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Exposure and Emissions Monitoring during Carbon Nanofiber Production—Part II: Polycyclic Aromatic Hydrocarbons

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Production of carbon nanofibers and nanotubes (CNFs/CNTs) and their composite products is increasing globally. High-volume production may increase the exposure risks for workers who handle these materials. Though health effects data for CNFs/CNTs are limited, some studies raise serious health concerns. Given the uncertainty about their potential hazards, there is an immediate need for toxicity data and field studies to assess exposure to CNFs/CNTs. An extensive study was conducted at a facility that manufactures and processes CNFs. Filter, sorbent, cascade impactor, bulk, and microscopy samples, combined with direct-reading instruments, provided complementary information on air contaminants. Samples were analyzed for organic and elemental carbon (OC and EC), metals, and polycyclic aromatic hydrocarbons (PAHs), with EC as a measure of CNFs. Transmission electron microscopy with energy-dispersive X-ray spectroscopy also was applied. Fine/ultrafine iron-rich soot, PAHs, and carbon monoxide were production byproducts. Direct-reading instrument results were reported previously [Evans DE *et al.* (Aerosol monitoring during carbon nanofiber production: mobile direct-reading sampling. *Ann Occup Hyg* 2010; 54:514–31)]. Results for time-integrated samples are reported as companion papers in this issue. OC and EC, metals, and microscopy results are reported in Part I [Birch ME et al. (Exposure and emissions monitoring during carbon nanofiber production—Part I: elemental carbon and iron–soot aerosols. Ann Occup Hyg 2011; 55: 1016–36.)] whereas results for PAHs are reported here. Naphthalene and acenaphthylene were the dominant PAHs with average concentrations ranging from 115 to 336 μg m^{-3} and 35 to 84 μg m^{-3}, respectively. Concentrations of other PAHs ranged from ∼1 to 10 μg m^{-3}.

Keywords: carbon nanofiber; nanomaterial; nanotube; occupational exposure; polycyclic aromatic hydrocarbon; ultrafine aerosol

INTRODUCTION

According to some projections, unprecedented growth in nanotechnologies will broadly impact many industrial sectors and require up to 2 million workers globally by year 2015 (Roco and Bainbridge, 2005). As discussed in a companion paper (Birch *et al.*, 2011), market value projections for nanotechnologies differ widely, e.g. from $26 billion to $4 trillion in 2015, depending on different assumptions and market definitions. The $26 billion estimate (BCC Research, 2010) may be more realistic. It includes only nanotechnology products ('nanomaterials', 'nanotools', and 'nanodevices') rather than all 'nanotechnology-enabled' products. The largest product segments in 2009 were nanomaterials, having an estimated value of $9 billion and a projected increase to ∼$19.6 billion in 2015 (BCC Research, 2010).

Carbon nanofibers and nanotubes (CNFs/CNTs) are an important class of nanomaterials due to their

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immense potential for industrial and scientific applications. Production of CNFs/CNTs and composite products is increasing globally, and manufacturing processes are rapidly changing. In 2004, an annual global production of CNFs and CNTs was reported as 65 tons per year (Cientifica 2005). Applications of CNTs include electronics, flat panel displays, batteries and fuel cells, thermoplastic additives (to impart conductivity), and biomedical science. At relatively low loadings, CNFs are being used to improve the thermal, electrical, and mechanical properties of a wide variety of polymer-based composite materials. Applications include high-performance products, such as coatings and composites for aerospace, automobiles, sports equipment, and construction.

High-volume production of CNFs/CNTs may pose an exposure risk for workers, especially manual handling in open areas. Inflammation, pulmonary fibrosis, granulomas, oxidative stress, and mutagenicity have been observed in inhalation studies of mice exposed to single-walled CNTs (SWCNTs) (Shvedova *et al.*, 2005, 2008). Dermal inflammation also has been reported (Murray *et al.*, 2009). More alarming is the prospect of asbestos-like pathology, as reported for multi-walled CNTs (MWCNTs) injected into the abdominal cavities of mice (Poland *et al.*, 2008). A similar study of CNFs has not been conducted, but acute inflammation and pulmonary fibrosis were observed in mice exposed by pharyngeal aspiration (Kisin *et al.*, 2010), and CNFs are similar to MWCNTs in some respects. Their diameters are comparable, with CNFs typically in the 50–200 nm range (Ku *et al.*, 2006) and MWCNTs having diameters up to 100 nm (Wang *et al.*, 2006); they have tubular structures; and the tubes/fibers typically form bundled/entangled structures. In contrast, SWCNTs have much smaller diameters (e.g. 1–3 nm) and form highly entangled structures (Shvedova *et al.*, 2005; Maynard *et al.*, 2007). The differences between and definitions of CNFs and CNTs are discussed in a companion paper (Birch *et al.*, 2011).

A review of the current toxicological literature and draft risk assessment on CNFs and CNTs was recently released by the National Institute for Occupational Safety and Health (NIOSH, 2010) for public comment. A single recommended exposure limit (REL) was proposed (7 μg m^{-3}); however, it is recognized that the diverse properties these materials may impart a range of toxicities. As an example, in a recent comparison of inflammatory responses to different types of CNTs administered to the peritoneum of mice, long thick MWCNTs caused DNA damage and severe inflammatory effects, whereas similar SWCNTs caused little effect and short thin MWCNTs had no effect (Yamashita *et al.*, 2010). These findings suggest important differences in the biological responses of CNFs/CNTs.

