



## The feasibility of isolation and detection of fullerenes and carbon nanotubes using the benzene polycarboxylic acid method

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### ABSTRACT

The incorporation of fullerenes and carbon nanotubes into electronic, optical and consumer products will inevitably lead to the presence of these anthropogenic compounds in the environment. To date, there have been few studies isolating these materials from environmental matrices. Here we report a method commonly used to quantify black carbon (BC) in soils, the benzene polycarboxylic acid (BPCA) method, for measurement of two types of single walled carbon nanotubes (SWCNTs), two types of fullerenes and two forms of soot. The distribution of BC products (BPCAs) from the high pressure and high temperature oxidation illustrates the condensed nature of these compounds because they form predominantly fully substituted mellitic acid (B6CA). The conversion of carbon nanoparticles to BPCAs was highest for fullerenes (average of  $23.2 \pm 4.0\%$  C recovered for both  $C_{60}$  and  $C_{70}$ ) and lowest for non-functionalized SWCNTs ( $0.5 \pm 0.1\%$  C). The recovery of SWCNTs was 10 times higher when processed through a cation-exchange column, indicating the presence of metals in SWCNTs compromises the oxidation chemistry. While mixtures of SWCNTs, soot and sediment revealed small losses of black carbon during sample processing, the method is suitable for quantifying total BC. The BPCA distribution of mixtures did not agree with theoretical mixtures using model polyaromatic hydrocarbons, suggesting the presence of a matrix effect. Future work is required to quantify different types of black carbon within the same sample.

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### 1. Introduction

As the industrial application for carbon nanotubes (CNTs) and fullerene production increases, their presence in the environment is an eventuality. While these compounds have much biomedical promise (Bianco et al., 2005), there is conflicting eco-toxic evidence (Oberdorster, 2004; Tong et al., 2007) about their impact on organisms in nature. The analytical methods used to isolate these materials from environmental matrices are limited, inhibiting our ability to directly quantify these compounds.

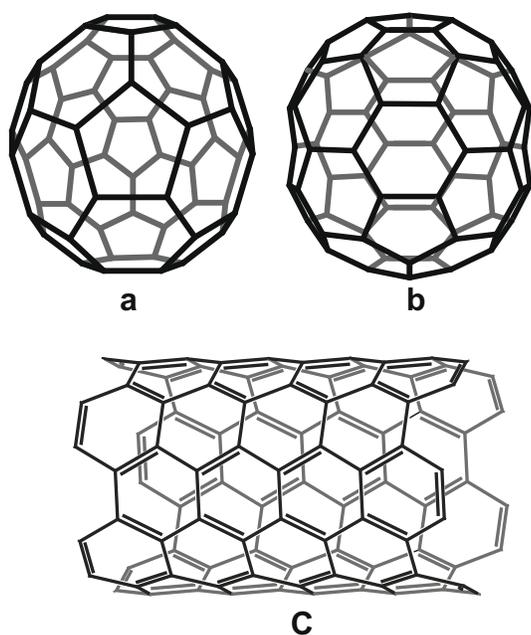
Fullerenes, also known as buckyballs, consists of twelve pentagonal rings surrounded by an appropriate number of aromatic hexagonal rings.  $C_{60}$ , first reported by Kroto et al. (1985) has 20 hexagon rings and is spherical, while  $C_{70}$  has 25 hexagons and an elongated shape. Used in industrial polymer products, such as thin films, electro-optical devices (Prato, 1999) and drug delivery agents (Bosi et al., 2003; Bianco et al., 2005), fullerene production has increased annually. Numerous techniques have been used to characterize fullerenes, such as mass spectrometry and UV–vis spectroscopy (Isaacson et al., 2007; Andrievsky et al., 2002), but few methods have successfully isolated fullerenes from environmental matrices. Carbon nanotubes exhibit different chemical

and physical properties depending on the method of production, removal of amorphous carbon and functionalization (Dai, 2002; Niyogi et al., 2002; Plata et al., 2008). Commercially available SWCNTs are typically produced on a metal catalyst and can be up to one-third metal by weight (Plata et al., 2008). To date, CNTs have been studied mostly by size exclusion chromatography (Bauer et al., 2007), electron microscopy (Rasheed et al., 2007) and chemo-thermal oxidation (Sobek and Bucheli, 2008).

