



NIOSH HEALTH HAZARD EVALUATION REPORT

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University of Dayton Research Institute
Dayton, Ohio

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DEPARTMENT OF HEALTH AND HUMAN SERVICES
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health



PREFACE

The Hazard Evaluation and Technical Assistance Branch (HETAB) of the National Institute for Occupational Safety and Health (NIOSH) conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health (OSHA) Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employers or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

HETAB also provides, upon request, technical and consultative assistance to federal, state, and local agencies; labor; industry; and other groups or individuals to control occupational health hazards and to prevent related trauma and disease. Mention of company names or products does not constitute endorsement by NIOSH.

ACKNOWLEDGMENTS AND AVAILABILITY OF REPORT

This report was prepared by Mark M. Methner, Ph.D., CIH of HETAB, Division of Surveillance, Hazard Evaluations and Field Studies (DSHEFS). Total carbon samples and analyses were performed by M. Eileen Birch, Ph.D., Division of Applied Research and Technology (DART). Real-time aerosol measurements were performed by Douglas Evans, Ph.D. (DART) and Robert McCleery, M.S., CIH (DSHEFS). Electrostatic precipitator samples were collected by Mark D. Hoover, Ph.D., CHP, CIH, Division of Respiratory Diseases (DRDS). Ventilation assessment was performed by Keith Crouch, Ph.D. (DART). All transmission electron microscopy (TEM) was performed by Bon-Ki Ku, Ph.D. (DART). Desktop publishing was performed by Robin Smith. Editorial assistance was provided by Ellen Galloway.

Copies of this report have been sent to management representatives at University of Dayton Research Institute (UDRI) and the OSHA Regional Office. This report is not copyrighted and may be freely reproduced. The report may be viewed and printed from the following internet address: <http://www.cdc.gov/niosh/hhe>. Copies may be purchased from the National Technical Information Service (NTIS) at 5825 Port Royal Road, Springfield, Virginia 22161.

For the purpose of informing affected employees, copies of this report shall be posted by the employer in a prominent place accessible to the employees for a period of 30 calendar days.

Highlights of the NIOSH Health Hazard Evaluation

On July 8, 2005, the National Institute for Occupational Safety and Health (NIOSH) received a management request to conduct a health hazard evaluation (HHE) at the University of Dayton Research Institute (UDRI) in Dayton, Ohio. The request asked NIOSH to evaluate potential sources of emissions from carbon nanofiber handling processes. No health complaints were reported by management or workers.

What NIOSH Did

- We observed work practices.
- We took air and surface samples for carbon nanofibers.
- We measured carbon nanofibers in the air using real-time instruments.
- We evaluated the laboratory ventilation system.
- We looked at the type of personal protective equipment (PPE) used by workers.

What NIOSH Found

- Most handling processes did not release carbon nanofibers. However, some processes (wet sawing of composite material and transferring carbon nanofibers to a mixing vessel) did raise the airborne particle concentration when compared to background levels.
- Carbon nanofiber materials are tracked out of the laboratory and into office areas (probably on the soles of footwear).

What University of Dayton Research Institute (UDRI) Managers Can Do

- Use local exhaust ventilation when transferring carbon nanofibers to mixing vessel and when using the wet saw.
- Train laboratory workers on proper carbon nanofiber handling techniques.
- Evaluate the ventilation system to ensure it is operating according to manufacturer's specifications.
- Install "sticky mats" at all doors leading to/from the laboratory. Change mats when they no longer feel sticky.
- Make sure a vacuum equipped with a high efficiency particulate air (HEPA) filter is used to clean up any spilled carbon nanofibers.
- Use gloves made of nitrile rubber instead of latex.

What the University of Dayton Research Institute (UDRI) Employees Can Do

- Wear PPE provided by management when handling carbon nanofibers.
- Make sure footwear is placed on "sticky mats" before entering/exiting the laboratory.



What To Do For More Information:
We encourage you to read the full report. If you would like a copy, either ask your health and safety representative to make you a copy or call 1-513-841-4252 and ask for HETA Report #2005-0291-3025



Health Hazard Evaluation Report 2005-0291-3025
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SUMMARY

On July 8, 2005, the National Institute for Occupational Safety and Health (NIOSH) received a management request to conduct a health hazard evaluation (HHE) at the University of Dayton Research Institute (UDRI) in Dayton, Ohio. The request asked NIOSH to evaluate potential sources of emissions from carbon nanofiber handling processes. No health complaints were reported by management or workers.

Measurements made with real-time instruments capable of sizing and determining airborne particle concentrations indicate that most processes did not release substantial quantities of carbon nanofibers when compared to background particle measurements. However, some processes (wet sawing of composite material and the transferring of carbon nanofibers to a mixing vessel) did elevate area airborne particle mass concentrations. Surface sampling indicated that carbon nanofiber material migrated from the laboratory to an adjacent office area, with employee footwear being the most likely means of transport. Despite the absence of occupational exposure criteria, UDRI management decided to take a cautious approach and instituted a policy requiring the use of personal protective equipment (PPE). The PPE used by lab workers included disposable Tyvek™ lab coats, latex gloves, and elastomeric half-mask respirators with a P100 pre-filter and organic vapor cartridge. A laboratory hood and local exhaust ventilation were evaluated with “smoke tubes” and appeared to operate as designed.

NIOSH investigators cannot conclude whether a health hazard exists to UDRI laboratory workers from exposure to nano-scale materials. There are currently no occupational exposure limits for carbon nanofibers nor clearly defined health effects, so no conclusions can be made regarding excessive exposure. The UDRI lab did have exhaust ventilation available to control potential releases of carbon nanofibers, but the ventilation was not operating during mixing outside the laboratory hood or wet saw cutting. The lab workers were wearing PPE; however, latex gloves should be replaced with nitrile gloves to avoid the potential development of latex allergy.

Keywords: NAICS 541710 (Research and Development in the Physical, Engineering, and Life Sciences), nanotechnology, nanoparticles, carbon nanofibers, composites, polymers, exposure assessment, particle concentration, nanomaterial handling practices, fugitive emissions.

