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Exposure Controls for Nanomaterials at Three Manufacturing Sites

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Abstract

Because nanomaterials are thought to be more biologically active than their larger parent compounds, careful control of exposures to nanomaterials is recommended. Field studies were conducted at three sites to develop information about the effectiveness of control measures including process changes, a downflow room, a ventilated enclosure, and an enclosed reactor. Aerosol mass and number concentrations were measured during specific operations with a photometer and an electrical mobility particle sizer to provide concentration measurements across a broad range of sizes (from 5.6 nm to 30 µm). At site A, the dust exposure and during product harvesting was eliminated by implementing a wait time of 30 minutes following process completion. And, the dust exposure attributed to process tank cleaning was reduced from 0.7 to 0.2 mg/m^3 by operating the available process ventilation during this task. At site B, a ventilated enclosure was used to control dust generated by the manual weigh-out and manipulation of powdered nanomaterials inside of a downflow room. Dust exposures were at room background (under 0.04 mg/m^3 and 500 particles/cm^3) during these tasks however, manipulations conducted outside of the enclosure were correlated with a transient increase in concentration measured at the source. At site C, a digitally controlled reactor was used to produce aligned carbon nanotubes. This reactor was a closed system and the ventilation functioned as a redundant control measure. Process emissions were well controlled by this system with the exception of increased concentrations measured during the unloading the product. However, this emission source could be easily controlled through increasing cabinet ventilation. The identification and adoption of effective control technologies is an important first step in reducing the risk associated with worker exposure to engineered nanoparticles. Properly designing and evaluating the effectiveness of these controls is a key component in a comprehensive health and safety program.

Keywords

Engineered Nanomaterials; Engineering Controls; Hazard Prevention; Airborne Contaminants; Control Evaluation

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INTRODUCTION

The specialized properties of manufactured nanomaterials have led to their increasing use. Nanomaterials refer to manufactured particles which have one dimension smaller than 100 nm.(1) These materials can be in the form of thin flakes, fibers, tubes, and pigments. Nanomaterials are used to improve product properties such as strength, conductivity, and flexibility. The small particle size, large surface area and enhanced biological activity of manufactured nanomaterials raise concerns about the potential for adverse health effects and a need to control worker exposures.(2–9) Enforceable regulations which specify exposure limits for these materials do not exist in the United States, but recommended exposure limits for carbon nanotubes (CNTs) and nanoscale particles of titanium dioxide (TiO_2) are available.(10) There have also been suggestions for lower, provisional occupational exposure limits as compared to bulk (or parent) materials.(5, 6, 11) As a result, decisions concerning engineering controls and personal protective equipment (PPE) need to be made by referring to the relevant exposure limits (if available) or exposure goals based on supplier recommendations or manufacturers' exposure goals.

In a review of exposure assessments conducted at nanotechnology plants and laboratories, Brouwer determined that activities which resulted in exposures included harvesting (e.g., scraping materials out of reactors), bagging, packaging, and reactor cleaning (12). 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. Particle concentrations during production activities ranged from about 10^3 to 10^5 particles/cubic centimeter. With the exception of leakage from reactors when primary manufactured nanoparticles may be released, workers are believed to be primarily exposed to agglomerates and aggregates.

Methner et al. summarized the findings of exposure assessments conducted in 12 facilities with a variety of operations, including: R&D labs, CNT, nanoscale metal and metal oxide producers and a nylon nanofiber manufacturer (13). The most common processes observed at these facilities were weighing, mixing, collecting product, manual transfer of product, cleaning operations, drying, spraying, chopping, and sonicating. Engineering controls used included portable vacuums with filters, laboratory fume hoods, portable LEV systems, ventilated walk-in enclosures, negative pressure rooms, and glove boxes. Tasks, such as weighing, sonicating, and cleaning reactors, showed evidence of nanomaterial emissions. The highest nanoparticle exposures measured occurred inside spray booth-type enclosures and during a spray dryer collection drum change-out. Other activities that resulted in higher exposures include reactor cleanout tasks (e.g., brushing and scraping slag material).

Control measures for hazards, including air contaminants such as nanomaterials, should be implemented as part of an occupational safety and health management system.(14, 15) These management systems are continuous improvement cycles that begin with the process's conceptual design. Before processes are put in place, control measures are planned so that exposures are limited and meet worker health and safety goals. During the planning phase, hazards can be identified by reviewing results from previous operations and by using the techniques of safety systems engineering.(16, 17) In considering control measures, process choices and equipment configurations that minimize occupational hazards have a higher priority than the use of local exhaust and dilution ventilation.(17) Using PPE in nanomanufacturing workplaces to protect workers is essential, because engineering controls and administrative controls may not completely remove the risk inherent in nanomanufacturing tasks. This combination of control measures is encouraged by the Occupational Safety and Health Administration (OSHA) to reduce worker exposure to nanomaterials.(10)

This paper presents the performance of a variety of control measures (including a ventilated enclosure, a downflow room, a fully enclosed reactor, and a process change/modification) observed at three nanomaterial sites producing or using CNTs and nanoscale graphene platelets (NGPs). The tasks sampled included product harvesting, reactor cleanout, and material handling. The effectiveness of each exposure control approach is quantified and discussed. Where exposures were not well controlled, potential solutions are presented.

METHODS

Each study site was unique so evaluation procedures were modified and adapted to the situation. These sites were small businesses that did not employ occupational safety and health professionals. During these studies, ventilation system and control measure performance was documented. Direct reading instruments were used to determine whether aerosol concentrations increased during specific tasks involving nanomaterials. (18–21) Background concentration measurements were taken to assist in the interpretation of the real-time measurements. Aerosol concentrations measured before and after these tasks are used to estimate in-plant local background concentrations that are a combination of ambient air pollution and emissions from other in-plant operations that can contribute to the overall measurement.(6) Local background concentrations were measured to assess the contribution from the process under study versus incidental and other process contaminants.