Recently the benzene polycarboxylic acid (BPCA) method has been employed to study BC in soils (Glaser et al., 1998; Brodowski et al., 2005), marine sediment (Sanchez-Garcia et al., 2007) and marine dissolved organic matter (Dittmar, 2008; Ziolkowski and Druffel, 2008). Using a high-temperature and high-pressure oxidation, the BC is chemically oxidized with concentrated nitric acid and converted to BPCAs. The number of carboxylic acid groups on each BPCA is a function of the number of aromatic carbons attached to it prior to oxidation (e.g. Fig. 2). Currently, the mechanism of this reaction is unknown. Fully substituted BPCAs (B6CA) are formed from aromatic rings surrounded on all sides by other aromatic rings, while less substituted BPCAs (i.e. B3CA) are formed from aromatic rings with only two adjacent aromatic rings. Thus by examining the relative distribution of BPCAs, information about the source BC material may be obtained. Post-oxidation, if a BPCA distribution is predominantly B6CA the original BC material was likely a condensed aromatic, while BC material that is less

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**Fig. 1.** Three of the six carbon nanoparticles studied in this paper. (a) Buckminsterfullerene,  $C_{60}$ , (b) Buckminsterfullerene,  $C_{70}$  and (c) SWCNT, non-functionalized.

condensed and more oxidized will form fewer B6CAs with a greater proportion of less substituted BPCAs.

Since BC and CNTs are similar in their condensed aromatic structure, it is likely that similar extraction techniques could be used. Here we test the feasibility of using the BPCA method to isolate and quantify carbon nanoparticles in the marine environment. In this paper we present the distribution of BPCAs and the percent carbon recovered for two fullerenes, two carbon nanotubes and two other carbon nanoparticles, hexane soot and carbon lampblack. Using mixtures of these carbon nanoparticles in marine sediment, we quantify CNTs and evaluate possible matrix effects.

## 2. Methods

We obtained polycyclic aromatic hydrocarbons, fullerenes ( $C_{60}$  and  $C_{70}$ ) and two single walled carbon nanotubes (SWCNT) from Sigma–Aldrich (Fig. 1). The first SWCNT was 1–2 nm O.D.  $\times$  0.5–2  $\mu$ m in length. The second was functionalized (SWCNT-F) with 3–6% carboxylic acid groups and was 4–5 nm O.D. by 0.5–1.5  $\mu$ m in length. Hexane soot obtained from D.M. Smith (University of Denver) was analyzed previously by Akhter et al. (1985) using spectroscopic techniques and quantified for BC by Hammes et al. (2007). Commercially available carbon lampblack (Fisher) was also analyzed. Perylene (Sigma–Aldrich) was used as a model com-

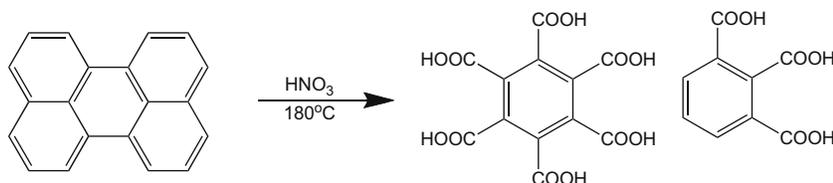
pound to investigate the oxidation process (Fig. 2). Marine sediment (NIST SRM 1941b) was used as an environmental matrix for mixed samples.

Two to seven milligrams carbon were digested in 2 mL 65%  $HNO_3$  at 180  $^{\circ}C$  for 8 h (unless otherwise noted) as reported by Glaser et al. (1998), Brodowski et al. (2005) and Ziolkowski et al. (submitted for publication). During the digestion BC is chemically oxidized to form BPCAs. The solution was passed through a 0.8  $\mu$ m pore size quartz fiber filter into a filtration flask and washed with 30 mL of deionized water. To remove polyvalent cations from the filtrate that interfere with sample analysis, a number of samples received additional treatment. This subset of samples was pretreated with 10 mL of 4 M trifluoroacetic acid for 4 h at 104  $^{\circ}C$ . Following nitric acid oxidation and filtration, samples were passed through a cation column ( $H^+$  form, Dowex 50 W-X8, 200–400 mesh, packed 18 cm ID  $\times$  10 cm high) that was subsequently rinsed with an additional 30 mL of deionized water and combined with the filtrate. Samples were then freeze-dried for 24 h.