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INTRODUCTION

On July 8, 2005, the National Institute for Occupational Safety and Health (NIOSH) received a request from the manager of a polymer nanocomposite research laboratory at the University of Dayton Research Institute (UDRI) to conduct a health hazard evaluation (HHE) at their facility in Dayton, Ohio. Specifically, NIOSH was asked to evaluate employee exposures to nanomaterials (carbon nanofibers) during various handling operations in the Kettering Laboratory Annex.

The Center for Basic and Applied Polymer Research at UDRI is staffed by professionals with expertise in polymer engineering and science. The UDRI laboratories conduct research, development, and technical service projects on polymeric materials. Activities at the Center include research on plastics, adhesives, elastomers, composites, and engineered nanomaterials.

On September 1, 2005, NIOSH investigators met with UDRI researchers and management staff to address their concerns and to observe engineered nanomaterial handling operations. On December 8, 2005, NIOSH investigators conducted air and surface sampling for nanomaterials during various material handling operations in the laboratory.

BACKGROUND

The scientific literature has limited information on adverse health effects related to exposure to engineered nanomaterials. Additionally, there are no occupational exposure limits regarding engineered nanomaterials. Therefore, nanomaterials present new challenges to understanding, predicting, and managing potential health risks to workers.¹ In the case of nanomaterials, the uncertainties are great because the characteristics of nanomaterials may be different from those of larger particles with the same chemical composition.

A nanometer (nm) is one billionth of a meter (10^{-9} meters) — about one ten-thousandth the diameter of a human hair, a thousand times smaller than a red blood cell, or about half the size of the diameter of deoxyribonucleic acid (DNA). For the purpose of this report, nanotechnology is defined as follows: research and technology development at the atomic, molecular, or macromolecular levels using a length scale of approximately 1 to 100 nanometers in any one dimension; the creation and use of structures, devices and systems that have novel properties and functions because of their small size; and the ability to control or manipulate matter on an atomic scale. The definition of nanotechnology does not include incidentally produced nanomaterials, nano-sized particles or materials that occur naturally in the environment, such as viruses or volcanic ash, nor nanoparticle byproducts of human activity, such as diesel exhaust particulates or other combustion aerosols.

Some manufacturing processes such as spray drying and calcining may produce nano-sized particles that may or may not have properties different from those of the bulk material from which they were developed. While there are often several sources of emissions in any manufacturing process, packaging and transfer operations involving nano-scale materials may provide the greatest potential for release and resultant occupational exposure.² The risk of particle release during production appears to be low because most production processes take place in closed systems with appropriate filtering systems. Contamination and exposure to workers is more likely to happen during handling and bagging of the material and during cleaning operations.

During the formulation of nanomaterials into products (e.g., coatings and composite materials), releases and exposures may occur during transfer/unloading operations; however, once the nanomaterial is incorporated into the formulation, the nanoparticles are typically immobilized in the matrix. For some products, release and exposure to nano-scale materials after incorporation into the finished product are

expected to be low.² However, there still remains a potential for nanomaterial release upon destructive processing of the nanomaterial matrix, for example by cutting, drilling, grinding, and machining.

Exposure Routes

The most common route of exposure to airborne particles in the workplace is inhalation. The deposition of discrete nanoparticles in the respiratory tract is determined by the particle's aerodynamic or thermodynamic diameter (depending on particle size). Agglomerates of nanoparticles will likely deposit according to the diameter of the agglomerate and not the constituent nanoparticles.³

Discrete nanoparticles are deposited in the lungs to a greater extent than larger respirable particles, and deposition increases with exercise (due to increase in breathing rate and change from nasal to mouth breathing^{3,4}) and among persons with existing lung diseases or conditions.⁵ Based on the findings from animal studies, discrete nanoparticles may enter the bloodstream from the lungs and translocate to other organs.^{6,7}

Ingestion is another route whereby nanoparticles may enter the body. Ingestion can occur from unintentional hand to mouth transfer of materials in the workplace. This can occur with traditional materials, and it is reasonable to assume that it also could occur during handling of nanomaterials. Ingestion may also accompany inhalation exposure because particles cleared from the respiratory tract via the mucociliary escalator may be swallowed.⁴ Little is known about possible adverse effects from the ingestion of nanoparticles.

Some studies suggest that nanoparticles also could enter the body through the skin during occupational exposure. The United Kingdom Royal Society and Royal Academy of Engineers have reported that unpublished studies indicate nanoparticles of titanium dioxide used in sunscreens do not penetrate beyond the epidermis.⁸ However, another study indicated

that particles smaller than 1000 nm in diameter may penetrate into mechanically flexed skin samples.⁹ A more recent study reported that nanoparticles with varying physicochemical properties were able to penetrate the intact skin of pigs.¹⁰ These nanoparticles were quantum dots of different size, shape, and surface coatings and were reported to penetrate the stratum corneum barrier by passive diffusion and to localize within the epidermal and dermal layers within 8 to 24 hours. The dosing solutions were two- to fourfold dilutions of quantum dots as commercially supplied and represent occupationally relevant doses. This study suggests that the skin is a potential route of exposure for nanoparticles in the workplace.

METHODS

Measuring Carbon Nanofiber Emissions

A potential issue when quantifying exposure is that mass dose may not be an appropriate metric to characterize exposure to nanomaterials. When considering mass as an exposure dose metric, a critical question is whether it is most appropriate to measure the mass of individual particles (which are less than 100 nm in one dimension) or agglomerates. The dynamics of nanomaterial agglomeration can play a critical role in determining the pulmonary deposition of respirable nanoscale material, where larger aggregates of particles tend to deposit in the upper airways, while dispersed nanomaterials often reach the alveoli region.

