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RESEARCH PAPER

Performance of particulate containment at nanotechnology workplaces

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Abstract The evaluation of engineering controls for the production or use of carbon nanotubes (CNTs) was investigated at two facilities. These control assessments are necessary to evaluate the current status of control performance and to develop proper control strategies for these workplaces. The control systems evaluated in these studies included ventilated enclosures, exterior hoods, and exhaust filtration systems. Activity-based monitoring with direct-reading instruments and filter sampling for microscopy analysis were used to evaluate the effectiveness of control measures at study sites. Our study results showed that weighing CNTs inside the biological safety cabinet can have a 37 % reduction on the particle concentration in the worker's breathing zone, and produce a 42 % lower area concentration outside the enclosure. The ventilated enclosures used to reduce fugitive emissions from the production furnaces exhibited good containment characteristics when closed, but they failed to contain emissions effectively when opened during product removal/harvesting. The exhaust filtration systems employed for exhausting these ventilated enclosures did not provide promised collection efficiencies for removing engineered nanomaterials from furnace exhaust. The exterior hoods were found to be a challenge for controlling emissions from machining nanocomposites: the downdraft hood effectively contained and removed particles released from the manual cutting process, but using the canopy hood for powered cutting of nanocomposites created 15–20 % higher ultrafine (<500 nm) particle concentrations at the source and at the worker's breathing zone. The microscopy analysis showed that CNTs can only be found at production sources but not at the worker breathing zones during the tasks monitored.

Keywords Engineering controls · Local exhaust ventilation · Emission mitigation · Nanomaterial manufacturing · Control evaluation · Carbon nanotubes (CNT) · Environmental, health and safety (EHS)

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Introduction

Engineered nanomaterials are those materials deliberately engineered and manufactured to have certain properties and have at least one primary dimension of less than 100 nm. Concerns for exposure to engineered nanomaterials released from manufacturing

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processes were raised since the published results of animal studies have shown that exposure to such nano-sized materials could potentially cause adverse health effects. Ultrafine size particles (20 nm) could easily penetrate into the interstitium of the lung and can evoke higher inflammation and overall toxicity than larger particles (Ferin et al. 1990). Much greater inflammation and cardiopulmonary health effects have also been observed for metal nanoparticles compared to larger respirable particles (Wolff et al. 1988; Ferin et al. 1991; Zhang et al. 2000). Of particular concern are studies indicating engineered nanoparticle (ENP) toxicity, such as those that found asbestos-like carcinogenic effects in mice (Poland et al. 2008; Takagi et al. 2008; Ryman-Rasmussen et al. 2009) from exposures to carbon nanotubes (CNTs) and cardiopulmonary health effects in rats (Sotiriou et al. 2011) from acute exposures to nanostructured Fe_2O_3.

The greatest exposures to raw nanomaterials likely occur in the workplace during production, packing, and transportation. In a review of exposure assessments conducted at nanotechnology plants and laboratories, Brouwer determined that activities that resulted in exposures included harvesting (e.g., scraping materials out of reactors), bagging, packaging, and reactor cleaning (Brouwer 2010). Downstream activities that may release nanomaterials include bag dumping, manual transfer between processes, mixing, or compounding, powder sifting, and machining of parts that contain nanomaterials. Bekker et al. summarized the findings of exposure assessments conducted in 15 downstream nanomaterial usage (nonproduction) companies in the Netherlands (Bekker et al. 2015). In these companies, across a range of industries, measurements showed that the highest exposure processes included the replacement of intermediate bulk material containers (aka big bags), mixing/dumping of powders, and the spraying of nanomaterial-containing liquids.

Maynard and Kuempel concluded that aerosol control methods have not been well characterized for nanometer-sized particles, although theory and limited experimental data indicate that conventional ventilation, engineering controls, and filtration approaches should be used in many situations (Maynard and Kuempel 2005). A properly designed enclosure at the source of release with a sufficient venting airflow system could significantly reduce particle number concentration in nanometer- and sub-micrometer (μm)-size ranges by four orders of concentration (Tsai et al. 2012b). In addition, the proper filtration of process effluents is essential for reducing ENP emissions to the environment. A recent study has shown that fabric filters with membrane coatings, such as Teflon membrane-coated woven polyester fabric filters, can provide a collection efficiency of 95 %, which is comparable to high-efficiency sampling filters in a laboratory setting (Tsai et al. 2012a). However, poor workplace environmental conditions and work practices can degrade the performance of engineering controls. To have proper control strategies for nanomanufacturing, the practicality of using engineering controls for containing nanoparticle contaminants in the workplace should be examined.

The use of engineering controls, such as enclosures, fume hoods, glove boxes/bags, cleanrooms, laminar flow clean benches, and other local exhaust ventilation (LEV), has been reported in nanomanufacturing workplaces (ICON 2006). LEV systems can be grouped into three major categories: enclosures, exterior, and receiving hoods (Burgess et al. 2004). Within the enclosure category, there are complete enclosures and partially enclosing hoods. Complete enclosures provide the highest level of protection for workers to keep processes or tasks operated inside the hood. Partially enclosing hoods are commonly used for containing a process emission from the rest of the work area. Some common examples of enclosing LEVs include glove boxes, spray paint booths, fume hoods, and biological safety cabinets (BSCs). Exterior and receiving LEVs do not surround (or contain) the source but are placed outside of the source to capture the air contaminant. These LEVs are more susceptible to external disturbances such as cross drafts than enclosures. In addition, the capture effectiveness is dependent on the positioning of the hood. If the hood is too far from the source, the system may not generate enough airflow to overcome the cross drafts. It is also possible with some hood designs that the worker may be able to be in the path between the hood and the contaminant source, resulting in exposure. Only limited data on the practical effectiveness of these engineering controls have been published to date. The primary objective of this research is to present field evaluations on existing control approaches in two workplaces, and to provide recommendations on measures for protecting workers from occupational exposure to nanoparticles. The study results will lead to the development of better recommendations for using engineering controls in nanomanufacturing workplaces.

Methods

The surveys were performed at two commercial nanomanufacturing workplaces (hereafter called Site A and Site B). The primary nanomaterials handled at these workplaces were CNTs, and other secondary ingredients used for fabricating their products were carbon fibers and metal oxides. Site A was a manufacturer to fabricate engineered nanomaterials in macro forms containing CNTs. Unlike Site A producing its own nanomaterials, Site B synthesized its products by integrating raw nanomaterials onto fabric substrates. The detailed processes cannot be described in this article because the products are proprietary. Both sites used the LEVs descried in the flowing sections to reduce particle emissions from their manufacturing processes.