Five mL of methanol was added to the dried BPCAs along with 500  $\mu$ L of a 1 mg  $mL^{-1}$  solution of biphenyl-2,2'-dicarboxylic acid (Sigma–Aldrich) in methanol that was used as a derivatization standard. Samples were then methylated by titration with (trimethylsilyl)diazomethane in diethyl ether (Sigma–Aldrich) until the sample solution remained yellow, indicating the presence of un-reacted diazomethane. Samples were then dried under a stream of ultra-high purity nitrogen. A fixed volume of dichloromethane was then added as a solvent.

All samples were separated on a Hewlett Packard 6890 GC outfitted with a Gerstel cooled injection system and a DB-XLB capillary column (30 m  $\times$  0.53 mm ID, 1.5  $\mu$ m film thickness) and a flame ionization detector (FID). After injection, the column temperature was maintained at 100  $^{\circ}C$  for 1 min, then raised 25  $^{\circ}C\ min^{-1}$  to 250  $^{\circ}C$ , then raised 5  $^{\circ}C\ min^{-1}$  to a final temperature of 280  $^{\circ}C$ . The detector temperature was 300  $^{\circ}C$ . The split-less injection volume was between 1 and 3 mL. Benzene polycarboxylic acids were identified by comparison of their retention times with those obtained by a commercially available mixture, verified by GC–mass spectrometry and quantified by GC–FID. All methylated BPCAs were quantified relative to the biphenyl-2,2'-dicarboxylic acid internal standard. No additional response factors were applied, as all methylated BPCAs exhibited an equal response to detection.

Initial work studying the oxidation products of PAHs with the BPCA method yielded BPCAs substituted with  $-NO_2$  groups, due to the nitric acid oxidation (Ziolkowski et al., submitted for publication). This study quantifies these nitrated BPCAs. Omitting these nitrated peaks from quantification would lead to an underestimate of the BPCAs formed in oxidation. Non-nitrated BPCAs are used as reference materials, as nitrated BPCAs are not commercially available. Phthalic acid and 3-nitro and 4-nitrophthalic acid exhibited nearly identical calibration curves, therefore we assumed the same relationship would hold true for larger nitrated BPCAs. All measurements were performed in triplicate, unless otherwise noted.



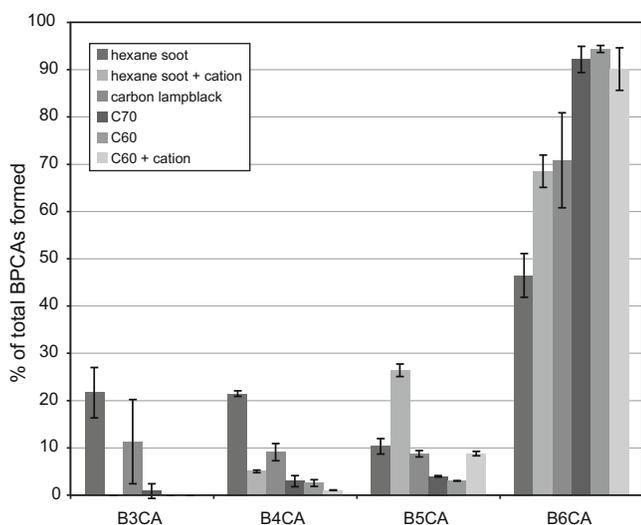
**Fig. 2.** Oxidation of the PAH perylene yields two BPCAs: 20% mellitic acid (B6CA) and 80% trimellitic acid (B3CA), suggesting that the oxidation products are reflective of the original structure of the condensed aromatic material (Ziolkowski et al., submitted for publication). The reported percentages are based on mg C recovered.