Studies have indicated that toxicity increases with decreasing particle size and that particle surface area may be a better metric for measuring exposures. This is of particular concern for nanomaterials, which typically have very high surface-area-to-mass ratios. Any material's biochemical reactivity is highly dependent upon its surface chemistry. Bioreactivity may be more pronounced in nanoscale particles where, for a given number or mass of particles, the total surface area delivered is dramatically larger than for the equivalent

number or mass of microscale particles. Studies in rodents have shown that the toxicity of some nanoscale particles correlates with increased particle surface area,¹¹ whereas other particles demonstrate no increase in toxicity with decreased size.¹² There are no wearable instruments that can monitor the surface area of particles in a worker's breathing zone. While there could be a correlation between mass and surface area (i.e., mass of each particle multiplied by the specific surface area of each particle), there are typically large variations between particle mass and surface area.¹³

The importance of particle number concentration as an exposure dose metric is currently unclear from the toxicology literature. In many cases, biological response may relate more to total particle surface area than to number of particles. However, in some cases the number of particles depositing in the respiratory system or penetrating beyond the respiratory system may be important.

The main goal of this NIOSH evaluation was to examine various processes and tasks involved in the handling of carbon nanofiber materials and determine whether the magnitude of emissions could lead to occupational exposure. The initial step in this emissions characterization survey was to identify sources on a process-by-process basis during a walk-through survey of the laboratory. Based on observations made during the walk-through, the following specific processes were identified for evaluation:

1. Chopping of extruded composite material containing carbon nanofibers.
2. Transferring approximately one pound of carbon nanofibers from a plastic receptacle outside a laboratory hood to a small beaker for weighing inside the hood.
3. Transferring and mechanically mixing carbon nanofibers with acetone inside a 5-gallon mixing vessel positioned on the floor outside the hood with no operating local exhaust ventilation.
4. Cutting composite material using a water-cooled table saw.

5. Sifting oven-dried, epoxy-coated carbon nanofibers on an open bench-top to remove impurities.

On a subsequent visit, various instruments assembled on mobile sampling carts were used to collect time-synchronized particle data (i.e., number of particles, size distribution, particle surface area, particle mass concentration) during each process. Air and surface samples for laboratory analyses also were collected. Equipment and methods used are described in the following sections.

Direct Reading Instrumentation

The following real-time instruments were used to measure particle number concentration, particle active surface area, particle mass concentration, and particle size distribution by number during various tasks:

- Condensation Particle Counter (CPC, Model 3007; TSI Inc. Shoreview, Minnesota): Measures total number of particles/cubic centimeter (cc) of air (10 nm–1000 nm range).
- Diffusion Charger (Model DC 2000-CE; Eco-Chem Analytics, League City, Texas): Measures total active particle surface area.
- Aerosol Photometer (DustTrak® Model 8520; TSI Inc., Shoreview, Minnesota): Measures total particle mass from 300 nm to 2500 nm diameter.
- Electrical Low Pressure Impactor (ELPI, Dekati, Ltd., Tampere, Finland): Measures number of particles/stage from 7 nm to 10,000 nm in 12 size stages.

Total Carbon

In addition to the real-time measurements described above, air and surface samples were collected at various laboratory and office locations to evaluate the potential migration of carbonaceous nanomaterials (powders/fibers) within the facility. Surface samples were

collected with a vacuum sampling method. Both air and surface samples were collected on high-purity, quartz-fiber filters (Pallflex 2500 QAT-UP, Pallflex Inc., Putnam, Connecticut) and analyzed by NIOSH Manual of Analytical Methods (NMAM) Method 5040, which is based on a thermal-optical analysis technique for carbon.¹⁴ The thermal-optical data analysis program calculates analytical results as micrograms carbon per square centimeter ($\mu\text{g}/\text{cm}^2$) of filter deposit. The total carbon (TC) on a filter is then determined by multiplying the result by the sample deposit area. To calculate the TC loading on a surface ($\mu\text{g TC}/\text{cm}^2$ surface), the TC on the filter was divided by the surface area sampled. TC air concentrations ($\mu\text{g}/\text{m}^3$) were calculated as follows:

$$TC (\mu\text{g}/\text{m}^3) = (PD/ft)1000$$

Where,

P = result for portion analyzed, ($\mu\text{g TC}/\text{cm}^2$)

D = total deposit area, square centimeters (cm^2)

f = flow rate, liters/minute (L/min)

t = time, minutes

Inhalable Dust

Area and breathing zone samples of inhalable dust were collected with the SKC Button™ Aerosol Sampler (SKC Inc., Eighty-Four, Pennsylvania) operated at 4 L/min. This sampler has a porous curved-surface inlet designed to improve the collection characteristics of inhalable dust, which is defined as particles that are hazardous when deposited anywhere in the respiratory tract¹⁵ ($< 100 \mu\text{m}$, or 100,000 nm aerodynamic diameter). Surface samples were collected by a vacuum sampling method. Surface particulate was vacuumed directly into a 25 millimeter (mm) plastic filter cassette operated at 20 L/min. This modified method is similar to the method published by the American Society for Testing and Materials (ASTM D 7144-05a),¹⁶ but an open-face sampling configuration and higher flow rate were used. A plastic ring with bristles around its periphery was attached to the spacer ring of the open-face cassette (ASTM D 7144-05a specifies a short

length of Tygon® tubing attached to the inlet hole of a cassette top). The attachment and open-face configuration were used to improve dust collection and provide a more even dust distribution on the filter. An even distribution is required because only a portion of the filter is normally analyzed (*note: if the deposit is not homogeneous, the entire filter must be analyzed*).

Filter/Transmission Electron Microscopy Grid Samples

A point-to-plane electrostatic precipitator (InTox Products, Albuquerque, New Mexico) was used to sample air during some processes. Air was drawn at 0.1 L/min across a 3-mm diameter carbon-lacey grid while a 5 kilovolt potential was applied between the grid and the tip of the electrostatic needle. Particles in the air stream were negatively charged in the corona between the needle and the grid and then electrostatically captured on the grid for later transmission electron microscopy (TEM) examination for particle size and shape.

Ventilation Assessment

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

EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for the assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime

without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects even though their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: (1) NIOSH Recommended Exposure Limits (RELs),¹⁷ (2) the American Conference of Governmental Industrial Hygienists' (ACGIH®) Threshold Limit Values (TLVs®), and (3) the U.S. Department of Labor, Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs).¹⁸ Employers are encouraged to follow the OSHA limits, the NIOSH RELs, the ACGIH TLVs, or whichever are the more protective criteria.

