char, PAHs, etc.) were used to generate this conversion factor. This is much higher than the 2.27 conversion factor reported in the original BPCA study (Glaser et al. 1998), but lower than the highest reported BPCA conversion factor (4.5, Brodowski et al. 2005). Activated charcoal, which was used to generate previous BPCA conversion factors, was not used in the determination of the conversion factor reported here. Although, carbon yields of oxidized activated charcoal ($23.5 \pm 1.0\%$ C yield, $n = 3$) agree with the conversion factor reported here.

For all materials assessed, our BC yields were higher than chemothermal oxidation, CTO-375, and the original BPCA method. Our results are similar to those generated using the chromic acid oxidation method (C_2O_2) for charred materials, however, results for the hexane soot are closer to those obtained by the thermal optical method (TOR/TOT). Whereas the laboratory-produced hexane soot may not represent typical soot-producing combustion, the urban aerosol (NIST 1649a), that Currie et al. (2002) established to contain mostly soot BC, also showed a higher BC yield than both the CTO-375 and original BPCA method (Hammes et al. 2007). The increased BC yield using this version of the BPCA method is due primarily to the quantification of nitrated BPCAs, and in small part, to the derivatization method. For wood char, if the 2.27 conversion factor was applied to the sum of nonnitrated BPCAs we observed, the BC yield was lowered from 478 g/kg to 213 g/kg, much closer to results from the original BPCA methods (Table 5). For hexane soot, if only the nonnitrated BPCAs were converted to BC with a 2.27 conversion factor, the BC is 334 g/kg and is still significantly higher than the previous BPCA estimates for hexane soot. Thus, it appears that the BPCA method presented here is not biased for char and can equally quantify char and soot BC. After the conversion factor and quantification of nitrated peaks are accounted for, the BC yield is still greater than previous versions of this method, likely due to the increased oxidation temperature and new derivatization method. Thus, this version of the BPCA method is suited for studies when a single method is needed for quantifying all forms of BC but not when quantitatively distin-

Table 4. Quantification of black carbon materials (g BC/ kg dry weight) by the BPCA and other methods. Data for CTO-375, BPCA, Cr₂O₇, TOR/TOT, and total organic carbon (TOC) are from Hammes et al. (2007). The quantity of BC in this work was converted from all BPCAs (including those nitrated) to BC using the conversion factor of 4 (the inverse of 25%). A dash indicated that no data were reported. The uncertainty of BC estimates, given in brackets, is either the propagated error of the BPCA to BC conversion factor (25 ± 6%) or the standard deviation of replicates, whichever is larger.

	TOC g/kg	BPCA this work	CTO-375	BPCA	Cr ₂ O ₇	TOR/TOT
Aerosol	178.4 (6.3)	32.7 (8.2)	14.9 (7.0)	14.5 (4.5)	63.9 (20.8)	66.5 (20.4)
Marine sediment	31.3 (2.3)	10.7 (8.1)	5.1 (1.4)	1.7 (1.5)	11.8 (6.6)	10.9 (6.5)
IHSS NOM	459.4 (37.6)	63.0 (15.8)	1.1 (1.9)	20.5 (25.1)	–	162.3 (135.1)
Hexane soot	921.3 (32.9)	945.5 (236.5)	410.0 (8.3)	239.5 (206.9)	469.9 (97.8)	887.6 (24.3)
Wood char	744.4 (45.6)	478.4 (119.7)	–	183.2 (96.3)	524.4 (106.7)	652.7 (93.5)
Grass char	591.4 (32.0)	488.0 (122.0)	9.0 (7.2)	154.6 (18.3)	205.8 (49.4)	478.0 (76.0)

Table 5. Wood char and hexane soot BC yield data (g BC/kg dry weight) using various scenarios. ΣnBPCA is the summation of all BPCAs, including those nitrated as reported in the body of this paper. ΣBPCA is the summation of all nonnitrated BPCAs. BPCAs (last column) are the data reported in the BC ring trial (Hammes et al. 2007) (nonnitrated BPCAs only). For the work presented here (ΣnBPCA and ΣBPCA), the uncertainty is the propagated error of the BPCA to BC conversion (25 ± 6%).

BPCA summation Conversion factor	ΣnBPCA 4.09		ΣBPCA 4.09		ΣBPCA 2.27		BPCA 2.27	
	mean	s	mean	s	mean	s	mean	s
wood char	478.4	119.6	385.2	96.3	213.8	53.4	183.2	96.3
hexane soot	945.5	236.5	616.8	154.2	334.0	83.5	239.5	206.9

guishing soot versus char is the aim of the study, such as in Elmquist et al. (2006).

Historically, some BC methods have exhibited false positives (Hammes et al. 2007). To test whether the high soot yields observed using this method were false positive, we studied the BPCAs resulting from the oxidation of the urban aerosol, NIST 1649a, in more detail. This material is a heterogeneous mixture of organic compounds and BC collected in a Maryland naval shipyard. The ratio of BC to total organic carbon (BC/TOC) in the urban aerosol using this version of the BPCA was 0.185, which is higher than that obtained for CTO-375 (0.079), yet lower than that obtained for Cr₂O₇ (0.520) (Currie et al. 2002). In contrast to the ¹⁴C content of the bulk organic carbon (Δ¹⁴C = –505‰, Currie et al. 2002), the BPCAs in the urban aerosols were depleted in radiocarbon (Δ¹⁴C = –936 ± 30‰). This result agrees with previous measurements for the Δ¹⁴C of BC in the urban aerosol that ranged from –935‰ to –849‰ (CTO-375 and Cr₂O₇, respectively, Currie et al. 2002). The Cr₂O₇ Δ¹⁴C values are more modern, suggesting a milder oxidation, which was supported by the higher BC/TOC ratio. If this version of the BPCA method was producing false positives, from non-BC material, the collected BPCAs would have higher Δ¹⁴C and BC/TOC values. This evidence suggests that the higher soot yields from this version of the BPCA method are not due to false positives.

Comments and recommendations

Using a revised BPCA method, we have shown that oxidation of nine PAHs results in nitrated BPCAs. On average, 26% of the

PAH carbon was recovered as BPCAs (including nitrated BPCAs). Although the number of acid groups is related to the original structure, the distribution of oxidation products does not systematically correlate with the structure of the original PAH. More highly substituted BPCAs are formed from larger PAHs. Time course experiments revealed that the ratio of oxidation products changed over time, favoring smaller BPCAs with longer oxidation times, whereas the carbon yield did not change.

We also found that quantifying the nitrated BPCAs is essential because the PAHs are nitrated before they are oxidized. Future work on the BPCA method should include assessment of the degree of nitrated BPCAs when oxidizing BC in environmental samples. Measurements of BC in reference materials reveal that this version of the BPCA method is overall more efficient for quantifying BC and not biased against the quantification of soot BC. The increased efficiency is a function of the oxidation conversion factor, quantification of nitrated peaks, derivatization method, and increased temperature of oxidation of BC to BPCAs.

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