Worker particulate exposures were monitored with an aerosol photometer (DustTrak Aerosol Monitor, model 8533, TSI Inc., Shoreview, MN) and Fast Mobility Particle Sizer (FMPS, Model 3091, TSI Inc.). To make task-specific measurements, sampling was done using conductive tubing approximately 1 meter in length to transport the aerosol from the source or the worker’s breathing zone (WBZ) to the instrument. Both instruments logged concentrations every second so that the relationship between worker task and exposures could be determined.

Real-time monitors were used to determine transient changes in size/number distributions of airborne nanomaterials released from tasks or processes. The FMPS determines particle sizes by measuring particle mobility in an electrical field in 32 distinct size channels. Because of inherent noise from each electrometer and particle charging efficiencies, however, the lower detection limits of the FMPS depend upon particle size and sampling interval. The upper limit of concentration is fixed but exponentially decreases as particle size increases. For the case of 1 second sampling, the detectable range of number concentration is from 100 to 10^7 particles/cm^3 at a mobility diameter of 5.6 nm, and from 1 to 10^5 particles/cm^3 at 560 nm.

The DustTrak is an aerosol photometer that detects particles based upon the quantity of scattered light. The concentration range for this instrument is 0.001 to 150 mg/m^3 for particles between 0.1 and 15 μm. The response of aerosol photometers is known to vary with particle size and optical properties.(22) Although aerosol photometer mass concentrations are highly correlated with gravimetrically determined mass concentrations, the response factors relating concentrations measured can vary by an order of magnitude.(23) Thus, aerosol photometer measurements are a good measure of relative concentration, and their use is a trade-off of accuracy for time resolution. As a result, these instruments are useful for studying how production process variations affect exposure.(24, 25)

Ventilation assessments included the measurement of air velocities and the air flow visualization using smoke tracers.(26) Air velocities were measured using a hotwire anemometer (VelociCalc plus model 8386, TSI Inc.) across enclosure faces and at key equipment interfaces. Smoke tracers were used to visualize flows to locate turbulence that might disrupt LEV performance or result in the leakage of contaminants out of enclosures.

Site A: Production of NGPs

Nanographene was produced in one of two proprietary processes shown in FIGURE 1. Although the equipment was similar, Process A was used for larger batches than Process B. For both processes, the final products were deposited in two stainless steel containers with larger particles being collected in container 1 and smaller particles in container 2. The collection container was then unscrewed from its bayonet mount and carried to a weigh-out booth. To prepare for further processing, workers used a scoop to transfer the materials from the collection container to a different container on a scale for weighing. Following production, the inside walls of process vessels were coated with residual materials and periodically required cleaning. To clean the process tanks, the operator opened the access hatch and used a hand tool to scrape accumulated powder from the walls, which created obvious dust exposure.

Process B had two design features that allowed for better containment of product and reduced emissions to the work environment, specifically: 1)the blower was located downstream of both product recovery vessels, and; 2) butterfly valves were incorporated on the upstream of the collection vessels. Since the fan was downstream of the process, all components of the process were under negative pressure during operation, minimizing the potential for system leakage to the work environment. In addition, the inclusion of butterfly valves on the bottom of the product recovery vessels allowed for system isolation during product harvest. Split butterfly valves have been widely used in the pharmaceutical industry to minimize particle emissions during transferring products or materials from one process vessel to another. These valves may be closed so that process leakage does not occur when collection containers are removed during product harvesting.

At Site A, the following task-based exposures and process evaluation were conducted to assess the impact of engineer controls and process changes on exposure mitigation:

Product Harvesting—Dust exposures were monitored at sources when the worker removed the product containers from the dischargers immediately following process completion. A 30 minute wait time was evaluated to allow for the stabilization of the system following the deactivation of the system fan. In addition, this wait time allowed the equipment surfaces to cool thus reducing the risk of a contact burn.

Process Tank Cleaning—Worker exposures were monitored during maintenance activities including equipment cleaning. Cleaning the process vessel was required to remove the accumulated materials on the inner wall which resulted in worker exposure to aerosolized nanomaterials. To control the dust and recover product, the system blower for Process A (FIGURE 1a) was operated when the process vessel was cleaned. When the system blower was activated during cleaning, the air velocity into the vessel was measured at the equipment access hatch. Since the task was shown to result in the aerosolization of larger agglomerates, the DustTrak was used to measure particulate mass at the source and in the WBZ.

Site B: Production of Nano Composite Paper

This study site was a small business whose main product was a thin, paper-like membrane coated with CNTs. These materials were combined to produce a nanocomposite paper. By optimizing the formulation, properties of interest such as mechanical strength, conductivity, handle-ability, thickness, weight, and other properties can also be customized to meet end-user requirements.

Dry powders were weighed out into a 2.5 liter beaker in a ventilated enclosure located inside a downflow room (FIGURE 2). During weighing, the enclosure ventilation was momentarily turned off, because air movement affected the accuracy of the scale. Solid ingredients in plastic bags or bottles were set in the enclosure and opened. A scoop was used to transfer the specified mass of various ingredients to the beaker. The total volume of solid nanomaterials transferred to the beaker was about 1 liter. Following weigh-out of materials, a solvent was added to the dry materials for initial mixing. The beaker was then taken out of the enclosure and more solvent was added to further mix the material, forming a slurry. The incorporation of nanomaterials into a slurry should suppress dust emissions during subsequent handling activities. Finally, the beaker was transferred to the production room where the customized sheets of membrane are produced.

A ventilated enclosure (Xpert Filtered Balance System, Labconco Co., Kansas City, Missouri) was used to weigh-out material on a perforated bench top. The face of the enclosure had an opening of 8 inches by 34 inches (20.3 cm by 86.4 cm) with a moveable front sash that allows for the moving of equipment into or out of the enclosure. This unit included a fan that exhausted air through a baffle plate in the back of the enclosure and discharged air through an ultra-low penetration air (ULPA) filter towards the ceiling of the room returning air to the lab. The ceiling panel directly over the position where the worker stands to perform the task is a light fixture; there is no ceiling air flow over the worker. Enclosure face velocities were measured using a hot wire anemometer, and air flow patterns were visualized with smoke tracers. Airborne concentrations were measured near the source during weigh-out of the dry nanomaterials and the mixing of the slurry using the DustTrak aerosol photometer and the FMPS. In addition, background concentrations both inside and outside of the down flow room were measured to assess non-process derived particulates.