CNFs/CNTs have been produced for some years now, yet relatively few studies at facilities that produce/use these materials commercially have been reported (Maynard *et al.*, 2004; Methner *et al.* 2007; Evans *et al.*, 2010; Lee *et al.*, 2010), and personal exposures were not monitored. Given the potential health hazards, there is an immediate need for toxicity and exposure data on CNFs/CNTs, with inhalation being the primary concern. An extensive study was conducted at a facility that manufactures and processes CNFs. Filter, sorbent, bulk sample, and microscopy analyses, combined with direct-reading instruments, provided complementary information regarding the composition, source, and concentrations of air contaminants. Samples were analyzed for organic and elemental carbon (OC and EC), metals, and polycyclic aromatic hydrocarbons (PAHs), with EC as a measure of CNFs. Transmission electron microscopy with energy-dispersive X-ray spectroscopy also was applied. Direct-reading results were reported previously (Evans *et al.*, 2010). Findings for time-integrated samples are reported as companion papers in this issue. In addition to CNFs, fine/ultrafine iron-soot aerosol, PAHs, and carbon monoxide were found as production byproducts. OC and EC, metals, and microscopy results are reported in Part I (Birch *et al.*, 2011), whereas PAH results are reported herein.

FIELD SURVEYS

Facility and process description

The facility surveyed manufactures and processes vapor-grown CNFs. At the time of the surveys, annual production was ∼31 000 pounds, and two different reactors, hereafter referred to as ‘A’ and ‘B’, were operating. The raw CNF products were collected in open boxes and taken to the processing area, where they were processed in multiple steps. As a final step, the CNF material was poured into a hopper feeding a thermal treatment system for removal of organic and metal impurities. The final product was discharged (openly) into a box containing a plastic bag. About 15 pounds were collected before the bag was manually removed, closed, and replaced. The facility had an open floor plan with ∼22 000 square feet of floor space and ceilings ∼18-feet high. Synthesis and processing operations were performed in different areas but these areas

were not separated. A separate room with a large window to the plant was used as a control room. A small interlock area separated the plant from the control room and from the administrative areas, but it was not operating during the surveys. The administrative areas included several offices, a conference room, and a small kitchen. A complete facility description and details on operations are reported elsewhere (Birch *et al.*, 2011; Evans *et al.*, 2010).

Products

The CNF products are formed in the gas phase as an entangled mass. Based on the manufacturer's specifications, the final product is a high-purity material that is 99.9% fibrous and has very low metal content. It is described as a highly graphitic, low-cost tubular material with walls composed of angled graphite sheets. The fibers have an outer chemically vapor deposited (CVD) layer of carbon and an inner, tubular graphitic layer beneath the CVD layer. The fiber structure, called 'stacked cup' or 'herringbone,' has exposed edge planes along the surface. These highly reactive edge sites allow chemical modification for maximum reinforcement in polymer composites. Fiber diameters range from 70 to 200 nm, significantly larger than SWCNTs (e.g. 1–3 nm). The length of the as-produced fibers is estimated to be from 50 to 200 μm. Different grades are available and depend on the type of thermal treatment received.

Air monitoring

Air monitoring was conducted over a total of 4 days: two consecutive days in December and on 1 day during the first and second weeks of February. Four locations inside the facility were monitored: (i) the CNF reactor (synthesis) area, (ii) the thermal treatment area, (iii) a plant background area, and (iv) a conference room in an office area. Samples also were collected outdoors as a measure of environmental background.

METHODS

Air samples were collected at 2 l min^{-1} (AirChek 2000 pumps, SKC Cat. No. 210-2002) with OVS-7 sorbent tubes (XAD-7 resin/glass fiber filter; SKC 226-57). Sampling periods were ~6h, and two (paired) tubes were used at each sampling location. For the PAH analyses, each section of the tube (front filter and front and back sorbent sections) was removed and placed into separate 40-ml vials. Ten microliter of a 100 p.p.m. surrogate standard solution containing nitrobenzene-d5, 2-fluorobiphenyl, and 4-terphenyl-d12 was spiked into each sample section. The individual sections were then desorbed in an ultrasonic bath for 30 min with 2 ml of methylene chloride. After sonication, 1 ml of desorption solvent was transferred to a 2-ml vial and 5 μl of a 1000 μg μl^{-1} internal standard solution containing naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12 was added. The sample was briefly mixed on a vortex mixer and analyzed by gas chromatography–mass spectrometry with selected ion monitoring (GC–MS SIM). Laboratory control samples included two media blanks and two sets of media spiked with standards.

The following equipment and conditions were used for PAH analyses: instrument: Hewlett Packard 5890 II GC and 5972 MS detector. GC conditions: Restek Rxi-5MS capillary column, 30 m, 0.25 mm inner diameter, and 0.25 μm film thickness; 1.5 ml min^{-1} column flow; injection temperature of 280°C; 2-μl injection volume; initial oven temperature at 85°C with 0.5 min hold time; 12°C min^{-1}–290°C and hold 0.5 min; 20°C min^{-1} to final temperature of 330°C with 1.0 min hold time. MS conditions: SIM scan mode with Group 1 scan starting at 2.0 min, Group 2 at 8.2 min, and Group 3 at 15.3 min (see Table 1 for quantitation and secondary ions). The limits of detection and quantitation (LOD and LOQ) were determined through analysis of media spikes. Because sections of the sorbent tube were analyzed separately, an LOD–LOQ study was performed for each section. The LOD–LOQ results (as micrograms per sample) were based on a 2-ml extraction volume.