These field study evaluations were conducted using direct-reading instruments to measure the levels of aerosol contamination where controls were in use. Airborne particles were collected for microscopic analysis on particle morphology, agglomeration, and elemental composition. The area particle concentrations were monitored before and after the investigated operations to characterize particle emission levels. Various devices (i.e., Pitot tube, thermal anemometers, and smoke generator) were also used to measure the associated operating conditions and air flow characteristics as described in ACGIH *Industrial Ventilation Manual* (ACGIH 2013) and ASHRAE method 110-1995 (ANSI/ASHRAE 1995).

Engineering controls used at study sites

Ventilated enclosures for nanomaterial production at Site A

Emission sources related to reactor operations, harvesting, and maintenance can be categorized as fugitive or task-based. As shown in Fig. 1a, ventilated enclosures with large dimensions were used at Site A to control particle emissions from full-scale production furnaces during manufacturing. Every furnace was contained by an enclosure whose exhaust was connected with the exhaust filtration systems as described below. Furnace access was available through hinged doors in the enclosures. Overall system exhaust flow rate was controlled by a frequency inverter. Enclosure exhaust flow rates were measured by Pitot traverse, and air velocities at open access doors were measured using thermal anemometers. The enclosure doors were generally kept closed during production, but were opened when products were unloaded. The performance of the enclosure during the material-accessing task was evaluated by real-time monitoring of particle concentrations.

Exhaust filtration systems at Site A

Two independent exhaust filtration systems (A and B, shown in Fig. 2) were used at Site A to connect to the exhaust ducts of ventilated enclosures (Fig. 1a) to remove air contaminants generated from production furnaces. Two ventilated enclosures were served by System A, and the other seven enclosures were served by System B. Panel pre-filters and main filters were installed in both exhaust filtration systems, and the pressure difference across the filters was routinely monitored. The primary filters used in the exhaust systems were $60 \times 60 \times 30$ cm, 95 % efficiency pleated filters (Flanders Co., Washington, North Carolina). These filters are rated at a resistance of 250 Pascals (Pa) at a flow rate of 5.7 m^3/min.

For each system, average duct air velocity was determined by 10-point orthogonal traverses performed on the ducts. Two sampling ports were located upstream and downstream from the primary filters to evaluate the filtration efficiencies of the exhaust systems. Dual Fast Mobility Particle Sizers (FMPSs) were used to measure upstream and downstream concentrations simultaneously for 5 min. The same 5-min measurement cycle was repeated by switching FMPSs to monitor different sampling ports of the systems.

BSC for nanomaterial handling at Site B

Fume hood-type ventilated enclosures are widely used for nanomaterial handling at manufacturing and user facilities. These commonly used controls are often used for tasks including transfer, weigh-out, and packaging of nanomaterials. At Site B, the tasks of

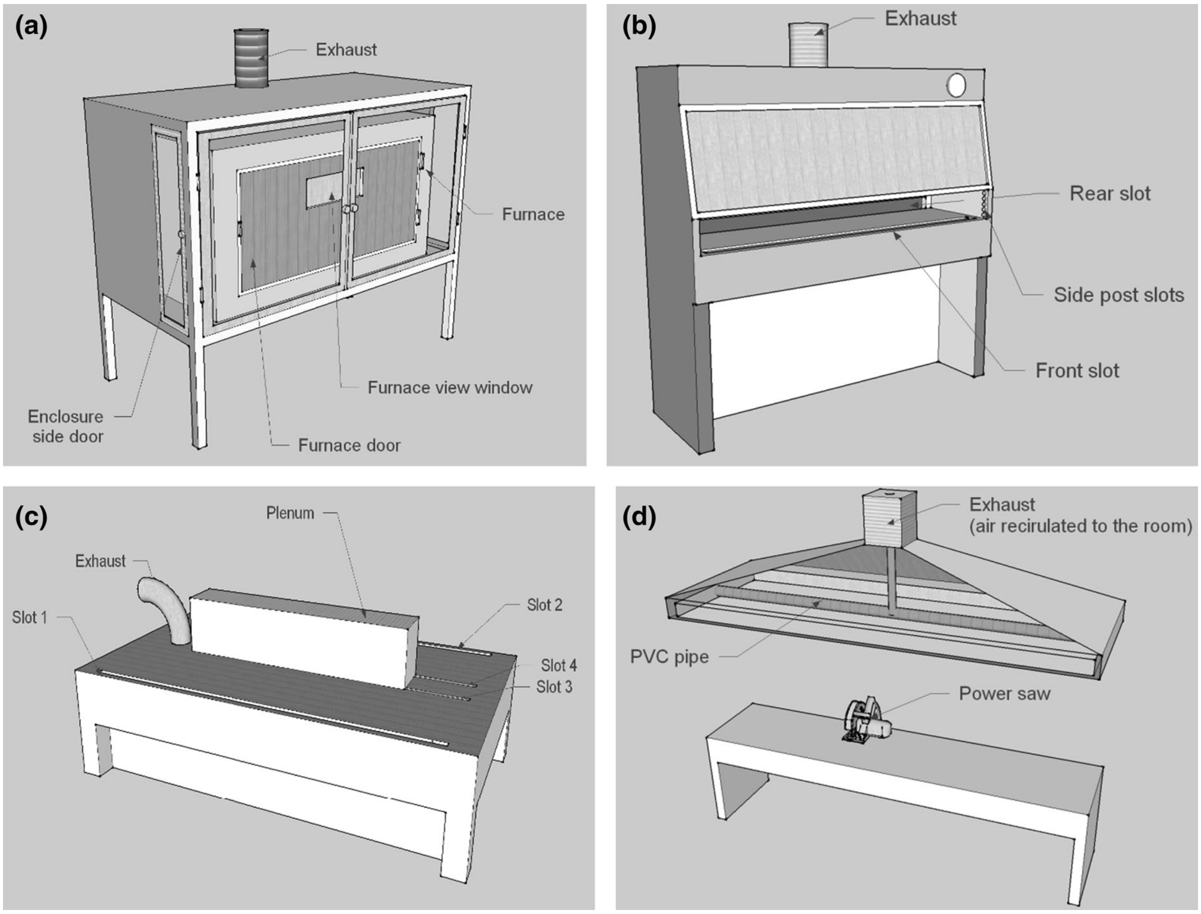

Fig. 1 LEV systems evaluated in this study: (**a**) the ventilated enclosure for nanomaterial production at Site A, (**b**) the BSC for weighing nanomaterials at Site B, (**c**) the downdraft hood for tailoring nanomaterial-containing substrates at Site B, and (**d**) the canopy hood operated during power cutting of nanocomposites at Site B

weighing and premixing of nanomaterials were performed in a BSC (Type II BSC, Baker Company, Sanford, Maine) shown in Fig. 1b. The BSC was 128 cm in width and 58 cm in depth and had a face opening of 20 cm. It included two perforated plate exhaust grilles (front and rear) with side post slots and provided a downward flow of filtered air over the work surface. This downward shower of air split as it approached the work surface; the front slot drew part of the air to the front grille, while the remainder was directed to the rear grille. The BSC typically recirculated a portion (up to 70 %) of the air after cleaning with a high-efficiency particulate air (HEPA) filter. In addition to the built-in recirculation fan, the BSC was also connected to a facility exhaust system operated by an independent blower with a variable frequency controller (VFC). This allowed the BSC to remain running even when the BSC fan was turned off to lower consumed air volume and to minimize disturbance of nanomaterials.

