



In-Depth Survey Report

Containment Assessment of Nanomaterial Handling Enclosures at Academic Research Laboratories using Carbon Nanotubes and Graphene

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Abstract

The NIOSH Control Technology Team and the Environmental Health and Safety Team of the University of Massachusetts Lowell (UMass Lowell) conducted an in-depth survey to assess nanoparticle emissions in a chemical laboratory at an academic institution in Boston, MA. The surveyed laboratory conducted lab scale research using carbon nanotubes (CNTs), neodymium oxide and graphene. The tasks evaluated in this study included weighing and mixing. All tasks were conducted in ventilated nanomaterial handling enclosures similar to pharmaceutical balance enclosures. The research team used direct-reading instruments to monitor the tasks and collected filter samples to characterize released nanomaterials by microscopy and chemical analysis. In addition, performance data on the nanomaterial handling enclosures were collected including face velocity and exhaust filter efficiency. The study results of nanoparticle emissions from this bench-top laboratory scale research evaluation provide information on exposure potential and control effectiveness for these common processes.

Overall, minimal exposure potential was identified during the tasks evaluated at these laboratories. This is more likely a result of the small quantities used and good handling techniques than the enclosure performance itself. The real-time monitoring did not identify noticeable particle emissions from the tasks evaluated. All of the elemental carbon (EC) concentrations obtained from filter samples in this study were either below the limit of detection (LOD) or between the LOD and limit of quantitation (LOQ). Although transmission electron microscopy (TEM) analyses identified a few CNTs outside of the ventilated enclosure, the overall concentrations were low. The highest concentration of airborne CNTs were identified during the weigh-out of CNT carpet sample coupons. This task was performed with the enclosure fan turned off to minimize disturbance to material during weigh-out.

Average face velocities of the nanomaterial handling enclosures assessed in the three laboratories ranged from 0.21-0.36 meters/second (m/s). Based on the current laboratory fume hood guidance, it would be prudent to increase the overall air flow rates to maintain each of these enclosures to the 0.41-0.51 m/s range for average face velocity. The proper use of personal protective equipment including lab coats, safety glasses and gloves should provide adequate dermal and respiratory protection. Currently, there are few published occupational exposure limits (other than the NIOSH REL of 1 $\mu\text{g}/\text{m}^3$) for carbon nanotubes. However, it is good occupational safety and health practice to maintain exposures to new and uncharacterized materials as low as possibly achievable.

Background

The National Institute for Occupational Safety and Health (NIOSH) is the primary Federal agency engaged in occupational safety and health research. Located in the Department of Health and Human Services, it was established by the Occupational Safety and Health Act of 1970. This legislation mandated NIOSH to conduct research and education programs separate from the standard setting and enforcement functions carried out by the Occupational Safety and Health Administration (OSHA) in the Department of Labor. An important area of NIOSH research deals with methods for controlling occupational exposure to potential chemical and physical hazards. The Engineering and Physical Hazards Branch (EPHB) of the Division of Applied Research and Technology (DART) has been given the lead within NIOSH to study the engineering aspects of health hazard prevention and control. Since 1976, EPHB has conducted a number of assessments of health hazard control technology on the basis of industry, common industrial process, or specific control techniques. The objective of each of these studies has been to document and evaluate effective control techniques for potential health hazards in the industry or process of interest and to create a more general awareness of the need for or availability of an effective system of hazard controls.

Occupational health risks associated with the manufacture and use of nanomaterials are not yet clearly understood. However, initial toxicological data indicate that there is reason for caution. Pulmonary inflammation has been observed in animals exposed to titanium dioxide (TiO₂) and carbon nanotubes (CNTs) (Shvedova, Kisin et al. 2005, Chou, Hsiao et al. 2008, Rossi, Pylkkanen et al. 2010). Other studies have shown that nanoparticles can translocate to the circulatory system and to the brain and cause oxidative stress (Elder, Gelein et al. 2006, Wang, Liu et al. 2008). Perhaps the most troubling finding is that CNTs can elicit asbestos-like responses in mice (Poland, Duffin et al. 2008, Takagi, Hirose et al. 2008). In light of these results, it is important for producers and users of engineered nanomaterials (ENMs) to reduce employee exposure and manage risks appropriately. Many universities and research labs have developed specialized guides for working with nanomaterials in recent years (Hallock, Greenley et al. 2009).

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

control to reduce worker 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 handling and manipulation (Tsai, Ada et al. 2009). This research evaluated exposures related to the handling (i.e., scooping and pouring) of powder nanoalumina and nanosilver in a constant air volume (CAV) hood, a bypass hood, and a variable air volume (VAV) hood. The study showed that the conventional fume hood in which face velocity varies inversely with sash height allowed the release of significant amounts of nanoparticles during pouring and transferring activities involving nanoalumina. Many users have adopted the laboratory fume hood as the primary exposure control given its ubiquitous nature and history as a standard control used in most research laboratories. New lower flow hoods are being marketed and used for the manipulation of nanomaterials. The use of lower flows may reduce the impact of turbulence and the body wake on the potential for fume hood leakage. However, there is little information on their performance.

This study evaluated the performance of new nanomaterial handling enclosures which were installed in several laboratories throughout the institution. For the tests, students conducted their standard tasks which typically included scooping, weighing and pouring nanomaterials inside the enclosure. Real-time instrumentation was used to evaluate the potential for release of materials out of the enclosure. Data were collected at three laboratories across tasks which commonly included weighing and transfer of nanomaterials such as carbon nanotubes (CNTs), graphene, and neodymium oxide.

Methodology

Description of Evaluated Hoods and Tasks

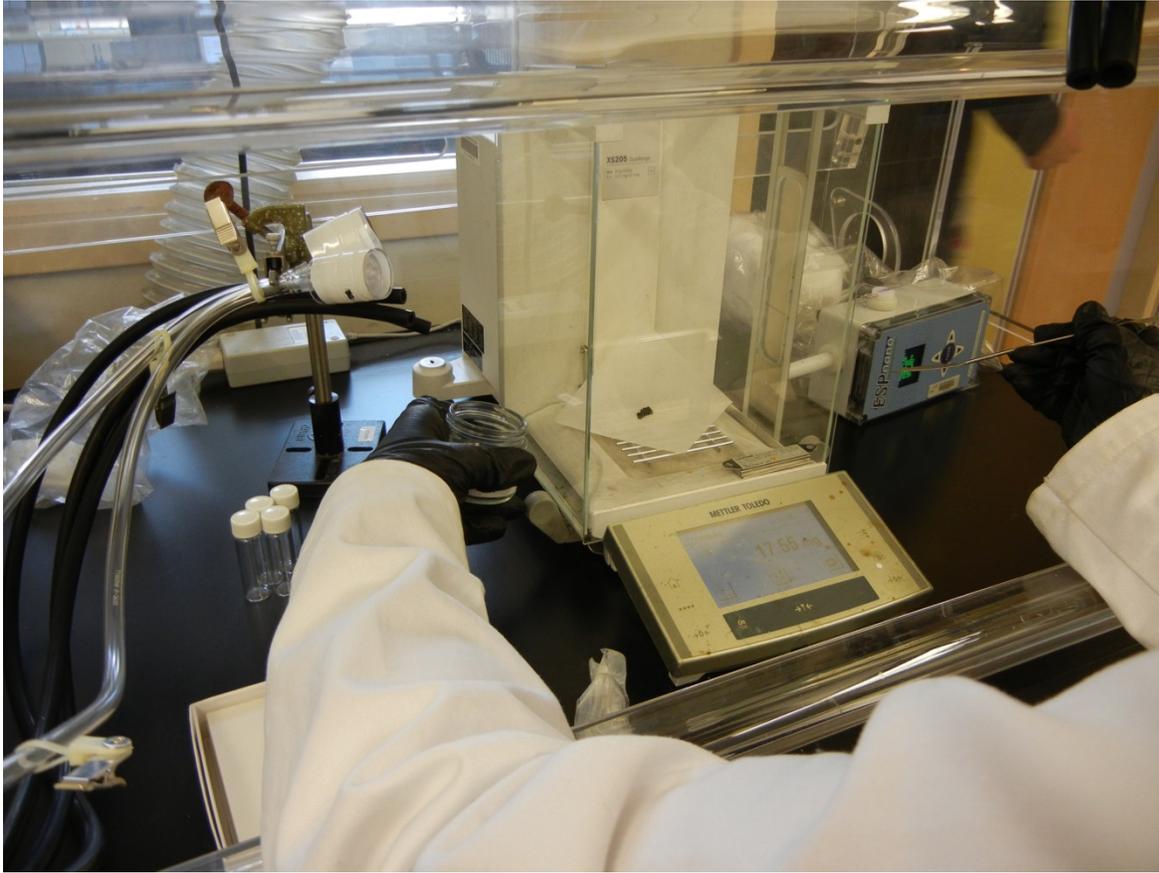
For each laboratory, the hood in use during the evaluation was a nanomaterial handling enclosure. These enclosures were originally designed to protect workers during handling of active pharmaceutical ingredients and to provide a low turbulence environment for the weighing of materials on microbalances.

Laboratory 1

The nanomaterial enclosure evaluated in this laboratory was the Pharmaceutical Containment Technologies (PCT) model 756000 Top Mounted Balance Enclosure System (Leland, NC). The enclosure evaluated in this study has interior dimensions of 51 centimeters (cm) (height) x 81 cm (width) with an internal working depth of 76 cm and a face opening of 25 cm (height) by 81 cm (width). It is constructed out of cast acrylic with a phenolic resin base. The enclosure includes a variety of features to reduce turbulence and improve containment performance. Molded airfoils are included at both side posts, at the base of the hood inlet, and along the bottom of the hood sash. The hood is exhausted through an integral high efficiency particulate air (HEPA) filter/fan unit which directs filtered exhaust to the laboratory.

During the evaluation, the student weighed out 20 mg of CNTs onto a sample paper and then transferred the material into a sample vial (Figure 1) inside the nanomaterial handling enclosure. This maneuver was completed 4 times during the evaluation.

Figure 1. Photo of balance and sampling equipment inside the enclosure located in Laboratory #1.

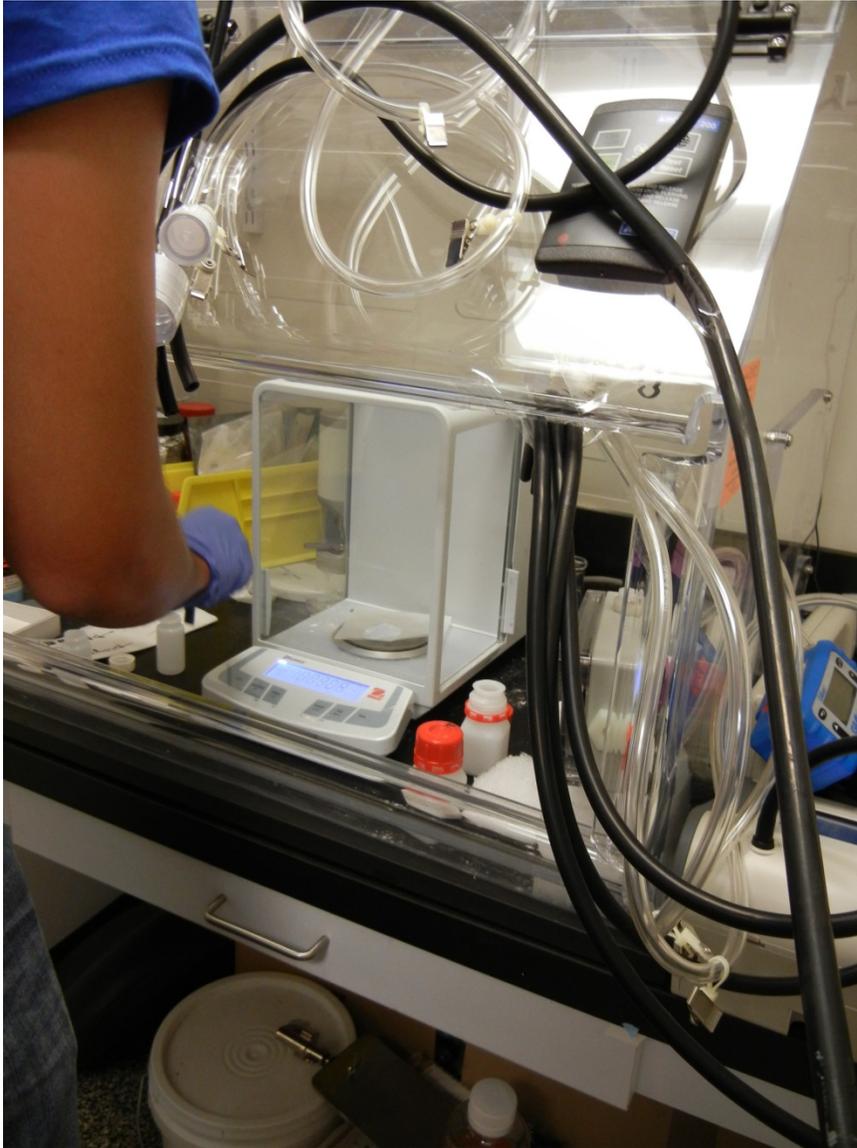


Laboratory 2

The enclosure evaluated in Laboratory 2 was identical to the unit in Laboratory 1 described above. During this evaluation, there were two primary tasks which were evaluated. The first was the weigh-out of 1.0 g of nanometer-scale neodymium (III) oxide (Nd_2O_3) powder and then transfer (by pouring) of that material into a small sample vial. The weigh-out process took approximately 4 minutes, and the pouring of the product into the sample vial took about 15-45 seconds. This task was repeated 4 times during the evaluation.