In addition to air samples, three bulk samples of CNFs were analyzed: two raw (unprocessed) CNF products, one from each reactor, and a final processed (heat treated) product. Samples were preweighed into amber glass vials and extracted three times with 10 ml of methylene chloride. Sample weights were as follows: Reactor A unprocessed CNF: 117.9 mg, Reactor B: 496.6 mg, and final product: 865.1 mg. The surrogate solution (nitrobenzene-d5, 2-fluorobiphenyl, and 4-terphenyl-d12) was added to the sample prior to extraction. With each extraction, the sample was shaken for 2 min. The three extracts were combined and concentrated to 1.0 ml except for one sample (Reactor A), which could only be concentrated to 5 ml. Analysis conditions were the same as those for the filter samples except the MS scan began at 1.5 min and was in full scan mode, from 35 to 500 amu. The LOD and LOQ and calibration ranges for the bulk samples are based on an initial weight of 1 kg and final extraction volume of 1 ml. The actual LOD and LOQ depend on the weight of sample extracted. The LODs and LOQs for the laboratory

Table 1. GC/MS quantitation and secondary ions and internal standard reference compounds for target PAHs. Air standards provided where available

Compound[a]	Group	Quantitation ion (m z^{-1})	Secondary ions (m z^{-1})	Internal standard	Exposure limit (mg m^{-3}) or classification
Naphthalene-D_8	I	136	—	—	—
Naphthalene	I	128	129, 126, 64	Naphthalene-D_8	50[b,c,d]
Acenaphthylene	II	152	153, 150, 76	Acenaphthene-D_{10}	—
Acenaphthene-D_{10}	II	164	—	—	—
Acenaphthene	II	153	154, 152, 150, 76	Acenaphthene-D_{10}	—
Fluorene	II	166	167, 165, 164, 82	Acenaphthene-D_{10}	—
Phenanthrene-D_{10}	II	188	—	—	—
Phenanthrene	II	178	179, 176, 89	Phenanthrene-D_{10}	0.2[b]
Anthracene	II	178	179, 176, 89	Phenanthrene-D_{10}	0.2[b]
Fluoranthene	II	202	203, 200, 101	Phenanthrene-D_{10}	—
Pyrene	II	202	203, 200, 101	Chrysene-D_{12}	—
Benz(a)anthracene	III	228	229, 226, 114	Chrysene-D_{12}	—
Chrysene-D_{12}	III	240	—	—	—
Chrysene	III	228	229, 226, 114	Chrysene-D_{12}	0.2[b], suspect carcinogen[c,d]
Benzo(b)fluoranthene	III	252	253, 250, 126	Chrysene-D_{12}	—
Benzo(k)fluoranthene	III	252	253, 250, 126	Chrysene-D_{12}	—
Benzo(a)pyrene	III	252	253, 250, 126	Chrysene-D_{12}	0.2[b], 0.1[c], suspect carcinogen[d]
Perylene-D_{12}	III	264	—	—	—
Indeno(1,2,3-cd)pyrene	III	276	277, 274, 138	Chrysene-D_{12}	—
Dibenz(a,h)anthracene	III	278	279, 276, 139	Chrysene-D_{12}	—
Benzo(g,h,i)perylene	III	276	277, 274, 138	Chrysene-D_{12}	—

[a]Compounds listed in order of elution.
[b]OSHA.
[c]NIOSH.
[d]ACGIH (see text for discussion of limits.)

control samples and blanks are based on an initial weight of 15 g, the amount of solid reagent used for blank extraction. The sample from Reactor B required dilution; the LODs and LOQs were adjusted accordingly. Laboratory control samples included one media blank (laboratory reagents only) prepared and analyzed with the sample set and one set of laboratory control spikes (standards spiked into the reagents).

RESULTS AND DISCUSSION

PAHs are pervasive environmental contaminants that result from incomplete combustion processes. In the workplace, they are commonly associated with industrial processes in which carbonaceous materials (e.g. coke, coal tar and pitch, asphalt oils) are produced or used (Bjerseth and Becher, 1986). The health hazards of PAHs are well established (Bjerseth and Becher, 1986; CRC Press, 1988; ATSDR 1996; Tsai *et al.*, 2001; Kuo *et al.*, 2003; Omar *et al.*, 2006; Yang and Xing, 2006; Srogi, 2007). Many are carcinogens thought to exert their effects through formation of PAH–DNA adducts (Miller and Miller, 1981; Jerina *et al.*, 1990; Kriek *et al.*, 1998; Rogan, *et al.*, 1993; Chakravarti, *et al.*, 1995). Several PAHs have caused cancer in animal studies when inhaled, ingested, or applied to the skin (ATSDR, 1996). Their toxicity is highly structure dependent, ranging from nontoxic to extremely toxic for isomers of a given compound. The US Environmental Protection Agency (US EPA) has promulgated 16 PAHs as priority pollutants (Table 1). Eight of these are considered possible carcinogens: benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene, and benzo(g,h,i)-perylene (ATSDR, 1996). The following PAHs have been recognized for carcinogenic, mutagenic, and teratogenic properties: benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)-fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene,

coronene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene, and ovalene (Luch, 2005). Benzo(*a*)pyrene in particular has been identified as being highly carcinogenic.