OSHA requires an employer to furnish employees a place of employment that is free from recognized hazards that are causing or are likely to cause death or serious physical harm [Occupational Safety and Health Act of 1970, Public Law 91-596, sec. 5(a)(1)]. Thus, employers should understand that not all hazardous chemicals have specific OSHA exposure limits such as PELs and short-term exposure limits (STELs). An employer is still required by OSHA to protect their employees from hazards, even in the absence of a specific OSHA PEL.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8- to 10-hour workday. Some substances have recommended STEL or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from higher exposures over the short term.

Nanotechnology is an emerging field. As such, there are many uncertainties as to whether the unique properties that underpin the commercial potential of nanomaterials also pose occupational health risks. These uncertainties arise because of gaps in knowledge about the factors that are essential for predicting health risks — factors such as routes of exposure, translocation of materials once they enter the body, and interaction of the materials with the body's biological systems. The potential health risk following exposure to a substance is generally associated with the magnitude and duration of the exposure, the persistence of the material in the body, the inherent toxicity of the material, and the susceptibility or health status of the person. More data are needed on the health risks associated with exposure to engineered nanomaterials. Results of existing studies in animals or humans on exposure and response to ultrafine or other respirable particles provide a basis for preliminary estimates of the possible adverse health effects, but data are lacking for engineered materials with nano-scale dimensions. A few reviews of nano-scale particle toxicological studies have recently appeared in the scientific literature.^{13,19,20}

Experimental studies in rodents and cell cultures have shown that the toxicity of nanoparticles is greater than that of the same mass of larger diameter particles of similar chemical composition.^{11,21,22,23,24,25,26} In addition to particle surface area, other characteristics may influence particle toxicity, including solubility, shape, and surface chemistry.^{27,28} Currently there are no occupational exposure limits for carbon nanofiber materials.

RESULTS

Photographic documentation of the various processes, personal protective equipment (PPE) used, and the position of the mobile sampling carts during the exposure monitoring appear in Figure 1.

Direct Reading Instrumentation

Condensation Particle Counter

A total of 11 different processes were evaluated using the CPC, and particle count data were compared to background concentrations inside the laboratory and outdoors (Figure 2). Some of the data collected inside the nanomaterial handling and mixing room (referred to as the “Cage”) were pooled and presented as “Weighing/Mixing Nanofibers.” None of the data collected exceeded the outdoor background concentrations (morning or afternoon). However, a slight increase in particle concentration relative to laboratory background was noted for weighing and mixing of carbon nanofibers as well as wet saw cutting of composite material.

Diffusion Charger

All data collected for the 11 processes using the diffusion charger showed no increases above background.

Aerosol Photometer (DustTrak®)

Particle mass concentrations for the 11 processes evaluated exhibited the same general pattern as the data collected using the CPC (Figure 3). Once again, data collected for the various processes occurring inside the Cage were pooled and graphically represented as Weighing/Mixing Nanofibers. The major finding when using the wet saw was that particle mass concentration increased approximately three times above the laboratory background level. Small repeated elevations were additionally observed during the weighing and mixing of carbon nanofibers.

Electrical Low Pressure Impactor

The particle number concentrations for each impactor size range, according to each process evaluated with the ELPI, are presented in Figure 4. The dominant particle sizes appear to be in the 30 nm to 200 nm range. Particles in this size range were most likely due to the intrusion of outdoor air, as modes present in the indoor background particle number size distributions appeared very similar to those outdoors, but at a lower concentration. Furthermore, regardless of process, the number concentration of particles indoors in this size range was lower than the background levels measured outdoors. Above the 400 nm particle diameter, particle number concentration increased for wet saw cutting and above 500 nm for measurements made above the vessel during mixing.

Total Carbon

TC results for air and surface samples are reported in Tables 1 and 2. Air concentrations (Table 1) within the laboratory processing area were 2 to 64 times higher than those in a nearby office area outside the laboratory, where the average TC concentration was measured at approximately $17 \mu\text{g}/\text{m}^3$. Relative to a surface sample from the floor in the common area, TC loadings ($\mu\text{g TC}/\text{cm}^2$) on seven laboratory surfaces were about 3 to 30 times higher. In addition, the TC loading on a floor surface (Table 2, sample 11) collected near the desk of a laboratory employee just outside the laboratory entry/exit door suggests tracking of nanomaterial from laboratory to office. The surface TC loading on the floor near the desk was 11 times higher than the sample from the more distant office area. The employee’s office was located just outside of the laboratory doors, while the common office area was further down the corridor. Results for two surfaces (Table 2, samples 7 and 8) in the processing laboratory showed little contamination, and they appeared to be clean based on visual inspection. One surface sample (Table 2, sample 5) taken from a benchtop in a different laboratory was less contaminated than the floor of the common area,

but the bench had been wiped with a wet cloth prior to the survey.

Filter/Transmission Electron Microscopy Grid Samples

A total of nine ESP samples were collected on TEM grids for subsequent microscopic analysis to determine particle morphology (shape) and size. A few samples exhibited fiber bundles of varying diameters and lengths (Figures 5 and 6).

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.²⁹ The majority of fibers appeared as loosely bundled agglomerates, rather than as single fibers, and this observation is in general agreement with the real-time aerosol instrument data collected.

Ventilation Assessment

The single-pass ventilation system used in the Cage, and for adjacent processing sites (drying, extrusion, and strength testing) has a dedicated exhaust fan with a high efficiency particulate air (HEPA) filter located on the roof of the two-story building. The lab is located in the basement of the building. The fan is rated at 4000 cubic feet per minute (CFM) at 5 inches water gauge (WG) pressure drop.

The ventilation system serves a lab hood (2' x 7' 3" opening) in the Cage area where small test batches of nanofibers are blended with a rotary mixer, first with acetone for approximately 30 minutes, then with an epoxy resin. The worker weighs out one pound (lb) of the dry nanofibers from a large bag outside the hood into a plastic container resting on a platform balance inside the hood. The container is then emptied slowly into a small container of acetone located in the hood, while a motorized stirrer stirs the mixture. After about 30 minutes, the epoxy resin (liquid) is added to the acetone/nanofiber mixture while mixing continues. The worker's breathing zone is close to any potential emissions of nanofibers, acetone, or epoxy resin during the transfer,

pouring, and mixing operations. After mixing, the mixture is carried through the building hallway to a lab where hardener is added before being poured into molds (not observed during this visit). Results of the smoke tube analysis indicated that the existing air flow patterns in and in front of the laboratory hood appeared to capture fugitive emissions from handling carbon nanofibers inside the hood.

