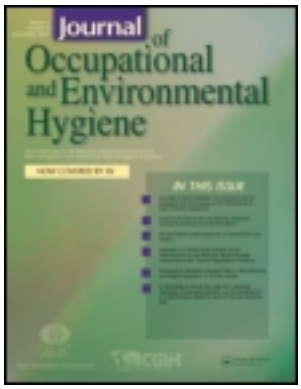

Journal of Occupational and Environmental Hygiene
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/uoeh20

Field Application of the Nanoparticle Emission Assessment Technique (NEAT): Task-Based Air Monitoring During the Processing of Engineered Nanomaterials (ENM) at Four Facilities

M. Methner [a], C. Beaucham [a], C. Crawford [a], L. Hodson [a] & C. Geraci [a]
[a] National Institute for Occupational Safety and Health, Cincinnati, Ohio

Accepted author version posted online: 05 Jun 2012. Version of record first published: 20 Jul 2012

To cite this article: M. Methner, C. Beaucham, C. Crawford, L. Hodson & C. Geraci (2012): Field Application of the Nanoparticle Emission Assessment Technique (NEAT): Task-Based Air Monitoring During the Processing of Engineered Nanomaterials (ENM) at Four Facilities, Journal of Occupational and Environmental Hygiene, 9:9, 543-555

To link to this article: http://dx.doi.org/10.1080/15459624.2012.699388

Journal of Occupational and Environmental Hygiene, 9: 543–555
ISSN: 1545-9624 print / 1545-9632 online
DOI: 10.1080/15459624.2012.699388

Field Application of the Nanoparticle Emission Assessment Technique (NEAT): Task-Based Air Monitoring During the Processing of Engineered Nanomaterials (ENM) at Four Facilities

M. Methner, C. Beaucham, C. Crawford, L. Hodson, and C. Geraci

National Institute for Occupational Safety and Health, Cincinnati, Ohio

In early 2006, the National Institute for Occupational Safety and Health created a field research team whose mission is to visit a variety of facilities engaged in the production, handling, or use of engineered nanomaterials (ENMs) and to conduct initial emission and exposure assessments to identify candidate sites for further study. To conduct the assessments, the team developed the Nanoparticle Emission Assessment Technique (NEAT), which has been used at numerous facilities to sample multiple engineered nanomaterials. Data collected at four facilities, which volunteered to serve as test sites, indicate that specific tasks can release ENMs to the workplace atmosphere and that traditional controls such as ventilation can be used to limit exposure. Metrics such as particle number concentration (adjusted for background), airborne mass concentration, and qualitative transmission electron microscopy were used to determine the presence, nature, and magnitude of emissions and whether engineered nanomaterials migrated to the workers' breathing zone.

[Supplementary materials are available for this article. Go to the publisher's online edition of Journal of Occupational and Environmental Hygiene *for the following free supplemental resource: a PDF file containing information on facilities, a description of processes/tasks, existing controls, and sampling strategy, and a PDF file containing TEM images according to facility and task.]*

Keywords airborne mass concentration, emissions, exposure, nanoparticles, particle number concentration, qualitative transmission electron microscopy

Correspondence to: Mark Methner, National Institute for Occupational Safety and Health, 4676 Columbia Parkway (R-11), Cincinnati, OH 45226; e-mail: MMethner@cdc.gov.

INTRODUCTION

Nanotechnology has the potential to revolutionize industries such as medicine, manufacturing, and pollution control because of unique properties exhibited by nanomaterials. However, the manipulation of matter at nanometer (nm) scales (1–100 nm, approximately) to produce new materials, structures, and devices may pose unique safety and health risks to those working with them. A recent review of the literature regarding risk assessment points to a common theme, namely, the need to collect more exposure data so that better risk assessments can be performed.[1–4]

Trout and Schulte[5] noted that the toxicity of the nanomaterial is likely to vary according to substance-specific toxicity, as well as size, shape, surface area, solubility, surface reactivity, charge, attached functional groups, crystalline structure, the agglomeration status of the particles, and their contaminants. Inhalation appears to be the primary route of exposure to airborne nanoparticles. However, other routes of exposure such as dermal uptake and gastrointestinal absorption should also be considered for further investigation. A thorough review of nanotoxicology has been published[6,7] but will not be discussed here.

To evaluate potential exposure in the workplace, the presence of engineered nanomaterials (ENMs) must be detected and characterized. Ultimately, a complete exposure assessment would require that they be quantified via a metric that is linked to an adverse health end point. The lack of specific, validated sampling and analytical methods necessary to measure exposure to ENMs has been identified as a critical research gap within the overall exposure/risk management paradigm related to these materials. Furthermore, existing instrumentation used to measure and characterize aerosols are not specific to ENMs, thereby indicating another critical knowledge and research gap. The absence of consistent protocols and methods makes attempts to reproduce or compare exposure assessments difficult. Additional difficulties arise from the differences in techniques used in exposure studies with those used in toxicology studies.

As a part of its nanotechnology research agenda, the National Institute for Occupational Safety and Health (NIOSH) created the nanotechnology field research team to assess

workplace processes, materials, and control technologies used in nanotechnology facilities and to conduct on-site assessments of potential occupational exposures to a variety of nanomaterials.[8] Such assessments have occurred in a variety of settings, including research and development laboratories, pilot plants, and full-scale manufacturing facilities.

The field research team developed the Nanoparticle Emission Assessment Technique (NEAT) to quantitatively identify sources of process emissions and evaluate the potential for worker exposure.[1] The NEAT employs a combination of field-portable, direct-reading hand-held instruments such as a condensation particle counter (CPC) and optical particle counter (OPC) to detect releases of airborne nanomaterials, on a task-by-task basis, coupled with filter-based air sampling and subsequent chemical and microscopic analyses for particle identification and elemental analysis.[2] As the technique evolved, it became clear that the NEAT is capable of determining whether an emission occurred as well as estimating the magnitude of an emission and whether the material reached the breathing zone of the worker. If a release of ENM was detected, each facility was provided with guidance on procedures or equipment that could control such releases.[9,10]

MATERIALS AND METHODS

Direct-Reading Instruments

Microscopy images and information pertaining to each facility, material, task descriptions, and existing engineering controls appear in two online supplementary files. Two direct-reading instruments were used in a side-by-side configuration during the assessments. The first was a hand-held CPC (Model 3007; TSI Inc., Shoreview, Minn.), which measures particles in the size range of 10–1000 nm. Data is expressed as total number of particles per cubic centimeter (1-cm^{-3}) of sampled air, with an upper limit of approximately 100,000 1-cm^{-3}. The value of this instrument for evaluating nanoparticle emissions is its ability to operate in continuous mode and provide a near instantaneous estimation of particle number concentration in the nanoscale range (10–100 nm), as well as larger particles up to 1000 nm. To estimate maximum emission magnitude on a task-by-task basis, only peak number concentration data was recorded manually on a field data sheet.