### 3. Results

#### 3.1. BPCA distributions

The BPCA method forms BPCAs only from condensed aromatic materials, such as char, soot or polycyclic aromatic hydrocarbons (PAHs) (Glaser et al., 1998; Brodowski et al., 2005; Ziolkowski et al., submitted for publication). Although some PAHs and BC materials form BPCAs with two carboxylic acids, only those compounds with three or more acids groups were quantified in this work. This assumption is employed to avoid erroneously quantifying BC as BPCAs from non-BC material, such as lignin. Initially, the PAH perylene was studied to understand the mechanism of high-temperature and high pressure nitric acid oxidation (Ziolkowski et al., submitted for publication). Upon oxidation of perylene we measured only two BPCAs: the tri-substituted hemimellitic acid (B3CA) and the fully substituted mellitic acid (B6CA) with the mole ratio of 4:1 (Fig. 2). These results suggest that the quantitative distribution of BPCAs can provide structural information about the material being oxidized.

Our results show that most of the oxidation products of the fullerenes ( $C_{60}$  and  $C_{70}$ ) and soots are the fully substituted mellitic acid (B6CA) with small portions of less substituted BPCAs (Fig. 3). Oxidation of both  $C_{60}$  and  $C_{70}$ , processed without cation removal, produces the greatest yield of B6CAs ( $94.4 \pm 0.7$  and  $92.2 \pm 2.8\%$  of total BPCAs, respectively). The BPCA distribution of  $C_{60}$  did not change significantly when processed through the cation column (Table 1). Based on the structure of  $C_{60}$  (Fig. 1a), only B6CA should be formed, which is confirmed by these results. Carbon lampblack, processed without the cation column, had almost equal proportions of B3CA, B4CA and B5CA (about 10% each) and  $70.8 \pm 10.0\%$  B6CA, suggesting that the structure of carbon lampblack is predominantly aromatic rings surrounded by other rings. Without the cation column, hexane soot produced the smallest proportion of B6CA of the materials in this study ( $46.5 \pm 4.6\%$ ) with  $10.3 \pm 1.6\%$  of B5CA,  $21.5 \pm 0.6\%$  B4CA and  $21.7 \pm 5.3\%$  B3CA. Processing soot through the cation column ( $n = 1$ ) drastically shifted the BPCA distribution. There was an increase in the proportion of B6CA and B5CA formed and a requisite decrease in the proportion of B4CA and B3CA. If one theorized about the structure of hexane soot using the BPCA distribution using the cation processed sam-



**Fig. 3.** Distribution of BPCAs formed upon high temperature and high pressure acid oxidation relative to total BPCAs formed from fullerenes, carbon lampblack and soot not processed through the cation column.

ples, a more condensed aromatic structure would be proposed than that using the non-cation processed samples.

The distribution of oxidation products formed from SWCNTs varied markedly depending on sample treatment (Fig. 4). The non-carboxylic acid functionalized SWCNTs exhibited significantly different distributions when processed with and without the cation column. Oxidation products of SWCNTs processed through the cation column were all B6CA ( $98.4 \pm 2.2\%$ ) and a trace of B4CA, while SWCNT samples not processed through the cation column contained a mixture of mostly B3CA and B4CA ( $37 \pm 13\%$  B3CA and  $43 \pm 8\%$  B4CA) with the remainder as B6CA ( $20 \pm 17$ ). B5CA were not observed in either sample. The SWCNT not processed through the cation-exchange resin had the greatest uncertainty associated with the distribution of oxidation products, due to the low carbon yield (as discussed in the next section). Theoretically, SWCNT should form predominantly B6CA because the structure consists of benzene rings surrounded on all sides by other benzene rings. In contrast, oxidation of SWCNT-F produced mostly B6CA regardless of cation processing ( $87.0 \pm 3.4\%$  with and  $68.3 \pm 3.5\%$  without cation processing). The other oxidation products (B4CA and B5CA) varied with cation processing, such that fewer B5CA and more B4CAs and B3CAs were formed when cation processing was not done. These results indicate a greater proportion of interfering cations, likely the metal catalyst, in SWCNTs that was not observed with the SWCNT-F samples.

We also investigated the effect of oxidation duration on the SWCNT BPCA distribution. After 16 h of oxidation (eight additional hours), the SWCNT-F oxidation products were predominantly B6CA ( $81.1 \pm 7.2\%$  with and  $61.9 \pm 9.6\%$  without cation processing). The 16 h oxidation of SWCNT did not yield a significantly different distribution of oxidation products for samples processed with and without cation column processing. These 16 h cationed distributions are not different from those obtained from shorter oxidations of SWCNT.

