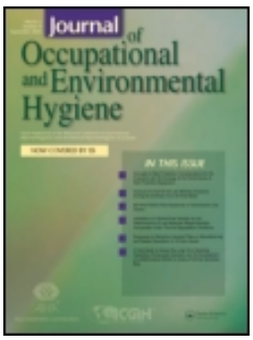

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Case Study
Identification and Characterization of Potential Sources of Worker Exposure to Carbon Nanofibers During Polymer Composite Laboratory Operations

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BACKGROUND AND INTRODUCTION

The National Institute for Occupational Safety and Health (NIOSH) received a request to conduct a health hazard evaluation (HHE) at a university-based research laboratory using carbon nanofibers (CNFs) to produce high-performance polymer composite materials. Though no health complaints had been reported, the laboratory management sought NIOSH assistance to assess potential CNF exposures. To address management and worker concerns, NIOSH investigators conducted air and surface sampling for CNFs during various material handling and processing operations within the laboratory.

There is limited published information on the potential adverse health effects of engineered nanomaterials[(1)] (human-made material possessing at least one size dimension between approximately 1 to 100 nanometers), but some materials do pose reasons for concern.[(2)] There are currently no occupational exposure limits governing workplace exposure to engineered nanomaterials. For these reasons, nanomaterials present new challenges to understanding, predicting, and managing potential health risks to workers.[(1)] In addition, uncertainties concerning exposure risk may be great because the nanomaterial characteristics may be quite different from those of larger particles with the same chemical composition. The most likely route of exposure to engineered nanomaterials is through inhalation; however, ingestion or dermal penetration may also occur.[(3–6)]

The goal of this study was to examine various operations involved in the handling or processing of CNF materials and to determine whether emission of these materials occurred. Potential sources were identified on a process-by-process basis during a walk-through survey of the laboratory. Based on initial observations, the following specific processes were identified for further evaluation:

1. Chopping of extruded composite material (proprietary formula) containing CNFs.
2. Transferring CNFs (approximately 1 lb) from a plastic receptacle outside a laboratory hood to a small beaker for weighing inside the hood.
3. Transferring and mechanically mixing CNFs with acetone inside a 5-gal mixing vessel positioned on the floor outside the hood without local exhaust ventilation.
4. Cutting composite material using a water-cooled, dust-suppressed table saw (wet saw).
5. Manually sifting oven-dried, epoxy-coated CNFs on an open benchtop to remove large clumps.

On a subsequent visit, various real-time aerosol instruments were assembled on mobile sampling carts and used to collect time-synchronized particle data during each process. Filter-based air and surface samples for laboratory analyses also were collected. The following equipment and methods were used in this investigation.

Filter-Based Samples. Filter-based air and surface samples were collected near various processes and in adjacent office locations to evaluate potential migration of carbonaceous nanomaterials within the facility. Samples were collected on quartz-fiber filters (Pallflex 2500 QAT-UP, Pallflex Inc., Putnam, Conn.) and analyzed by *NIOSH Manual of Analytical Methods (NMAM)* method 5040, based on a thermal-optical analysis technique for carbon.[7] NIOSH 5040 was evaluated for measurement of diesel particulate matter (DPM), but it has application to other carbonaceous materials. Routine application requires an even filter deposit because only a portion of the filter is analyzed (i.e., it must be representative of the entire deposit). CNFs collected in this study, and in another survey, were unevenly deposited on the filter. To address this issue, the entire filter was analyzed.

Inhalable Dust. Process-specific and worker breathing zone samples of inhalable dust (e.g., particles capable of entering the nose or mouth) were collected with the SKC Button Aerosol Sampler (SKC Inc., Eighty Four, Pa.) operated at 4 L/min. Surface samples were collected by a modified vacuum sampling method (ASTM D 7144-05a).[8] Surface particulate matter was vacuumed directly into an open-faced 25-mm, plastic filter cassette incorporating plastic bristles around its periphery and operated at 20 L/min. This configuration improved dust collection and provided a more even dust distribution on the filter.

Real-Time Instrumentation. Real-time aerosol instruments were used to monitor temporal changes in particle number, PM_{10} mass, and active surface area concentrations, and size distribution by number at various locations and processes. Instruments included: a condensation particle counter (CPC, model 3007; TSI Inc. Shoreview, Minn.); an aerosol photometer (DustTrak model 8520; TSI Inc.); a diffusion charger (model DC 2000-CE; Eco-Chem Analytics, League City, Texas), where response is a function of particle size;[9] and an electrical low pressure impactor (ELPI; Dekati, Ltd., Tampere, Finland).