The second task was the weigh-out of a CNT carpet sample—a growth of CNTs mounted on a microchip. The CNTs were reportedly several nanometers in diameter. The researcher weighed out 10-20 samples during a typical run. However, only one CNT carpet sample was weighed out for this assessment. Each CNT carpet sample weighs approximately 1 mg. During this task, the researcher turned off the enclosure fan since it “blows the sample away.” Once the weigh-out task was complete, the researcher turned the containment blower back on.

Figure 2. Photo of balance and sampling equipment inside of the enclosure located in Laboratory #2.



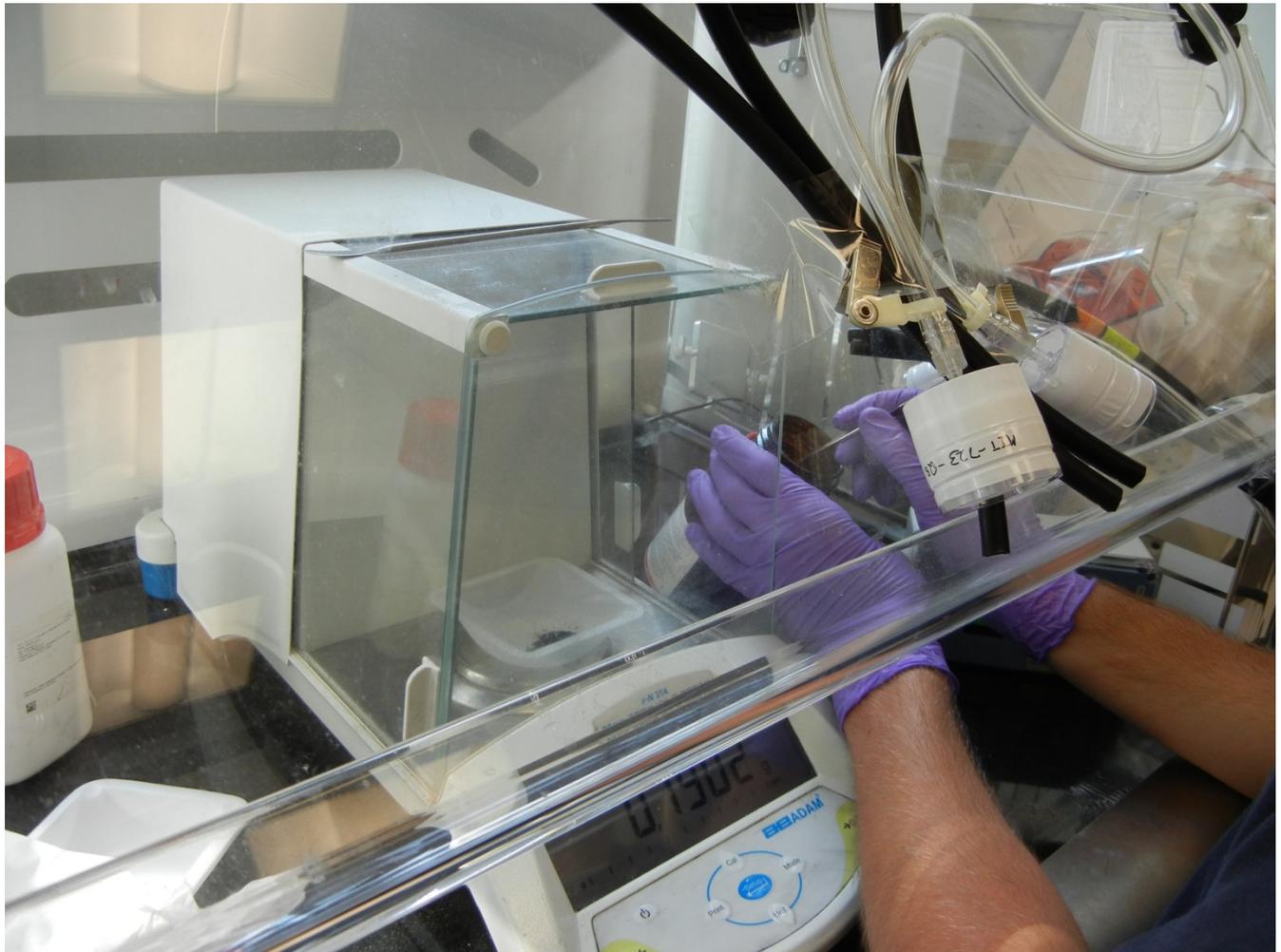
Laboratory 3

The nanomaterial handling enclosure evaluated in Laboratory 3 was the a1 safetech ST1 (Dusseldorf, Germany) Potent Powder Weighing Enclosure. The enclosure has dimensions of 61 cm (height) x 91 cm (width) with an internal working depth of 64 cm. Molded airfoils are included at both sideposts and along the bottom of the hood sash. In addition, a stainless steel airfoil is in place at the front sill of the hood. The unit has an airflow

alarm that provides the user with an indication of proper airflow into the hood using two sensors located along the bottom of the hood opening. The exhaust of the hood is routed through a HEPA/fan unit, which removes powders and filters the air prior to recirculation to the laboratory.

During this evaluation, there were four primary tasks which were evaluated. A mixture of sodium dodecyl sulfate (SDS) and either graphene platelets or CNTs (or both) were weighed out and then poured into deionized water. The CNTs were multi-walled with an outside diameter of 6-9 nm and a length of 9 μm . The graphene platelets were 6-8 nm thick and 5 μm wide. During Tasks #1 and #2, 800 mg of SDS were weighed out and added to the deionized water. Following that, 200 mg of CNTs were weighed out and added to the SDS/DI solution. There was an approximately 32 minute break (10:37-11:09 am) in Task #2 to address a low battery on an air sampler. Following the installation of new batteries, the task was re-started and completed. For Task #3, the same general tasks were performed, however, using 400 mg of graphene and 1600 mg of SDS. For Task #4, a graphene/CNT mixture was synthesized using 200 mg of graphene, 40 mg of CNTs and 1000 mg of SDS.

Figure 3. Photo of balance and sampling equipment inside the enclosure located in Laboratory #3.



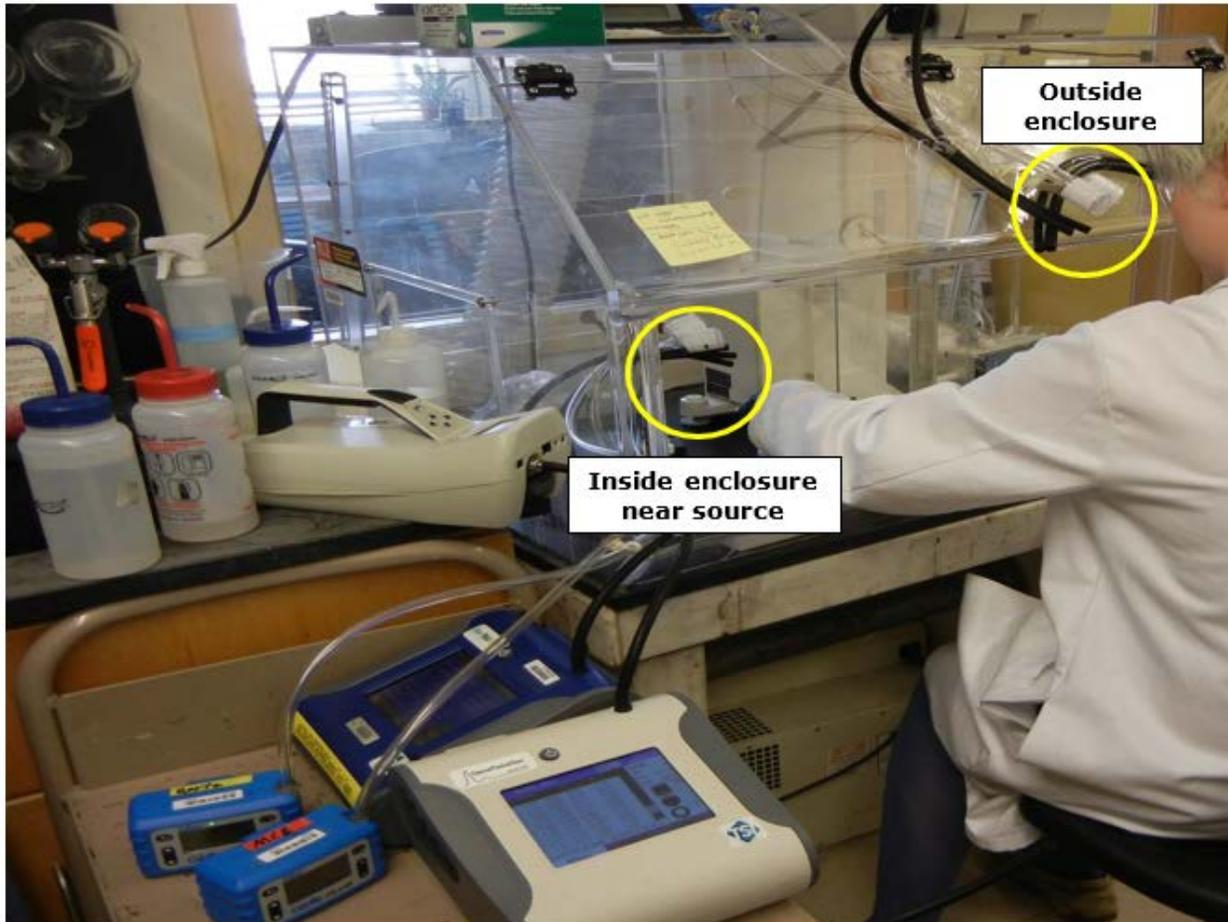
Ventilation measurements

Airflow measurements were used to characterize the inlet air velocity profile at the face of the nano enclosure. A traverse of the enclosure face was conducted with a hot wire anemometer to evaluate the spatial variation in air velocities entering the hood. The air velocity measurements were collected using a model 9555 multi-function ventilation meter outfitted with a hot wire transducer (TSI, Inc. Shoreview, MN) having a range of 0.15 to 50 meters per second (m/s), an accuracy of 3% of reading or 0.015 m/s and a response time of 200 milliseconds (ms). The velocity profile was measured at the mid-plane of the hood face opening at 5 points.

Air Sampling Methods

Direct-reading instruments were used in the survey to evaluate the effectiveness of enclosures (Brouwer, Gijssbers et al. 2004, Demou, Peter et al. 2008, Peters, Elzey et al. 2009). An array of air samples was taken both inside of the enclosures (near the source) and directly outside of the enclosures (see Figure 4). This approach helps assess the emissions from the process as well as the containment effectiveness of the enclosure. These instruments were operated in real-time mode to provide continuous measurements of concentrations for correlation with work processes. An evaluation of the efficiency of the integral HEPA filters which filter the enclosure exhaust air before recirculating it into the laboratories was also conducted. In addition, filter samples were collected to provide elemental and microscopy-based analyses to help differentiate process-related particles from background, ambient aerosols.

Figure 4. Photo of air sample locations and instrumentation set up both inside and outside of the nanomaterial handling enclosure.



Direct-reading, real-time instruments

Three direct-reading, real-time field-portable instruments were used to characterize process emissions by determining the number or mass concentration and approximate size ranges of airborne particles. The TSI model 3007 (TSI, Inc., Shoreview, MN) handheld condensation particle counter (CPC) counts airborne particles in the size range of 10 to 1,000 nm. The data are expressed as total number of particles per cubic centimeter (cc) of sampled air with an upper dynamic range limit of approximately 100,000 particles per cc of air (pt/cc). The CPC operates by drawing air into the instrument, passing it through a heated saturator filled with isopropyl alcohol, and then cooling the air stream via a condenser chamber. In the condenser chamber, particles serve as condensation nuclei and adsorb

alcohol vapor until each particle “grows” large enough to be detected. These larger particles then pass through an optical detector where they are counted.

The TSI model 8533 (TSI, Inc., Shoreview, MN) DustTrak DRX™ Aerosol Monitor simultaneously measures mass and size fraction of airborne particulate using laser light scattering. The sampled air passes through a chamber illuminated by a laser light. Light scattered by particles is measured at 90° using a solid state silicon photo detector. The intensity of the scattered light is a function of the particle mass concentration, the size distribution of the aerosol, and the composition of the aerosol drawn into the detector. This instrument can estimate mass concentrations between 0.001 and 150 mg/m³ for particles ranging from 100 to 10,000 nm. It displays mass fractions in the modes of PM₁, PM_{2.5}, respirable particulate matter, PM₁₀, and total mass concentration. Aerosol photometers provide estimates based upon assumed density and particle size distributions. However, detector sensitivity is lower for particles smaller than 250 nm diameter, and the instrument efficiency when measuring fiber-like aerosols is less than that obtained when sampling an aerosol composed of spherical particulate.