Average PAH concentrations in different areas of the facility during the first two survey days are reported in Fig. 1 (n = 4; error bars represent 1 SD). Naphthalene and acenaphthylene (Fig. 1a) were the dominant PAHs with average concentrations ranging from 115 to 298 μg m^{-3} and 35 to 63 μg m^{-3}, respectively. Concentrations of other PAHs (Fig. 1b), including phenanthrene, fluorene, fluoranthene, anthracene, acenapthene, and pyrene, ranged from ~1 to 6 μg m^{-3}. Results for two media blanks and two samples collected outdoors were non detect.

Similar findings (Fig. 2a,b) were obtained for samples collected on 2 days, 2 months later (in February). Naphthalene concentrations near Reactor A were 453 μg m^{-3} and 219 μg m^{-3}, giving an average concentration of 336 μg m^{-3} (Fig. 2a) for the 2 days, which is consistent with that found previously (298 μg m^{-3}). Corresponding concentrations in the thermal treatment area were 109 μg m^{-3} and 142 μg m^{-3}, similar to the previous average (115 μg m^{-3}). The concentrations of acenaphthalene in these areas were 84 μg m^{-3} in the Reactor A area and 44 μg m^{-3} in the thermal treatment area on the first day, and, respectively, 83 μg m^{-3} and 61 μg m^{-3} on the second, again comparable to results found previously. Concentrations of other PAHs (Fig. 2b) also were similar to previous results, ranging from ~0.5 μg m^{-3} to 10 μg m^{-3}. Average air concentrations of naphthalene and acenaphthylene and other

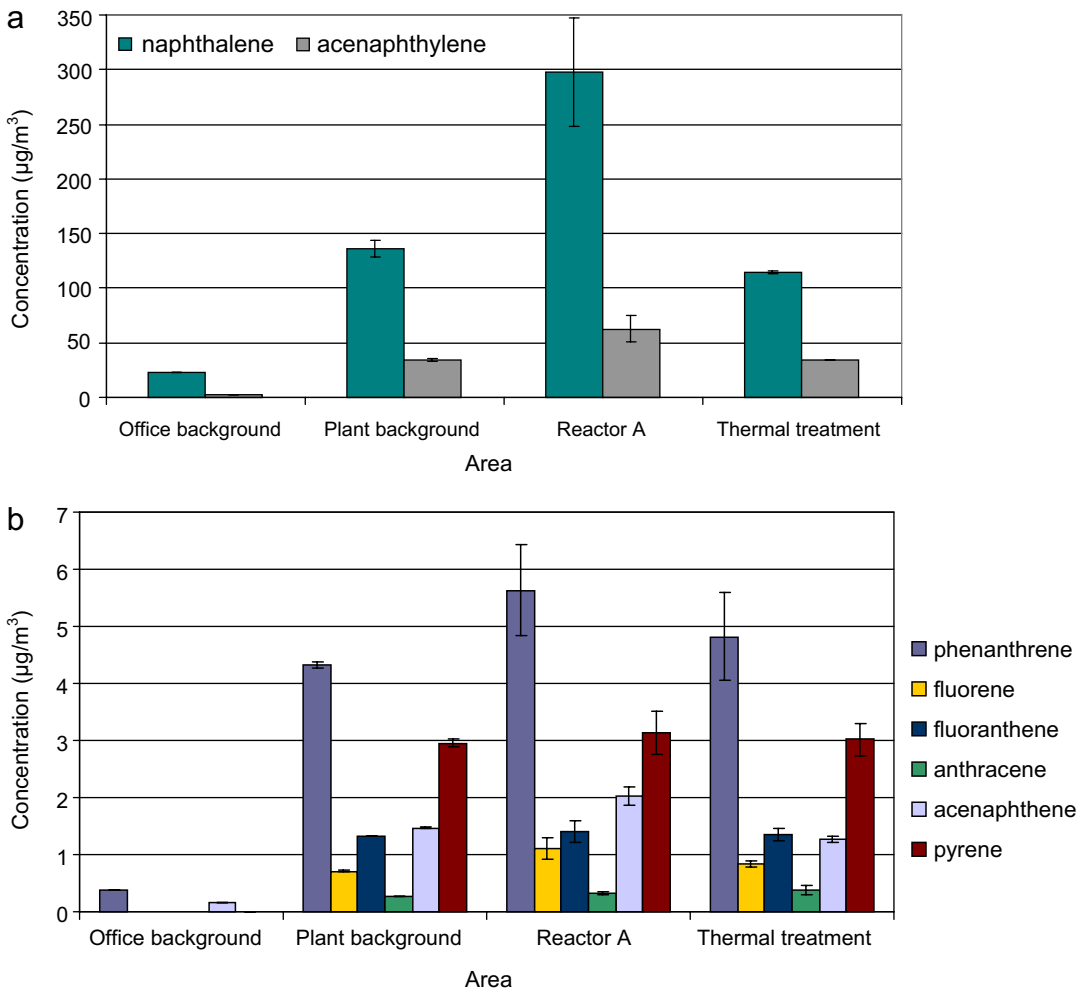

Fig. 1. a) Average concentrations of naphthanene and acenaphthylene in different areas over two survey days in December. (b) Average PAH concentrations in different areas over two survey days in December.