The second instrument, the Hand Held Particle Counter (HHPC-6 OPC; ART Instruments, Grants Pass, Ore.), is an optical particle counting (OPC) device that measures the total number of particles per liter (1-L^{-1}) of air within six specific size channels: 300–500 nm, 500–1000 nm, 1000–3000 nm, 3000–5000 nm, and 5000–10,000 nm with an upper response limit of 70,000 1-L^{-1}. The OPC was operated in differential mode where the count data include all particles that are larger than or equal to the particle size selected but smaller than the next greatest particle size. Each task was sampled for 21 sec so that a total volume of 1 L of air was measured.

The sampling inlet of each instrument was positioned as close as possible to the potential emission source (AS = At source) and, when possible, the workers' personal breathing zone (PBZ). The use of these particle sizing and counting instruments was intended to provide an indication of the number concentration of emitted particulate, on a task-by-task basis, within a specific size range that encompasses nanoscale particulate (defined as particulate with at least one dimension of 100 nm or less). To approximate the size range that contains nanoscale particulate, measured particle number concentrations using the OPC size channels 300–500 nm and 500–1000 nm were added together and subtracted from the CPC measurement, which yields a particle number concentration value covering the size range of 10–300 nm.

To address the potential influence of incidental nanoparticles on task-specific measurements, background number concentration measurements for each instrument were obtained based on a 21-sec sampling interval both before and after each task. An average of these background measurements was calculated and used to adjust, via subtraction, task-specific direct-reading instrument measurements. If the difference between the measured particle number concentration for a specific task was the same as or lower than the average background number concentration, the adjusted particle number concentration was considered zero.

Filter-Based Air Sampling

Filter-based air sampling in combination with microscopy provides more specific information on the nature of the aerosol emission by evaluating the airborne mass concentration, size, shape, degree of agglomeration, and chemical composition. PBZ samples were collected as close as possible to the subject's face (e.g., the lapel of the lab jacket), whereas the AS samples were collected as close as possible to the potential source of emission (e.g., just above the beaker opening during the weighing process). Since this strategy was used primarily to identify worst-case scenarios and also to increase the probability of capturing released ENMs, this type of sampling is not intended to represent full-shift worker exposure. Because of the short duration of many of the tasks studied, filter-based samples were often collected at a high sampling rate (7 L/min) to increase the volume of sampled air, thereby increasing the probability of particle capture on the filter media. Occasionally, some tasks were of such short duration (e.g., a few seconds or minutes) that conducting filter-based air sampling was not feasible owing to the inadequate sample volume. In such cases, data collected with the direct-reading instruments were used to determine whether a release occurred. In addition to the PBZ and AS samples, general area air samples were also collected to measure the concentration of any ambient nanoscale particulate (incidental or ENMs).

Appropriate air sampling filter media were selected according to the nanomaterial type and desired analytical information. At most of the field studies, Leland Legacy sampling pumps (SKC Inc., Eighty Four, Pa.), operating at 7 L/min were used to collect air samples. Because CNTs and CNFs are composed of carbon, the airborne mass concentration measurements for these ENMs were collected on 37-mm-diameter open-face quartz fiber filters (QFFs) and analyzed for

elemental carbon (EC) according to *NIOSH Manual of Analytical Methods* (NMAM) Method 5040.[11] Alongside each mass-based air sample, a simultaneous air sample was collected on a 37-mm-diameter open-faced mixed cellulose ester (MCE) filter and examined for the presence of nanomaterial by means of transmission electron microscopy (TEM). In one case (Facility 1), scanning electron microscopy (SEM) was used to generate images and characterize the aerosol.

RESULTS

Across the four facilities, a total of 39 tasks were studied. For these 39 tasks, a total of 45 filter-based air sample pairs (elemental mass and TEM/SEM) were collected and analyzed (19 PBZ, 26 AS). In addition, eight general area (GA) filter-based samples were collected across all four facilities, and all GA results were either below the analytical limit of detection (mass-based samples) or devoid of ENMs when analyzed using microscopy (data/images not shown).

At Facility 1, a total of nine tasks were studied, which resulted in 11 filter-based air samples (3 PBZ and 8 AS) being collected (Table I). All filter-based PBZ mass concentration air samples were below the analytical limit of detection (LOD) for both vapor grown carbon fibers (VGCFs) and boron carbide (BC) (10-μg sample and 40-μg sample, respectively). However, the two AS samples did have measureable amounts of material. These samples, which were collected during the transfer of material to a mixing vessel, ranged from 476 μg/m^3 for VGCFs to 5238 μg/m^3 for blended BC (Table I). For samples examined using SEM, all but three samples (73%) showed visual evidence of either VGCFs or BC (Table I). All three PBZ samples showed evidence of material, whereas five of eight AS samples also showed material (Figures 1 and 2). The remaining three AS samples that showed no evidence of material were associated with the oven exhaust port during the drying cycle and with the loading and operating of the vibrating shaker/sieve. Nearly all particulates examined via SEM were present as agglomerates (Figures 1 and 2; online supplementary Figures 11–16).

Table I also illustrates the particle number concentration emitted in the 10–300 nm size range during each task. Similar to the filter-based air samples, nearly all activities emitted particulate. The highest particle number concentration was observed during the weighing of fine grade BC. The lowest particle number concentration was measured during the operation of the vibrating shaker.

At Facility 2, a total of 14 filter-based air samples were collected under two-directional ventilation conditions (off vs. on) (Table II). These short duration samples resulted in air concentrations of EC ranging from below the LOD (8-μg sample) to 252 μg/m^3. Only two of the 14 filter-based air samples (11%) analyzed for EC had concentrations above the LOD. Samples containing measureable amounts of EC were collected during the spray/filtration process and indicated air concentrations of 148 μg/m^3 (ventilation on), and 252 μg/m^3 (ventilation off). Filter analysis via TEM indicated that 12 of the 14 samples (86%) showed evidence of CNFs either in the PBZ or AS. The majority of the samples, regardless of the ventilation status, showed the presence of a few discrete CNFs (Figures 3 and 4). Samples collected during the spray/filtration process, regardless of ventilation status, showed diffuse clusters of CNFs (online supplementary Figures 19–22). For the tearing/crumbling operation, no evidence of CNFs was noted for the PBZ sample when the ventilation system was operating. However, CNFs were found on the PBZ sample when the ventilation was off (online supplementary Figure 23) and also on the AS samples regardless of ventilation (online supplementary Figures 24, 25).