The BSC was used for CNT weigh-out and for the dispersion of CNTs into solution. The BSC was tested in the as-used condition with equipment and supplies located inside the hood. The equipment and supplies blocked some areas of the face and exhaust grilles. Face velocity measurements were made with a thermal anemometer at seven equally spaced points across the opening of the BSC. The measurement locations were at the center of each grid and perpendicular to the plane of the opening. A Pitot tube was used to measure velocity pressure in the BSC exhaust duct. Two 10-point orthogonal traverses were performed in the

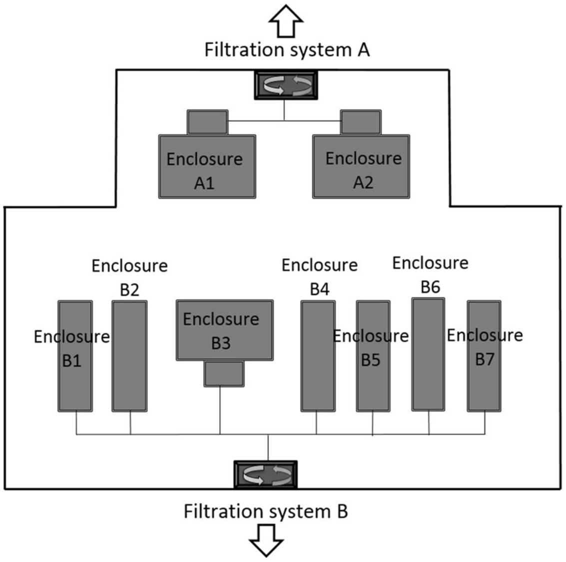

Fig. 2 Exhaust filtration systems used at Site A to connect to the exhaust ducts of ventilated enclosures each containing a production furnace

BSC exhaust duct to determine average duct air velocity (ACGIH 2013). Air velocity in the duct was calculated using the velocity pressures and volumetric flow rate through each duct and was determined by multiplying the average velocity by the cross-sectional area of the duct. Direct-reading measurements were taken inside and outside the BSC, and in the worker's breathing zone to evaluate particle releases during the task of nanomaterial weighing.

Downdraft hood used for manually cutting of nanomaterials at Site B

A custom-made downdraft hood (Fig. 1c) was an exterior LEV used at Site B to inspect and finish substrates containing nanomaterials. For this process, nanocomposite materials were manually cut to size by a rotary cutting wheel to meet product specifications. Air contaminants generated during the tasks were removed by the downdraft hood through its four surface slots connected to a fan and a dust collector equipped with filter cartridges. The slots were labeled 1–4 based on location. Slots 1 and 2 ran the length of the downdraft hood (246 cm) along the edge with Slot 1 being 0.6 cm wide, while Slot 2 was 0.3 cm wide. Slots 3 and 4 were located near the center of the hood, outside the plenum, and both were 0.6 cm wide and 36 cm long. The exhaust was filtered by a HEPA filter before being exhausted into the adjacent office area. The overall exhaust volumetric flowrate from this engineering control was estimated based on a Pitot traverse conducted in the exhaust duct. To monitor the emissions of contaminants from the cutting task in the downdraft hood, particle concentrations were measured simultaneously using two FMPSs; one was located near the worker's breathing zone, and the other one was located close to the cutting wheel (i.e., emission source).

Canopy hood used for power cutting of nanocomposites at Site B

As an exterior hood, canopy hoods require that sufficient capture velocity is created at the source to overcome any secondary airflows such as cross drafts. Overhead canopy hoods are typically used for hot processes to receive contaminants mixed with hot process air, but their control can be ineffective because of poor air distribution and their open faces (ACGIH 2013). At Site B, cutting nanocomposites with a power saw was performed under a custom-built canopy hood (Fig. 1d). According to the study site, this hood was not used very regularly for power cutting of nanocomposites. The area of the hood measured 105 cm in width by 305 cm in length and was 140 cm above the cutting table. Different from other regular canopy hoods, air was exhausted from this hood by a long PVC pipe running along the rear of the hood with a series of 6.35-cm holes about 30 cm apart (on center). Four holes were along the left side and four were along the right side, with a distance of 70 cm on center between the holes located near the center from each side. Unlike other control measures reported in this study, the exhaust air from the canopy hood was recirculated into the room after filtration.

The centerline velocity of each exhaust hole along the canopy hood was measured to estimate the overall exhaust flow rate. To evaluate the potential impact of utilizing this canopy hood during cutting, the hood exhaust fan was turned on and off alternatively, while a worker cut eight identical nanocomposite samples with the power saw. Cutting a nanocomposite material required 1 min. The same sampling strategy mentioned above (using dual direct-reading instruments) was applied for emission monitoring at the worker's breathing zone and the source.

Process monitoring by direct-reading instruments

Real-time measurement of aerosolized particles, including primary nanoparticles and agglomerates, plays an important role in identifying nanomaterial emissions and evaluating control systems during field study (Brouwer et al. 2004; Demou et al. 2008; Tsai et al. 2008, 2009b; Peters et al. 2009). Direct-reading instruments were used in this study to evaluate the emissions from processes and equipment and to help assess effectiveness of engineering controls. The monitoring data we collected from site surveys included the particle concentrations before tasks or processes (area sampling), during processes, and after processes. The FMPS spectrometer (Model 3091, TSI, Inc., Shoreview, Minnesota), Aerodynamic Particle Sizer (APS) spectrometer (Model 3321, TSI, Inc., Shoreview, Minnesota), and DustTrak aerosol monitor (Model 8533, TSI, Inc., Shoreview, Minnesota) were used to measure airborne particle concentrations. Air flow velocities and exhaust flow rates of the LEV systems were measured by a VelociCalc Plus multi-parameter ventilation meter (Model 8386, TSI, Inc., Shoreview, Minnesota) outfitted with a thermal anemometer for airspeed measurement and an electronic manometer for duct velocity assessment. All the instruments used in this study had been calibrated and maintained by manufacturers before site studies. During field investigations, the instruments were checked, re-zeroed, and synchronized in the beginning of days.