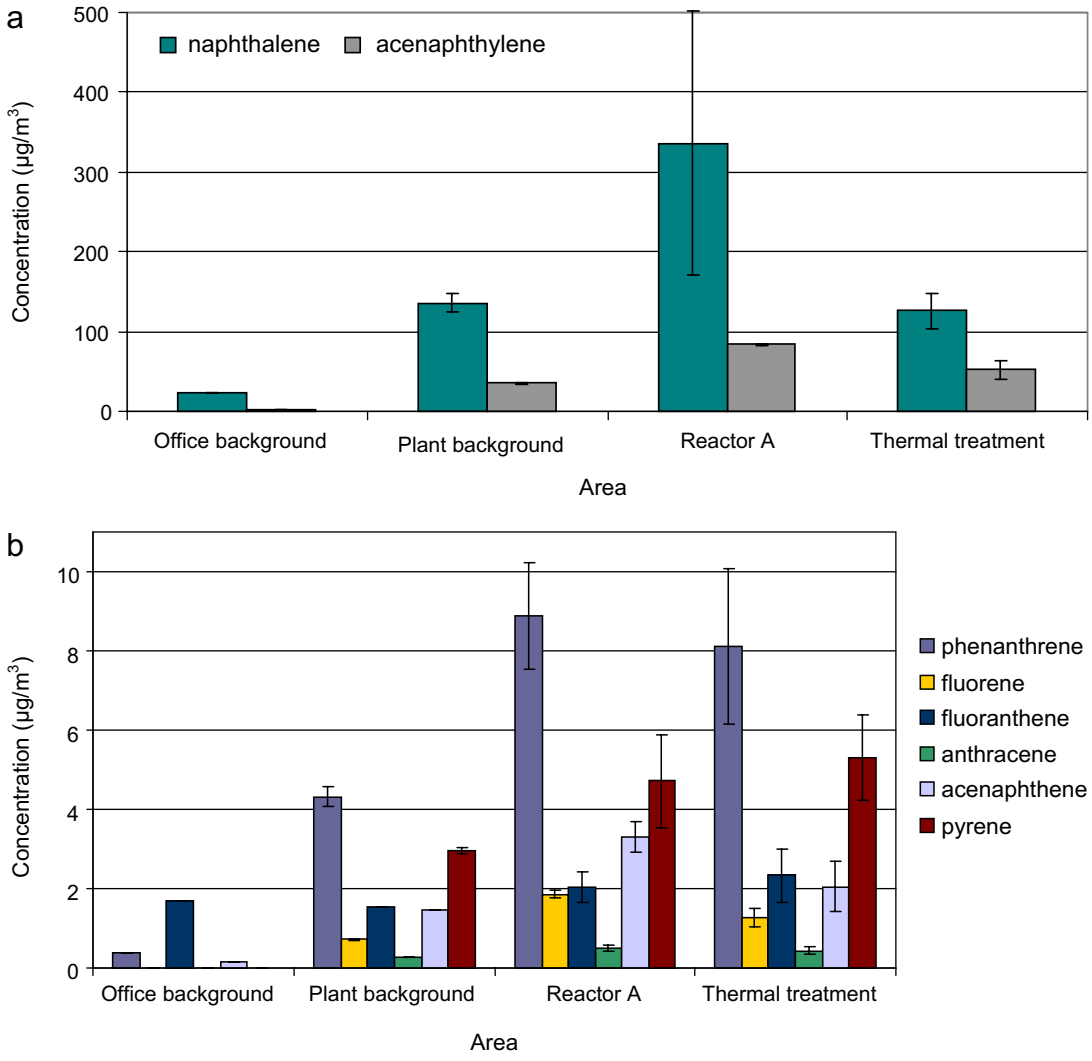

Fig. 2. a) Average concentrations of naphthalene and acenaphthylene in different areas over two survey days in February. (b) Average PAH concentrations in different areas over two survey days in February.

PAHs in different areas of the facility over all four survey days are reported in Fig. 3a,b ($n = 8$; error bars represent 1 SD).

Except for naphthalene, all results for the front filter sections of the OVS samplers were below the LOD (0.1–0.4 µg per sample) or LOQ (0.34 to 1.0 µg per sample) on all survey days. During the December surveys (Fig. 1), in the thermal treatment area, naphthalene on the front filter would have contributed only a minor amount (1.81 µg m^{-3}) to the air concentration (115 µg m^{-3}) determined with the front sorbent result, which is expected given its volatility. The amount of acenaphthylene and benzo(g,h,i)perylene on the front filter corresponded to air concentrations of 0.46 µg m^{-3} and 0.62 µg m^{-3}, respectively, both between the LOD and LOQ for these compounds. The acenaphthylene concentration determined with the result for the front sorbent was ~34 µg m^{-3}, whereas benzo(g,h,i) perylene was found only on the front filter (and in bulk samples as discussed below), indicating its particulate form rather than vaporous. Similar results for front filters were found in the Reactor A area: 6.20 µg m^{-3} for naphthalene (298 µg m^{-3} with front sorbent), 0.89 µg m^{-3} for acenaphthylene (63 µg m^{-3} with front sorbent), and 2.23 µg m^{-3} for benzo(g,h,i)perylene (on front filter only). The same trend was found for the plant background samples. The front filter contributed 2.96 µg m^{-3} naphthalene, relative to 136 µg m^{-3} for