The TSI model 3091 (TSI, Inc., Shoreview, MN) Fast Mobility Particle Sizer (FMPS) was used to determine particle concentrations in sizes ranging from 5.6 to 560 nanometers (nm) in 32 equally spaced (log-scale) size channels with a resolution time of 1 second. The FMPS uses a corona charger to positively charge particles which strike an array of electrometers and transfer their charge. A particle with high electrical mobility strikes an electrometer near the top, whereas a particle with lower electrical mobility strikes an electrometer lower in the stack. Real-time measurement allows the determination of fluctuations of size/number distributions of released nanoparticles in the nano-manufacturing workplace. The FMPS has been previously used in field studies for exposure assessment (Bello, Wardle et al. 2009, Tsai, Ada et al. 2009).

Air filter samples—Microscopy and elemental analyses

In addition to the real-time monitoring, filter-based samples were collected on 25-mm diameter quartz fiber filters (QFF) and analyzed for the airborne mass concentration of elemental carbon (EC), a marker of exposure to CNTs

or graphene according to NMAM 5040 (NIOSH 1994). Task-based area samples for EC were collected using an open-faced, 25-mm diameter cassette with a GilAir Plus pump (Sensidyne, St. Petersburg, FL) set at approximately 4 liters per minute (lpm) in order to estimate the inhalable size fraction. Inhalable particles are less than about 100,000 nm in size and when these particles are breathed in, they can deposit in the nose, mouth, windpipe (trachea), and the upper portions of the lung.

Area samples were collected on 25-mm mixed cellulose ester filters (0.8 μm pore size) for analysis by transmission electron microscopy (TEM) using a JEOL 2100F and a modified NMAM 7402, Asbestos by TEM (NIOSH 1994). These modifications to NMAM 7402 primarily consisted of eliminating all steps necessary to positively identify asbestos. Three, 3-mm copper TEM grids from each collected sample (filter) were examined at low magnification to determine the loading and preparation quality. Multiple grid openings from each TEM grid were then examined. Samples collected in Laboratory 2 were also analyzed using electron energy-loss (EELS) spectra and energy-dispersive X-ray spectroscopy (EDS) to identify the presence of other elements such as Nd_2O_3 which was handled in that lab enclosure. Samples in Laboratory 3 were analyzed using EELS to identify graphene which was used in the enclosure being evaluated.

GilAir Plus pumps (Sensidyne, St. Petersburg, FL) operating at 4 lpm were used to collect the TEM samples. Air samples analyzed by TEM were collected to provide visual evidence of airborne CNTs as well as providing an indication of the structure of the particles collected, which included general size, shape and degree of agglomeration. All "structures" containing CNTs, which may possibly range from single CNTs to large agglomerates, were counted, with no size or shape restrictions.

Air filter samples were also collected in the Laboratory 2 for neodymium oxide and analyzed in accordance with NIOSH Method 7302 (NIOSH 1994). Quartz filters were used for this sample set since they were available based on plans for measuring carbonaceous nanomaterials. The quartz filters were not digested during the sample preparation. Using NMAM 7302, Nd_2O_3 bulk and Nd spikes on quartz filters were quantitatively recovered.

Results

Hood Face Velocity Testing

Ventilation measurements were taken at the face of each nanomaterial handling enclosure. The face velocities are shown in Table 1 and consist of 5 measurements across the face of each hood (from left to right).

Table 1. Hood face velocity traverse measurements for enclosures in each laboratory.

Hood/Lab	Face Velocity (meters/second)					
	1	2	3	4	5	Average
Laboratory 1	0.28	0.23	0.18	0.15	0.20	0.21
Laboratory 2	0.33	0.33	0.36	0.31	0.36	0.34
Laboratory 3	0.38	0.30	0.30	0.43	0.36	0.36

Air sample Results

Direct-reading, real-time instruments

Laboratory 1

The real-time data from the CPC, DustTrak, and FMPS are shown in Figures 5, 6 and 7, respectively. From the CPC data (Figure 5), it can be seen that the smallest particulate (100-1000 nm) concentrations are generally consistent with background levels seen in the ambient environment. Also, the concentrations measured inside the enclosure near the source are slightly lower than those measured outside of the enclosure with the background laboratory concentration (approximately 3-4.6 meter from the enclosure) being the highest. This may represent a source in the lab not associated with the tasks being evaluated or changes in outdoor environmental levels that infiltrate into the lab space.

For the larger particles, measured by the optical photometer (DustTrak), the concentrations during the weigh-out of CNTs were very low with no tasks showing a marked increase in concentration either inside or outside of the enclosure (Figure 6). There were two instantaneous peaks measured

between tasks likely associated with operations from other research being conducted in the lab.

Finally, a check of the ultrafine particle concentrations at the HEPA filtered exhaust on the enclosure showed excellent filtration in the 0-100 nm range with an increase in output of particles in the 100-400 nm range (Figure 7). This result is unexpected and should be further investigated. Overall, the concentrations in this range are low but should be near zero for a HEPA filter that is installed and functioning properly. It's possible that a poorly fitted HEPA filter, a pin-hole leak, or entrainment of ambient particles to the sampler could result in the reduced collection efficiency seen in the 100-300 um range. However, over the full range of FMPS measurement sizes (5-560 nm), the total filter efficiency (on a particle concentration basis) was 88%. NOTE: A follow-up survey of the HEPA outlet for the ventilated enclosure was conducted using a CPC. The Lab background concentration was about 9000 p/cc with HEPA exhaust concentrations between 1-4 p/cc.

Figure 5. Laboratory #1 fine and ultrafine particle concentration measurements collected by the CPC. The concentrations represent real-time measurements of particles from 10-1,000 nm in size.

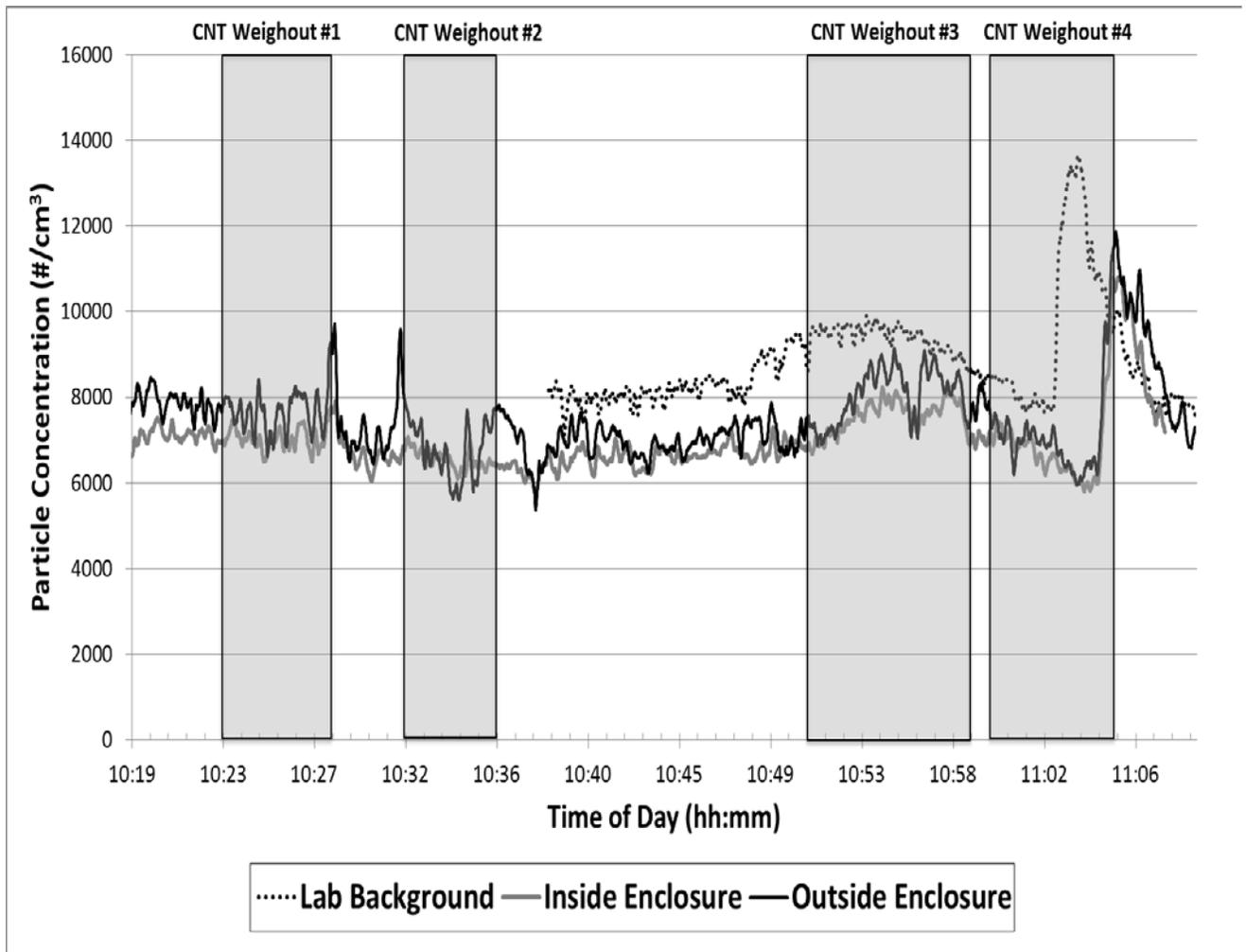


Figure 6. Laboratory #1 mass concentration measurements collected by the Dustrak. The concentrations represent real-time measurements of particles from 100-10,000 nm in size.