Transmission Electron Microscopy (TEM) Samples. A point-to-plane electrostatic precipitator (ESP, InTox Products, Albuquerque, N.M.) was used to sample air during select processes. Particles were directly deposited onto 3 mm diameter carbon grids for subsequent analysis by transmission electron microscopy (TEM).

Ventilation Assessment. The ventilation system was evaluated using "smoke tubes" that allowed visualization of airflow patterns in and around a laboratory hood used for weighing carbon nanofibers. Visual inspection of local exhaust ventilation flow controllers (dampers) and a rooftop air handler was also conducted to determine if any deficiencies were present, such as slipping drive belts, heavy particulate loading on filter media, low airflow, and closed or blocked dampers.

RESULTS

The mass of total carbon (TC) on the singular, filter-based samples was employed as an elemental marker for the presence of CNFs (Tables I and II). Air concentrations (Table I) within the laboratory processing area were 2 to 64 times those in a nearby office area. Relative to a surface sample from the floor in the common area, TC loadings (μg TC/cm^2) on seven laboratory surfaces ranged from 3 times to 30 times (Table II). In addition, the TC loading on a floor surface (Table II, Sample 11) collected near the desk of a laboratory employee, suggested transfer of CNFs from the laboratory to a nearby office. The surface TC loading on the floor near the desk was 11 times that in a sample from a more remote office area. Results for two surfaces (Table II, Samples 7 and 8) in the processing laboratory showed little contamination. One surface

TABLE I. Total Carbon Concentrations from Inhalable Dust Samples

Sample No.	Sampling Location and Operation	TC (μg/m^3)	Multiple of Average Office TC Concentration[A]
1	Weighing out CNF[B] material	64	4
2	Mixing CNF with solvent	93	5
3	General area (on shelf near hood)	55	3
4	Lab bench: handling bulk, partially dry product	221	13
5	Wet saw: cutting CNF composite	1094	64
6	Cart with real-time instruments: different areas	33	2
7	Cart with real-time instruments: different areas	30	2
8	Office background (sampler located near printer in common area)	15	N/A
9	Office background (sampler located on piano in common area)	19	N/A

[A]Relative to average office background TC concentration of 17 μg/m^3.
[B]CNF = carbon nanofiber.

TABLE II. Total Carbon Concentrations from Surface Samples

Sample No.	Sampling Location	Surface Area Sampled (cm^2)	Surface TC Loading ($\mu g/cm^2$)	Multiple of Surface TC Loading Found in Office[A]
1	Floor in office common area outside laboratory	155	0.57	N/A
2	Near milling apparatus	77	3.68	6.5
3	Bottom shelf of metal rack near hood	100	1.40	2.6
4	Second shelf of metal rack near hood	100	1.64	2.9
5	Right laboratory bench near balances (different laboratory)	300	0.39	0.7[b]
6	Laboratory hood surface (inside) near balance after weighing out CNF[c] material.	36	1.44	2.6
7	Middle of fume hood surface (inside)	36	0.65	1.1
8	Floor just outside mixing area (beyond existing sticky mat)	155	0.76	1.3
9	Right side of sink nearest lab entry/exit door	36	17.5	30.7
10	Left side of circuit breaker box near wet saw (Note: top of box visually contaminated)	36	7.25	12.7
11	Office floor near laboratory worker's desk (dark area visible)	155	6.26	11.0

[A] TC surface loading relative to floor of office common area (Sample 1).
[B] Laboratory bench was cleaned by staff prior to survey.
[C] CNF = carbon nanofiber.

sample (Table II, Sample 5) taken from a benchtop in a different laboratory was less contaminated than the floor of the common area, but the bench had reportedly been wiped with a wet cloth prior to the survey.

A total of 11 different processes were evaluated using the CPC. Particle counts were compared with background measurements both inside the laboratory and outdoors (Figure 1). Data collected inside the nanomaterial handling and mixing room (the "Cage") were pooled and are presented as "Weighing/Mixing Nanofibers." No indoor particle concentrations exceeded the outdoor background concentrations (morning or afternoon). However, slight increases in particle concentration