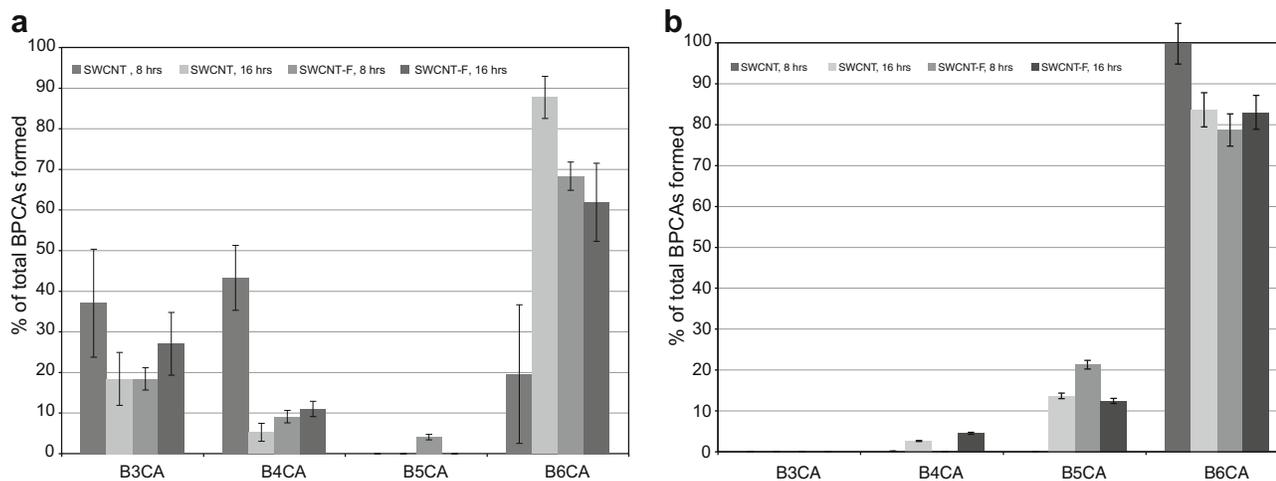
#### 3.2. Carbon yield

Carbon recoveries were calculated as a percentage of mg BPCA C formed relative to the mg C used in each experiment (Table 1). The BPCA carbon yields of the compounds in this study ranged from 0.8% to 26% and 6.0–17% for samples processed with and without the cation column. The range of the carbon yields decreases with cation processing and the overall recoveries were lower. These losses, due to additional sample handling, may be accounted for in the future by incorporating an additional recovery standard that could be added before chemical oxidation. For fullerenes not cation processed, the carbon yield was equal;  $C_{70}$  exhibited a carbon yield of  $26.0 \pm 3.2\%$  and  $C_{60}$  had a carbon yield of  $20.3 \pm 2.1\%$ . Processed through the cation, there was a small loss of  $C_{60}$  (17% recovery). A sample of  $C_{70}$  was not processed through the cation column. By definition, this method cannot recover 100% of the carbon from fullerenes because carbon is lost due to the breakup of adjacent rings. The maximum number of B6CA molecules that could form from one  $C_{70}$  is three (i.e.: 36 carbons), corresponding to only 51.4% carbon yield. If the carbon yield is adjusted to account for only the carbon available to form BPCAs, then the C yield for  $C_{70}$  would be  $47.0 \pm 6.4\%$  within this study. Similarly, if only the carbon available to form BPCAs was used to calculate the carbon yield for  $C_{60}$  then the maximum possible carbon yield would be  $33.5 \pm 3.5\%$ . Adjusting the carbon yield to reflect only the available BPCAs formed is not always practical or possible, because the correct structures of the compounds studied are not always known.

Although carbon lampblack and hexane soot exhibited significantly different BPCA distributions (Fig. 3), the C yields of these materials ( $20.0 \pm 4.1\%$  and  $25.3 \pm 4.0\%$  respectively) are statistically equivalent and equal to the  $C_{60}$  yield. The C yield for perylene was

**Table 1**  
Percent carbon yield for the carbon nanoparticles in this study. Unless otherwise noted, all samples were treated for 8 h. *s* is the standard deviation of three replicates.