The preparation of the slurry for the process was conducted inside a down flow room. Unidirectional flow booths, or down flow booths are commonly used in pharmaceutical applications for large-scale powder packing, process loading, and tray dryer loading (27). In general, these booths supply air from overhead over the full depth of the booth. Particles generated by processes carried out in the booths are captured and carried to the exhaust registers, which are located along the back wall of the booth. The down flow room in this facility was 14 feet (4.3 m) wide, 28 feet long (8.5 m), and 9 feet (2.7 m) high. The majority of air in the room was recirculated by 36 2-ft (0.6 m) x 4-ft (1.2 m) fan-powered HEPA filters (Model No. SAM 24 MS GS, Clean Rooms International) located in the ceiling. Except for the air exhausted by the fume hood and the ventilated enclosure, the remaining air returned to these fan-powered HEPA filters through a bank of seven filters that covered the inlets to the return air plenum. There were no provisions for make-up air; leakage into the return air plenum and around the room’s door was likely. During this study, air flow from the fan-powered HEPA filters was measured using an air capture hood (model 8371, TSI Inc.) where possible. Because access to some of the fan-powered HEPA filters was obstructed (e.g. sprinkler heads for fire suppression), a hot wire anemometer was used to measure some filter face velocities and estimate system flow.

Site C: Production of Aligned CNTs

The small company produced vertically aligned CNTs for use in electronics. These CNTs can be processed into a fiber or thread that is highly electrically conductive, flexible, bendable, fatigue-resistant, and load-bearing for multifunctional applications.

Aligned CNTs were manufactured in an EasyTube™ 3000 reactor (First Nano, Ronkonkoma, NY). This system is a customizable chemical vapor deposition/annealing process tool for nanomaterials synthesis, thin film depositions and anneals. The unit included digital control of production and maintenance parameters. The only human interaction during the operation of this reactor occurred during the loading and unloading of the reactor. To load the reactor, the access door was opened to allow the worker to mount the collection substrates on a holder. The reactor was sealed after the holder moved into the reactor. Then, gases such as argon, helium, methane, ethane, ethylene, acetylene, and hydrogen flowed into the reactor and, in the presence of a proprietary catalyst, formed aligned CNTs on the substrate. At the end of the process, the reactor was opened, and the collection substrate was moved into the loading/unloading port. The substrate was then placed in a container for shipping.

The reactor was comprised of four cabinets, including: the control cabinet, load compartment, reactor and burn box cabinet (see Figure 3). Each cabinet was maintained under negative pressure with respect to the room to prevent leakage.

The function of each cabinet is listed below:

1. **Control Cabinet:** This cabinet contained electronics and computers used to control the process.
2. **Load Compartment Cabinet:** The access door was typically opened to load or unload a substrate from a holder that moves in and out of the reactor in the next cabinet. The design air flow into the loading compartment was 100 cfm (2.8 m^3/min). This air flowed through HEPA filters before being discharged to the outdoors.
3. **Reactor Cabinet:** This cabinet contained a reactor which can achieve temperatures up to 1100°C. The reactor was sufficiently hot that thermal decomposition products may be emitted from the external surfaces. The cabinet ventilation was intended to remove these emissions and the heat of production. The design ventilation rate was 200 cfm (5.7 m^3/sec).
4. **Burn Box Cabinet:** Airborne process effluents from the reactor were pyrolized and scrubbed in the burn box. The design air flow into the burn box is 30 cfm (0.68 m^3/sec).

This system uses a hierarchical process control scheme to prevent process leakage:

1. Interlocks were used to ensure that some events cause production to abort, e.g. opening cabinet panels during operation or operating the reactor without ventilation.
2. Programmable logic controllers were used to make sure that production steps follow the prescribed sequence of events so that adverse events do not occur.
3. Supervisory control ensured that the recipes or maintenance activities do not cause adverse incidents. This system also requires periodic calibration of all sensors. This system supervises the abort of production so that life, property, and product are protected.

Cabinet inlet air velocities and static pressures were measured using a hot wire anemometer in front of the slots of loading/unloading modules and the inlet port of the burn box. During routine production operations, the DustTrak and FMPS monitored the area concentrations in front of the reactor. Worker exposures were monitored when CNTs were unloaded from the reactor.

RESULTS

Site A: Process Controls and Changes for Product Harvest

The difference between similar Processes A and B provide us a good case for exploring the effects of engineering controls on reducing worker aerosol exposure during product harvest. FIGURE 4 shows dust exposures measured at the source with the DustTrak and FMPS when collection containers were removed from Processes A and B following completion. The dust exposures measured by the DustTrak (FIGURE 4a) did not increase when the collection containers were removed from Process B. However, mass concentrations measured by the DustTrak exceeded 1 mg/m^3 (Container 1) and 10 mg/m^3 (Container 2) when harvesting product from Process A. Product harvest from Process B showed an increase of 0.002

mg/m^3 above background, but the same task performed on Process A resulted in a much higher WBZ concentration of 2.25 mg/m^3. Worker exposure during the harvest task for Process B was 99.9% lower than that from Process A.

The data from the FMPS (FIGURE 4b) showed similar trends as the DustTrak, however, the magnitude of the fluctuation in fine particle concentrations (5.6–560 nm) was much smaller than that shown on the DustTrak during product harvest. Unlike the DustTrak, the FMPS also did not show any significant increases in fine particle concentrations during the transfer of nanomaterials inside a ventilated enclosure. These results suggest that the contaminants released from these tasks were primarily larger agglomerates.

The implementation of a waiting time prior to product harvest was evaluated on Process A because no dust exposure was found during this task on Process B. The monitoring results have shown that the particulate mass concentrations measured on Process A were largely unaffected by container removal and brief concentration spikes were below 0.5 mg/m^3. The average concentrations at the WBZ decreased from 2.36 to 0.01 mg/m^3 while removing Container 1 and from 0.32 to 0 mg/m^3 while removing Container 2 after implementing a 30 minute wait. Overall, the implementation of the wait time resulted in a reduction of 99.6% and 100% dust concentrations measured at the WBZ during the removal of Containers 1 and 2, respectively.