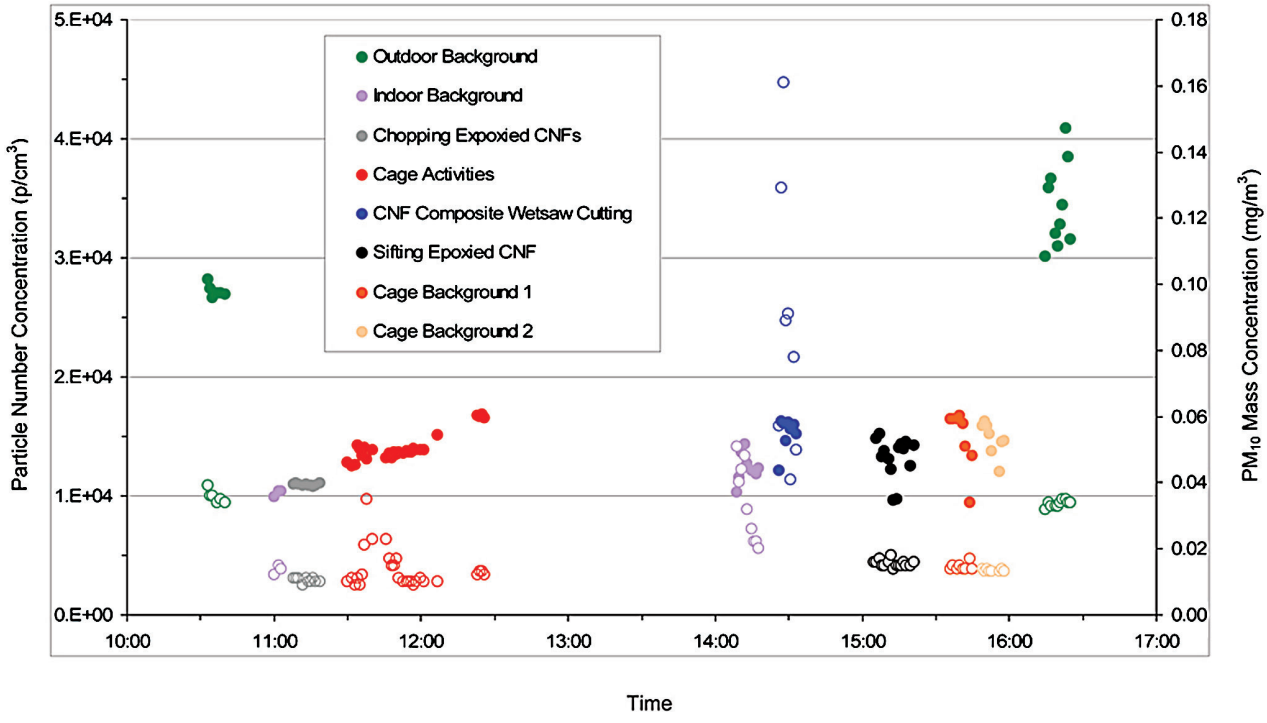

FIGURE 1. Time series of simultaneous particle number and PM_{10} mass concentrations for all processes, activities, and locations. Solid symbols denote particle number concentration (particles/cm^3) and open symbols denote PM_{10} mass concentrations (mg/m^3).

relative to laboratory background were noted for weighing and mixing of CNFs as well as for wet-saw cutting of composite material. All surface area (diffusion charger) data collected for the 11 processes showed no discernable increases above background.

Relative PM_{10} particle mass concentrations for the 11 processes evaluated and the data collected using the CPC revealed similar trends (Figure 1). When cutting composite material with the wet saw, the relative particle mass concentration was approximately three times greater than the laboratory background concentration, while small, repeated increases were observed during the weighing and mixing of carbon nanofibers.

Particle size distributions by number (obtained with the ELPI) indicated that the dominant particle sizes appeared to be in the 30 to 200 nm range. Particles observed in this size range were most likely due to the intrusion of outdoor air rather than indoor activities. Particle size modes present in the indoor background measurements appeared very similar to those outdoors but at lower concentration. Furthermore, regardless of process, indoor particle number concentrations in this size range were lower than background levels measured outdoors and similar to CPC measurements. Particles having a diameter of about 400 nm or greater were found in greater number during wet-saw cutting, while the number of particles having a diameter of about 500 nm or greater were elevated during the weighing and mixing of CNFs.