An interesting finding occurred when the worker created a suspension by adding isopropanol to dry CNFs. The PBZ sample collected during this task (Figure 5), with the ventilation system operating, showed evidence of CNFs; whereas other samples for this task (PBZ, ventilation off; AS, ventilation on and off) showed no evidence of CNFs. Finally, no

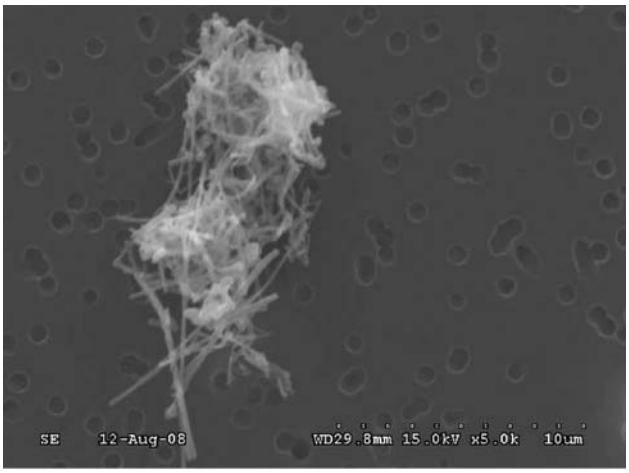

FIGURE 1.

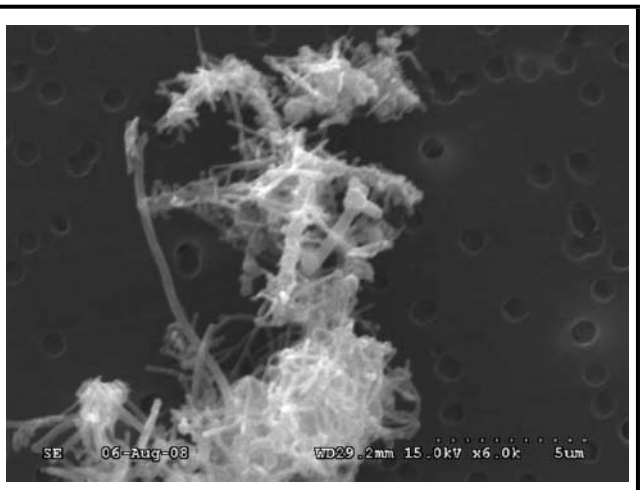

FIGURE 2.

TABLE I. Facility 1—Blending VGCFs and BC for Shipment to End User

Type of Material	Process Description	Engineering Controls	Task	CPC – OPC 10–300 nm (1 cm^3)	PBZ Conc ($\mu g/m^3$)	PBZ Evidence via SEM	AS Conc ($\mu g/m^3$)	AS Evidence via SEM	Figure No.
Vapor grown carbon fibers (VGCFs) 150 nm diameter, 5–10 μm in length; boron carbide (BC) 700-nm diameter	Handling and blending VGCFs/BC	Ventilated, negative pressure room	Scooping/weighing 200 g VGCFs on open benchtop	870	ND	Yes	ND	Yes	1,2
			Transferring 200 g VGCFs to mixing vessel	1228	N/A	N/A	476	Yes	11
			Weighing 4 kg of *blended* (coarse and fine) BC on open benchtop	11,601	N/A	N/A	ND	Yes	12
			Transferring 4 kg of *blended* (coarse and fine) BC to mixing vessel	12,975	ND	Yes	5238	Yes	13,14
			Weighing 4 kg of *fine* grade BC on open benchtop	15,751	ND	Yes	ND	Yes	15,16
			Oven exhaust outlet during drying cycle	93	—	—	ND	No	—
			Loading vibrating shaker/sieve with dried material	144	N/A	N/A	ND	No	—
			Operating vibrating shaker/sieve with sealed lid closed	0	N/A	N/A	ND	No	—
			Transferring material from vibrating shaker via gravity to plastic bag	13,714	N/A	N/A	N/A	N/A	—

Notes: All particle number concentration data have been adjusted for background via subtraction.
ND = none detected; N/A = task too short for filter-based air sampling; no analysis performed.

TABLE II. Facility 2—Processing/Handling CNFs for Use in Manufacturing Buckypaper

Type of Material	Process Description	Engineering Controls	Task	CPC – OPC 10–300 nm (1 cm^3)	PBZ Conc ($\mu g/m^3$)	PBZ Evidence via TEM	AS Conc ($\mu g/m^3$)	AS Evidence via TEM	Figure No.
CNFs 100 nm diameter, 4–20 μm in length	Use CNFs to produce Buckypaper	Ventilated processing room with directional airflow and perforated benchtops	Weighing CNF – vent off	3893	ND	Yes	—	—	3
			Weighing CNF – vent on	0	ND	Yes	—	—	4
			Weighing CNF – vent off	1748	—	—	ND	Yes	17
			Weighing CNF – vent on	0	—	—	ND	Yes	18
			Adding isopropanol to form CNF suspension – vent off	2898	ND	No	—	—	—
			Adding isopropanol to form CNF suspension – vent on	0	ND	Yes	—	—	5
			Adding isopropanol to form CNF suspension – vent off	500	—	—	ND	No	—
			Adding isopropanol to form CNF suspension – vent on	0	—	—	ND	No	—
			Spraying and filtration – vent off	0	ND	Yes	—	—	19
			Spraying and filtration – vent on	46	ND	Yes	—	—	20
			Spraying and filtration – vent off	0	—	—	252	Yes	21
			Spraying and filtration – vent on	77	—	—	148	Yes	22
			Tearing/crumbling Buckypaper – vent off	0	ND	Yes	—	—	23
			Tearing/crumbling Buckypaper – vent on	50	ND	No	—	—	—
			Tearing/crumbling Buckypaper – vent off	0	—	—	ND	Yes	24
			Tearing/crumbling Buckypaper – vent on	150	—	—	ND	Yes	25
			Opening grinder lid/removing product – vent off (PBZ)	60	N/A	N/A	—	—	—
			Opening grinder lid/removing product – vent on (PBZ)	0	N/A	N/A	—	—	—
			Opening grinder lid/removing product – vent off (AS)	67,747	—	—	N/A	N/A	—
			Opening grinder lid/removing product – vent on (AS)	23,935	—	—	N/A	N/A	—

Notes: All particle number concentration data have been adjusted for background via subtraction. All supply air to the room was HEPA filtered and resulted in very low particle counts with the ventilation system on.