Primary nanoparticles released from nanomaterial production processes tend to quickly agglomerate into large-sized particle clusters (Kumar et al. 2008; Hotze et al. 2010). The APS and FMPS help provide a full spectrum of airborne particle size and number distributions to cover nano-sized primary particles up to large agglomerate sizes typically seen in production plants. The FMPS is capable of measuring particle sizes ranging from 5.6 to 560 nm in 32 discrete size channels with a time resolution of 1 s. The APS can detect airborne particles ranging from 500 to 20,000 nm in 52 channels with a time resolution of 1 s. The DustTrak laser photometer was used to measure the particle mass concentration, which is traditionally used as a metric for exposure assessment consistent with toxicology studies. The DustTrak aerosol monitor measures mass concentrations of particles ranging from 100 to 15,000 nm with a 1-s time resolution. The measurement capability of these instruments allows for the determination of real-time fluctuations in airborne particle size/number or mass distributions in the nanomanufacturing workplace, but the direct-reading instruments cannot characterize engineered nanomaterial exposures.

Aerosol characterization by microscopy

In addition to direct-reading instrument measurements, nanoparticle emissions were characterized using electron microscopy of air sampling filters. These methods help determine the physical and chemical properties of airborne nanomaterials and are useful in separating background nanoparticles from engineered nanomaterials of interest, based on size, shape, morphology, etc. A nanoparticle aerosol filter sampler as described below was used in these studies to collect airborne nanoparticles for transmission electron microscopy (TEM) analysis (Tsai et al. 2009b). Unlike NIOSH method 7402, which uses cellulose ester membrane filters to characterize asbestos (NIOSH 1994), this method was modified to use 25-mm cassettes with TEM-copper grids (SPI 400 mesh with a formvar/carbon film, Structure Probe, Inc., West Chester, PA) taped on 25-mm-diameter polycarbonate membrane filters (0.2 μm pore size) to collect particles on both filters and grids. Sampled filters and grids could be directly analyzed by TEM. Agglomerates were seen on filters, and individual or small agglomerate nanoparticles were seen on grids. Air flow was driven by a sampling pump at a flow rate of 0.3 l/min, and particles were collected on the grid for analysis. For this study, TEM samples were taken along with the direct-reading instruments near production equipment to characterize contaminant sources and at the worker's breathing zone to evaluate the control performance. TEM images of the samples were taken using an electron microscope (EM400, Philips, Eindhoven, Netherlands) operated at an accelerating voltage of 100 kV. TEM provides an indication of the relative abundance of nanostructures per air volume, as well as other characteristics such as size, shape, and degree of agglomeration.

Results and discussion

Ventilated enclosures

Controlling fugitive emissions of nanomaterials from production processes at Site A

During the evaluation of the furnace enclosure (Fig. 1a), the real-time monitoring data showed that transient peaks in the measured concentrations of nanoparticles occurred after opening and closing the doors of the enclosure and access to the furnace for product removal (Fig. 3a). Particle concentration levels increased at least one order of magnitude higher than area concentration levels [$\sim 2.0 \times 10^4$ #/cm^3] when both the doors of enclosure and production equipment were fully open for nanomaterial handling. The area concentration remained at a higher level ($\sim 5.0 \times 10^4$ #/cm^3) even after the task was completed. Particle size distributions during different stages are presented in Fig. 3b. The air flow measurement showed that the average face velocity on the ventilated enclosure was 11 cm/s when the enclosure front and side doors were open. This low face velocity is not sufficient to provide effective containment of the nanoparticles and cannot prevent their release into the workplace. The particles around 10 nm at the room area were detected by FMPS at a concentration of about 1.0×10^5 #/cm^3 after accessing the product. This concentration was much higher than before accessing the product, indicating the release of the nanoparticles from the task into the workplace.

After the task was completed, the sampling port was kept inside the enclosure to monitor the temporal concentration variations when the enclosure door was closed (Fig. 3a). The particle concentrations were decreased linearly from $\sim 6.2 \times 10^5$ to $\sim 1.3 \times 10^5$ #/cm^3, a reduction of 79 % in 6 min under normal operations. The volume of air exhausted from each enclosure was generally too low when the enclosure was opened as indicated by the low capture velocity. The airflow was not adjustable to maintain the air velocity when the enclosure was opened, and the designed airflow was not sufficient to provide the air velocity needed at the access opening.

Controlling airborne nanoparticles from nanomaterial handling at Site B

For the BSC (Fig. 1b), a Pitot traverse of the exhaust duct indicated exhaust airflows of 0.2 m^3/min at the low VFC setting and 2.7 m^3/min at the high VFC setting without the integral BSC fan operating. Very low face velocities were measured when the integral BSC fan was turned off with average velocities of 0 cm/s at the low VFC setting and 3.6 cm/s at the high VFC setting. Therefore, when the integral BSC fan was turned off, the facility exhaust blower did not provide adequate exhaust flow to contain contaminants inside the BSC. Turning on the integral fan significantly increased the exhaust airflow rates to 5.2 m^3/min and the face velocity to 33 cm/s. The current consensus of the literature is that the average face velocity for a laboratory chemical hood should be in the range of 41–61 cm/s (80–120 ft/min) (Burgess et al. 2004). The reduced face velocity of the BSC at the study site would allow particle release.

A series of measurements with FMPSs were conducted to evaluate the performance of the BSC used for the weighing process (Table 1). When the BSC fan was turned off, the task of weighing nanoparticles inside the hood resulted in particle concentrations up to 2.5 times higher than the area concentration levels measured before weighing (Table 1, Tasks W2 and W4). The average particle number concentration in the worker's breathing zone (Table 1, Tasks W5 and W7) was 4381 #/cm^3 during weighing nanomaterials when the fan was turned off. However, turning on the BSC fan during the weighing task decreased the concentration in the worker's breathing zone down to 2749 #/cm^3, which is about a 37 % reduction. According to the data for Task W8, the operation of the BSC fan throughout the weighing task produced a 42 % lower post-weighing area concentration outside the BSC; this reduced concentration was associated with the BSC fan use.