A total of nine ESP samples were collected on TEM grids for subsequent microscopic analysis to determine particle morphology and size. A few fiber bundles of varying diameters and lengths were also observed (Figure 2). Some fibers observed on the TEM grids had diameters clearly larger than the 100 nm criterion used to define a nanofiber, which is consistent with previous observations.[10] The majority of fibers appeared as loosely bundled agglomerates rather than as single fibers, an

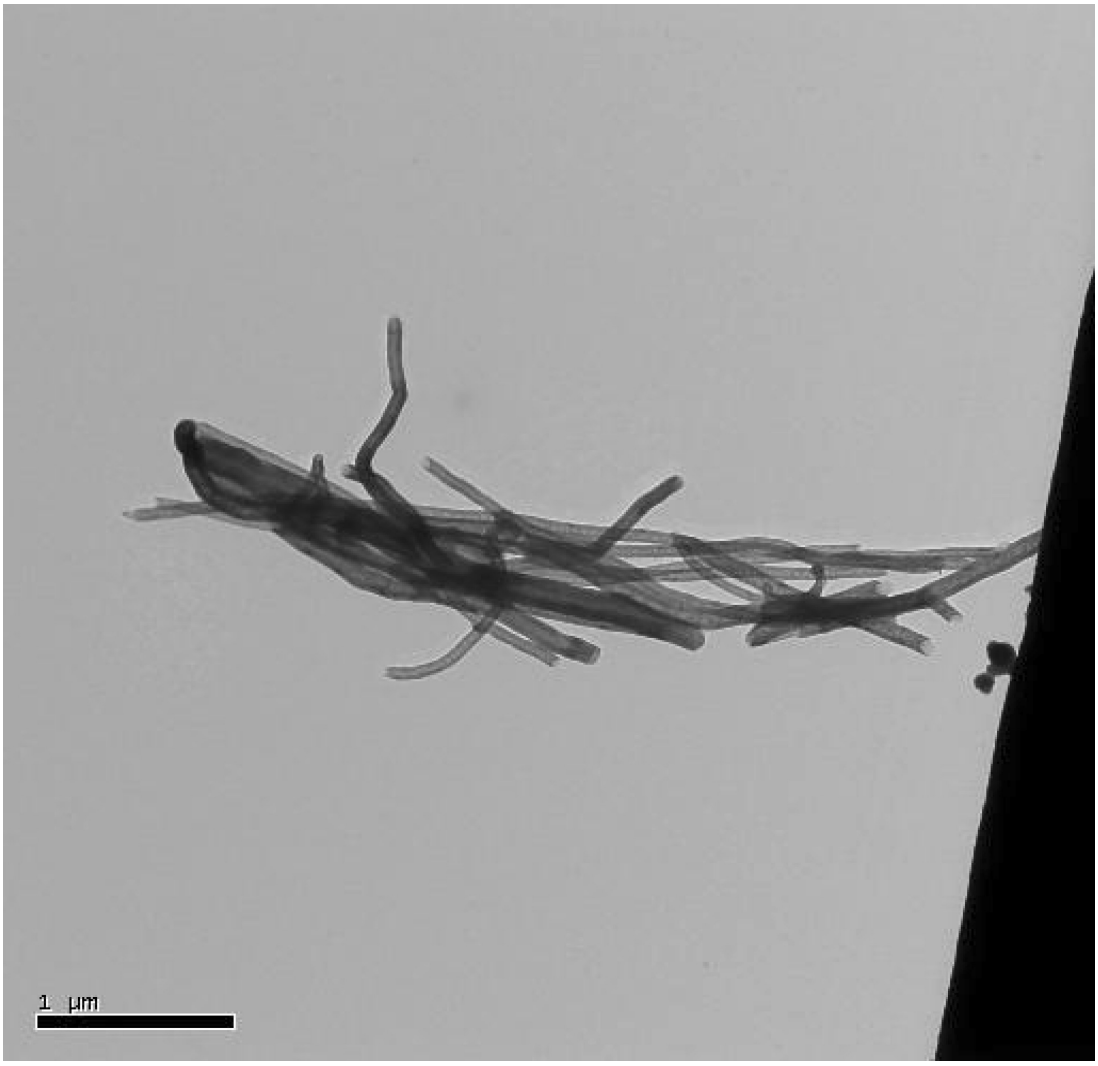

FIGURE 2. TEM micrograph of fibers collected during mixing with acetone

observation that is in general agreement with real-time aerosol instrument data.

Ventilation Assessment

The single-pass ventilation system used in the laboratory had a dedicated exhaust fan (4000 ft^3/min [113 m^3/min]) with a high-efficiency particulate air (HEPA) filter located on the roof of the two-story building. Smoke tube analysis of the airflow patterns in and in front of the laboratory hood indicated that the hood appeared to be functioning adequately and, therefore, was believed to capture fugitive emissions from handling carbon nanofibers within the hood. Of course, the hood would not have prevented exposure to any emissions from manual scooping of material prior to weighing, since that procedure was conducted outside the hood.