			C <sub>70</sub> n = 3	C <sub>60</sub> n = 3	Carbon lamp black n = 3	Hexane soot n = 3	SWCNT n = 3	SWCNT-F n = 3	SWCNT, 16 h n = 3	SWCNT-F, 16 h n = 3
No cation column used	Average BPCA distributions	B3CA	0.89	0.0	11.3	21.7	37.1	18.4	7.0	27.1
		<i>s</i>	1.54	0.0	8.9	5.3	13.3	2.7	6.5	7.7
		B4CA	3.0	2.6	9.1	21.5	43.3	9.2	5.3	11.0
		<i>s</i>	1.2	0.7	1.8	0.6	8.1	1.5	2.2	1.9
		B5CA	4.0	3.0	8.8	10.3	0.0	4.1	0.0	0.0
	<i>s</i>	0.2	0.0	0.7	1.6	0.0	0.7	0.0	0.0	
	Yield	B6CA	92.2	94.4	70.8	46.5	19.6	68.3	87.7	61.9
		<i>s</i>	2.8	0.7	10.0	4.6	17.1	3.5	5.2	9.6
		% C	26.0	20.3	20.0	25.3	0.8	8.2	7.8	11.1
		<i>s</i>	3.2	2.1	4.1	4.0	0.2	1.5	1.2	2.7
				n = 1	n = 1	n = 2	n = 2	n = 2	n = 2	
Cation column used	Average BPCA distributions	B4CA	–	1.1	–	5.03	1.2	2.1	11.0	13.7
		<i>s</i>	–	–	–	–	1.8	0.3	4.7	3.4
		B5CA	–	8.8	–	26.4	0.0	10.9	5.9	5.2
		<i>s</i>	–	–	–	–	0.0	3.7	8.4	3.8
		B6CA	–	90.1	–	68.6	98.4	87.0	83.0	81.1
	<i>s</i>	–	–	–	–	2.2	3.4	13.1	7.2	
	Yield	% C	–	17.0	–	15.7	7.2	7.2	6.0	8.8
		<i>s</i>	–	–	–	–	1.6	1.5	1.9	0.3



**Fig. 4.** Distribution of BPCAs formed upon high temperature and high pressure acid oxidation relative to total BPCAs formed for two types of single walled carbon nanotubes for 8 h oxidations and 16 h oxidations. (a) Samples processed without cation column and (b) samples processed through cation column.

also similar to these values ( $22.6 \pm 1.3\%$ , Ziolkowski et al., submitted for publication), suggesting an average C yield of  $22.9 \pm 4.2\%$  for the non-SWCNT materials in this study. The conversion of BPCAs to BC was previously been made using activated charcoal as a model BC material (Glaser et al., 1998; Brodowski et al., 2005). This average C yield is in agreement with the BPCA conversion factor reported by Brodowski et al. (2005) for activated charcoal but about half of the original conversion factor reported by Glaser et al. (1998).

After oxidation of SWCNTs, there was always black particulate material left in the flask that was most likely undissolved SWCNTs. When processed without the cation column, the non-functionalized SWCNT had the lowest carbon yield at  $0.8 \pm 0.2\%$  and the functionalized SWCNT had a carbon yield of  $8.2 \pm 1.5\%$ . If the oxidation duration was increased to 16 h, the SWCNT carbon yield increased to  $7.3 \pm 0.7\%$  with no change for the SWCNT-F. When processed with the cation column both SWCNTs had the same carbon yield ( $7.2 \pm 1.6$  and  $7.2 \pm 1.5\%$ ) after 8 h and longer oxidations did not show a significant change in carbon yield ( $6.0 \pm 1.9\%$  SWCNT and  $8.8 \pm 0.3\%$  SWCNT-F) from the shorter oxidations. Carboxylic acid

functionalized SWCNTs are produced as a bi-product of metal catalyst removal using  $\text{HNO}_3$  alone or in combination with  $\text{H}_2\text{SO}_4$  (Liu et al., 1998). Since the carbon yield for the 16 h functionalized SWCNT was not significantly different from that of the non-functionalized SWCNT, it is plausible that the oxidation procedure that functionalized the SWCNT initially made it more susceptible to BPCA formation. Future experiments should include longer oxidation times (i.e.: 32 h) to assess the effect on the SWCNT C yield. Acid treatment has also been shown to shorten the length of the CNTs (Chen et al., 2001; Liu et al., 1998) and to form carbonaceous impurities (Hu et al., 2003).