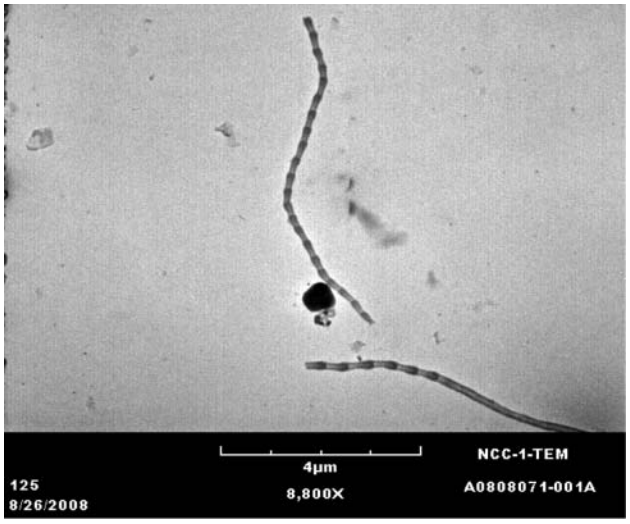

FIGURE 3.

filter-based samples were collected during the opening of the grinder task because of the brief time required to complete the task.

With regard to the particle number concentrations according to tasks, the largest emission occurred during the grinder opening/product removal process, and generally, larger releases were observed with the ventilation off (Table II). However, AS sampling during the spraying/filtration process yielded no reduction in particle number concentration with the ventilation system on. In fact, the particle number concentration data for larger particles were higher when the ventilation system was operating, as compared with the data collected when the system was off.

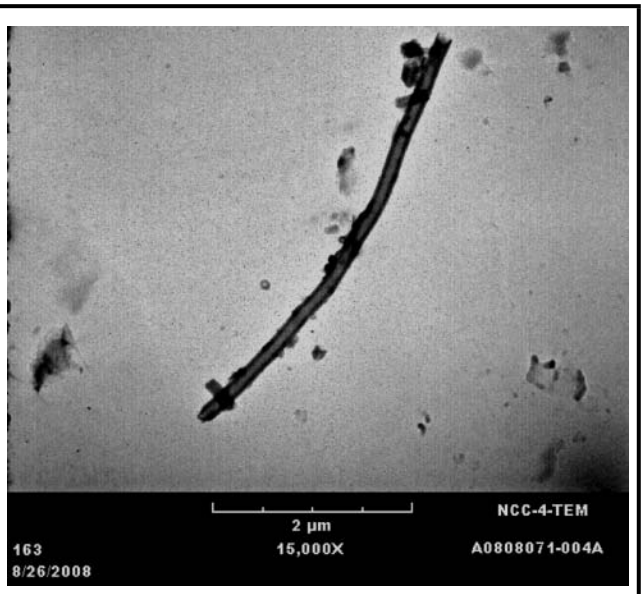

FIGURE 4.

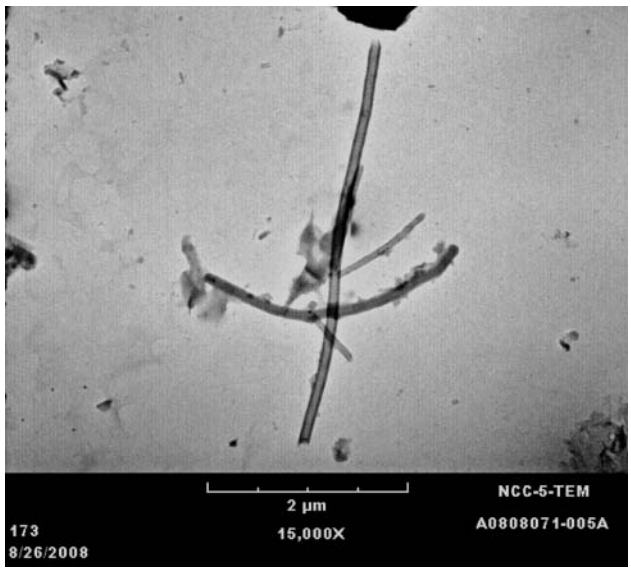

FIGURE 5.

At Facility 3, a total of eight filter-based air samples were collected for eight different tasks (Table III). All air samples analyzed for EC were below the LOD (<2-µg sample) and only two of eight samples analyzed via TEM showed evidence of CNTs (Table III, Figures 6 and 7). The AS sample that showed evidence of CNTs was collected inside the ventilated enclosure surrounding Sheet Furnace 4 during a roller-cleaning task (Figure 6), while the PBZ sample that showed evidence of CNT material was collected on the operator of Yarn Furnace 2 (Figure 7). Both images indicated that large agglomerates of amorphous carbon soot are emitted, with CNTs attached around the periphery of the soot particles. All other samples

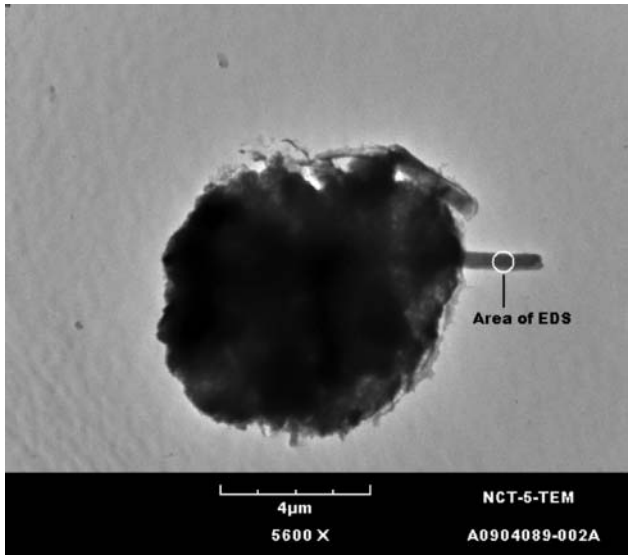

FIGURE 6.