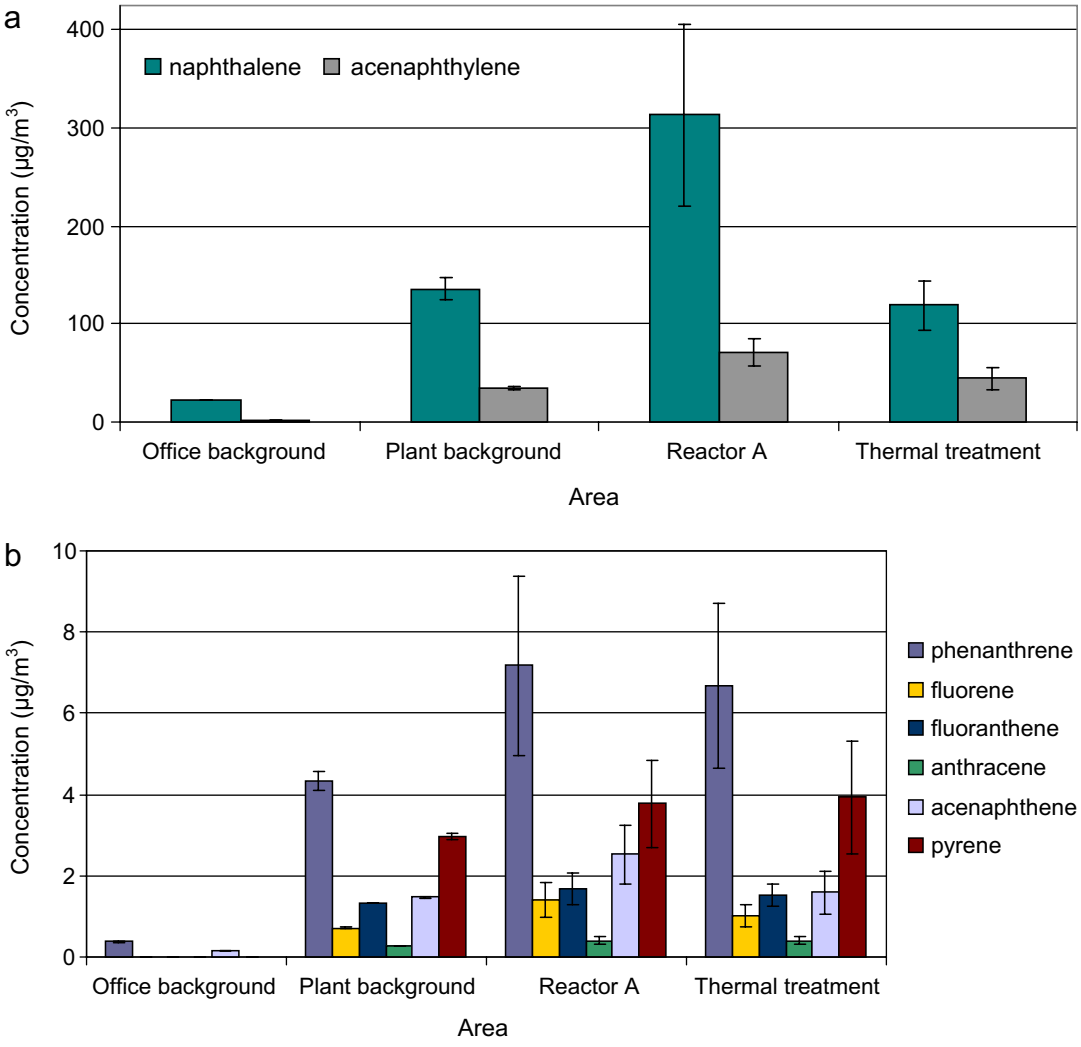

Fig. 3. a) Average concentrations of naphthalene and acenaphthylene in different areas over all survey days (four total). (b) Average PAH concentrations in different areas over all survey days (four total).

the front sorbent; 0.65 µg m^{-3} acenaphthylene, relative to 35 µg m^{-3} for the front sorbent; and 0.96 µg m^{-3} benzo(g,h,i)perylene, with nondetect for the front sorbent.

Except for naphthalene, the amounts of PAHs on the back sorbent sections of the OVS samplers were negligible and therefore not reported. During the first two survey days (in December), the amount on the back section (i.e. breakthrough) was typically <2% of that found on the front section. Results were similar for the samples collected in February, but for several samples (with highest loadings), the amounts on the back section were higher, between ~6 and 10% of that on the front section.

Results for the three bulk materials, two raw CNF products from Reactors A and B and a final, processed product, are reported in Fig. 4 and Table 2. All results for bulk samples were either nondetect or above the LOQ, which depended on the amount of sample extracted and the individual PAH. Limits for target analytes in the three materials were LOD = 3.0–4.0 mg kg^{-1} and LOQ = 11.0–13.0 mg kg^{-1} for Reactor A, LOD = 0.2–2.0 mg kg^{-1} and LOQ = 0.5–5.7 mg kg^{-1} for Reactor B, and LOD = 0.1 mg kg^{-1} and LOQ = 0.3–0.4 mg kg^{-1} for the final product. Several non-target analytes also are reported based on a library (MS) search. Results for non-target analytes are considered estimates.