A survey was conducted of producers and users of engineered carbonaceous nanomaterials (ECNs) in the US at a research and development or pilot scale plant with plans to scale up within 5 years (Dahm et al. 2011). All participating companies reported using some sort of engineering control to reduce worker

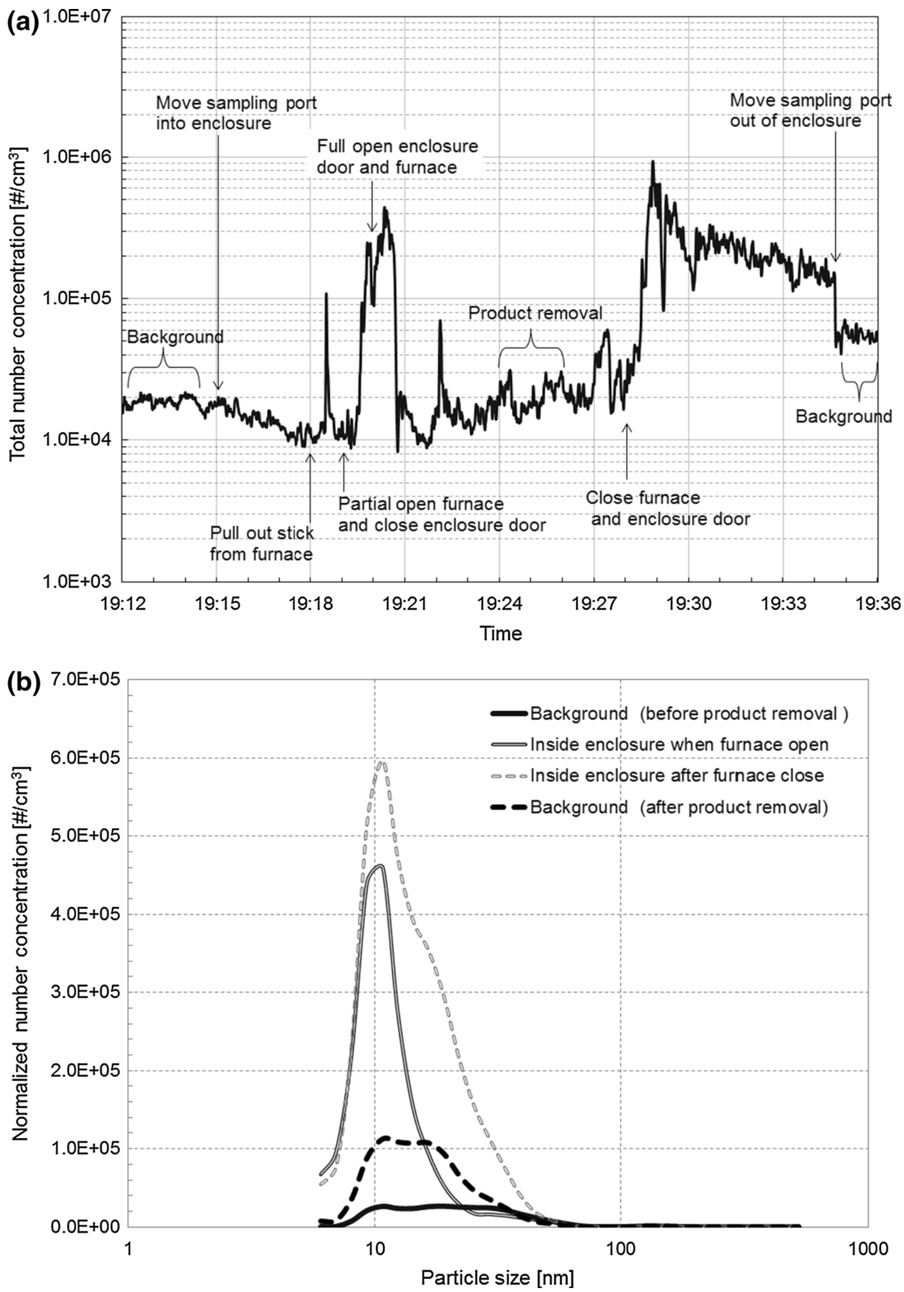

Fig. 3 Process monitoring by FMPS for product removal from a production furnace contained by a ventilated enclosure at Site A: (**a**) particle concentration over entire process, and (**b**) average particle size distributions during different stages

exposure to ECNs. The most commonly reported control used to minimize workplace exposures to ECNs was the chemical fume hood. Recent research has shown that the fume hood may allow releases of nanomaterials during their handling and manipulation in some situations (Tsai et al. 2009a; Tsai 2013). The use of enclosures with appropriate design and operating features along with good work practices is the fundamental requirement for controlling nanoparticle exposure at workplaces.

For this weighing operation, the user turned off the integral fan to reduce air turbulence within the BSC. This action, in turn, resulted in the loss of containment of the material being handled. Dahm et al. conducted

Table 1 Summary of FMPS data during the nanomaterial weighing process performed inside the BSC at Site B

Task IDs	Task and measuring locations		Average total particle number concentration[a] (#/cm^3)	
	Task	locations	Fan off	Fan on
W1	Area concentration check before weighing	Outside hood	2800	3209
W2	Area concentration check before weighing	Inside hood	3515	NA
W3	Area concentration check during weighing	Outside hood	4027	NA
W4	Weighing CNTs	Inside hood	8564	1207
W5	Weighing CNTs	Worker's breathing zone	4381	2749
W6	Weighing CNTs	Inside hood	6292	1170
W7	Weighing CNTs	Worker's breathing zone	4200	NA
W8	Area concentration check after weighing	Outside hood	5234	3059

[a] Concentration data were averaged from 120 data of 2 min measurement

exposure assessments at six sites identified as CNT/nanofiber primary or secondary manufacturers (Dahm et al. 2012). During these evaluations, samples collected during dry powder handling task/processes were generally found to have the highest concentrations of respirable elemental carbon compared to other processes/tasks, including sonication and harvesting. Overall, the two highest exposures occurred at secondary manufacturing facilities during dry powder handling processes/tasks that included mixing and weighing operations within fume hoods that were not always in operation or being utilized properly during material handling procedures. The authors noted that it was common to shut down fume hoods during the handling of CNTs to reduce the amount of product loss from air disturbance. New lower flow hoods adapted from pharmaceutical powder handling enclosures are being marketed and used for the manipulation of nanomaterials. The design features and use of lower flows may reduce the impact of turbulence on the potential for fume hood leakage. However, there is little information on their performance for controlling nanomaterial exposures in the scientific literature.