Larger scale test batches (2 lbs) are also weighed out in the hood, but a larger mixer is used to prepare the batch on the floor approximately 8 feet from the front of the hood opening. The local exhaust hood for this mixing process captures emissions before they enter the workroom environment. However, the blast gate that controls the airflow through the flexible overhead duct was closed. A hand-held vacuum cleaner containing a HEPA filter was used by NIOSH researchers during a brief trial to temporarily provide local exhaust for this process. Measurements made with the ELPI indicated that using the vacuum near the opening of the mixing container appeared to control fugitive emissions. This finding is supported by the fact that no increase in particle concentrations, compared to background levels, was observed. Additionally, no increase in particle concentrations was observed with the other real-time instruments when the vacuum was in operation.

The wet sawing process had no exhaust ventilation and was located in a part of the lab not controlled by the single-pass ventilation system. The water-cooled circular saw was used to cut the hardened nanomaterial product into small squares which were then sent to other laboratories for analysis. Cutting of this hardened product, containing nanofibers and epoxy resin, generated an aerosol plume that spun off the saw blade and impinged onto a vertically suspended plastic sheet several feet behind the saw. This process resulted in an increase in particulate matter as observed with real-time particle measurements, filter samples (TC), and TEM samples.

Personal Protective Equipment

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. All employees designated to wear respirators are medically monitored and fit-tested in accordance with guidelines set forth in the OSHA respiratory protection standard.

DISCUSSION

In general, direct reading instrumentation used in this evaluation is unable to distinguish between incidental background particles (i.e., those from outdoors) and airborne engineered nanomaterials generated by the processes described in this report. An exception may be situations where a process generates a sufficiently high concentration of particles resulting in a rapid increase in particle concentrations measured by the direct-reading instruments. In addition, if filter measurements or TEM analysis indicate a specific release of nanomaterial, one may be confident that any real-time instrument response observed at that same time was due to an actual nanomaterial release.

After analyzing the direct-reading instrument data collected during this survey, it appears that no particular process was identified as a substantial source of airborne carbon nanofiber emissions. However, two processes (mixing in a vessel on the floor and wet saw cutting) did elevate airborne particle concentrations relative to background levels. Additionally, TC results for air and surface samples indicated that some carbon nanofiber material is being released by the processes monitored and appears to be migrating outside of the laboratory area and into an office near the laboratory exit door. It is unknown whether the carbon nanofibers are being transported via air currents or carried on footwear and/or clothing. However, transport by footwear is a likely explanation for the office

floor contamination because a dark, localized deposit was visible on the floor.

A critical issue when characterizing exposure using particle number concentration is selectivity. Nanoparticles are ubiquitous in many workplaces from sources such as combustion, vehicle emissions, and infiltration of outside air. Particle counters are generally insensitive to particle source or composition, making it difficult to differentiate between incidental and process-related nanoparticles using number concentration alone. In a study of aerosol exposures while bagging carbon black, a researcher found that peaks in number concentration measurements were associated with emissions from fork lift trucks and gas burners in the vicinity, rather than the process under investigation.³⁰ Furthermore, in an engine machining facility, direct gas-fired heating systems dominated the nanoparticle number concentrations observed in the workplace compared to process-related emissions.³¹ Although this issue is not unique to particle number concentration measurements, orders of magnitude difference can exist in aerosol number concentrations, depending on concomitant sources of particle emissions. Fortunately, potential confounders such as gas burners and combustion sources were not present during this survey.

CONCLUSIONS

Because this evaluation was designed to determine the magnitude of carbon nanofiber fugitive emissions during various handling processes, it is not appropriate to make a determination regarding personal exposures. By using the mobile sampling carts, NIOSH investigators were for the most part within a few feet of any potential source of emission. Therefore, all data collected with the instruments on the carts provides information pertaining to general area concentrations and are not to be construed as representative breathing zone concentrations. Additionally, there are no accepted occupational exposure criteria specific to nano-scale materials 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 nano-scale materials does exist during various processes. First, transferring carbon nanofibers to the mixing vessel on the floor did result in a slight increase in the airborne concentration (both by number and mass) of particle sizes greater than approximately 500 nm (as indicated by the ELPI), suggesting some release of aggregated nanofiber material. Second, utilization of the wet saw resulted in a subtle increase in the airborne number concentration of particles larger than 400 nm, along with a corresponding increase in the mass concentration indicated with the aerosol photometer. Local exhaust ventilation, achieved via flexible connections to a main exhaust duct that is HEPA-filtered, is available at some locations in the laboratory. The system is equipped with manually-operated blast gates and is reportedly used whenever carbon nanofiber handling occurs outside a laboratory hood (except during large batch mixing and wet sawing).

RECOMMENDATIONS

Until further information on the possible health risks and extent of occupational exposure to nanomaterials becomes available, interim precautionary measures should be developed and implemented. The following recommendations focus on the implementation of a risk management program and the development of safe working practices tailored to the specific processes and materials where workers might be exposed.

1. Educate workers in the proper handling of nanomaterials (e.g., good work practices).
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, specifically during large-scale mixing and wet sawing. Establish written procedures for installing and evaluating these controls at locations where exposure to nanoparticles might occur.

3. Use good work practices to minimize worker exposures to nanomaterials. Examples include cleaning of work areas using a HEPA-filtered vacuum cleaner and wet wiping; prohibiting the consumption of food or beverages in workplaces where nano-scale materials are handled; and providing hand-washing facilities and facilities for showering and changing clothes.

4. "Sticky mats" should be placed on the floor at each laboratory exit/entry door and changed on a regular basis (i.e., when adhesive no longer feels sticky to one's footwear).