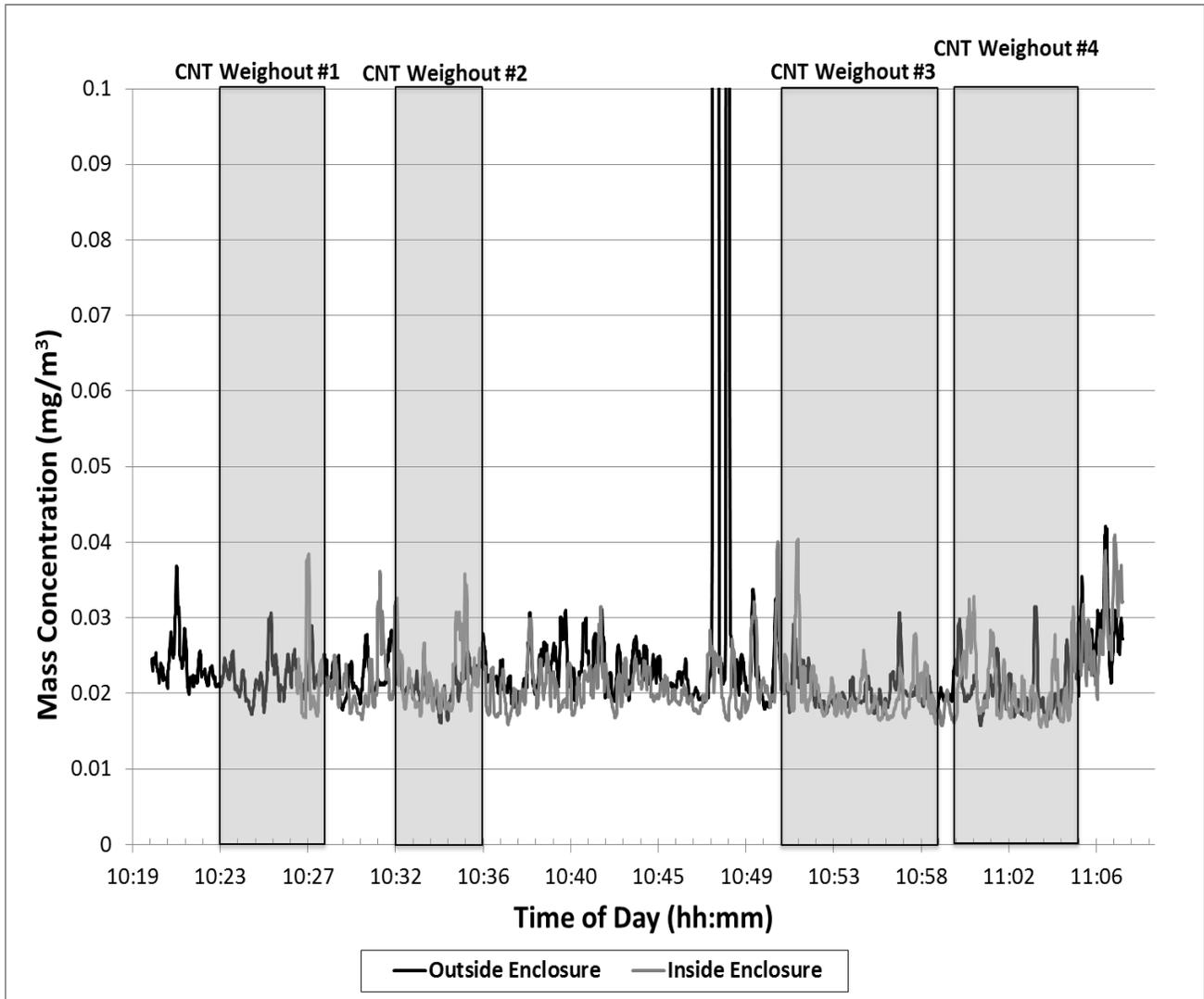
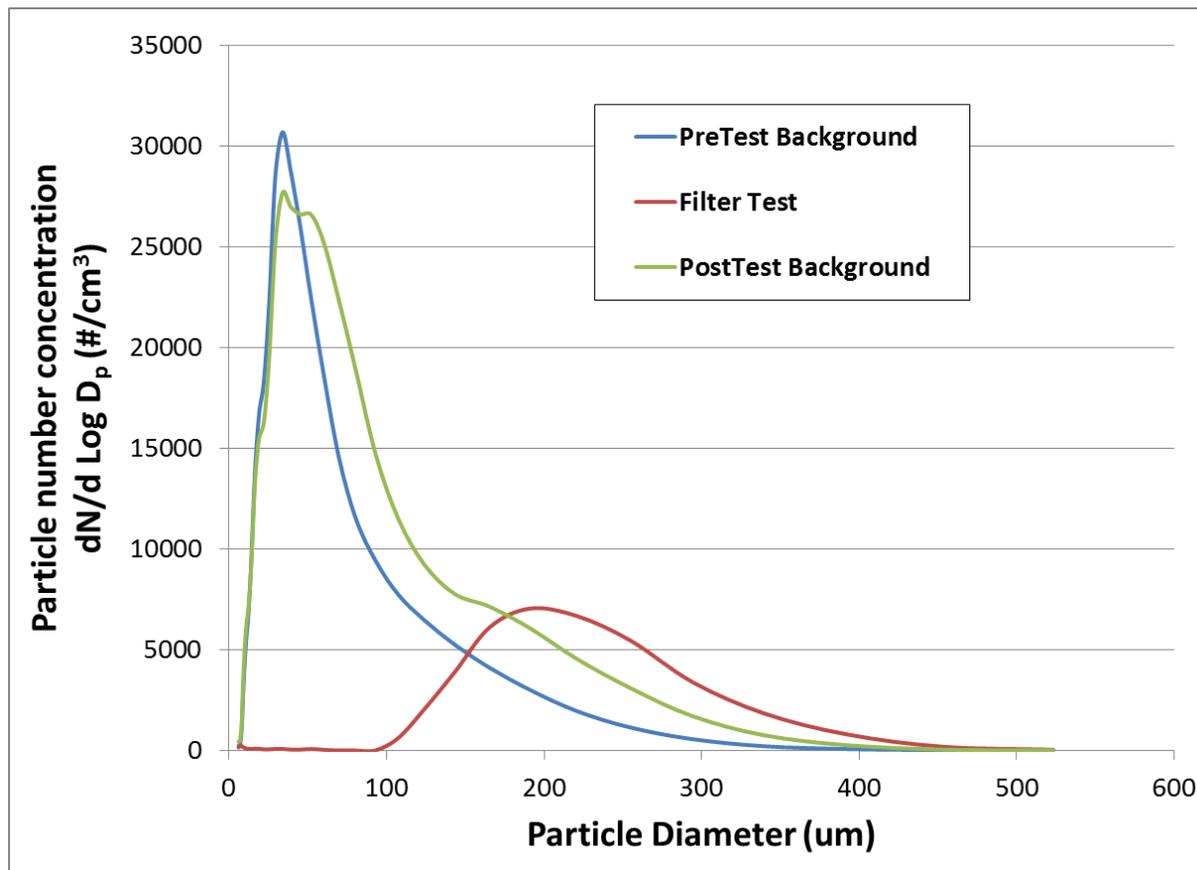


Figure 7. Laboratory #1 normalized particle size distribution during check of enclosure HEPA filter exhaust.



Laboratory 2

The real-time data from the CPC, DustTrak, and FMPS are shown in Figures 8, 9, 10 and 11. The CPC data (Figure 8) showed a decreasing trend throughout the evaluation consistent with levels in the laboratory background. Overall, the ultrafine particle concentrations in the lab were low compared with typical levels seen in the ambient environment likely due to effective filtration on the room air flows. As seen in Laboratory 1, the levels inside the enclosure were lower than those directly outside the enclosure with the highest levels seen in the lab background away from the enclosure; although all levels were similar and within reasonable levels of temporal and spatial variability.

For the larger particles, as measured by the DustTrak optical photometer (Figure 9), the concentrations measured during the weigh-out of neodymium oxide and the CNT carpet samples were very low with no tasks showing a marked increase in concentration either inside or outside of the enclosure. The concentrations measured inside and outside of the enclosure were similar with a few transient excursions occurring outside the enclosure at times when no tasks were being evaluated within the enclosure.

Finally, the ultrafine particle concentrations measured by the FMPS mirror those of the CPC (which cover similar ranges of particle sizes) and showed a general decrease in concentrations throughout the period of evaluation (Figure 10). The particle size distribution was similar in all phases of the evaluation and showed a decreasing trend in concentrations as seen in the real-time plot (Figure 11). Likewise, a check of ultrafine particle emissions at the HEPA filtered exhaust on the enclosure showed excellent filtration in the 0-100 um range and a noticeable increase in output of particles in the 100-300 um range. This particle size range is referred to as the most penetrating particle size since the two dominant filtration mechanisms (diffusion and interception) are less efficient in this range. However, HEPA filters should have an efficiency of greater than 99% in this range; so this result is unexpected. It's possible that a poorly fitted HEPA filter or pin-hole leak could result in the reduced collection efficiency seen in the 100-300 um range. Over the full range of measurement sizes (5-560 nm), the total filter efficiency (on a particle concentration basis) was 90%. NOTE: A follow-up survey of the HEPA outlet for the ventilated enclosure was conducted using a CPC. The Lab background concentration ranged between 1300-1400 p/cc with HEPA exhaust concentrations of 0-2 p/cc.

Figure 8. Laboratory #2 fine and ultrafine particle concentration measurements collected by the CPC. The concentrations represent real-time measurements of particles from 10-1000 nm in size.

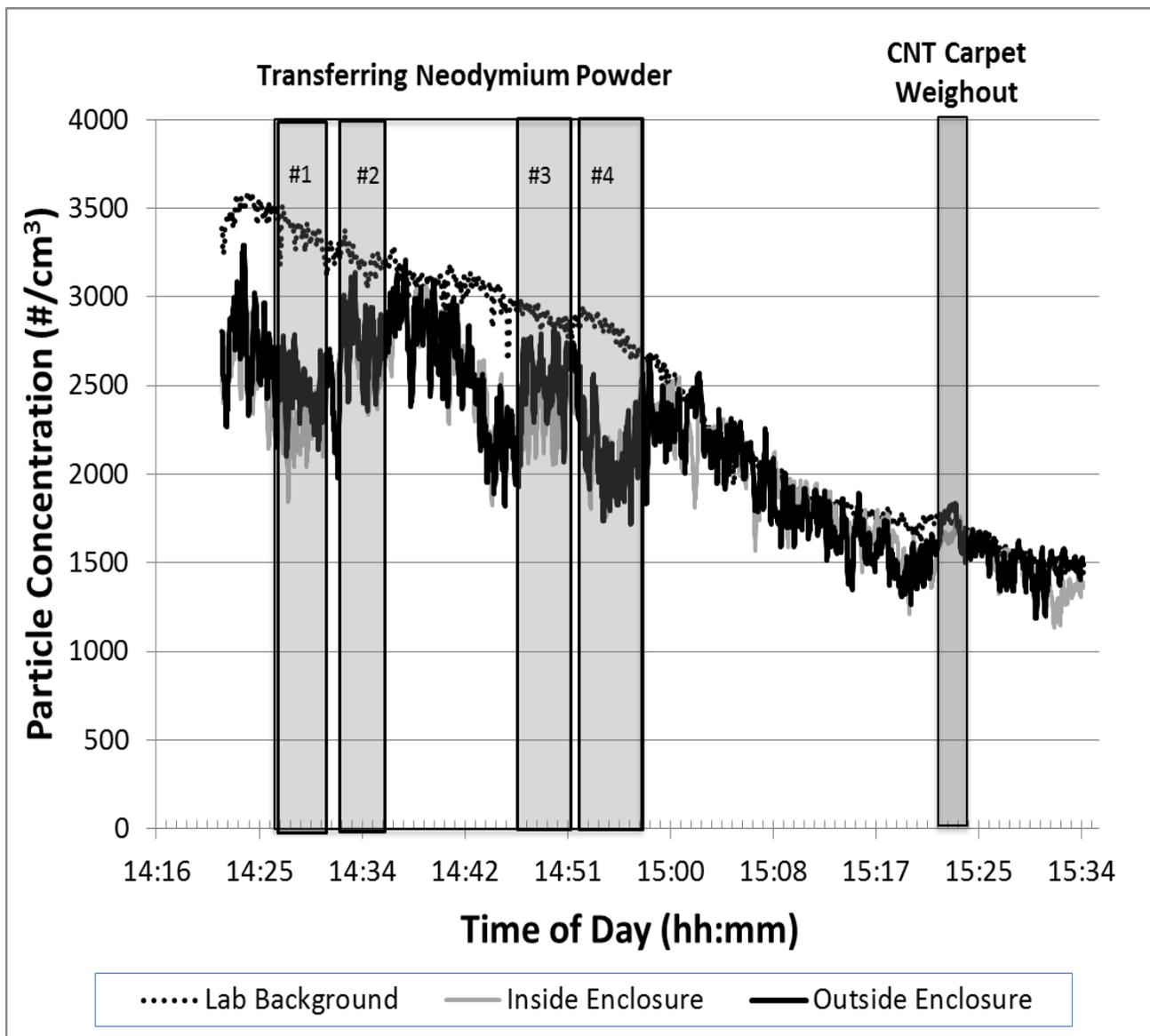


Figure 9. Laboratory #2 mass concentration measurements collected by the Dustrak. The concentrations represent real-time measurements of particles from 300-10,000 nm in size.

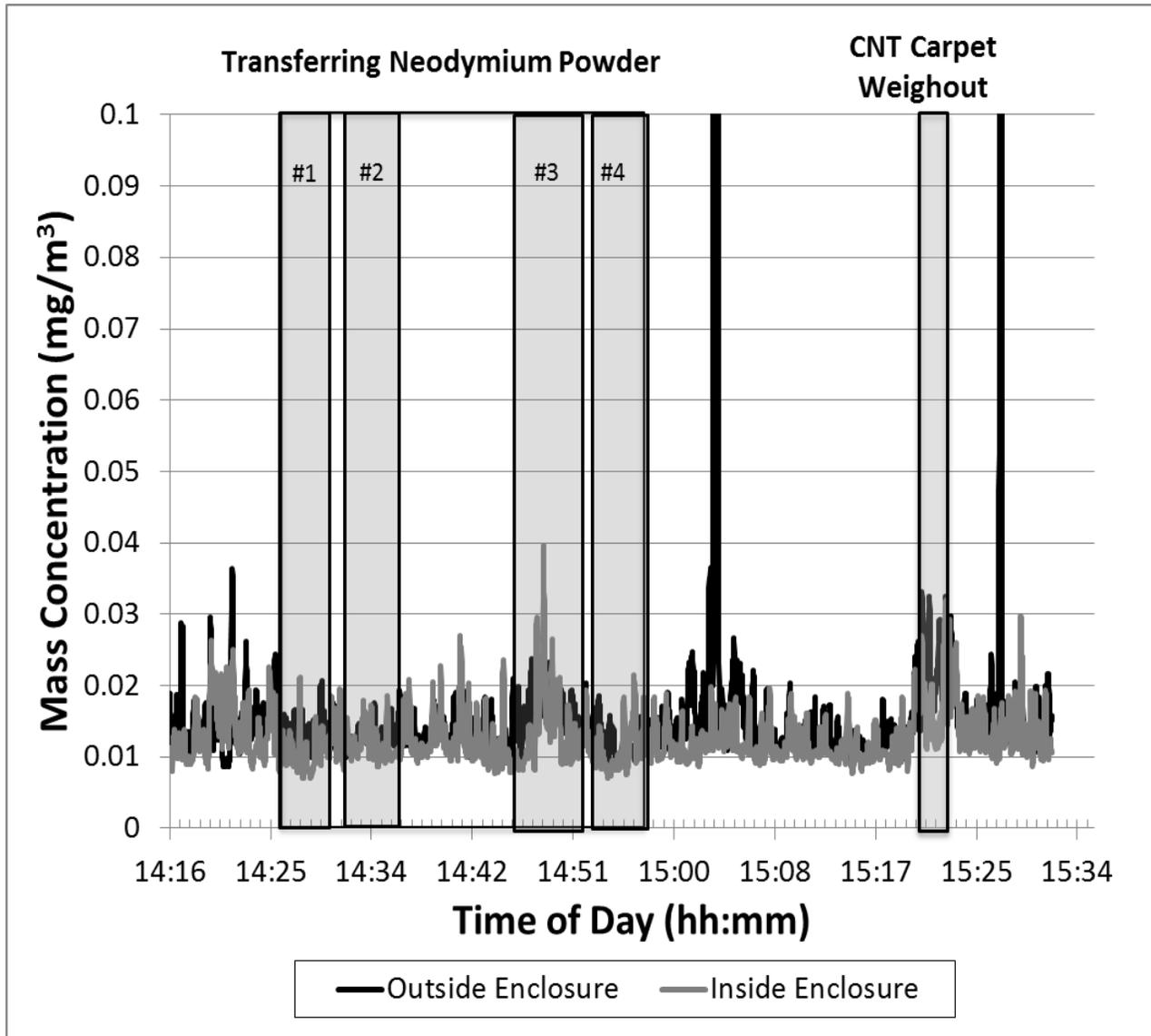


Figure 10. Laboratory # 2 particle concentration measurements collected by the FMPS. The concentrations represent real-time measurements of particles from 5-560 nm in size.