Site A: Use of System Ventilation for Process Tank Cleaning

Operating the process blower (see FIGURE 1a) while cleaning the process tank significantly reduced worker dust exposure. When the downstream fan was tuned on, an average inward air velocity of 130 feet per minute (fpm) (40 m/min) was measured at the face of the open access door. The release of smoke tracers near the access door also showed that the smoke was being effectively captured. FIGURE 5 shows that the operation of the process ventilation reduced dust exposures during tank cleaning. The mass concentration in the WBZ averaged 0.71 mg/m^3 (FIGURE 5a) and 0.18 mg/m^3 (FIGURE 5b), when the process ventilation was turned off and on, respectively. The implementation of this simple process change resulted in a nearly 75% reduction in exposure during harvesting.

Site B: Use of Ventilated Enclosure and Downflow Room

In down flow rooms, the air flows from the ceiling moves toward the floor and away from the WBZ before being captured at floor level air return registers. The ventilation measurements for the downdraft room showed that the total estimated air flow was 19,000 cubic feet per minute (cfm) (538 m^3/min). The chemical fume hood located inside the room exhausted 1,100 cfm (31 m^3/min) from the room. The ventilated enclosure had an average face velocity of 98 fpm (30 m/min) and recirculated this flow into the room following integral HEPA filtration.

As shown in FIGURE 6, the dust concentrations measured within the room at 0.002 mg/m^3 were lower than that of the general facility due to the HEPA filtration (0.035 mg/m^3 measured outside of the room). WBZ dust concentration measured with the DustTrak during weigh-out activities in the ventilated did not differ from the room background measurement of 0.002 mg/m^3. Likewise, the nanoparticle number concentrations measured with the FMPS in the downflow room were below 500 particles/cm^3, a factor of 10 to 40 less than the typical urban number concentrations of reportedly 5,000 to 20,000 particles/cm^3.(28, 29) The fine particle number concentration did not show significant increases above background during weigh-out and handling of material inside the ventilated enclosure. However, when materials were handled outside of the ventilated enclosure, the DustTrak detected some transient increases in mass concentration likely due to contaminant emissions from the mixing operation suggesting that this task should be conducted inside the ventilated enclosure.

Site C: Fully Closed Manufacturing Reactor

The observed air flow into the load compartment (84 cfm or 2.38 m^3/min) was slightly lower than the design air flow (100 cfm or 2.83 m^3/min). This minor difference between the measured and design air flows may have been due to measurement difficulties. However, static pressures measured were approximately −0.03 inches of water (or −7.5 Pa) inside the cabinets indicating that they were under slight negative pressure with respect to the ambient environment.

Particle number concentrations at Site C were below 1,000 particles/cm^3, much less than the 5,000 to 20,000 particles/cm^3 reported for urban environments.(28, 29) The average background mass concentration obtained from the DustTrak was as low as 0.004 mg/m^3 at Site C. Workplace ambient mass concentrations during task monitoring were generally under 0.04 mg/m^3 (FIGURE 7) consistent with ambient PM10 concentrations which ranged between 0.006 and 0.06 mg/m^3 for this area.(30) The average concentration measured during the task of loading and unloading of the reactor was 0.01 mg/m^3. Although most of the particulate mass is likely due to ambient air pollution background, there were concentration spikes approaching 1 mg/m^3 (FIGURE 7) over 2–4 seconds. These spikes were due to the handling of the CNTs outside of the enclosure. Neither real-time nor filter-based concentration measurements detected leakage from the Easy Tube 3000 reactor. These findings indicate that the proper enclosure and ventilation of the reactor and associated process cabinets effectively contained process-generated nano-aerosols.

Summary of Results

The results from these field surveys are summarized in Table I. Overall, the engineering controls and process changes had resulted in substantial reductions in airborne contaminants from tasks or processes involving nanomaterials. They showed promise for eliminating particle emissions at sources (e.g., the use of process ventilation and harvest wait time at Site A, and the application of a down flow booth and ventilated enclosure at Site B) and minimize particle release into the workplace (e.g., the use of a closed production system at Site C). The use of process ventilation at Site A largely mitigated particle emissions from the task of tank cleaning resulting in worker exposure to agglomerated nanomaterials. And the implementation of a 30 minute waiting time for product harvesting at Site A also reduced potential for exposure to nanomaterials as well as contact burns due to high equipment surface temperature.

DISCUSSION

Hazards involved in processing and manufacturing nanomaterials should be managed using control measures set within the framework of an occupational safety and health management system.(15, 17, 31, 32) The techniques of safety systems engineering such as preliminary or initial hazard analysis facilitate hazard recognition and the selection of design choices that minimize or avoid worker exposures.(17, 33) During a preliminary or initial hazard analysis conducted as part of the design process, the process design is reviewed, hazards are identified, and control measures are selected so that exposures are acceptable. Occupational safety and health management systems also require the monitoring of control measure performance. The assessment of control effectiveness is essential for ensuring that the exposure goals continue to be successfully met.

Site A: Product Harvesting

The harvesting of material from reactors has been identified as a potentially high exposure activity in several manufacturing plants (34–38). In addition, the cleanout of the reactors has contributed to increasing facility concentrations and exposures to operation and maintenance workers. Leakage from pressurized reactors can also contribute to background concentrations and result in exposure to employees throughout the facility. At site A, the airborne concentration at the source during the collection of products from the discharge vessel was measured at 2.27 mg/m^3 and 0.017 mg/m^3 for Processes A and B, respectively. This difference was due to differences in the process design, specifically, the use of isolation valves at the collection vessel for Process B.