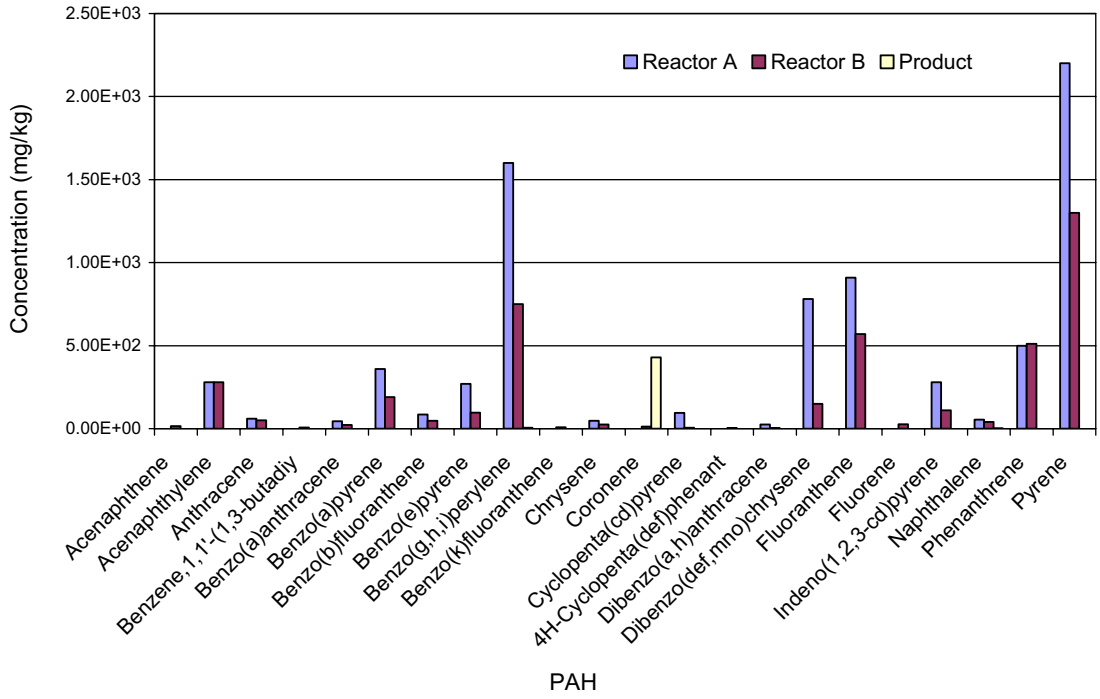

Fig. 4. PAH results for three bulk CNF samples of unprocessed products from Reactors A and B and a final product.

The top three PAHs in both of the raw products were pyrene, benzo(g,h,i)perylene, and fluoranthene, with concentrations of 2200, 1600, and 910 mg kg^{-1} for the Reactor A material and 1300, 750, and 570 mg kg^{-1} for the Reactor B material. In general, the PAHs common to both the products were higher in the Reactor A product. In ascending order, with concentrations ranging from 780 to 25 mg kg^{-1}; other PAHs in product A included dibenzo(def,mno)chrysene, phenanthrene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene and acenaphthylene, benzo(e)pyrene, cyclopenta(cd)pyrene, benzo(b)fluoranthene, anthracene, naphthalene, chrysene, benz(a)anthracene, and dibenz(a,h)anthracene. Product B also contained these PAHs, but the relative distribution differed. In addition, product B contained the following PAHs not found in product A: fluorene, coronene, benzo(k)fluoranthene, benzene,1,1′-(1,3-butadiyene-1,4-diyl)bis, acenaphthene, and 4H-cyclopenta(def)phenanthrene. Excluding the top three PAHs (i.e. pyrene, benzo(g,h,i)perylene, and fluoranthene), the PAH concentrations for product B ranged from 510 to 4.2 mg kg^{-1}. As expected, due to thermal treatment, PAH levels in the final product were much lower, with the exception of coronene at 430 mg kg^{-1}. Coronene was not found in the Reactor A product and was at 13 mg kg^{-1} in the Reactor B product. Other PAHs in the final product were benzo(g,h,i)perylene (5.1 mg kg^{-1}), naphthalene (1.7 mg kg^{-1}), pyrene (0.68 mg kg^{-1}), and acenaphthylene (0.62 mg kg^{-1}).

Occupational exposure to PAHs should be controlled to an extent that is practically feasible, but there are few set limits for assessing exposure to individual PAHs. Air concentrations (Figs. 1,2) of target PAHs having established exposure limits were well below those limits (Table 1). By comparison, the mean phenanthrene concentration reported for a study population of 284 workers 'highly exposed' to PAHs during the manufacture of refractory products (graphite electrode production, coke oven operation, tar distillation, and steel production) was 4.81 μg m^{-3} (Pesch *et al.*, 2007), while it ranged from ~5 to 9 μg m^{-3} in this study. In another cross-industry study (Unwin *et al.*, 2006), 8-h time-weighted average (TWA) concentrations of BaP ranged from <0.01 to 6.21 μg m^{-3}, with a geometric mean of 0.036 μg m^{-3}. In this study, BaP was found in the bulk materials, but it was not detected in the air samples. Differences in the relative abundances and types of PAHs present depend on their sources and processes by which they are formed. All the PAHs found in this study are EPA priority pollutants, and seven (Reactor A sample) and eight (Reactor B sample) of the PAHs found in two unpurified products are considered possible carcinogens (ATSDR, 1996).