TABLE III. Facility 3—Creating Multi-Walled and Single-Walled CNTs (MWCNTs and SWCNTs) for Use in Manufacturing Sheets and Yarns

Type of Material	Process Description	Engineering Controls	Task	CPC – OPC 10–300 nm (1 cm^3)	PBZ Conc. ($\mu g/m^3$)	PBZ Evidence via TEM	AS Conc. ($\mu g/m^3$)	AS Evidence via TEM	Figure No.
SWCNTs (1 nm diameter) or MWCNTs (10 200 nm diameter)	Production of carbon nanotube sheets (4 ft wide by 32 ft length) and yarns (length = miles)	Ventilated enclosures around each furnace, ducted to single, HEPA-filtered exhaust	Sheet Furnace 4 during roller cleaning	118,330[A]	ND	No	ND	Yes	6
			Sheet Furnace 4 during sheet production	0	N/A	N/A	ND	No	—
			Sheet Furnace 4 during harvesting	175	ND	No	ND	No	—
			Sheet Furnace 4 during reactor cleanout	11,573	ND	No	ND	No	—
			Sheet Furnace 6 during growth of CNTs	368	N/A	N/A	ND	No	—
			Yarn Furnace 2 during growth of CNTs	51,371	ND	Yes	ND	No	7
			Yarn Furnace 2 during winder spool change	18,379	N/A	N/A	N/A	N/A	—
			Yarn Furnace 2 during reactor cover removal	36,379	N/A	N/A	N/A	No	—

Note: All particle number concentration data have been adjusted for background via subtraction.
[A]Value exceeded the upper range of the CPC instrument (100,000 1 cm^3).

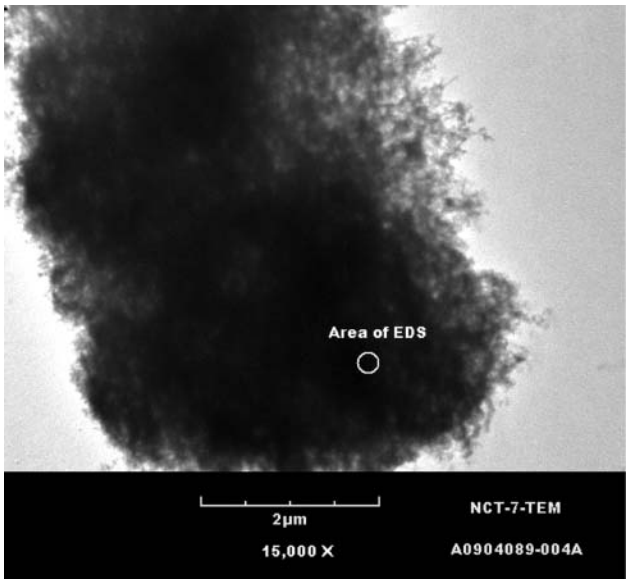

FIGURE 7.

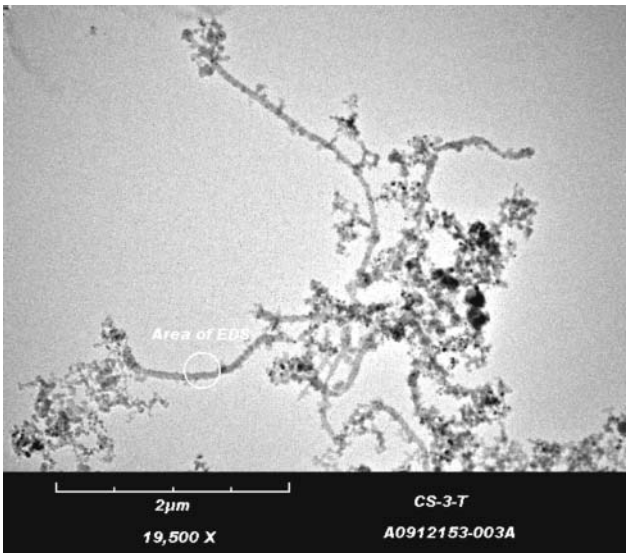

FIGURE 8.

analyzed via TEM showed evidence of agglomerated amorphous carbon soot, which is considered a byproduct of the CNT formation reaction. The largest increase in particle number concentration inside the ventilated enclosure occurred during cleaning of the Furnace 4 collection roller with a brush. Also, each furnace was found to emit particulate during the CNT growth phase (Table III).

At Facility 4, a total of eight filter-based air samples were collected for four different tasks (Table IV). Of the filter-based air samples analyzed for EC, air concentrations ranged from below the LOD (2 µg/sample) to 39 µg/m^3. The highest PBZ concentration (38 µg/m^{-3}) occurred during the harvesting of single-walled carbon nanotubes (SWCNTs) from the reactor, while the highest AS sample (39 µg/m^3) was collected during the loading of flasks. Of the eight filter-based air samples analyzed by TEM, seven showed evidence of SWCNTs (88%). All the PBZ samples showed evidence of SWCNTs (Figure 8), and three of four AS samples showed evidence of SWCNTs (Figure 9). The majority of samples showed clusters of bundled SWCNTs attached to metallic catalyst particles, along with numerous particles of amorphous carbon (Figure 10). The most common size of individual SWCNTs was approximately 50 nm in diameter and 2 µm in length. However, the bundled SWCNTs often appeared in larger formations that ranged in size from 500 nm to approximately 10 µm. Particle number concentration data presented in Table IV indicated emissions occurred during three different tasks: (1) harvesting material from the reactor, (2) wet wiping/mopping of room, and (3) loading trays.

DISCUSSION

As ENMs continue to be developed for use in a range of applications, interest in potential occupational exposure will increase. Over the past few years, studies to assess exposure have occurred and often utilize large, sophisticated often expensive instrumentation that is beyond the scope of routine industrial hygiene surveys.[12–19]

Over time, the NEAT has demonstrated its utility in the field for conducting initial baseline assessments to determine whether emissions occur. Since its inception, when direct-reading CPC and OPC were the sole instruments used to measure emissions, the NEAT has evolved whereby additional direct-reading instrumentation (e.g., for surface area measurements) and more filter-based air sampling techniques (e.g., respirable aerosol fraction) can be used to better characterize

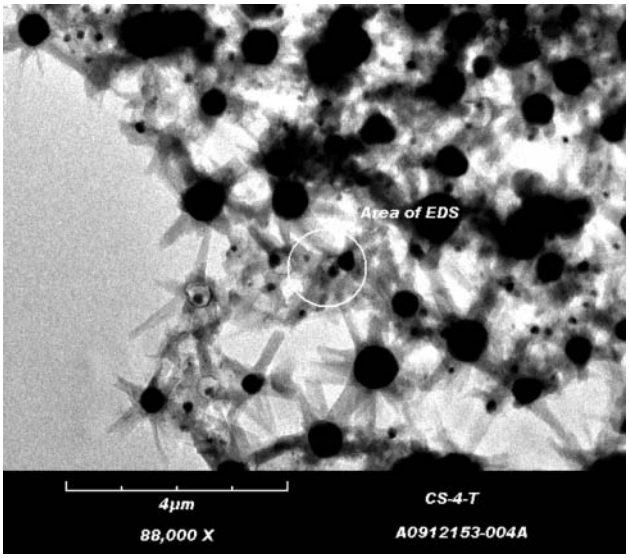

FIGURE 9.