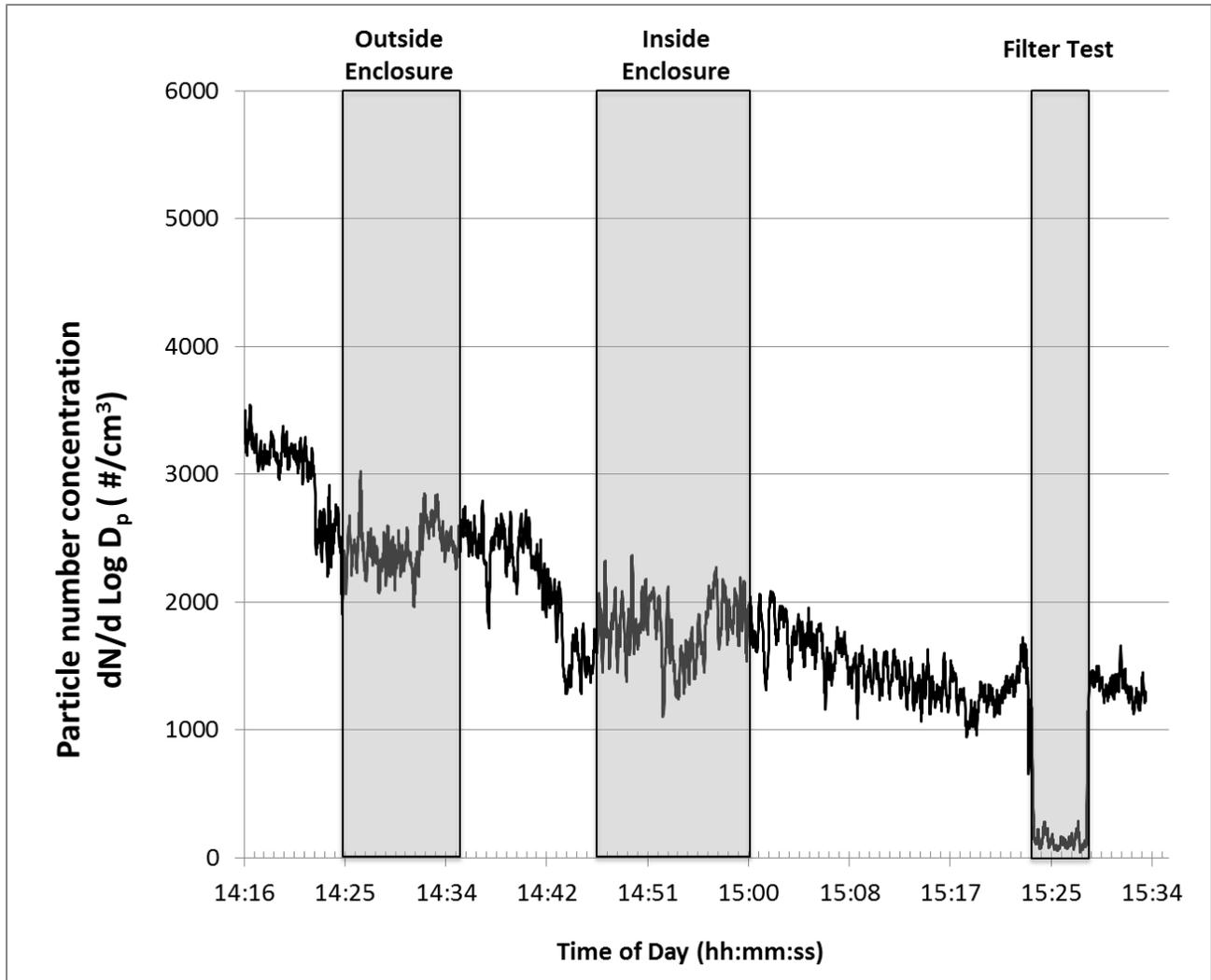
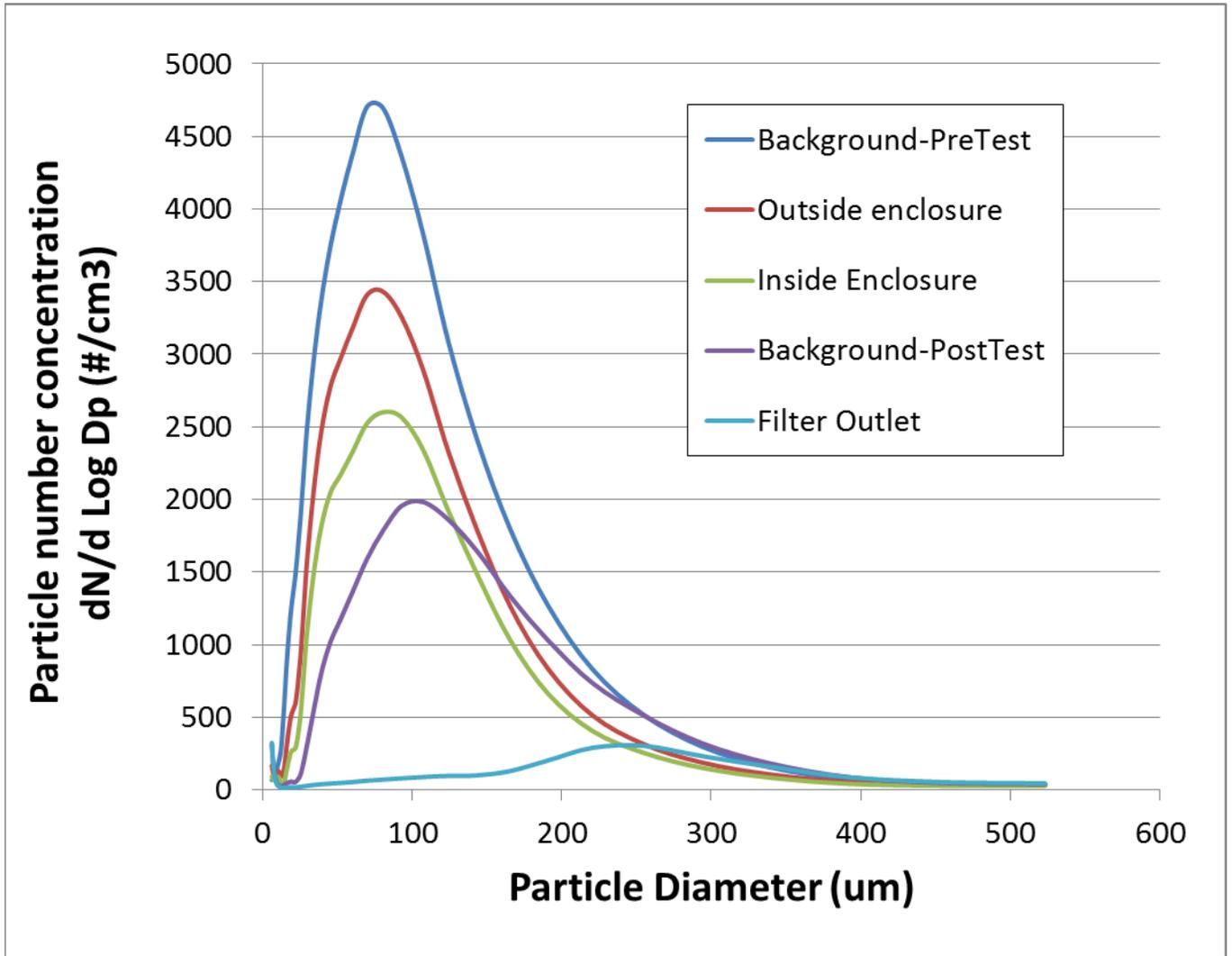


Figure 11. Laboratory #2 normalized particle size distribution during the weigh-out of powders and check of enclosure HEPA filtered exhaust.



Laboratory 3

The real-time data from the CPC, DustTrak, and FMPS are shown in Figures 12, 13, 14 and 15, respectively. The CPC data (Figure 12) showed a consistent concentration between 1200 and 1600 particles/cm³ throughout the evaluation period. The CPC located inside the enclosure was not logging during the initial tasks. However, once started, the concentrations followed those of the CPC located just outside the enclosure and were lower, consistent with results from the other laboratories. Overall, the ultrafine particle concentrations in the lab were very low compared with typical levels seen in the ambient environment likely due to effective filtration on the room

air flows. No correlation of increases in concentrations was noted based on the tasks being performed inside the enclosure.

For the larger particles, as measured by the DustTrak optical photometer (Figure 13), the total particulate concentrations measured during the weigh-out of sodium dodecyl sulfate (SDS), CNTs and graphene were very low with only one task showing a marked increase in concentration either inside or outside of the enclosure. In the graphene weigh-out task, a small transient concentration increase occurred which might have been due to a noted spill of SDS powder by the operator (Figure 13). Overall, the concentrations measured inside the enclosure were slightly higher than outside, however, within reasonable limits of variability.

Finally, the FMPS showed a dramatic increase in particle concentrations associated between the first and second CNT weigh-out tasks (Figure 14). The FMPS indicated particle concentrations much higher than the CPC with measurements above 30,000 pt/cc at times during the evaluation. However, an error was recorded by the FMPS during this evaluation which makes the validity of the data collected uncertain. When evaluating the data from all but the second CNT weigh-out task, the size distributions and concentrations from the other weigh-out procedures are fairly consistent in size and similar to background levels (Figure 15). NOTE: A follow-up survey of the HEPA outlet for the ventilated enclosure was conducted using a CPC. The Lab background concentration was about 1100 p/cc with the HEPA exhaust concentration ranging between 1-2 p/cc.

Figure 12. Laboratory #3 fine and ultrafine particle concentration measurements collected by the CPC. The concentrations represent real-time measurements of particles from 10-1000 nm in size.

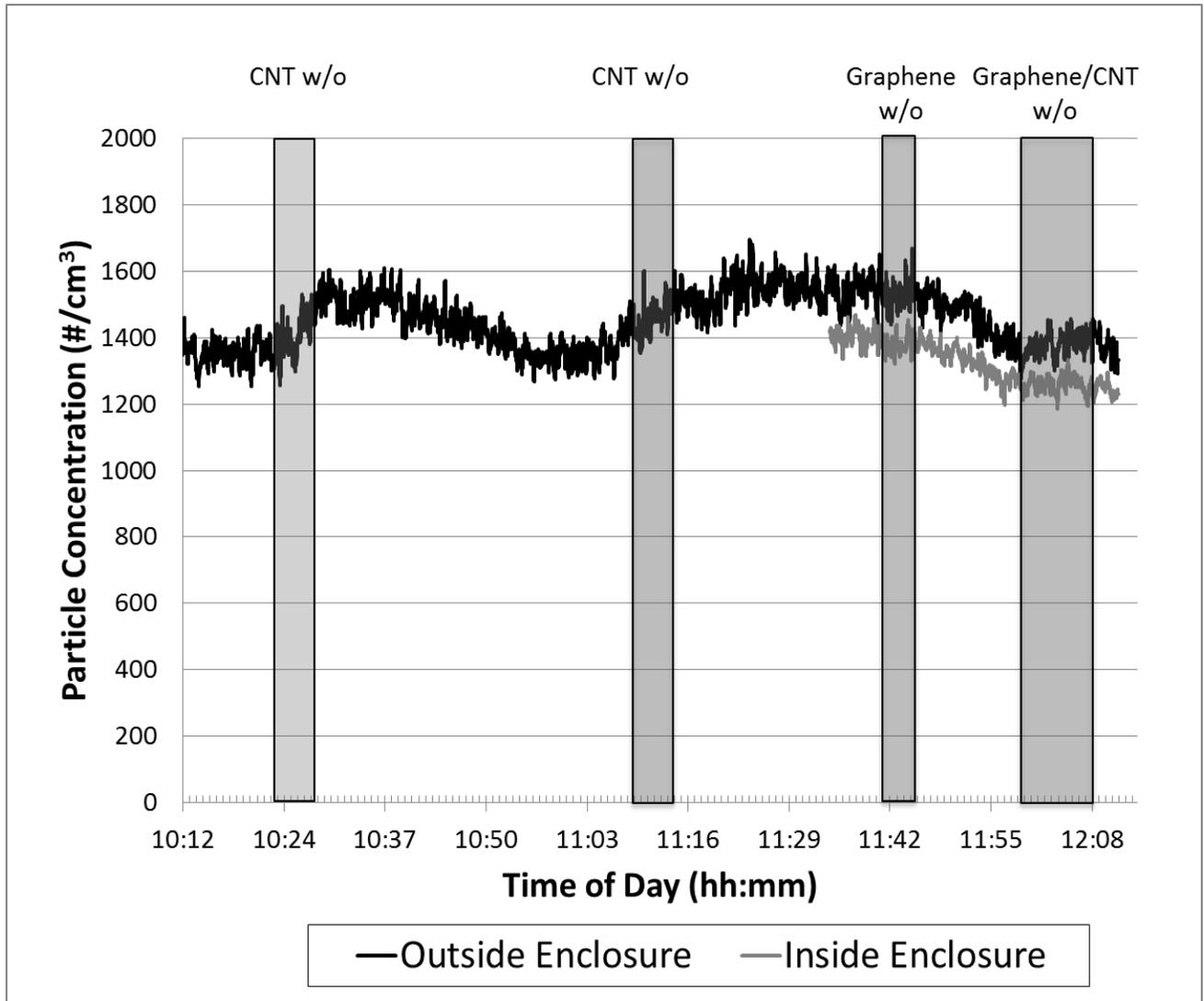


Figure 13. Laboratory #3 mass concentration measurements collected by the Dustrak. The concentrations represent real-time measurements of particles from 300-10,000 nm in size.