To investigate the potential for reducing worker exposure through the implementation of a simple process changes at Process A, a 30 minute wait time was added to allow the aerosol within the process to settle. The addition of this wait time nearly eliminated the worker exposure during product harvesting (Table I) showing a reduction in worker breathing zone concentration from 2.4 mg/m^3 to 0.06 mg/m^3. This simple process change could be used until more permanent control measures can be put into place including the isolation of the collection vessel from the process using butterfly (or other) valves and/or the implementation of an enclosure around the collection point. The use of isolation valves in the Process B effectively eliminated emissions during harvesting at this site. Another approach could be to use a ventilated enclosure around the discharge point to prevent the loss of nanomaterials into the work environment during product harvesting (FIGURE 8). Two studies have shown that when a reactor is housed in a well-designed and operated enclosure, particle loss to the work environment is low. (38, 39)

Site A: Process Tank Cleanout

As part of normal operations, a worker cleaned the process tank with a hand tool creating a personal exposure of 0.71 mg/m^3. To reduce worker exposure during this task, the system exhaust fan was operated keeping the process equipment under negative pressure. Worker breathing zone concentrations were reduced to 0.18 mg/m^3 when the blower was kept on during reactor cleaning. The use of ventilation has been evaluated during reactor cleaning in other settings. Methner assessed the use of a portable LEV unit for controlling exposure during cleanout of a vapor deposition reactor used for producing nanoscale metal catalytic materials comprised of manganese, cobalt or nickel (37). Analysis of real-time data and airborne metals showed an average reduction in concentrations of 88–96% during cleanout procedures when using a portable fume extractor. In this case, the operation of an exhaust fan during process cleaning operations reduced worker exposures while not requiring the purchase of any additional hardware.

Site B: Dry Material Handling/Mixing

Small-scale weighing and handling of nanoscale powders are common tasks; examples include working with a QA/QC sample, processing smaller quantities, and packaging/opening nanomaterials in production and downstream facilities. In these processes, workers may weigh out a specific amount of nanomaterials to be added to a process such as mixing or compounding. The tasks of weighing out nanomaterials can lead to worker exposure primarily through the scooping, pouring, and dumping of these materials. At site B, the use of a down flow booth significantly reduced particulate levels from ambient background pollution. In general, dust concentrations in the room were about an order of magnitude lower than the ambient facility background (0.002 vs. 0.059 mg/m^3). However, when the nanofibers were manually mixed with solvent, some release of particulates was measured. Concentrations measured at the source showed transient peak concentrations of up to 0.08 mg/m^3 when the nanofibers were manually stirred on the benchtop.

Methner et al. evaluated a university-based research lab that used CNFs to produce high performance polymer materials. (40) Several processes were evaluated during the survey: chopping extruded materials containing CNFs, transferring and mixing CNFs with acetone, cutting composite materials, and manually sifting oven-dried CNFs on an open bench top. Real-time monitoring did not identify any process as a substantial source of airborne CNF emissions; however, weighing/mixing of CNFs in an unventilated area resulted in elevated particle concentrations compared to background. Other studies have shown that bench top activities such as probe sonication of nanomaterials in solution can also result in emission of airborne particles. (36, 41) Conducting the mixing tasks inside the ventilated enclosure used for weigh-out is an effective means for mitigating the noise and aerosol exposure.

Many different types of commercially available laboratory fume hoods can be employed to reduce exposure during the handling of nanopowders. Other controls have also been used in the pharmaceutical and nanotechnology industries for containment of powders during small quantity handling and manipulation. They include glove boxes, glove bags, biological safety cabinets or cytotoxic safety cabinets, and homemade ventilation enclosures. Newer nano hoods based on pharmaceutical weigh-out enclosures may be a reasonable alternative to larger fume hoods when only small-scale, bench-top manipulation of powders is needed. Overall, the published studies suggest that the selection of a fume hood with improved operating characteristics such as a variable air volume hood provides better operator protection than conventional fume hoods when handling dry nanomaterials.(42) When using any hood, the worker should strive to maintain the face velocity in the recommended range of 80–120 ft/min. (43) Additionally, proper use of the engineering control by the operator and validation of the performance of the control equipment is essential for risk mitigation.

Site C: Enclosed Process Operations

Site C used automated and closed processing systems designed and built to significantly control process emissions. Hazard control for this carbon nanotube reactor is largely integral to the equipment's design and is intended to contain air contaminants. There are interlocks on the doors or access panels to safely shut down the operation if these doors are inadvertently opened. Ventilation is used as a secondary, redundant control measure that removes any process leakage, thermal decomposition products from the reactor exterior, and heat from the enclosed spaces around the reactor. Air samples suggested that the operation of the equipment did not contribute to air contamination in the workplace. Individual fibers were not detected in the workplace air, and elemental carbon concentrations were less than 1 $\mu g/m^3$. However, short transient peak concentrations were seen when the worker unloaded the CNTs from the process suggesting that a higher exhaust flow for the cabinet may be required to fully contain the contaminants.

CONCLUSIONS

Exposure to engineered nanomaterials can be controlled by process modification and the use of engineering controls. Control measures are best implemented as a component of an occupational safety and health management system. During the initial process design, the techniques of safety systems engineering, such as preliminary or initial hazard analysis, should be used to identify hazards appropriate control measures early in the design process. For these sites, the implementation of control measures helped reduce worker exposure to air contaminants across common process tasks consistent with other published studies.(44–49) Many of the hazards seen at these facilities could have been identified and controlled as part of the initial design through the implementation of process safety principles such as job hazard assessments.

Direct reading instruments can be useful for identifying exposure sources and assessing whether process changes affect exposures to air contaminants. This assessment can be done without the cost or delays caused by submitting filter samples to a laboratory for offline analysis. However, one must interpret the results cautiously as direct reading instruments respond to all aerosols regardless of their source; the instrument response may not be solely due to process generated aerosols.(4, 6, 50)