TABLE IV. Facility 4—Production and Handling of SWCNTs

Type of Material	Process Description	Engineering Controls	Task	CPC – OPC 10–300 nm (1 cm^3)	PBZ Conc. ($\mu g/m^3$)	PBZ Evidence via TEM	AS Conc. ($\mu g/m^3$)	AS Evidence via TEM	Figure No.
SWCNTs (1 nm diameter)	Production of SWCNTs	General room ventilation-ceiling mounted supply and exhaust	Harvesting material from reactor	2273	38	Yes	15	Yes	8,9
			Wet wiping and mopping of room	1800	ND	Yes	ND	No	26
			Loading flasks with material	56	33	Yes	39	Yes	10,27
			Loading trays with material	1775	ND	Yes	ND	Yes	28,29

Note: All particle number concentration data have been adjusted for background via subtraction.

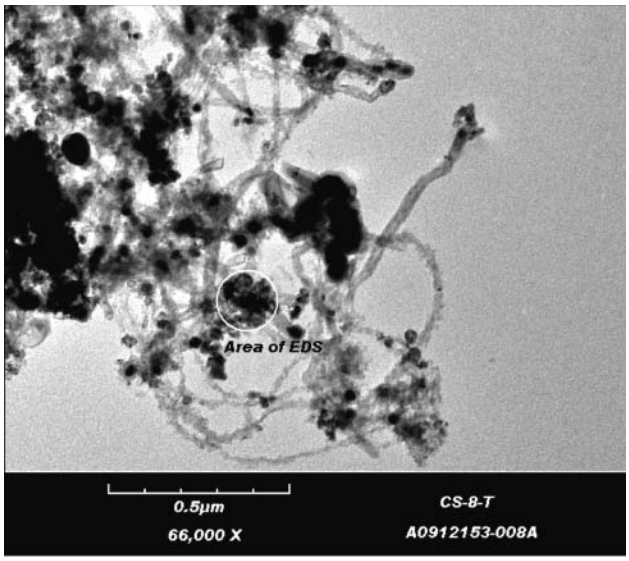

FIGURE 10.

worker exposure. The NEAT also provides critical information that could identify jobs or processes in need of more detailed assessment studies. Given the results presented here, it appears that there are numerous tasks at each facility that emit ENMs, which could pose a risk for exposure and may warrant further study.

At Facility 1, all weighing and transferring activities released particulate to the general plant atmosphere (VGCFs, BC, or the blended material). In particular, weighing and transferring BC resulted in the highest concentration obtained on both a mass and number concentration basis. Despite the visual evidence of either VGCFs or BC in the majority of the filter-based air samples analyzed via SEM, all but two filter-based air samples collected to determine the airborne mass concentration yielded no detectable amount of either EC or BC (Table I). This finding is most likely due to the very low mass of these ENMs, in combination with relatively short sampling times (and lower sampling volumes) at all the facilities. An exception to this finding occurred at Facility 2 and involved the AS samples collected during the spraying/filtration process, where large, visible droplets of isopropanol containing CNFs were observed exiting the spray nozzle and directly impacting the filter cassette media. If the visible droplets contained a relatively high concentration of CNFs, it is plausible that the droplets could have deposited a detectable amount of CNFs onto the air sample filter media. A similar finding was noted in a study in which droplets that became airborne via sonication contained agglomerates of multi-walled CNTs.[20] An event such as this could lead to an overestimation of the airborne concentration of CNFs and should be interpreted with caution.

At Facility 2, three processes yielded filter-based samples that showed evidence of CNFs in the PMZ despite the ventilation system operating: (1) weighing, (2) adding isopropanol to form a suspension, and (3) spraying/filtration. This finding could be due to the turbulence of the airflow as well as possible eddy currents of air forming in front of the worker's body when air approaches the worker from behind. When such events occur, the airflow pattern changes direction and flows back toward the body in a spiral pattern, carrying airborne particulate back toward the worker.[21] This phenomenon may also be the reason why the PBZ air sample collected during isopropanol addition to form a suspension with ventilation on resulted in visible evidence of CNFs when analyzed via TEM (Figure 5). During this process, liquid isopropanol is squirted into a beaker containing dry CNFs. If eddy currents around the worker's body are present, the force of the stream of isopropanol could result in CNFs becoming airborne and traveling along the streamlines of eddy currents back toward the worker. In addition, air movement across the opening of the balance enclosure may create a Venturi effect and draw particulate out of the enclosure and toward the worker. Similar results have been noted in a study that evaluated hoods used during ENM handling in a laboratory setting and indicate the need for more research on the effectiveness of low flow controls.[22]

The particle number concentration results presented in Table II (weighing, adding isopropanol) indicate virtually 100% control of emissions was achieved at the source and in the PBZ when directional ventilation was operating. However, results indicate that the task of grinder opening and product removal was not well controlled at the source. This finding is probably due to the very large release of CNFs at the source, in combination with airflow turbulence and eddy currents near the surface of the perforated tabletop.

In an examination of the effect of directional ventilation on emissions related to the spraying/filtration process and the tearing and crumbling of Buckypaper, the particle number concentration results indicate that no control was achieved (Table II). In fact, the data indicate that the particle number concentration increased very slightly when the ventilation system was operating. Such a finding may be due to subtle differences in the variability of each instrument, or changes in the background particle number concentration. Also, air turbulence at the surface of the perforated tabletop may provide enough of a buoyant force to cause the droplets to remain suspended in the air and be counted.

At Facility 3, despite visual evidence of CNTs on some of the filter-based air samples, all samples collected to determine the airborne mass concentration of CNTs yielded no detectable amount of EC (LOD = 2 µg/sample) (Table III) and is again most likely due to the very low mass of CNTs in combination with relatively short sampling times for some of the tasks studied. The majority of the filter-based air samples analyzed via TEM indicated that the particulate emitted during various tasks was in the form of agglomerates (amorphous carbon soot).