Downdraft hood at Site B

For the downdraft hood at Site B (Fig. 1c), four exhaust slots pulled air downward from the work surface. Air flow measurements showed that the highest flow rate was found at Slot 1 (5.55 m^3/min at slot velocity of 637 cm/s), nearly five times higher than the lowest at Slot 2 (1.08 m^3/min at slot velocity of 250 cm/s). The flow rates of Slots 3 and 4 were close (2.12 m^3/min at 1507 cm/s and 2.01 m^3/min at 1422 cm/s). This control used a velocity that is 5–30 times higher than the recommended velocity of 50 cm/s applied to the typical hood operation (ACGIH 2013). The estimated total exhaust flow rate was approximately 10.8 m^3/min. A qualitative (visual) smoke test was conducted to study the airflow profiles on the table surface: Slot 1 showed good capture up to 5–7 cm from the slot, Slot 2 up to 2.5 cm, and Slots 3 and 4 up to 7.5–10 cm. As expected, Slot 2 had the lowest effective capture, because it had the lowest overall slot velocity and was 0.32 cm wide versus the other three slots, which measured 0.64 cm wide.

The task of manually cutting product materials performed on the downdraft hood was monitored by a FMPS and an APS near the worker's breathing zone with a second FMPS and APS at the emission source. Two transient peak concentrations were measured by the FMPS at the source, but no noticeable change was detected in the worker's breathing zone. For research and development of their products, this study site also performed a similar task of manually cutting a small-scale nanocomposite substrate on a laboratory worktable with no engineering controls (i.e., a downdraft hood). This allowed us to evaluate particle emissions from this manual cutting process. The activities of manual cutting, weighing, and worktable cleaning in the laboratory were monitored by DustTrak to check particle emissions. As shown in Fig. 4, the activity of cutting substrates with a manual rotary cutter on the laboratory table released particles. The highest instantaneous concentration at the source reached over 3.5 mg/m^3, but the average concentration for the

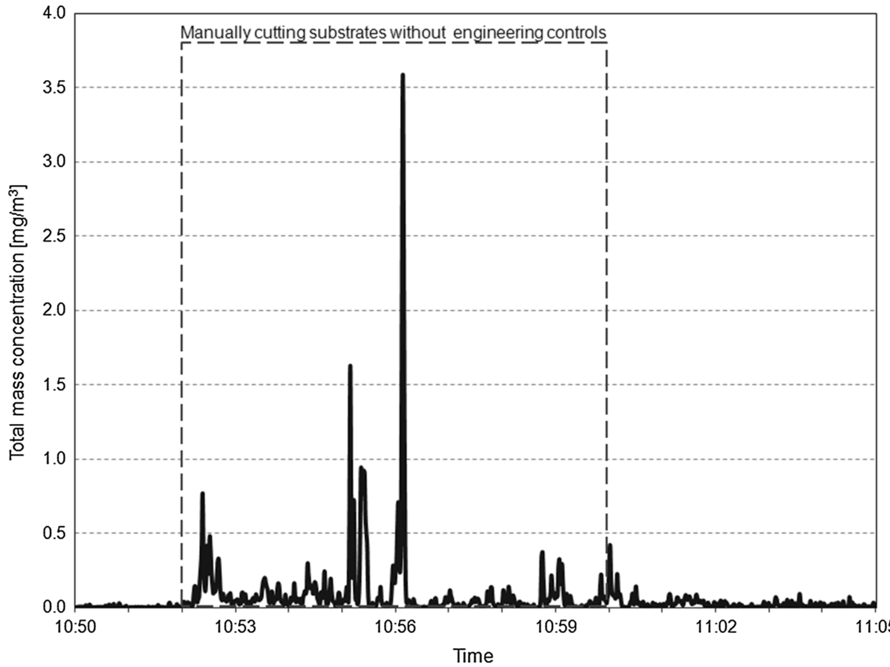

Fig. 4 Mass concentration variations of manually cutting nanocomposite substrates on a laboratory worktable at Site B. The activity was monitored by DustTrak to check particle emissions

whole process was 0.1 mg/m^3 (over 10 times higher than area concentration $\sim$0.009 mg/m^3). Comparing these two cases discussed above, the downdraft hood used for the manual cutting task is effective in reducing contaminant concentrations, but the task would need to be carried out very close to the slots (within about 5 cm) for this control measure to be effective.

Canopy hood at Site B

To evaluate the effect of using a canopy hood for the power cutting process, a group of instruments (including a FMPS, an APS, and a DustTrak) were used to monitor particle levels in the worker's breathing zone. Another group (a FMPS and an APS) was used to measure the emissions source. Before the power cutting process, these instruments were used to monitor the area concentration level. The average area particle concentrations measured by the FMPSs, APSs, and DustTrak were 6650 #/cm^3, 67 #/cm^3, and 0.056 mg/m^3, respectively.

The data in Table 2 show that the canopy hood did not reduce fine particle emissions and therefore did not prevent worker exposure to airborne particles released during the powered cutting task. In fact, the FMPS data showed that operating the hood created 15–20 % higher ultrafine particle concentrations at the source and at the worker's breathing zone than when the hood fan was turned off. The average concentration of larger-size particles (>0.5 μm) obtained from APSs was increased by 23 % at the source when using the hood.

According to air velocity measurements, the overall exhaust flow rate of the canopy hood was estimated to be 5.5 m^3/min. The overall low exhaust flow rate and the distance of the exhaust pipe from the worktable dramatically reduced the canopy hood effectiveness. More important, however, is that the design of the hood placed the worker between the source of emissions and the exhaust. This design means that the particulates generated during cutting would likely be carried through the worker's breathing zone. The LEV systems with recirculating exhaust like the canopy hood installed at Site B are not recommended for control of airborne nanoparticles, especially for CNTs.

Initial studies have shown that machining some nanocomposite materials can result in the release of nanoscale particles to the work environment. Engineering controls when machining materials are available for most common processes. They range from ventilation of handheld tools using a high velocity–low volume system to the use of wet cutting techniques commonly adopted for silica control

Table 2 Summary of average particle concentrations during power cutting of nanocomposites under the studied canopy hood at Site B

Sampling locations		Sources		Worker's breathing zones		
Canopy hoods	Roll #	FMPS2 (#/cm^3)	APS2 (#/cm^3)	FMPS1 (#/cm^3)	APS1 (#/cm^3)	DustTrak (mg/m^3)
On	1	12,384	209	10,027	93	0.092
	3	8675	245	6873	71	0.053
	5	10,036	310	6543	70	0.046
	7	10,013	360	5678	61	0.057
Overall average concentration		10,277	281	7288	74	0.062
Off	2	9000	220	7377	85	0.075
	4	8890	237	6818	75	0.065
	6	8774	277	5927	82	0.111
	8	7497	182	5279	66	0.054
Overall average concentration		8540	229	6350	77	0.076

Table 3 Test results of efficiency evaluation for the exhaust filtration systems at Site A[a]