When pure compounds are assessed using the BPCA method (e.g.: perylene), cation column processing is not required. However, environmental samples most often contain a significant concentration of metals and other polyvalent cations that require removal by cation column. Internal standard, biphenyl-2,2'-dicarboxylic acid, recoveries are lower when polyvalent cations are present, suggesting that the presence of polyvalent cations compromises the derivatization reaction. Since the BPCA distributions of samples processed without the cation column were distinctly

different from those processed with the cation column, polyvalent cations apparently change the mechanism of the oxidation process. Hexane soot did not exhibit a loss of the internal standard when processed without the cation column, yet the BPCA distribution was significantly different under the two processing regimes. Further study is required to determine under what conditions cation column processing affects BPCA distributions. Samples containing polyvalent cations not processed through the cation column form a smaller proportion of B6CA and a larger proportion of smaller BPCAs. Therefore estimated structures of BC for samples processed without the cation column would be a less condensed aromatic structure than for those samples processed through the cation column, underestimating the aromaticity of the original structure.

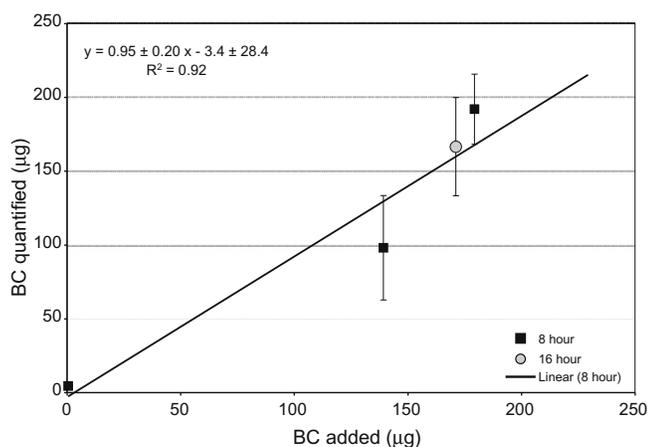
### 3.3. Mixtures in sediments

A key challenge remains for applying this methodology to environmental matrices, such as coastal sediments. In environmental samples it will be important to not only quantify the amount of BC present, but also to determine the relative contributions of dif-

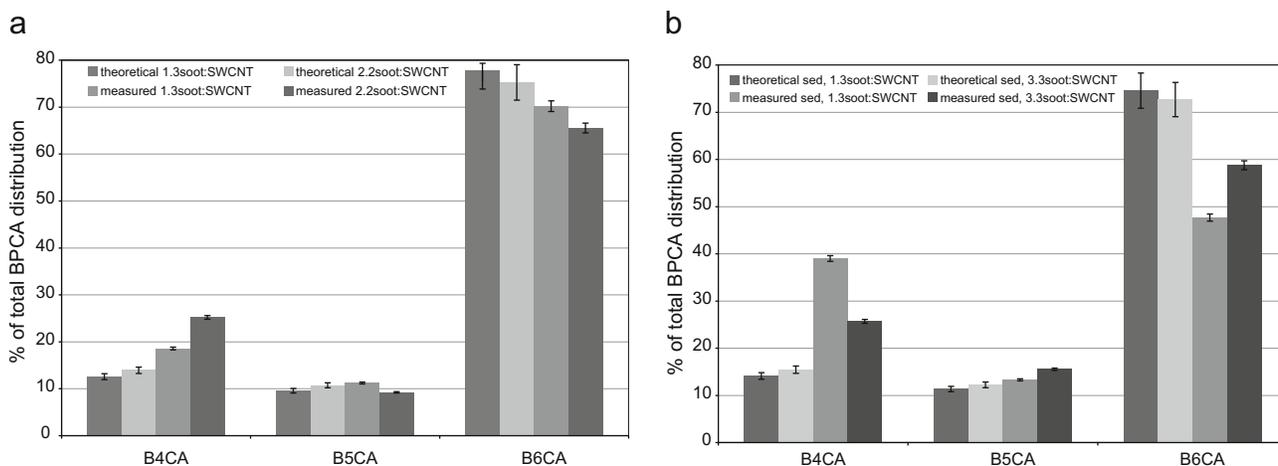
ferent BC sources. Two methods were used to evaluate matrix effects that may occur during oxidation. First, using standard addition of SWCNT we quantified BC in known mixtures of marine sediment, soot and SWCNT (Fig. 5). Marine sediment (NIST 1941b), without any additional BC, was found to contain  $4.4 \pm 0.4$  g/kg BC, which is greater than previous BPCA estimates and not significantly different than chemo-thermal oxidation (Hammes et al., 2007). While these measurements were converted from BPCAs to BC using the 22.9% conversion factor determined in this study other loss processes must be present. Since we do not know the types of BC materials being quantified we must use this average value. In some cases this may lead to an over estimate of BC abundance. The slope of the data from the standard addition experiments indicates recovery of  $95 \pm 20\%$  of the BC when the samples were oxidized for 8 h. Prolonged oxidation, of 16 h, also fell on the observed trend, indicating that the duration of oxidation did not affect the observed matrix effect. SWCNTs oxidized in isolation were found to have a low carbon yield (7.2%) and in mixture samples a conversion factor of 20.7% was applied, yet the BC yield is lower than expected. The lower than expected BC yield in mixture samples demonstrates that a small matrix effect is present. In other words, the presence of sedimentary material, mainly clay, causes the nitric acid oxidation of BC to proceed less efficiently than when no sedimentary material is present.