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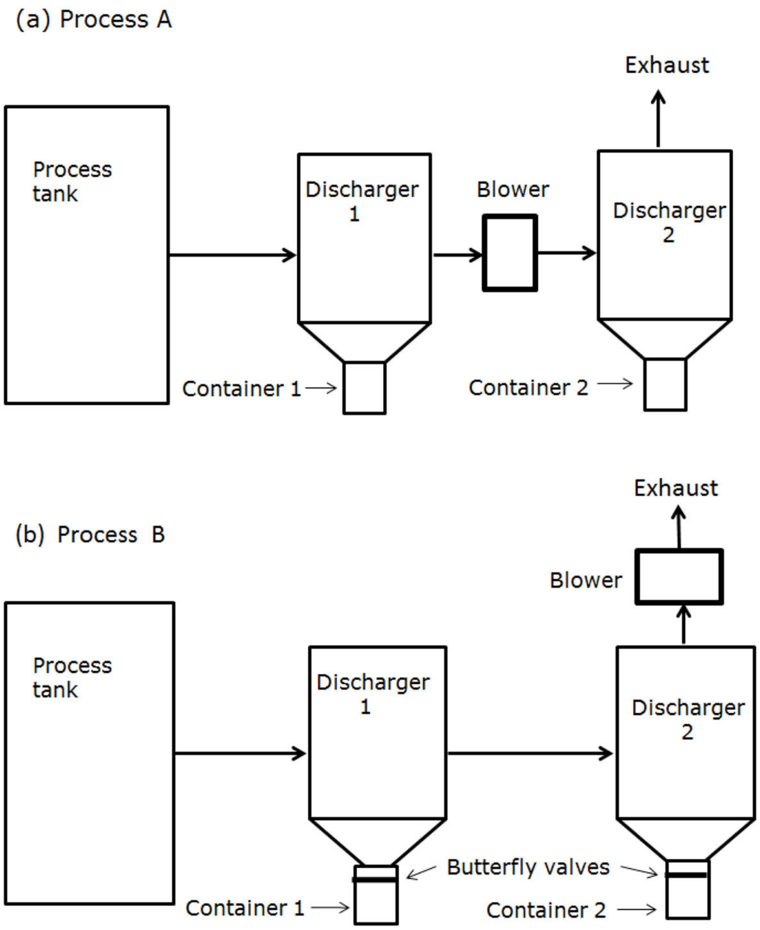

FIGURE 1.

Schematic illustration of process flow at Site A: (a) Process A; and (b) Processes B with design features that may minimize dust exposures.

Note: The butterfly valves can be closed during product recovery so that process containment is maintained.

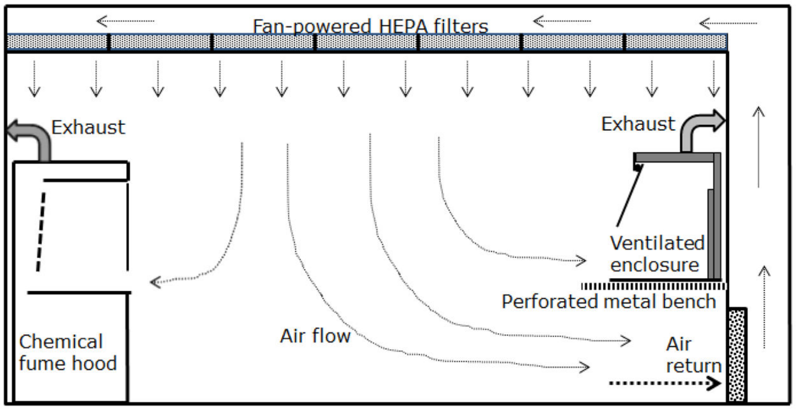

FIGURE 2.
Layout of the downflow room at Site B.

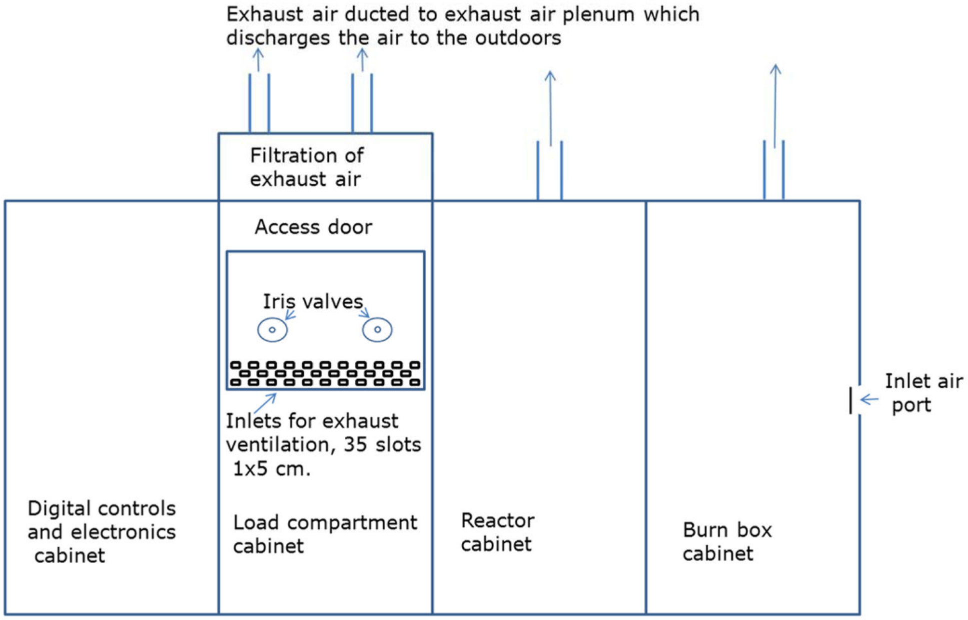

FIGURE 3.

Schematic illustration of Easy Tube 3000 Reactor (CVD Equipment Corporation, Ronkonkoma, NY) used at Site C.

Note: the reactor cabinet's exhaust air enters through slots behind the filtration module that sits on top of the Load compartment cabinet.