Tests	Exhaust filtration systems	Average total number concentration[b] (#/cm^3)		System efficiency (%)
		Upstream	Downstream	
Test 1	A	55,831 (FMPS2)	88 (FMPS1)	99.84
	B	335,548 (FMPS1)	23,395 (FMPS2)	93.03
Test 2	A	63,015 (FMPS1)	5196 (FMPS2)	91.75
	B	746,063 (FMPS2)	56,472 (FMPS1)	92.43

[a] The pressure drops of both exhaust filtrati on systems were at 175 Pa during testing

[b] The measurement data reported in this table represent the mean values of total number concentrations from 5-min measurements

during construction activities. The use of standard dust controls such as those described by the Health and Safety Executive for woodworking (HSE 2011) as well as those identified in the ACGIH *Industrial Ventilation Manual* for machining processes provides a source of guidance that can be used to identify controls for machining processes. Bello et al. showed that the use of wet suppression techniques during sawing of nanocomposites reduced exposures down to background levels (Bello et al. 2009). A recent study has also shown that the ventilated enclosure built to contain a power sawing machine efficiently captured the dust generated by cutting and sanding nanocomposite panels (Heitbrink and Lo 2015).

Filtration efficiency of exhaust system at Site A

Before taking measurements, both FMPSs were re-zeroed and then conducted a 5-min monitoring of area concentrations. The pre-checks for the instruments indicated that the average total number concentration from the FMPS1 ($\sim 1.19 \times 10^5$ #/cm^3) was comparable to that from the FMPS2 ($\sim 1.09 \times 10^5$ #/cm^3). Flow measurements indicated that both exhaust systems had nearly the same capacity at 40.7 and 41.3 m^3/min and showed pressure drops of 175 Pa during testing.

The 5-min sampling results are summarized in Table 3. The results of filtration efficiency from every test were calculated from the ratio of the removal concentrations to the upstream concentrations. The data showed that System B managed higher concentrations of contaminants from process equipment than System A. The highest filtration efficiency (99.84 %) was found at System A from the first test, due to the extreme low average concentration from downstream (88 #/cm^3). However, the second test on System A showed the lowest efficiency (91.75 %). For System B, both tests showed comparable results of filtration efficiency around 92–93 %. The two filtration systems measured in this study used filters that theoretically provided 95 % efficiency, but the measured efficiency was slightly reduced on both systems except the first test for System A. Tests on filtration performance at workplaces should be considered as a routine practice to maintain optimum performance.

Research on common air filter materials has shown that fractional efficiency for collection of particles of different sizes is consistent with the single fiber theory (Heim et al. 2005; Kim et al. 2007; Shin et al. 2008). One study found that humidity has little effect on particle collection efficiency (Kim et al. 2006). Research has determined that the use of electrostatic filters (commonly used for respirators) improves particle collection in the 0.1–1-µm particle size range (Huang et al. 2007). Testing of respirator filters showed that the most penetrating particle size shifted from 30–60 to 200–300 nm following treatment of respirators by liquid isopropanol, which removes electrostatic charges on the filter materials (Rengasamy et al. 2009). This result suggests that capture by electrostatic forces is important for particles in the 250–300-µm range. Overall, filters appear to behave in a manner consistent with theoretical predictions that common filter materials allow for efficient collection through diffusion of nanoparticles down to 2 nm (Givehchi and Tan 2014).

Particle morphology

Collecting a sufficient quantity of such nanoparticles from fugitive emissions and short operating processes on filters was challenging. For morphology analysis using TEM, airborne particle samples were collected at locations associated with the studied processes and control equipment investigated in this study. As shown in Fig. 5, CNTs were identified on the filter samples collected from production sources: (a) the sample collected near the production furnace inside the ventilated enclosure, and (b) the sample collected on the downdraft hood during manual cutting. However, no CNTs were found from the filter samples collected from different locations other than sources. Representative TEM images of these samples are presented in Fig. 6. No significant TEM results were found from the power cutting process performed under the canopy hood (Fig. 1d). Most of these contaminants were carbonaceous particles. Two categories of particle structure were observed among these samples: a hollow object (Fig. 6a, c), and a layering object (Fig. 6b, d–f). These TEM results indicated that nanomaterials did not reach worker breathing zones during the tasks monitored. Therefore, the control measures (Fig. 1a–c) used at study sites could provide effective protection for workers, when they are used appropriately.

It is interesting to compare the data of aerosol monitoring by FMPS presented in Fig. 3 with the TEM results shown in Figs. 5a and 6a. The FMPS detected a large amount of particle below 100 nm, but most of them were not CNTs. As discussed by other researchers (Peters et al. 2009), direct-reading instruments can be used for activity-based monitoring to identify emission sources, but costly microscopy analysis is required to