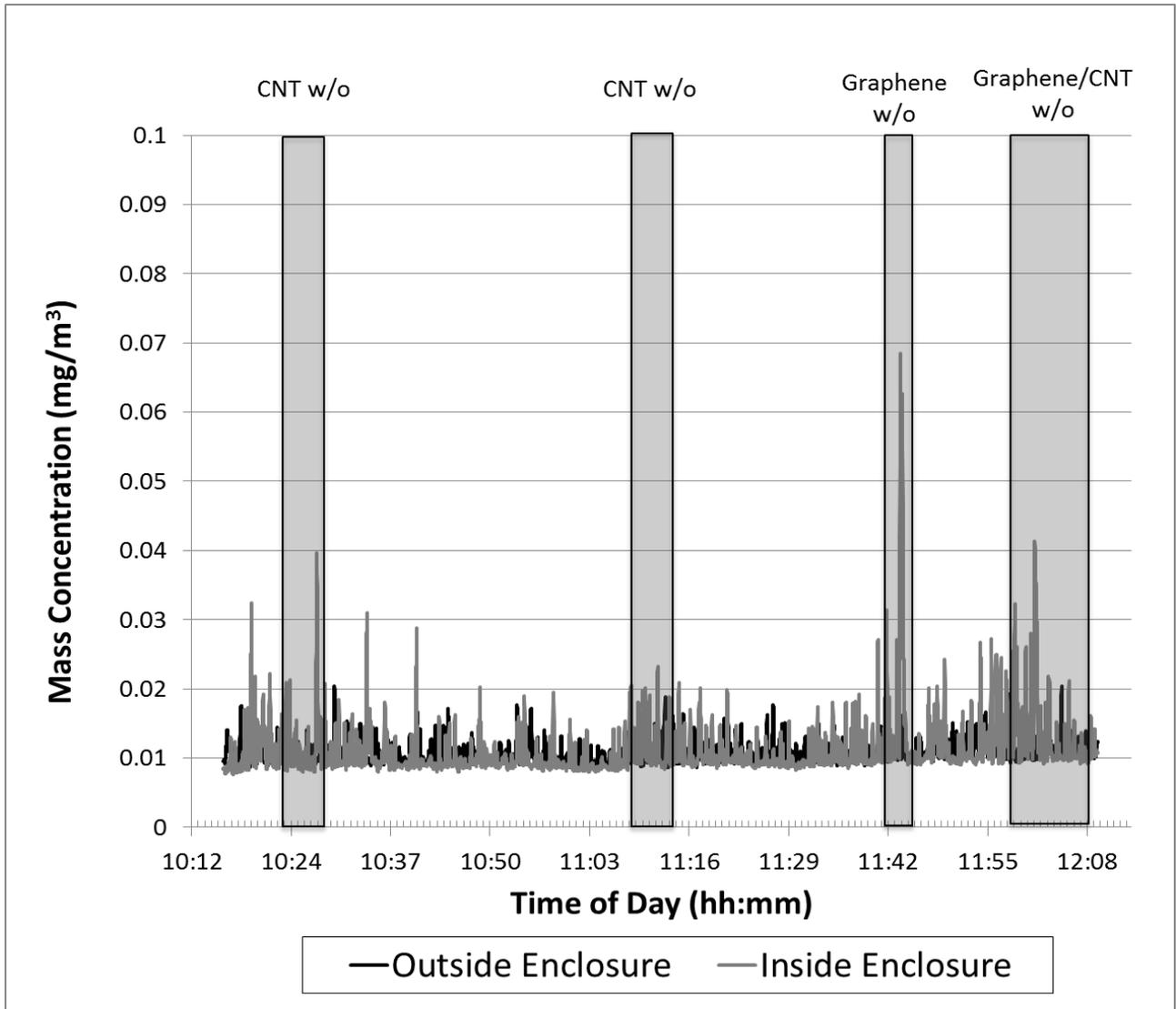


Figure 14. Laboratory #3 particle concentration measurements collected by the FMPS. The concentrations represent real-time measurements of particles from 5-560 nm in size.

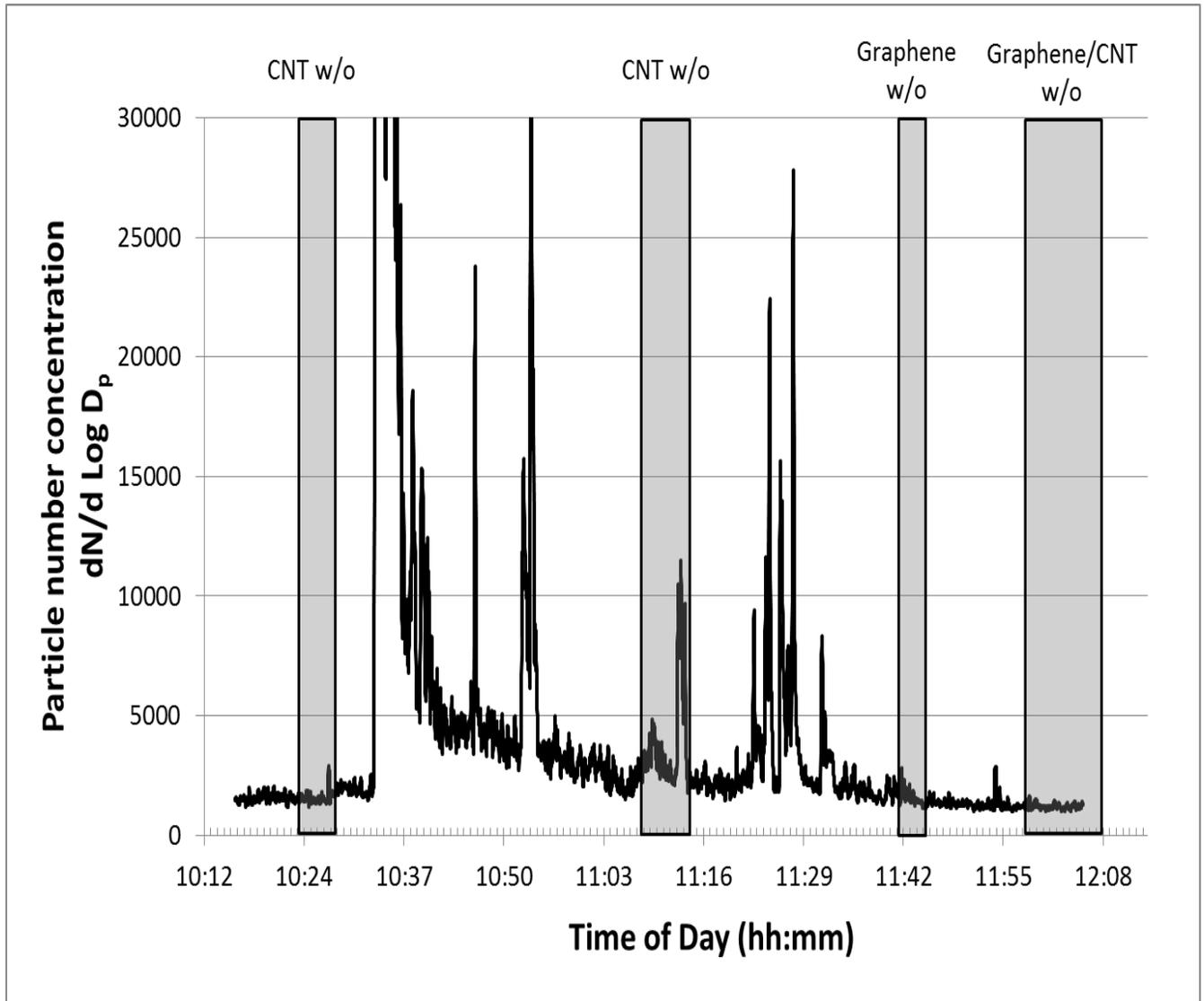
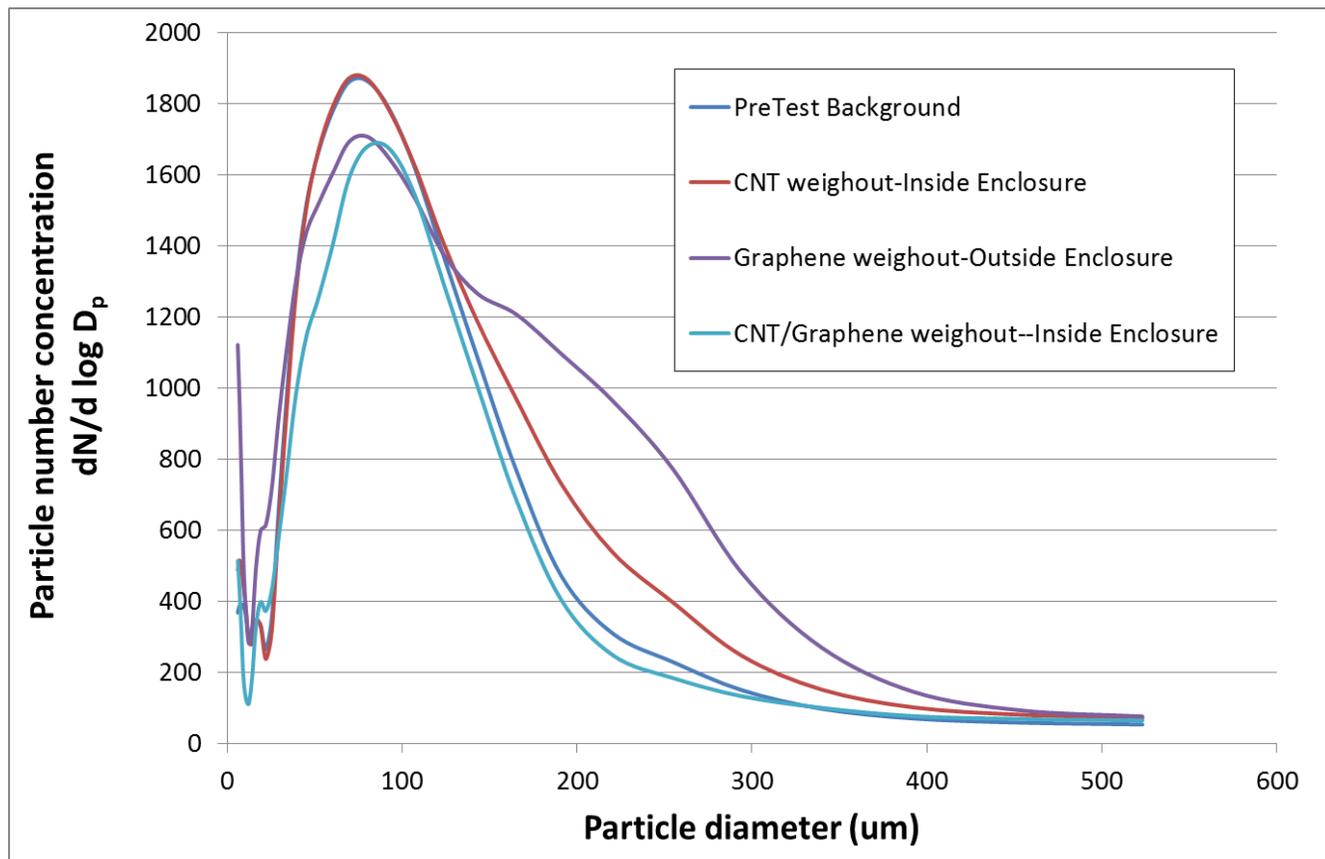


Figure 15. Laboratory #3 normalized particle size distribution during weigh-out of powders and check of enclosure HEPA filtered exhaust.