5. Develop written procedures for the selection of personal protective equipment (e.g., clothing, respirators, gloves).

6. Use disposable laboratory coats during all laboratory processes and remove them when exiting the laboratory. These coats can be reworn upon returning, provided the coats are not heavily soiled, at which time they should be discarded and replaced with a new garment. 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. Latex gloves should be replaced with gloves made of nitrile rubber.

7. Currently, there are no specific exposure limits for airborne exposures to engineered nano-scale materials, although occupational exposure limits do exist for larger particles of similar chemical composition as well as for many of the solvents and epoxies used in these processes. Therefore, the decision to use respiratory protection should be based on professional judgment that takes into account 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 nano-scale material inhalation.

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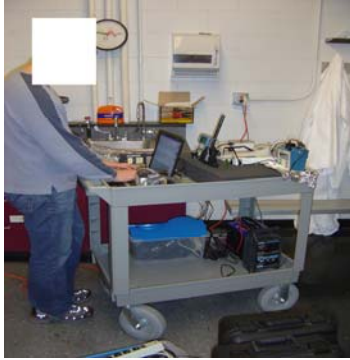
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Figure 1: Process Photographs

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a. Mobile Sampling Cart



b. "Cage" Area



c. Laboratory Hood Used in Weighing Carbon Nanofibers



d. Weighing Carbon Nanofibers



Figure 1: Process Photographs (cont'd)

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e. Mixing Apparatus



f. PPE Currently Used



g. Extruded Nanofiber Composite



h. Chopping Extruded Nanofiber Composite



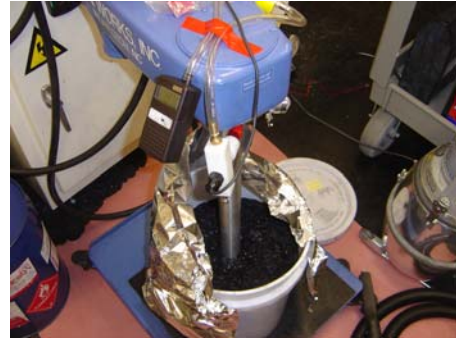
Figure 1: Process Photographs (cont'd)

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i. Transferring Carbon Nanofibers to Mixing Vessel



j. Mixing Apparatus



k. Mobile Sampling Carts Adjacent to Wet Saw



l. Wet Saw in Use



m. Benchtop Sifting of Oven Dried, Epoxied Carbon Nanofibers



Figure 2: Particle number concentrations based on Condensation Particle Counter (CPC) data
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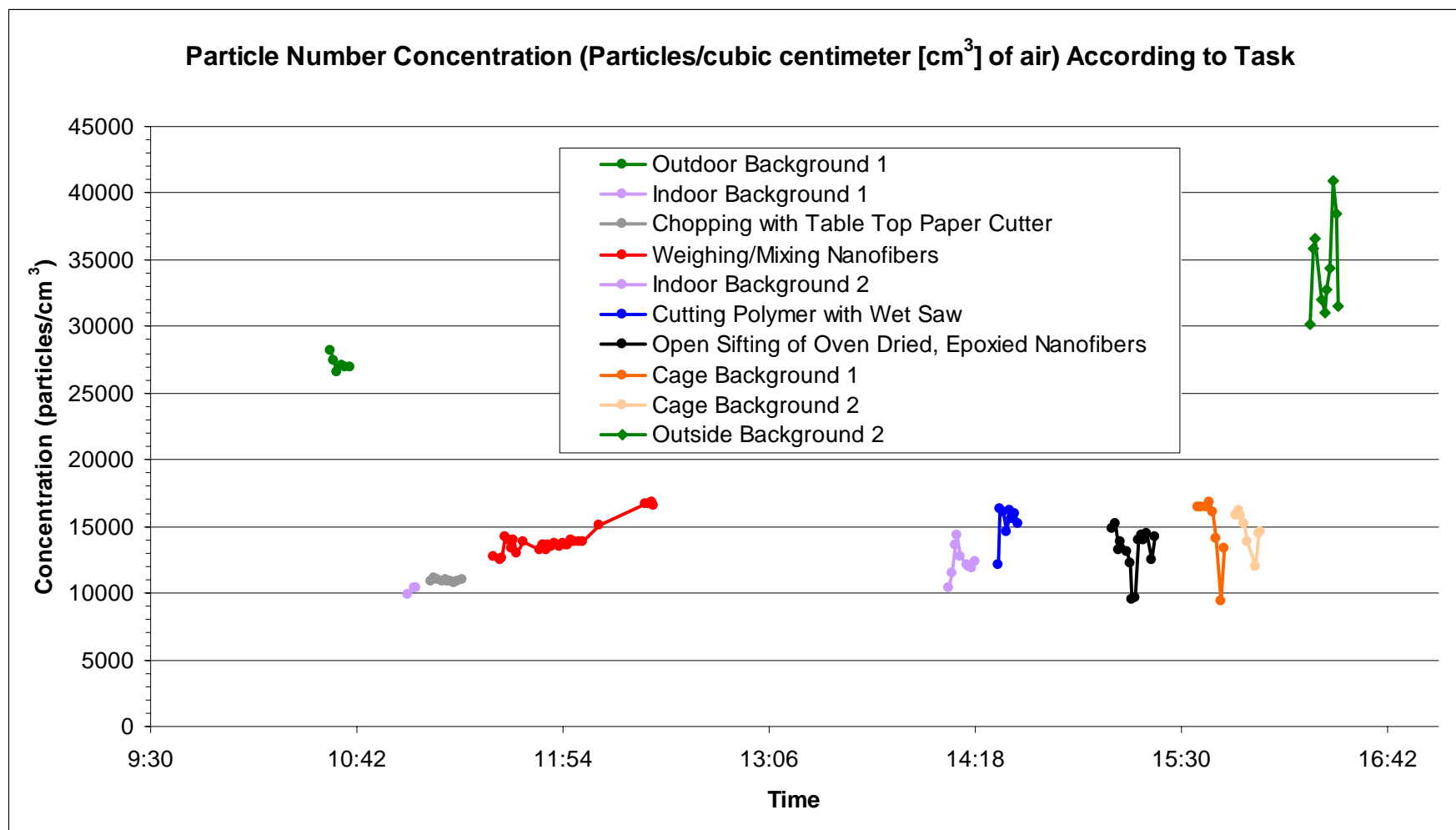