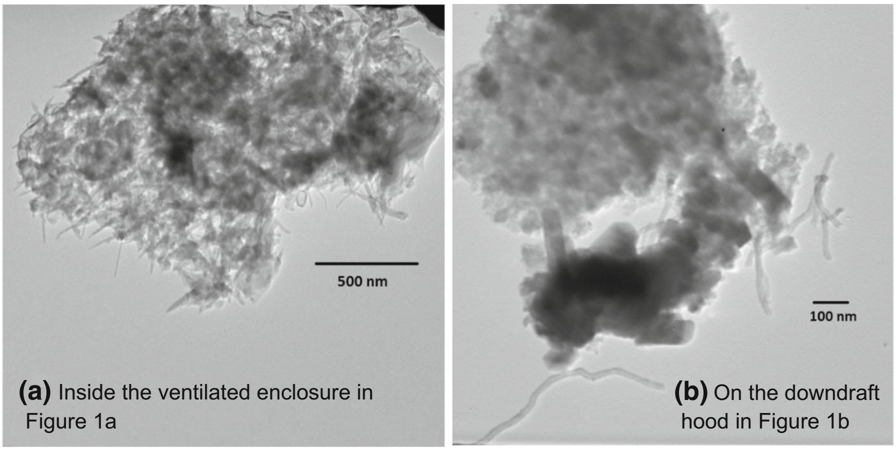

Fig. 5 TEM image of CNTs found at production sources

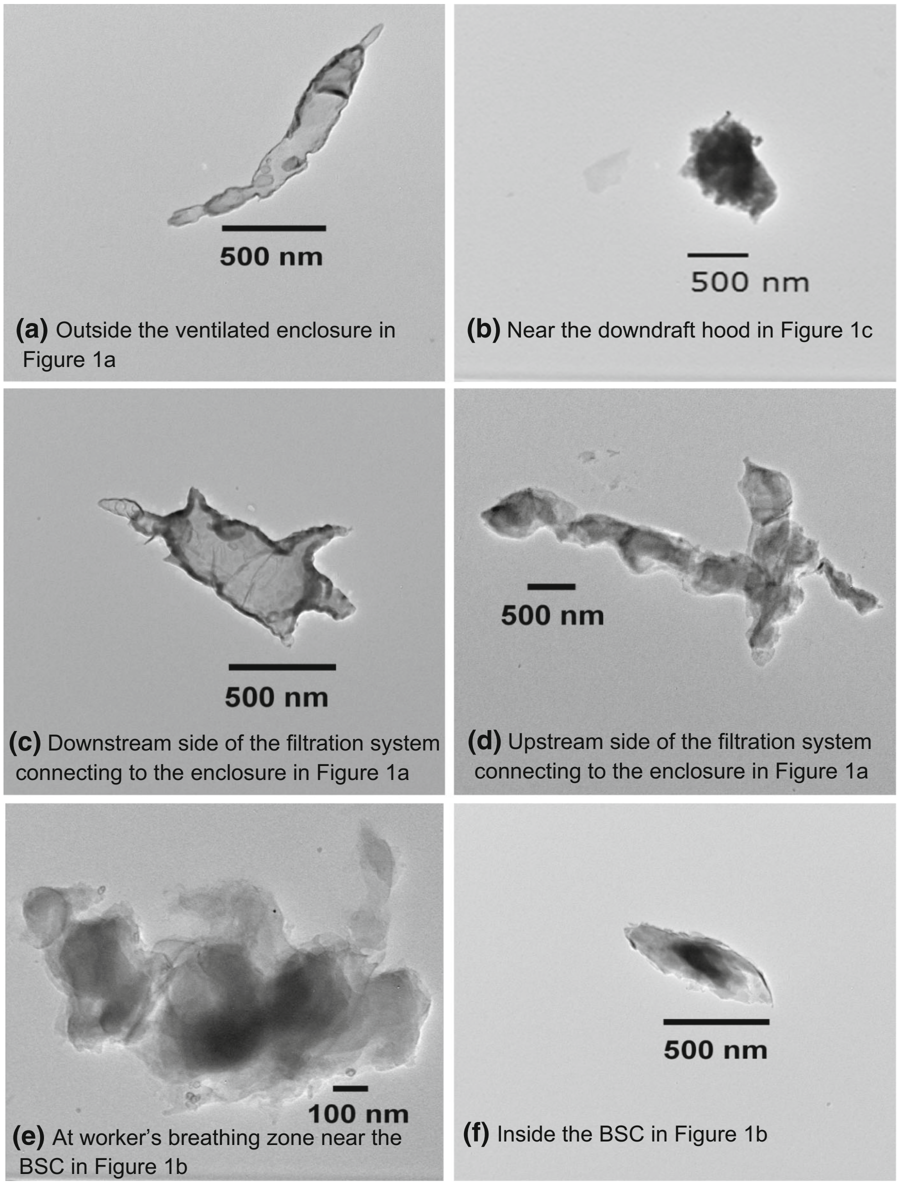

Fig. 6 TEM images of carbonaceous particles sampled at various controls equipment

provide detailed compositional and structural information for understanding and controlling worker exposures to engineered nanomaterials.

Conclusions

The evaluation of engineering controls in the nanomaterial production and use facilities showed varying levels of control effectiveness. The use of a BSC for weighing and handling nanomaterials showed good containment only when the integral fan was on, but the integral fan was typically turned off to minimize the turbulence resulting from the BSC airflows. Many options (such as glove boxes and containment enclosures) are available to facilities that require worker protection during small-scale material handling operations.

As reported by other research done in several manufacturing plants (Demou et al. 2008; Methner 2008; Yeganeh et al. 2008a), our study also showed that the task of harvesting nanomaterials from a furnace is a potentially high-exposure activity. Leakage from pressurized reactors has contributed to increasing facility background concentrations and exposures to operation workers and other employees throughout a facility. As shown by the TEM results and the FMPS data, the ventilated enclosures used to reduce fugitive emissions from the production furnaces exhibited good containment characteristics when closed. However, when the enclosures were opened during product removal/harvesting, the air flows were not sufficient to provide a negative pressure inside the enclosures. The airflows would need to be increased to provide an inward airflow of approximately 41–61 cm/s through the opening to contain any potential emissions into the work environment. The exhaust filtration systems employed for exhausting these ventilated enclosures did not provide promised collection efficiencies for removing engineered nanomaterials from furnace exhaust. Routine monitoring and maintenance of exhaust filtration systems should be implemented in nanomanufacturing facilities to keep optimum performance.

When machining composite materials coated or impregnated with nanomaterials, good dust suppression techniques should be used. In this study, we evaluated the exterior hoods including a downdraft hood and a canopy hood for the cutting of nanocomposite materials. The TEM analysis showed that CNTs were released from the manual cutting of nanocomposite sheets on the downdraft hood, but the direct-reading data showed low concentrations in the worker's breathing zone. This may have been due to low emissions of materials during the manual cutting process. The canopy hood, however, resulted in increased worker breathing zone concentrations when the exhaust fan was turned on during power cutting. This is likely due to the fact that the canopy hood design places a worker between the emissions source and exhaust. Guidance on dust suppression techniques from ventilation-based (woodworking-type) or mist/water-based (silica/construction-type) controls may be adopted to reduce worker exposures to emissions from machining nanocomposites. In addition to engineering controls, safe work practices and personal protection equipment (respirators, gloves, and protective clothing) are highly recommended to be used when working with nanomaterials (OSHA 2013).

Engineering controls protect workers by removing hazardous conditions or placing a barrier between the worker and the hazard, and, with good safe handling techniques, they are likely to be the most effective control strategy for nanomaterials. The identification and adoption of control technologies that have been shown effective in other industries are important first steps in reducing worker exposures to ENPs. Several studies have shown that the use of engineering controls can reduce operator exposure, and one study showed that a poorly designed enclosure actually increased exposure (Methner et al. 2007; Yeganeh et al. 2008b; Tsai et al. 2009c, 2010; Cena and Peters 2011).

Properly designing, using, and evaluating the effectiveness of these controls is a key component in a comprehensive health and safety program. Both activity-based monitoring by direct-reading instruments and filter sample microscopy analysis are recommended to be used to develop strategies of controlling engineered nanomaterials in the workplace. Several government reports and guidelines have described the recommended work practice (NIOSH 2009; HSE 2011; SWA 2012) and engineering control use in general (NIOSH 2013), but the actual use of engineering controls at workplaces was not fully understood nor was it reported. The results of this investigation help fill the knowledge gap between the recommended guidance of controls and the on-site practices of control operations.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no actual or potential conflict of interest in relation to this article.

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