One sample in particular (Figure 6) showed a formation of carbon soot with a CNT protruding from the main particle. Another interesting finding involved the presence of soot material on all samples collected, regardless of their location (inside/outside ventilated enclosure) or furnace type.

This finding indicates that, although no free CNT material was present in the production area atmosphere (Figures 6 and 7), particulate appears to be escaping from the ventilated enclosures that surround each furnace.

Similar to the findings at Facility 3, the results obtained at Facility 4 indicate that the majority of TEM images show evidence that specific tasks are emitting a small amount of SWCNTs, but the aerosol appears to be dominated by amorphous carbon in both bound and unbound forms.

As stated previously, NIOSH Method 5040 was used to measure the airborne concentration of EC, which is intended to serve as an indicator of the mass concentration of CNTs and/or CNFs in air. However, three limitations of the method involve the specificity related to the identification and contribution of different sources of EC that are collected on the filter. First, some of the samples yielded detectable amounts of EC, yet the accompanying filter sample analyzed via TEM indicated no evidence of CNTs but, rather, amorphous carbon particles from the production process (Table IV). Second, the method is unable to distinguish free airborne CNTs from those embedded in or attached to an agglomeration of amorphous carbon particles. Finally, when sampling times are limited to the normal duration of each task, the low volume of sampled air can result in samples being reported as being below the LOD.

Therefore, the airborne mass concentration data presented in Table IV should be interpreted with caution, as not all mass of EC will be indicative of free CNTs. Such a finding further supports the need for collection and qualitative analysis of filter samples by means of electron microscopy. To address the limitations associated with short-duration, task-based air sampling, the use of full-shift sampling appears necessary to ensure an adequate volume of air is collected to meet the analytical needs of the sampling method.

CONCLUSIONS

Because the direct-reading instrumentation is not material-specific (e.g., for CNTs or CNFs only) and cannot identify the chemical composition of the particles detected, one cannot definitively conclude that increases in particle number concentration during a specific task is due to a release of particulate from that process. In fact, using particle number concentration as the sole indicator of emissions or as an exposure metric may be problematic in certain work environments, especially those with highly variable sources and concentrations of background nanoparticles.[13,23] Therefore, the method of computing an average background particle number concentration based on measurements made before and after a task and subtracting it from a task-specific measurement may introduce additional variability and result in a low magnitude emission not being detected.[24]

To further illustrate the influence of variability and the need for careful interpretation of the particle number concentration data, two different studies arrived at opposite conclusions regarding number concentration and the correlation with airborne mass. In a study conducted at a metal oxide facility, number concentration correlated well with processes, yet mass concentration did not.[14] Conversely, a study conducted at a nanoscale lithium titanate plant revealed that airborne mass correlated well with process activities, whereas number concentration did not.[24] Such instruments are known to have limitations, such as the following:

1. Decreased OPC counting efficiencies in the lower size ranges (300–500 nm)
2. Susceptibility to particle coincidence in measurements of high concentrations (OPC and CPC), which would lead to underestimation of the true particle number-concentration
3. Differences in OPC instrument response, due to the refractive index and shape of materials (e.g., background particulate vs. VGCFs vs. BC).[25]

Therefore, these issues, coupled with a recent study that evaluated the CPC and OPC responses to different materials, indicate the need for careful interpretation of data collected with these instruments.[26] For example, subtracting the OPC concentration from the CPC concentration is intended to generate data within a size range that approximates the nanoscale region of the size distribution (10–300 nm). However, even though this size range includes nanoscale particles, it also includes particulate slightly larger than the traditional definition of a nanoscale particle. Despite this limitation, the use of these instruments can be relied on to be field-portable tools that can semiquantitatively identify emissions related to a specific task so that future resources and sampling efforts can be guided toward more detailed worker exposure characterizations.

Because particle number concentrations in the lower size range (10–300 nm) are higher than background, and the results of the TEM/SEM analysis yielded evidence of ENMs, one can conclude that a release occurred and the potential for exposure exists. This type of information is important to facilities that are concerned about the release of ENMs in the workplace. In an effort to be proactive with respect to reducing worker exposure, the facilities studied here indicated that because a release was detected, they plan on either installing engineering controls or improving controls that are already in place.

Since these studies were designed to be range finding in an effort to identify emissions by task, and given the limited number of samples collected during these studies and the variety of tasks, the data presented are not amenable to statistical analyses and therefore should not be used to make statistical inferences, nor should they be utilized to generate an estimate of full-shift personal exposure. Currently, there are no legally enforceable regulatory occupational exposure limits specific to individual ENMs or classes/groups of such materials. However, NIOSH is currently in the process of establishing recommended exposure limits (RELs) for a variety of ENMs. For example, a Current Intelligence Bulletin (CIB) for nanoscale titanium dioxide that describes a REL has been published.[27] A similar document for CNTs/CNFs is currently under development. Nonetheless, it is considered good practice to eliminate or

reduce potential exposure to new and uncharacterized ENMs until clear guidance on acceptable exposure concentrations is established.

RECOMMENDATIONS

Because the data presented indicate that releases occur and are associated with specific tasks, the following recommendations can be made with regard to the control of such releases that in turn will reduce or eliminate potential worker exposure:

1. Although research is continuing on the efficacy of different types of respirators in removing nanoparticles from inspired air, preliminary evidence indicates that, at a minimum, a NIOSH-certified N95 respirator is useful in protecting workers from nanoparticle exposure via inhalation.[28]
2. Conduct all weighing and dry material handling tasks inside a ventilated enclosure equipped with a HEPA-filtered exhaust. The exhaust duct should be routed out of the facility and discharged in accordance with appropriate environmental regulations. Such a device should be of a low-velocity, laminar flow design so that airflow turbulence does not cause particulates to be directed back into the work area or toward the breathing zone of the worker. The most effective face velocity for such an enclosure can be derived empirically with additional on-site monitoring where one could vary the average face velocity, conduct air sampling, and determine whether a reduction in emissions occurred.
3. "Sticky mats" should be installed on both sides of doors that lead into or out of production areas. Use of such mats will aid in preventing ENMs from being carried out on footwear. These mats should be replaced when they become heavily soiled or the adhesive no longer feels sticky on footwear.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of Paul A. Schulte, manager of the NIOSH nanotechnology cross-sector program, and John Howard, director of NIOSH. The authors also extend sincere thanks to the facilities and employees who collaborated with us during each assessment. Partial support for this research was provided by the National Institute for Environmental Health Sciences, through Interagency Agreement No. 1-ES-9026-01.