A second method used to evaluate matrix effects was to examine the BPCA distributions of the mixtures, comparing the theoretical and measured BPCA distributions. When oxidized together, soot and SWCNTs were not as fully substituted as predicted by a theoretical mixture of these compounds (Fig. 6a). This shift towards the production of less substituted BPCAs was more dramatic when soot and SWCNTs were oxidized with marine sediments present (Fig. 6b). Although the matrix effect generates BPCA distributions similar to those not processed through the cation column (Fig. 4), these observed results are not due to residual cations. If cations were present, the internal standard recovery would have diminished, whereas this was not observed in the mixture samples. Thus, this shift could be due to interactions with the cation column.

The presence of this matrix affect limits the applicability of identifying the types of BC present in mixtures using the BPCA method alone. Compound specific isotopic analysis of BPCAs, for the purpose of isolating the source of BC, is not likely to be feasible when mixtures of BC are present. Stable carbon isotopes are not suitable as SWCNTs show a wide range of  $\delta^{13}\text{C}$  values ( $-53.2$  to



**Fig. 5.** Standard addition of soot and SWCNTs to marine sediment (NIST 1941b) after 8 h (filled squares) and 16 h (grey circle). The trend line, generated using only 8 h oxidation samples, indicates the recovery of SWCNT. The y-intercept corresponds to the BC content in the marine sediment and the negative value indicates loss of BC. Error bars represent propagated errors.



**Fig. 6.** Theoretical and measured BPCA distributions in mixtures of (a) soot and SWCNT and (b) marine sediment, soot and SWCNT. Error bars on theoretical BPCA distributions are 5% while measured BPCA distribution errors are propagated errors.

–23.5%, Plata et al. (2008)), which may be from the carbon source material or fractionation during fabrication and post-production treatments. Since carbon source materials for SWCNTs, fullerenes and most soots are mostly fossil in origin, radiocarbon ( $\Delta^{14}\text{C}$ ) analysis of BPCAs would not garner information about the source of BC. BC oxidization techniques will not be able to parse the source of BC when mixtures of soot and SWCNTs are present due to their structural similarity. Therefore, for BC source appointment, additional analytical techniques must be employed.

#### 4. Conclusions

This paper investigated the suitability of using the BPCA method to isolate two SWCNTs, two fullerenes and two types of soot from natural samples. The materials studied exhibit distinct BPCA distributions, favoring the production of larger BPCAs. Mixtures of BC do not exhibit BPCA distributions predicted by oxidation of single compounds. Although the BPCA method is suitable for isolating and quantifying BC mixtures in environmental samples, matrix effects complicate the feasibility of identifying the relative contributions of different types of BC using this method.

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