Table 2. PAH results for samples of raw (unprocessed) CNFs from Reactors A and B and a final processed product

Compound	Formula	Molecular weight (g mol)	Concentration (mg kg) Reactor A	Reactor B[a]	Final product[a]
Acenaphthene[b]	$C_{12}H_{10}$	154.21	nd	16	nd
Acenaphthylene[b]	$C_{12}H_8$	152.19	280	280	0.6
Anthracene[b]	$C_{14}H_{10}$	178.23	60	51	nd
Benzene,1,1′-(1,3-butadiyne-1,4-diyl)bis	$C_{16}H_{10}$	202.25	nd	6.6[c]	nd
Benz(a)anthracene[b,d]	$C_{18}H_{12}$	228.29	45	23	nd
Benzo(a)pyrene[b,d]	$C_{20}H_{12}$	252.31	360	190	nd
Benzo(b)fluoranthene[b,d]	$C_{20}H_{12}$	252.31	85	47	nd
Benzo(e)pyrene	$C_{20}H_{12}$	252.31	270	97[d]	nd
Benzo(g,h,i)perylene[b,d]	$C_{22}H_{12}$	276.33	1600	750	5.1
Benzo(k)fluoranthene[b,d]	$C_{20}H_{12}$	252.31	nd	8.7	nd
Chrysene[b,d]	$C_{18}H_{12}$	228.29	47	25	nd
Coronene	$C_{24}H_{12}$	300.35	nd	13[d]	430
Cyclopenta(cd)pyrene	$C_{18}H_{10}$	226.28	95	5.8[d]	nd
4H-Cyclopenta(def)phenanthrene	$C_{15}H_{10}$	190.25	nd	4.4[d]	nd
Dibenz(a,h)anthracene[b,d]	$C_{22}H_{14}$	278.35	25	4.2	nd
Dibenzo(def,mno)chrysene	$C_{22}H_{12}$	276.33	780	150[d]	nd
Fluoranthene[b]	$C_{16}H_{10}$	202.25	910	570	nd
Fluorene[b]	$C_{13}H_{10}$	166.22	nd	26	nd
Indeno(1,2,3-cd)pyrene[b,d]	$C_{22}H_{12}$	276.33	280	110	nd
Naphthalene[b]	$C_{10}H_8$	128.17	54	40	1.7
Phenanthrene[b]	$C_{14}H_{10}$	178.23	500	510	nd
Pyrene[b]	$C_{16}H_{10}$	202.25	2200	1300	0.7

nd, nondetect.
[a]Several siloxane polymers found in Reactor B sample (e.g. $C_{14}H_{38}O_6Si_5$) and especially final product (e.g. $C_{16}H_{50}O_7Si_8$).
[b]USEPA 16 priority pollutants.
[c]Non-target analytes; results are estimates (see text).
[d]Compounds (Car-PAH) considered carcinogenic, especially benzo[a]pyrene.

Concentrations of naphthalene were highest but still well below current occupational exposure levels. The Occupational Safety and Health Administration (OSHA) permissible exposure limit (OSHA, 2001), NIOSH REL (NIOSH, 2005), and American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV) (ACGIH, 2009) are all 50 mg/m^3 as an 8-h TWA, but there is uncertainty about whether the standard is protective enough. Concerns about naphthalene exposure and efforts to reassess the inhalation risks have been in a state of flux (NTP, 2004; Jia and Batterman, 2010) since its potential carcinogenicity was reported (NTP, 2000). The US EPA had set a chronic reference concentration (RfC) of 3 μg m^{-3} (US EPA, website), while the Agency for Toxic Substances and Disease Registry (ATSDR) set an inhalation minimal risk level (chronic) at 3.6 μg m^{-3} (ATSDR, 2009), and the Office of Environmental Health Hazard Assessment (OEHHA, California) set an inhalation REL (chronic) at 9 μg m^{-3} (OEHHA, 2000). A revision to a 1998 EPA risk assessment (US EPA, 1998) was made that updates the inhalation cancer risk, along with noncancer and oral risks (US EPA, 2004). The update was based mainly on a National Toxicology Program (NTP) animal inhalation study that found increased risk of rare nasal tumors (NTP, 2000). Naphthalene's carcinogenic potential was increased by a factor of three and it was listed as a probable human carcinogen (US EPA, 2004); however, both the EPA (US EPA, 2004; Magee *et al.*, 2010) and IARC (IARC, 2002) considered the epidemiological evidence for determining the human carcinogenicity of naphthalene inadequate. Still, new information and risk assessment methods used in the revision lower the exposure limit substantially, to 0.01 μg m^{-3} for chronic inhalation and cancer risk of 10^{-6}; the final assessment is expected in 2012 (Jia and Batterman, 2010). Limit values for other countries have been summarized by IARC

(IARC, 2002), and a report on development of indoor air guidelines for naphthalene was issued by the World Health Organization (WHO, 2006).

CONCLUSIONS

Filter, sorbent, impactor, microscopy, and bulk samples, combined with direct-reading monitoring, provided complementary information on air contaminants generated during manufacture and processing of CNFs. Worker exposure was to a complex mixture of CNFs, fine/ultrafine iron-rich soot (Birch *et al.*, 2011), CO (Evans *et al.*, 2010), and PAHs. The presence of PAHs in unpurified CNFs is a health concern and suggestive of their presence in unpurified CNF/CNT products generally. PAHs are formed under conditions employed for synthesis of vapor-grown CNFs (and CNTs), and these materials can have high sorptive capacity for PAHs and other organic compounds (Yang and Xing, 2006).

Raw and purified products, byproducts, and other workplace emissions should be considered when assessing the exposure risks of CNFs/CNTs and other nanoscale carbons. The potential health effects may be additive or synergistic with co-exposures. Systematic studies of complex mixtures are needed to better understand how interactions between components may influence aerosol toxicity. Inhalation of CNFs/CNTs is the primary health concern and was the focus of this study, but dermal contact and ingestion are potential exposure routes that merit future investigation. Given the potential inhalation risks suggested by animal studies, efforts to reduce and control exposure to CNFs/CNTs are prudent.

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