REFERENCES

1. **Methner, M.M., L. Hodson, and C. Geraci:** Nanoparticle emission assessment technique (NEAT) for the identification and measurement of potential inhalation exposure to engineered nanomaterials: Part A. *J. Occup. Environ. Hyg*. *7*:127–132 (2010).
2. **Methner, M.M., L. Hodson, and C. Geraci:** Nanoparticle Emission Assessment Technique (NEAT) for the identification and measurement of potential inhalation exposure to engineered nanomaterials: Part B. Results from 12 field studies. *J. Occup. Environ. Hyg*. *7*:163–176 (2010).
3. **Savolainen, K., H. Alenius, H. Norppa, et al.:** Risk assessment of engineered nanomaterials and nanotechnologies: A review. *Toxicology*. *269*:92–104 (2010).
4. **Brouwer, D.:** Exposure to manufactured nanoparticles in different workplaces. *Toxicology*. *269*:120–127 (2010).
5. **Trout, D., and P.A. Schulte:** Medical surveillance, exposure registries, and epidemiologic research for workers exposed to nanomaterials. *Toxicology 269*:128–135 (2010).
6. **U.K. Institute of Medicine:** "Welcome to SAFENANO." http://www.safenano.org (accessed February 15, 2011).
7. **Ostrowski, A.D., T. Martin, J. Conti, et al.:** Nanotoxicology: Characterizing the scientific literature, 2000–2007. *J. Nano. Res*. *11*:251–257 (2009).
8. **National Institute for Occupational Safety and Health (NIOSH):** *Approaches to Safe Nanotechnology: Managing the Health and Safety Concerns Associated with Engineered Nanomaterials* (Pub. No. 2009-125). Cincinnati, Ohio: Department of Health and Human Services, Centers for Disease Control and Prevention, NIOSH, 2009.
9. **Methner, M.M.:** Effectiveness of local exhaust ventilation (LEV) in controlling engineered nanomaterials emissions during reactor cleanout operations. *J. Occup. Environ. Hyg*. *5*:D63–D69 (2008).
10. **Methner, M.M.:** Effectiveness of a custom-fitted flange and local exhaust ventilation (LEV) system in controlling the release of nanoscale metal oxide particulates during reactor cleanout operations. *Int. J. Occup. Environ. Health*. *16*:475–487 (2010).
11. **National Institute for Occupational Safety and Health (NIOSH):** Method 5040. Elemental Carbon (Diesel Particulate). In *NIOSH Manual of Analytical Methods,* 4th ed. (DHHS/NIOSH Pub. No. 94-1130). Cincinnati, Ohio: NIOSH, 2006.
12. **Heitbrink, W.A., D.E. Evans, B.K. Ku, et al.:** Relationships among particle number, surface area, and respirable mass concentrations in automotive engine manufacturing. *J. Occup. Environ. Hyg*. *6*:19–31 (2009).
13. **Evans, D.E., B.K. Ku, M.E. Birch, and K.H. Dunn:** Aerosol monitoring during carbon nanofiber production: Mobile direct-reading sampling. *Ann. Occup. Hyg*. *54*(*5*):514–531 (2010).
14. **Demou, E., P. Peter, and S. Hellweg:** Exposure to manufactured nanostructured particles in an industrial pilot plant. *Ann. Occup. Hyg*. *52*(*8*):695–706 (2008).
15. **Park, J., B.K. Kwak, and E. Bae:** Characterization of exposure to silver nanoparticles in a manufacturing facility. *J. Nanopart. Res*. *11*:1705–1712 (2009).
16. **Park, J.Y., G. Ramachandran, P.C. Raynor, et al.:** Comparing exposure zones by different exposure metrics using statistical parameters: Contrast and precision. *Ann. Occup. Hyg*. *54*(*7*):799–812 (2010).
17. **Pfefferkorn, F.E., D. Bello, and G. Haddad:** Characterization of exposures to airborne nanoscale particles during friction stir welding of aluminum. *Ann. Occup. Hyg*. *54*(*5*):486–503 (2010).
18. **Bello, D., A.J. Hart, A. Kwangseog, et al.:** Particle exposure levels during CVD growth and subsequent handling of vertically aligned carbon nanotube films. *Carbon*. *46*:974–981 (2008).
19. **Bello, D., B.L. Wardle, N. Yamamoto, et al.:** Exposure to nanoscale particles and fibers during machining of hybrid advanced composites containing carbon nanotubes. *J. Nanopart. Res*. *11*:231–249 (2009).
20. **Johnson, D.R., M.M. Methner, A.J. Kennedy, and J.A. Steevens:** Potential for occupational exposure to engineered carbon-based nanomaterials in environmental laboratory studies. *Environ. Health Perspect*. *118*(*1*):49–54 (2010).
21. **Flynn, M.R., and B. Lindquist:** A review of wake effects on worker exposure. *Ann. Occup. Hyg*. *39*(*2*):211–221 (1995).
22. **Tsai, S., R.F. Huang, and M.J. Ellenbecker:** Airborne nanoparticle exposures while using constant-flow, constant-velocity, and air-curtain isolated fume hoods. *Ann. Occup. Hyg*. *54*(*1*):78–87 (2010).

23. **Yeganeh, B., C. Kull, M.S. Hull, and L.C. Marr:** Characterization of airborne particles during production of carbonaceous nanomaterials. *Environ. Sci. Technol*. *42*:4600–4606 (2008).
24. **Peters, T.M., S. Elzey, R. Johnson, et al.:** Airborne monitoring to distinguish engineered nanomaterials from incidental particles for environmental health and safety. *J. Occup. Environ. Hyg*. *6*:73–81 (2009).
25. **Hinds, W.C.:** *Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles,* 2nd ed. New York: John Wiley & Sons, 1999. pp. 292–378.
26. **Schmoll, L.H., T.M. Peters, and P.T. O'Shaughnessy:** Use of a condensation particle counter and an optical particle counter to assess the number concentration of engineered nanoparticles. *J. Occup. Environ. Hyg*. *7*:535–545 (2010).
27. **National Institute for Occupational Safety and Health (NIOSH):** *Current Intelligence Bulletin 63:* Occupational exposure to titanium dioxide (Pub. no. 2011-160). Cincinnati, Ohio: NIOSH, April 2011.
28. **Shaffer, R.E., and S. Rengasamy:** Respiratory protection against airborne nanoparticles: A review. *J. Nanopart. Res*. *11*:1661–1672 (2009).