Air filter samples—microscopy and elemental analyses

The results of the EC analyses from the task-based air filter samples are shown in Table 2. The limits of detection and quantitation were 1 and 3.4 $\mu\text{g}/\text{sample}$, respectively. Only two of the samples collected were above the limit of detection (LOD). But both of these samples were between the LOD and the limit of quantitation (LOQ). The first sample was collected outside of the enclosure inside Laboratory 1 during the weigh-out of CNTs while the second was collected inside the enclosure during the weigh-out of CNTs in the Laboratory 3. Because the uncertainty in exact exposure concentrations between the LOD and LOQ is higher than for samples above the LOQ, there may be a positive or negative bias in these results that may limit the usefulness and generalizability of the data. Also, note that the concentrations are for total EC not respirable EC.

Table 2. Elemental carbon air filter sample results. Note: LOD = 1 µg and LOQ = 3.4 µg for these samples. The samples have been media blank corrected.

Sample number	Location	EC mass (ug)	Sample Time (min)	Sample Volume (l)	EC air concentration (ug/m ³)	Notes
722-Q1	Laboratory 1- Inside enclosure	<LOD	73	292	<LOD	Collected during the weigh-out of CNTs
722-Q2	Laboratory 1- Outside enclosure	1.7	73	292	5.8	Collected during the weigh-out of CNTs
722-Q5	Laboratory 2- Inside enclosure	<LOD	22	89	<LOD	Collected during the weigh-out of CNT carpet sample
722-Q6	Laboratory 2- Outside enclosure	<LOD	19	78	<LOD	Collected during the weigh-out of CNT carpet sample
723-Q7	Laboratory 3- Inside enclosure	1.6	80	322	5.0	Collected during the weigh-out of CNTs
723-Q8	Laboratory 3- Outside enclosure	<LOD	84	339	<LOD	Collected during the weigh-out of CNTs
723-Q9	Laboratory 3- Outside enclosure	<LOD	45	183	<LOD	Collected during the weigh-out of graphene/CNTs
723-Q10	Laboratory 3- Inside enclosure	<LOD	48	196	<LOD	Collected during the weigh-out of graphene/CNTs

Air filter samples collected both inside and outside of the enclosure in Laboratory 2 for *neodymium oxide* were below the limits of detection. The limits of detection and quantitation for neodymium oxide were 0.74 and 2.47 µg/sample, respectively. These samples were collected during the weigh-out of 4g of neodymium oxide powder conducted in four successive 1g weigh-out procedures.

The results of the TEM analyses from the task-based air filter samples are shown in Tables 3 and 4. Table 3 lists the CNT structure concentrations for each sample. Since the samples collected for EC were generally below the sensitivity of the method, the samples analyzed by electron microscopy

provide an increased capability of detecting CNTs. Example TEM images from several filters are shown in Figures 16-21. Overall, the loading on the filters was light but CNT structures were identified on all filter samples except 723-M10 taken inside the enclosure in Laboratory 3 when weighing graphene. The TEM results indicate that the highest exposure potential came during the weigh-out of the CNT carpet samples in Laboratory 2 with the concentration outside of the hood being slightly higher than that inside the hood (0.337 versus 0.262 CNT Structures/cm³).

Table 4 displays the longest measured dimension of each CNT structure by air sample, which was analyzed using TEM. Two-dimensions were measured from the semi-spherical agglomerates and averaged to give an approximate diameter for each CNT structure. A majority of CNTs were seen as individual tubes with lengths less than 1 μm . CNT materials were also detected in clusters (Fig. 16, 17, 19, and 21) as agglomerates and matrix particles which were mostly seen in the size bins of 2-5 μm and 5-10 μm . In addition, an agglomerated TiO₂ nanoparticle was identified on 722-m3, which was located inside the ventilated enclosure in Laboratory #2 during the weigh-out of Nd₂O₃ (see Figure 20).

Table 3. TEM air filter sample results.

Sample ID	Laboratory	Sample Location/Material Handled	Air Volume (l)	CNT Containing Structures/cm ³
722-m1	1	Inside of enclosure/CNT	281	0.032
722-m2	1	Outside of enclosure/CNT	294	0.011
722-m3	2	Inside of enclosure/neodymium	177	0.006
722-m4	2	Outside of enclosure/neodymium	164	0.014
722-m5	2	Inside of enclosure/CNT carpet	89	0.262
722-m6	2	Outside of enclosure/CNT carpet	76	0.337
723-m7	3	Inside of enclosure/CNT	328	0.024
723-m8	3	Outside of enclosure/CNT	344	0.013
723-m9	3	Outside of enclosure/graphene	183	0.018
723-m10	3	Inside of enclosure/graphene	196	0

Table 4. CNT structures by longest measured dimension.

Sample ID	Process	Individual			
		CNT	< 1um	1-2 um	2-5 um
722-m1	Inside of enclosure/CNT (Lab 1)	1	5	2	1
722-m2	Outside of enclosure/CNT (Lab 1)	3	3	0	0
722-m3	Inside of enclosure/neodymium (Lab 2)	1	1	0	0
722-m4	Outside of enclosure/neodymium (Lab 2)	1	2	0	0
722-m5	Inside of enclosure/CNT carpet (Lab 2)	9	17	3	1
722-m6	Outside of enclosure/CNT carpet (Lab 2)	19	23	0	0
723-m7	Inside of enclosure/CNT (Lab 3)	3	7	0	0
723-m8	Outside of enclosure/CNT (Lab 3)	4	4	0	0
723-m9	Outside of enclosure/graphene (Lab 3)	0	1	1	1
723-m10	Inside of enclosure/graphene (Lab 3)	0	0	0	0

Figure 16. CNT cluster from sample 722-m1.

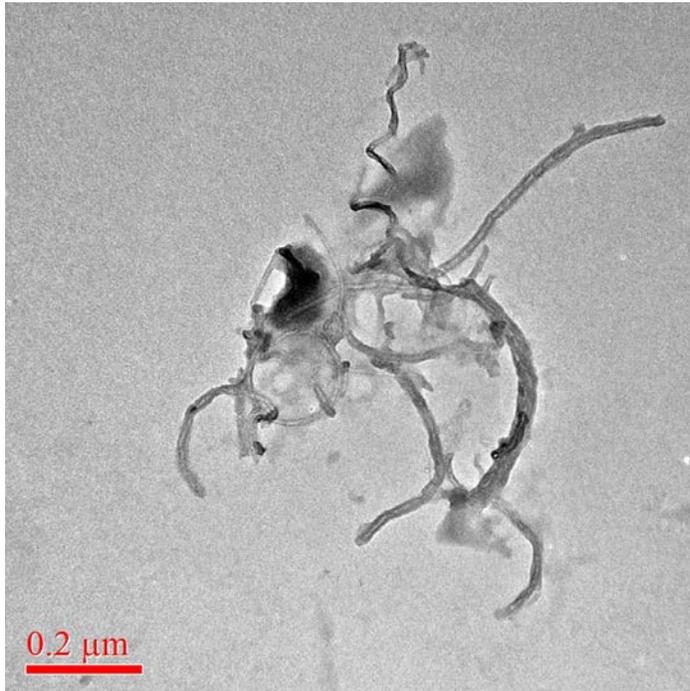


Figure 17. Individual CNT fiber from sample 722-m1.

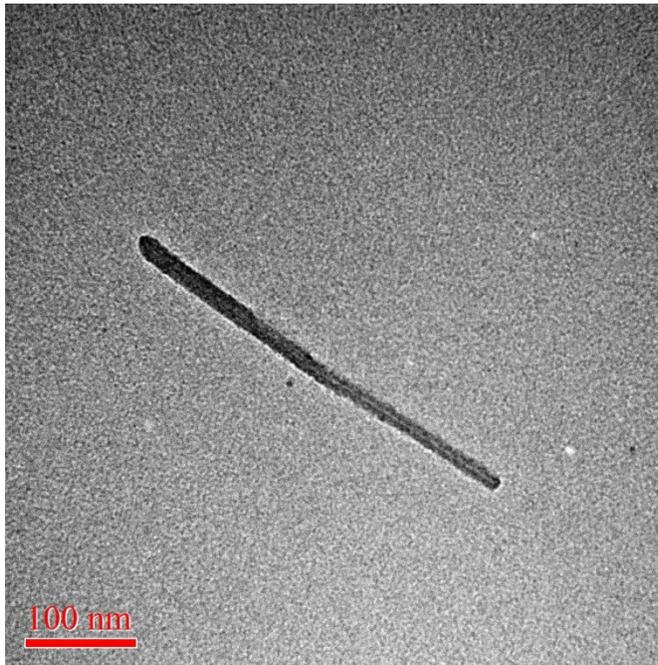


Figure 18. Agglomerated TiO₂ nanoparticle from 722-m3.

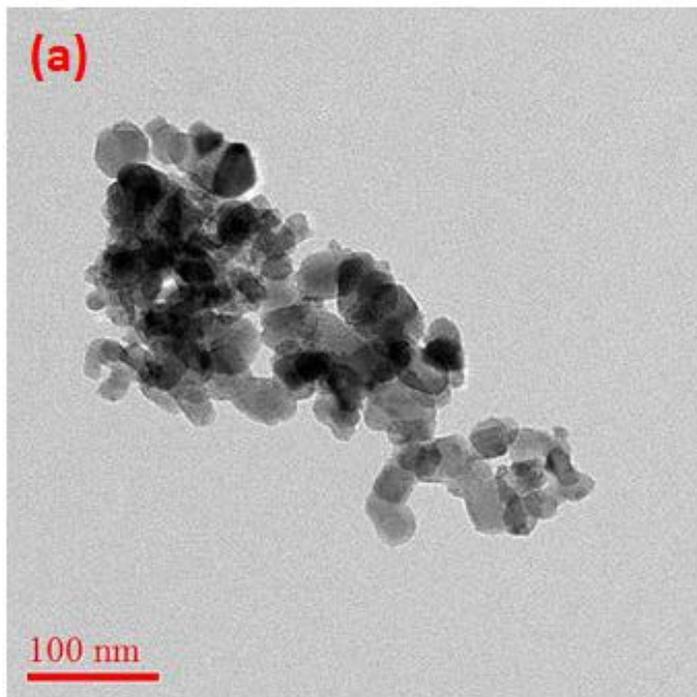


Figure 19. CNT matrix structure from sample 722-m5.

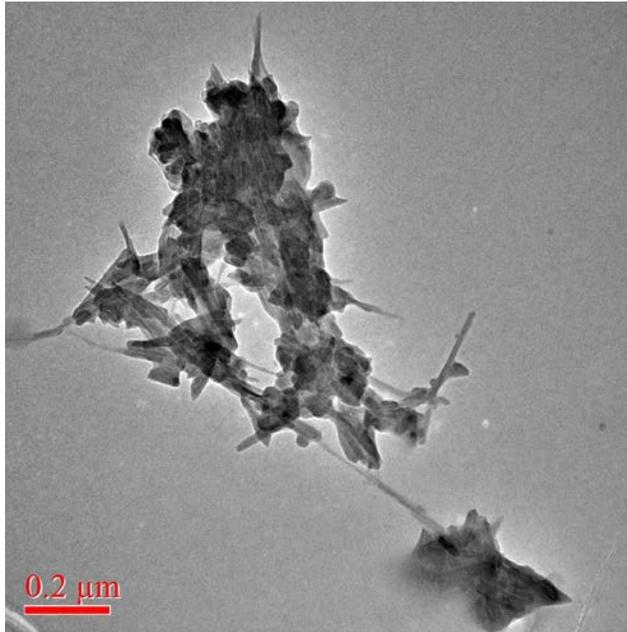


Figure 20. CNT bundle from sample 723-m7.