Figure 3: Particle mass concentrations based on aerosol photometer data
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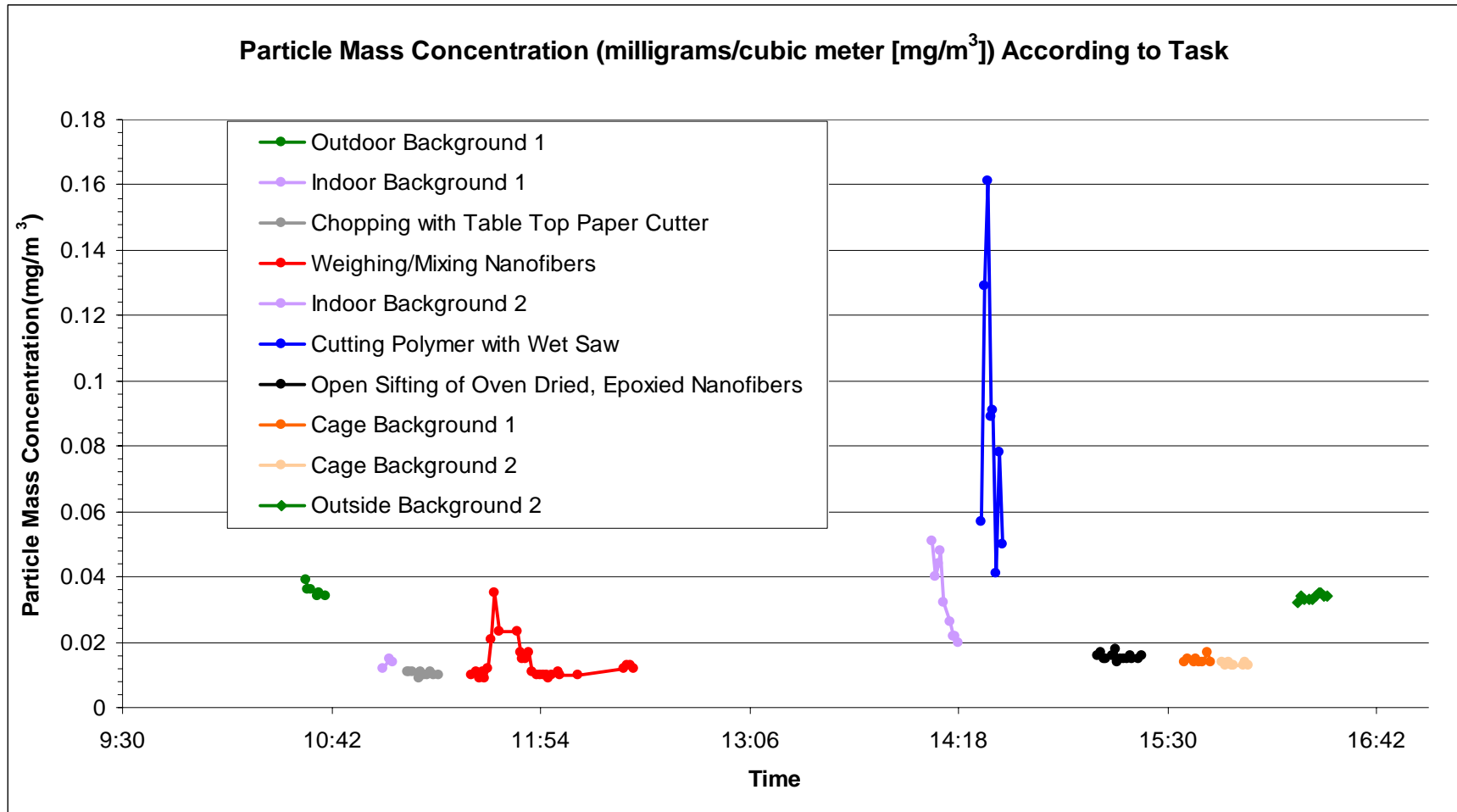