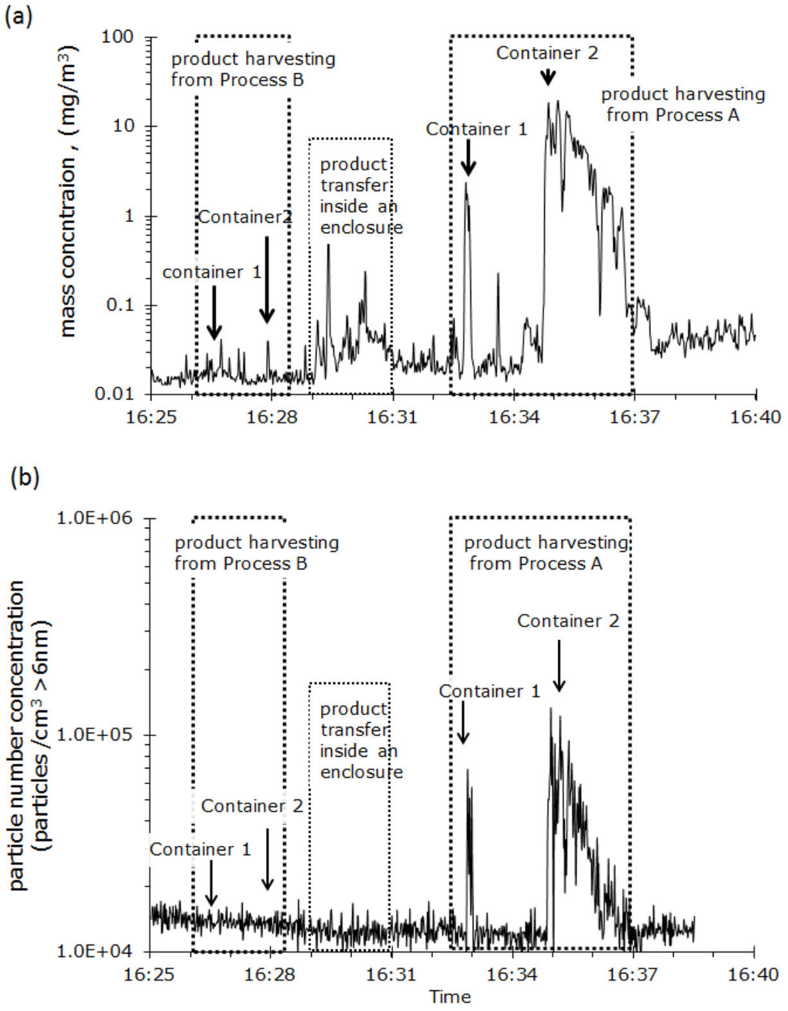

FIGURE 4.

Dust exposure measured at source with (a) DustTrak and (b) FMPS during product harvesting from processes and product transfer inside a ventilated enclosure at Site A.

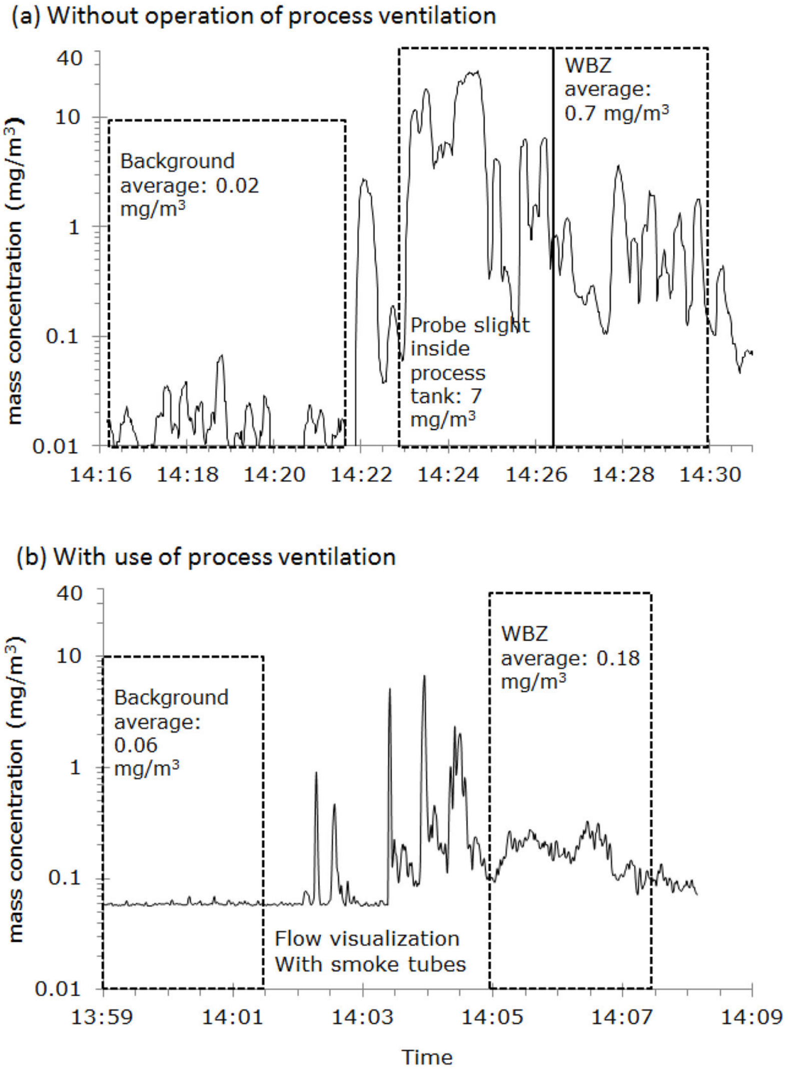

FIGURE 5.

Real-time monitoring of nanomaterials released from the cleaning for Process tank A at Site A. The cleaning process was performed (a) without and (b) with the use of the process ventilation.

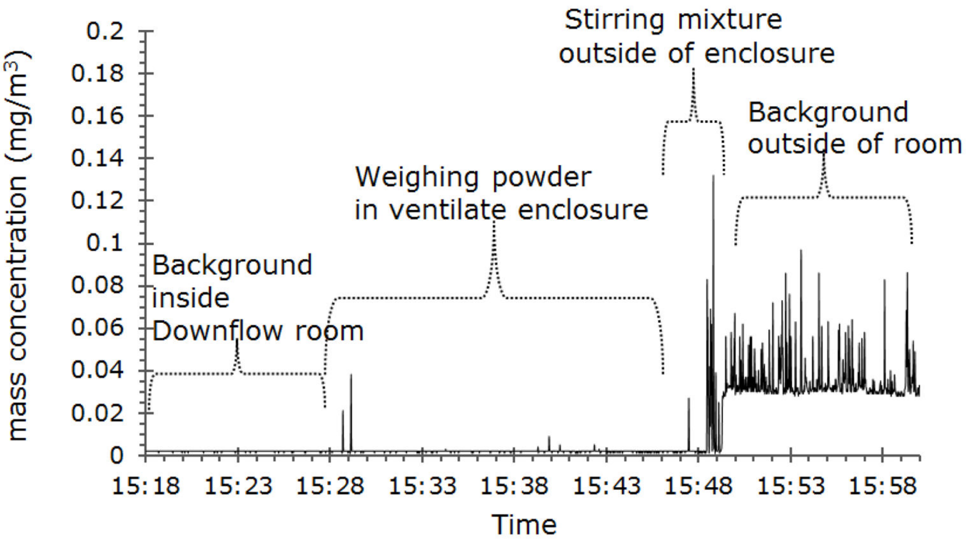

FIGURE 6.