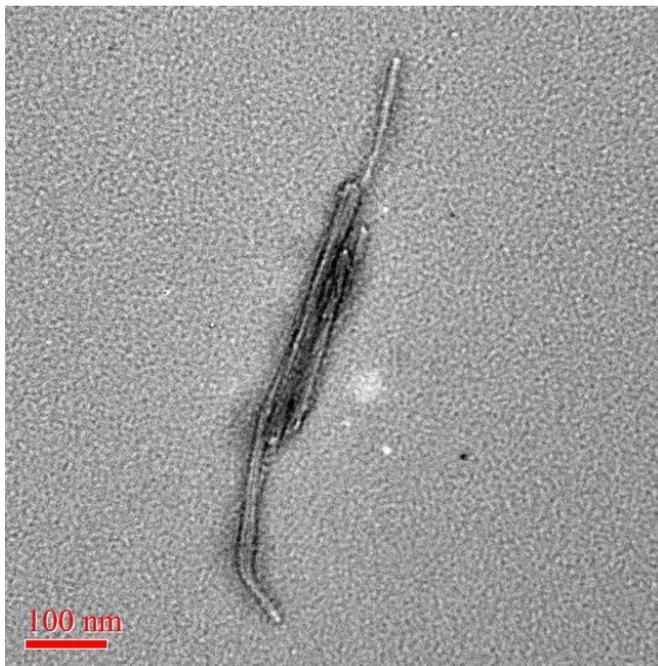
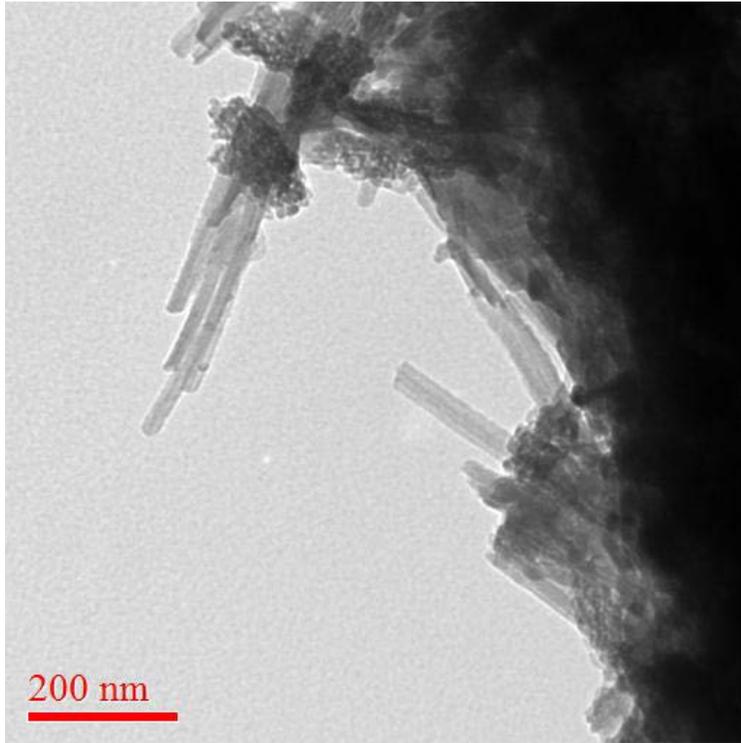


Figure 21. CNT Structure from sample 723-m9.



Discussion

Overall, minimal indication of leakage of nanomaterials was detected from any of the enclosures during the evaluated tasks based on real-time and air filter sample results. This is not surprising since the quantity of materials handled was small and the researchers appeared to use slow, careful movements when weighing out and transferring materials. Further, these types of enclosures have been used for containing powdered active pharmaceutical ingredients for several years. Particulate concentrations from both inside and outside of the enclosures, as measured by the real-time instrumentation, appeared to be driven primarily by environmental concentrations inside the laboratory. TEM analyses of area samples showed that the primary nanoparticles seen were single CNTs with a few agglomerates in the size ranges of 1-2 μm and 2-5 μm . These analyses showed light loading on the filters overall. However, the highest concentrations were detected during weigh-out of CNT carpet samples in Laboratory 2 when the ventilated enclosure fan was turned off.

Small-scale handling of nanopowders is a common task; this includes weighing 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. Dahm et al. conducted exposure assessments at six sites identified as carbon nanotube/nanofiber primary or secondary manufacturers (Dahm, Evans et al. 2012). During these evaluations, samples collected during dry powder handling task/processes were generally found to have the highest concentrations of respirable EC 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/CNFs to reduce the amount of product loss from air disturbance.

A recent study on the unintended emission of nanoparticles during common operations showed that the handling of small amounts (500-1500 mg) of nanopowders did not result in high particle concentrations inside enclosures similar in size to those used in these laboratories (Gomez, Irusta et al. 2014). Those experiments showed a differential increase in enclosure concentration between 200-400 particles/cm³ during pouring, transferring (with spatula) and spilling of nanopowders. These concentrations are approximately 1-2 orders of magnitude lower than those encountered in the background environment within the laboratories evaluated here—between 1,000-14,000 particles/cm³. This might make the identification of exposures related to the handling of these materials difficult to identify in typical laboratory environments using direct-reading instruments alone.

The average face velocity measurements taken across the enclosure faces evaluated ranged from 0.21-0.36 m/s (table 1). These enclosures typically operate between 0.36-0.41 m/s on average at the enclosure face opening. A recently published study evaluating a nanomaterial handling enclosure, similar to those seen in these labs, showed that an average face velocity of 0.30 m/s was not adequate to prevent the escape of tracer nanoparticles or tracer gas when a room air supply diffuser was located above the hood face (Dunn, Tsai et al. 2014). Even at an average face velocity of 0.41 m/s, some face leakage was identified. Only at the highest face velocity of 0.51 m/s was the hood effective regardless of room air conditioner

operation. However, the handling of nanopowders in the enclosure did not result in the release of measurable particles at the hood face or in the breathing zone of the operator in that study at the lowest studied face velocity of 0.30 m/s.

When deciding on the location of these types of hoods, placement away from potential disturbing factors such as room supply air vents, doors, windows and aisle ways can help reduce the impact on the performance. Research has shown the adverse impact of room air conditioning (or makeup air) on the performance of fume hood containment (Caplan and Knutson 1982, DiBerardinis, First et al. 1991, Altemose, Flynn et al. 1998). Altemose et al. found that the magnitude of cross draft velocities relative to hood face velocity is an important factor in determining whether a hood will leak. Likewise, Caplan and Knutson suggested that the terminal velocity of supply air jets is as important as hood face velocity in hood containment effectiveness noting that the center of the hood experiences better containment than the sides (Caplan and Knutson 1982).

Conclusions and Recommendations

Overall, minimal exposure potential was identified during the tasks evaluated at the laboratories. This is likely a result of the small quantities used and good handling techniques as well as the enclosure performance. The results provided from the filter-based samples analyzed for EC and by TEM, however, show that the potential for minimal airborne exposures to CNT exists. The proper use of personal protective equipment including lab coats, safety glasses and gloves should provide adequate dermal and respiratory protection. Currently, there are few published occupational exposure limits (other than the NIOSH REL of 1 $\mu\text{g}/\text{m}^3$) for carbon nanotubes. However, it is good occupational safety and health practice to maintain exposures to new and uncharacterized materials as low as possibly achievable.

Based on the face velocities measured, it would be prudent to increase the overall air flow rates to maintain each of these enclosures to the 0.41-0.51 m/s range for average face velocity, if possible. Most of these units have potentiometers on the units which allow the simple adjustment of flow. In addition, it would be prudent to work with the researchers from Laboratory 2 to evaluate methods of using the enclosure fan during CNT carpet weigh-out

procedures. It's possible that even operating the enclosure at a lower than optimal face velocity (like 0.25-0.30 m/s) might provide improved protection while minimizing disruption to the process. More guidance on the operation and performance of these enclosures as well as other types of fume hoods is available in the NIOSH document, General Safe Practices for Working with Engineered Nanomaterials in Research Laboratories (NIOSH 2012).

References

- Altemose, B. A., M. R. Flynn and J. Sprankle (1998). "Application of a tracer gas challenge with a human subject to investigate factors affecting the performance of laboratory fume hoods." Am Ind Hyg Assoc J **59**(5): 321-327.
- Bello, D., B. L. Wardle, N. Yamamoto, R. Guzman deVilloria, E. J. Garcia, A. J. Hart, K. Ahn, Ellenbecker. M. J. and M. Hallock (2009). "Exposure to nanoscale particles and fibers during machining of hybrid advanced composites containing carbon nanotubes." J. Nanopart. Res. **11**(1): 231-249.
- Brouwer, D. K., J. H. J. Gijssbers and M. W. M. Lurvink (2004). "Personal exposure to ultrafine particles in the workplace: exploring sampling techniques and strategies." Ann. Occup. Hyg. **48**(5): 439-453.
- Caplan, K. J. and G. W. Knutson (1982). "Influence of room air supply on laboratory hoods." Am Ind Hyg Assoc J **43**(10): 738-746.
- Chou, C. C., H. Y. Hsiao, Q. S. Hong, C. H. Chen, Y. W. Peng, H. W. Chen and P. C. Yang (2008). "Single-walled carbon nanotubes can induce pulmonary injury in mouse model." Nano Lett **8**(2): 437-445.
- Dahm, M. M., D. E. Evans, M. K. Schubauer-Berigan, M. E. Birch and J. E. Fernback (2012). "Occupational exposure assessment in carbon nanotube and nanofiber primary and secondary manufacturers." Ann Occup Hyg **56**(5): 542-556.
- Dahm, M. M., M. S. Yencken and M. K. Schubauer-Berigan (2011). "Exposure control strategies in the carbonaceous nanomaterial industry." J Occup Environ Med **53**(6 Suppl): S68-73.
- Demou, E., P. Peter and S. Hellweg (2008). "Exposure to manufactured nanostructured particles in an industrial pilot plant." Ann. Occup. Hyg. **52**(8): 695-706.
- DiBerardinis, L. J., M. W. First and R. E. Ivany (1991). "Field Results of an in-place, quantitative performance test for laboratory fume hoods." Appl Occup Environ Hyg **6**(3): 227-231.
- Dunn, K. H., C. S. Tsai, S. R. Woskie, J. S. Bennett, A. Garcia and M. J. Ellenbecker (2014). "Evaluation of leakage from fume hoods using tracer gas, tracer nanoparticles and nanopowder handling test methodologies." J Occup Environ Hyg **11**(10): D164-173.
- Elder, A., R. Gelein, V. Silva, T. Feikert, L. Opanashuk, J. Carter, R. Potter, A. Maynard, Y. Ito, J. Finkelstein and G. Oberdorster (2006). "Translocation of inhaled ultrafine manganese oxide particles to the central nervous system." Environ Health Perspect **114**(8): 1172-1178.
- Gomez, V., S. Irusta, F. Balas, N. Navascues and J. Santamaria (2014). "Unintended emission of nanoparticle aerosols during common laboratory handling operations." Journal of hazardous materials **279**: 75-84.

- Hallock, M. F., P. Greenley, L. DiBerardinis and D. Kallin (2009). "Potential risks of nanomaterials and how to safely handle materials of uncertain toxicity." Journal of Chemical Health and Safety **16**(1): 16-23.
- NIOSH (1994). ASBESTOS by TEM Method 7402. Cincinnati Ohio, National Institute for Occupational Safety and Health.
- NIOSH (1994). Elemental Carbon (Diesel Particulate). Cincinnati Ohio, National Institute for Occupational Safety and Health.
- NIOSH (2012). General Safe Practices for Working with Engineered Nanomaterials in Research Laboratories. Cincinnati, OH. Cincinnati, Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health.
- Peters, T. M., S. Elzey, R. Johnson, H. Park, V. H. Grassian, T. Maher and P. O'Shaughnessy (2009). "Airborne monitoring to distinguishing engineered nanomaterials from incidental particles for environmental health and safety." J. Occup Environ. Hyg. **6**: 73-81.
- Poland, C. A., R. Duffin, I. Kinloch, A. Maynard, W. A. H. Wallace, A. Seaton, V. Stone, S. Brown, W. MacNee and K. Donaldson (2008). "Carbon nanotubes introduced into the abdominal cavity of mice show asbestos-like pathogenicity in a pilot study." Nature Nanotechnology **3**: 423-428.
- Rossi, E. M., L. Pylkkanen, A. J. Koivisto, M. Vippola, K. A. Jensen, M. Miettinen, K. Sirola, H. Nykasenoja, P. Karisola, T. Stjernvall, E. Vanhala, M. Kiilunen, P. Pasanen, M. Mäkinen, K. Hameri, J. Joutsensaari, T. Tuomi, J. Jokiniemi, H. Wolff, K. Savolainen, S. Matikainen and H. Alenius (2010). "Airway exposure to silica-coated TiO₂ nanoparticles induces pulmonary neutrophilia in mice." Toxicol Sci **113**(2): 422-433.
- Shvedova, A. A., E. R. Kisin, R. Mercer, A. R. Murray, V. J. Johnson, A. I. Potapovich, Y. Y. Tyurina, O. Gorelik, S. Arepalli, D. Schwegler-Berry, A. F. Hubbs, J. Antonini, D. E. Evans, B. K. Ku, D. Ramsey, A. Maynard, V. E. Kagan, V. Castranova and P. Baron (2005). "Unusual inflammatory and fibrogenic pulmonary responses to single-walled carbon nanotubes in mice." Am J Physiol Lung Cell Mol Physiol **289**(5): L698-708.
- Takagi, A., A. Hirose, T. Nishimura, N. Fukumori, A. Ogata, N. Ohashi, S. Kitajima and J. Kanno (2008). "Induction of mesothelioma in p53^{+/-} mouse by intraperitoneal application of multi-wall carbon nanotube." J Toxicol Sci **33**(1): 105-116.
- Tsai, S.-J., E. Ada, J. A. Isaacs and M. J. Ellenbecker (2009). "Airborne nanoparticle exposures associated with the manual handling of nanoalumina and nanosilver in fume hoods." J Nanopart res **11**: 147-161.
- Tsai, S. J., E. Ada, J. Isaacs and M. J. Ellenbecker (2009). "Airborne nanoparticle exposures associated with the manual handling of nanoalumina in fume hoods." J Nanopart Res **11**(1): 147-161.
- Wang, J., Y. Liu, F. Jiao, F. Lao, W. Li, Y. Gu, Y. Li, C. Ge, G. Zhou, B. Li, Y. Zhao, Z. Chai and C. Chen (2008). "Time-dependent translocation and

potential impairment on central nervous system by intranasally instilled TiO₂ nanoparticles." Toxicology **254**(1-2): 82-90.



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