Figure 4: Particle size distributions based on electrical low pressure impactor data
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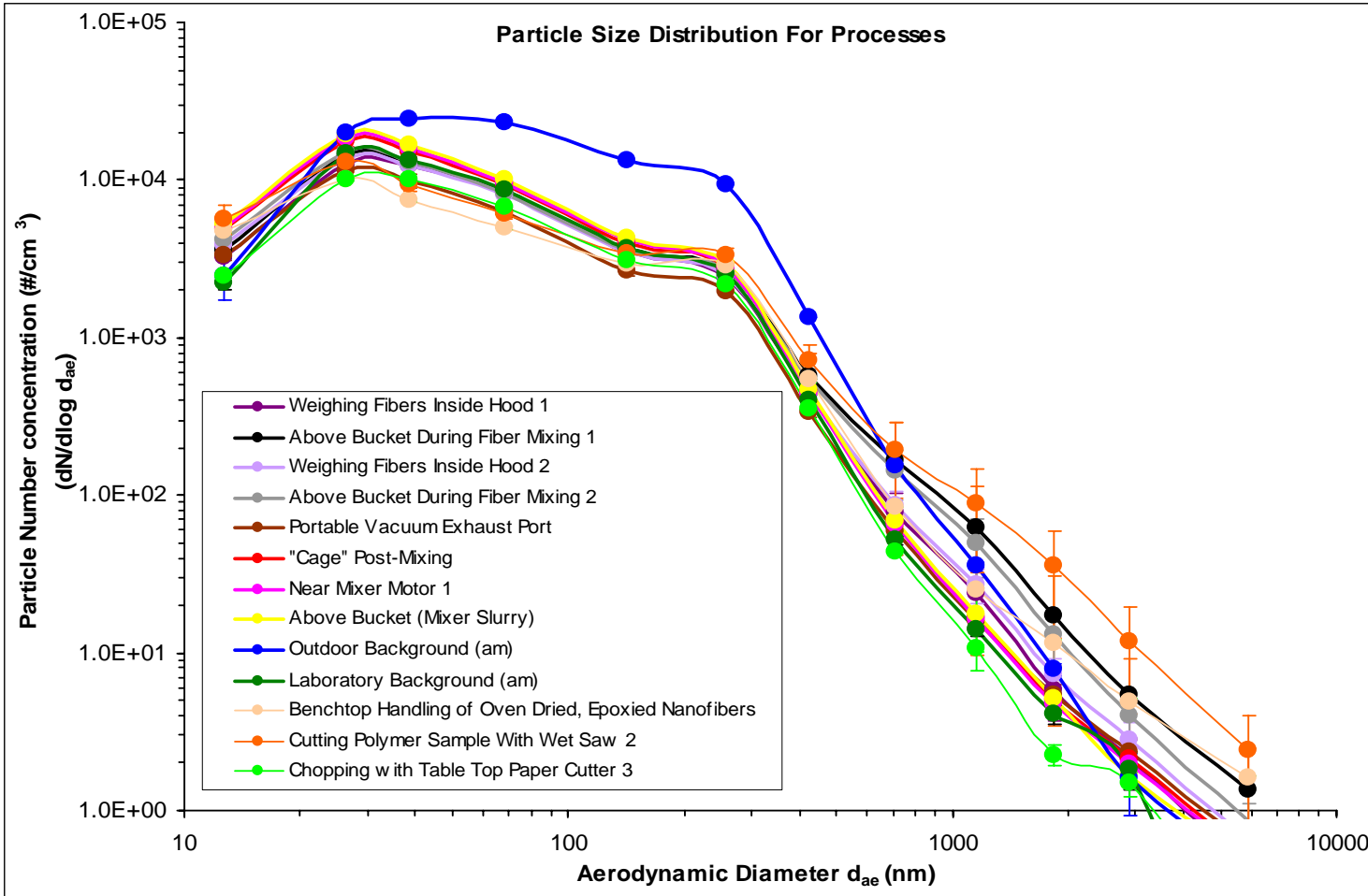


Figure 5: Fibers collected during mixing with acetone

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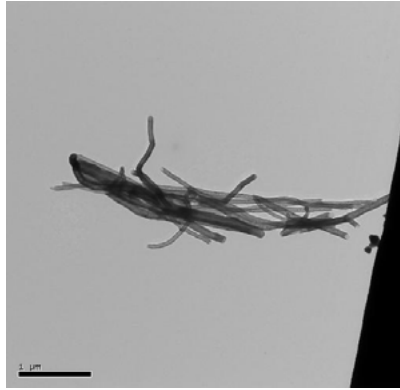


Figure 6: Collected during wet saw cutting of nano-composite material

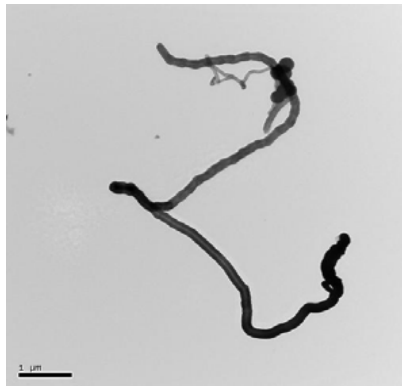


Table 1. Total carbon concentrations from inhalable dust samples

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| Sample No. | Sampling location and operation [†] | TC ($\mu\text{g}/\text{m}^3$) ^a | Multiple of average office (background) TC concentration ^b |
|------------|---|--|---|
| 1 | Cage: weighing out CNF ^c material | 64 | 4 |
| 2 | Cage: mixing CNF with solvent | 93 | 5 |
| 3 | Cage: 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 $\mu\text{g}/\text{m}^3$ = micrograms per cubic meter

^b Increase relative to average background TC concentration of $17 \mu\text{g}/\text{m}^3$

^c CNF = carbon nanofiber

[†] Samples collected for the duration of a task in the breathing zone of the worker

Table 2. Total carbon concentrations from surface samples

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| Sample No. | Sampling location | Surface area sampled (cm ²) | Surface TC loading (µg/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 | Cage: near mill | 77 | 3.68 | 6.5 |
| 3 | Cage: bottom shelf of metal rack near hood | 100 | 1.40 | 2.6 |
| 4 | Cage: second shelf from top | 100 | 1.64 | 2.9 |
| 5 | Right laboratory bench near balances (different laboratory) | 300 | 0.39 | 0.7 ^b |
| 6 | Cage: fume hood base near balance. Surface sample taken after weighing out CNF ^c material. | 36 | 1.44 | 2.6 |
| 7 | Cage: middle of fume hood base | 36 | 0.65 | 1.1 |
| 8 | Floor just outside cage door (beyond sticky mat) | 155 | 0.76 | 1.3 |
| 9 | Right side of sink nearest lab entry door | 36 | 17.5 | 30.7 |
| 10 | Left side of circuit breaker box near wet saw (note: top of box very contaminated) | 36 | 7.25 | 12.7 |
| 11 | Office floor near laboratory worker's desk (dark area visible) | 155 | 6.26 | 11.0 |

^aFactor increase in TC surface loading relative to floor of office common area (sample 1)

^bLaboratory bench was cleaned by UDRI staff prior to survey.

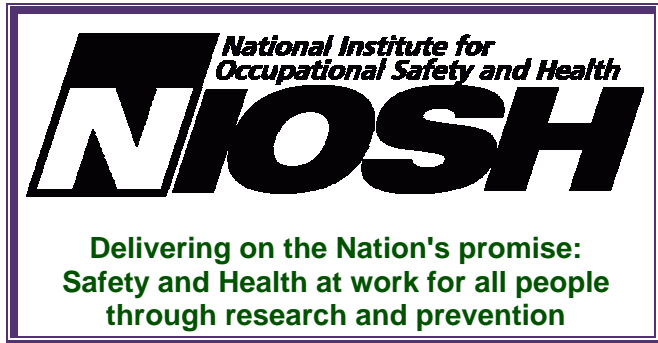
^cCNF = carbon nanofiber

cm² = square centimeter

µg/cm² = micrograms per square centimeter

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