Aerosol concentrations measured during powder weigh-out at Site B.

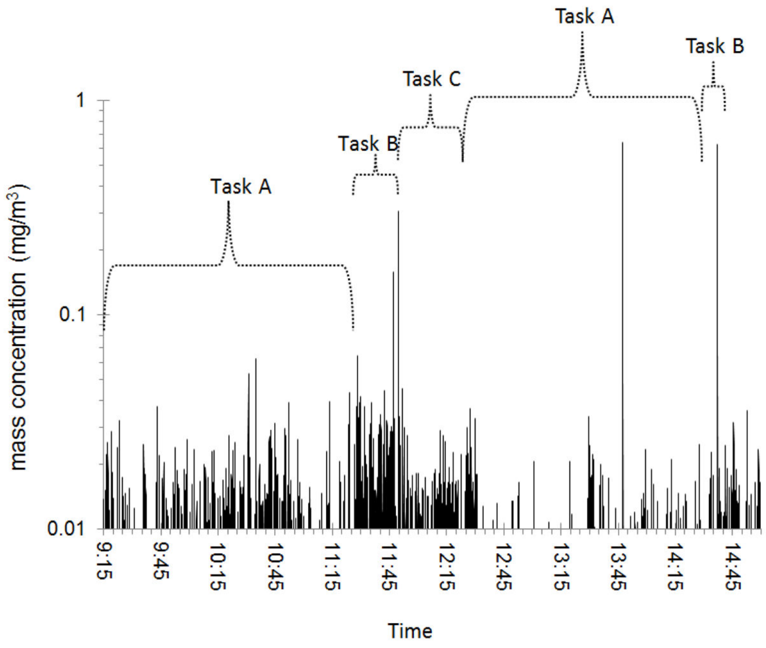

FIGURE 7.

Particle (A) number and (B) mass concentrations in front of reactor at Site C: Task A – routine operation of reactor, Task B – loading and unloading of reactor, and Task C – away from reactor during other activities.

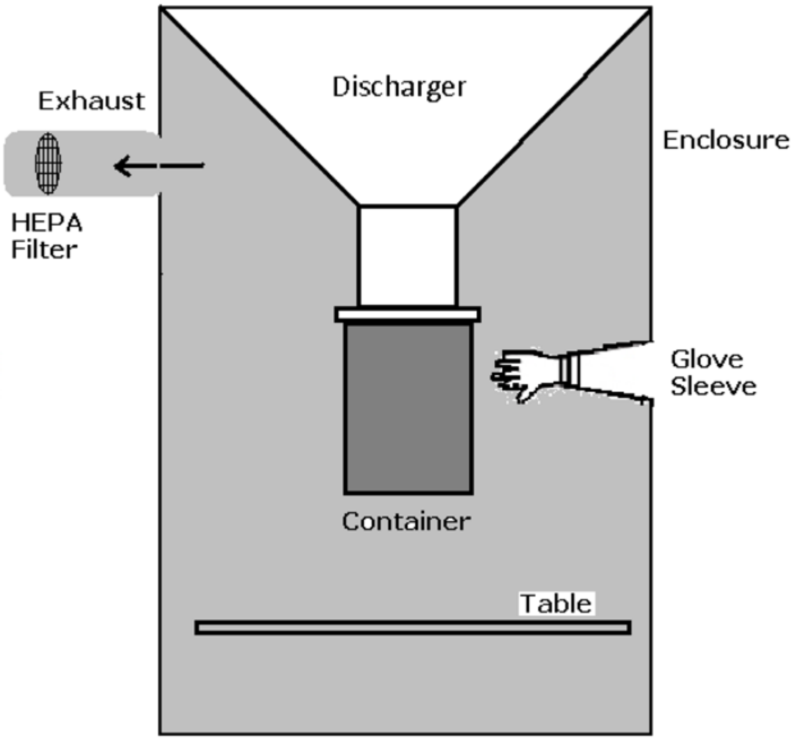

FIGURE 8.
Flexible enclosure for product harvesting.

TABLE I

Summary of the results from the field surveys.

Study Site	Task	Engineering Controls or Process Changes	Background Concentration [mg/m^3]	Aerosol Concentration [mg/m^3]	(Net) Efficiency
A	Harvesting	Process A (exhaust)	0.024	2.27 (source)	Particle emissions from Process B 99.9% lower than that from Process A.
		Process B (exhaust, butterfly valves)	0.015	0.017 (source)	
	Harvesting	Process A (no waiting)	0.04	Container 1: 2.4 (WBZ) Container 2: 0.36 (WBZ)	Container 1: 99.6 % reduction in WBZ.
		Process A (30 min waiting)	0.05	Container 1: 0.06(WBZ) Container 2: 0.05 (WBZ)	Container 2: 100% reduction in WBZ.
	Tank Cleaning	Process A (no controls)	0.013	6.87 (source) 0.71 (WBZ)	82.6% reduction in WBZ.
		Process A (exhaust on)	0.059	0.18 (WBZ)	
B	Mixing	Downflow room and ventilated enclosure	0.002	0.002 (source)	Particle emissions eliminated at source if the task was performed inside the ventilated enclosure.
		Downflow room only	0.002	0.008 (source)	
C	Loading unloading	Closed production system	0.004	0.01 (source)	Low particle emissions found and consistent with local ambient PM10.