The wet-sawing process produced a visible plume emanating from the saw blade and had no dedicated exhaust ventilation. Increases in both particle number and mass concentrations above background were observed in the general vicinity during cutting. The TC result (Table I, Sample 5) for a filter sample collected in this area was 64 times background.

Personal Protective Equipment (PPE)

PPE routinely used by laboratory employees consisted of disposable Tyvek laboratory coats, safety glasses, latex gloves, and a 3M model 7501 elastomeric, half-mask respirator equipped with an organic vapor cartridge and a P100 filter. Workers reported that they are medically monitored and fit tested in accordance with guidelines set forth in the Occupational Safety and Health Administration respiratory protection standard.

DISCUSSION

A critical issue when characterizing source emissions and potential exposure using particle number concentration is specificity. Nanoparticles are ubiquitous in many workplaces, originating from sources such as combustion,[11] vehicle emissions,[12] and infiltration of outside air. Direct-reading instruments, as used in this evaluation, are generally insensitive to particle source or composition, making it difficult to differentiate between exogenous and process-related nanoparticles.

However, short-term elevations in concentrations above the background that coincided with a particular action, process, or task may generally be ascribed to those actions or processes. Fortunately, potential confounders such as forklifts, gas burners, and other combustion sources were not present during this survey.

Real-time monitoring identified no particular process as a substantial source of airborne CNF emissions in this laboratory. However, two processes: (1) weighing/mixing CNFs in an unventilated area within the cage, and (2) wet-saw cutting of a composite material did elevate airborne particle concentrations (number and mass) relative to background concentrations. Additionally, TC results for air and surface samples indicated that some CNF material is being released, and it appears to be migrating from the laboratory to a nearby office. Transport by footwear is a likely explanation for the office floor contamination because a dark, localized deposit was visible on the floor.

CONCLUSIONS

Because this study was designed to determine the magnitude of CNF emissions during various handling processes, it is not appropriate to make a determination regarding personal exposures. The mobile sampling carts used were, for the most part, within a few feet of any potential source of CNF emission. Therefore, all data collected provide information on general area concentrations and are not to be construed as representative breathing zone concentrations.

In addition, there are no accepted occupational exposure criteria specific to engineered nanomaterials with which to compare the findings of this survey. Despite the limitations imposed on this survey by these factors, it can be concluded that the potential for release of engineered nanomaterials does exist during various processes. First, transferring of CNFs prior to weighing and mixing with solvent resulted in a slight increase in the airborne concentration (number and mass) of particle sizes greater than approximately 500 nm (as indicated by the ELPI), suggesting some release of aggregated nanofiber material. Second, operation of the wet saw resulted in a subtle increase in the airborne number concentration of particles larger than 400 nm (as indicated by ELPI), along with a corresponding increases in both the mass concentration measured by the aerosol photometer and TC concentration.

RECOMMENDATIONS

Until further information on the possible health risks and extent of occupational exposure to nanomaterials becomes available, the following recommendations should be implemented:

1. Educate workers in the proper handling of nanomaterials (e.g., cleaning work areas with a HEPA-filtered vacuum cleaner, use wet wiping to clean up spilled material, prohibiting the consumption of food or beverages in workplaces where nanoscale materials are handled, and providing handwashing facilities and facilities for showering and changing clothes.
2. Use engineering controls such as source enclosure (i.e., isolating the generation source from the worker) and HEPA-filtered local exhaust ventilation to capture airborne nanomaterials (http://www.cdc.gov/niosh/topics/nanotech/safenano/control.html), specifically during large-scale mixing and wet sawing.
3. "Sticky mats" should be placed on the floor at each laboratory exit/entry door and changed on a regular basis.
4. Use disposable laboratory coats during all laboratory processes and remove them when exiting the laboratory. These coats can be reworn on returning, provided the coats are not heavily soiled, at which time they

should be discarded and replaced with new garments. Although no guidelines are currently available for the prevention of dermal exposure to nanomaterials, some clothing standards incorporate testing with nanometer-sized particles and therefore provide some indication of the effectiveness of protective clothing with regard to nanoparticles.

5. Latex gloves should be replaced with gloves made of nitrile rubber to reduce the possibility of a worker developing a latex allergy.

Since there are no specific exposure limits for airborne engineered nanomaterials, the decision to use respiratory protection should be based on toxicity information, exposure measurement data, and the frequency and likelihood of the worker's exposure. Preliminary evidence suggests that NIOSH-certified N95 filtering face-piece respirators will be adequate for protecting workers from nanoscale material inhalation.

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