Current Issues in Exposure Assessment for Nanoparticles

John Baker, MS, MBA, CIH
Manager, Environmental and Technical Services
Total Safety EHS Services
Houston, Texas

Introduction

Nanoparticles are defined in several ways, the most common of which is a particle with at least one dimension which falls within the size range of 1 to 100 nanometers (nm, i.e., 10^{-9} meter). "Ultrafine particles" also fall within this size range, which include many naturally occurring aerosols with a wide particle-size distribution. Therefore the term *engineered nanoparticle* has been coined to describe particles which have been specifically manufactured to fall within a narrow segment of the nano size range. The ASTM E2456-06, Standard Terminology Relating to Nanotechnology, definition adds two more elements: (1) that novel physical or chemical properties emerge within the nano size range that are not observed at either the bulk scale or the atomic scale; and (2) that there is a capability of manipulating particles on the nano scale. Or, as the National Science Foundation more eloquently puts it: "One nanometer (one billionth of a meter) is a magical point on the dimensional scale. Nanostructures are at the confluence of the smallest of human-made devices and the largest molecules of living systems" (Consortium of Nanoscale Science and Engineering Centers).

How small are particles on the nano scale compared to objects that we commonly discuss? A single atom measures on the order of 0.1 nm, while protein macromolecules and viruses generally fit in the upper half of the nano scale, from 50 to 100 nm. Bacteria often measure 1000 nm, and a red blood cell is approximately 10,000 nm, or 10 micrometers (µm). Welding fumes can range typically from less than 200 nm to 1 µm. Ambient air quality standards for particulates focus on particles with a mass median diameter less than 10 micrometers (10,000 nm), referred to as PM_{10} and the U.S. EPA also defines a sub-set of fine particulate with a median diameter less than 2.5 micrometers (2,500 nm) as $PM_{2.5}$, often termed "soot" in the popular press. These emissions are typically associated with diesel exhaust and wood burning fireplaces.

What "novel physical and chemical properties" may emerge on the nano scale? For example, nano-scale iron particles have much greater magnetic susceptibility than individual iron atoms or compared to an iron bar. This has been suggested as a means of treating drinking water in developing countries where naturally occurring arsenic levels in the soil and groundwater pose public health risks.

As particles become extremely small, on the order of a few nanometers, the number of molecules or atoms that make up the particle become so few that a high proportion of them reside at the surface of the particle. It has been estimated that a 10 nm particle has 25 percent of its

molecules at the surface. Even the concept of a "surface" is altered because the properties of the particle are strongly influenced by the way in which the quantum mechanical properties of individual molecules interact (Vincent, 1999, p. 226).

The World Technology Evaluation Center has defined four generations of nanomaterials. The first generation is comprised of *passive nanomaterials,* such as carbon black, carbon nanotubes, nano silicon dioxide, nano titanium dioxide, and nano gold, the properties of which are dependent on size alone. *Active nanomaterials* constitute the second generation defined by properties that change or evolve while functioning due to a signal or stimulus external to themselves. Examples include carbon nanotubes "functionalized" with antibodies to seek out target tissues. The third generation includes *integrated nano systems*, such as nanoscale electronic circuitry for computation and networked sensor systems. The fourth generation is comprised of *molecular nanosystems*, including atomic or molecular devices not found in nature but designed by humans (Murashev et al, 2012).

As safety and health professionals, we recognize that dealing with very small particles is nothing new. Gases and vapors, being composed of small molecules of a few atoms, are well below the typical nano scale. However, we do recognize that having a very precisely limited size range of particles from which emerge new electrical, magnetic, chemical or other properties brings with it the potential for safety or health hazards that have not previously been anticipated or recognized. A very active area of toxicology is the study of nanomaterials for this reason.

How shall we monitor potential exposure to these "exotic" new materials? Surely there must be a reliable, inexpensive, direct-reading, hand-held instrument that we can point at the problem and get an instant answer that characterizes the risk? I am here to say, "Sorry, not yet available to my knowledge!"

The current situation brings to mind the ancient parable of the blind men and the elephant. As described in one tradition of India:

> Six blind men were asked to determine what an elephant looked like by feeling different parts of the elephant's body. The blind man who feels a leg says the elephant is like a pillar; the one who feels the tail says the elephant is like a rope; the one who feels the trunk says the elephant is like a tree branch; the one who feels the ear says the elephant is like a hand fan; the one who feels the belly says the elephant is like a wall; and the one who feels the tusk says the elephant is like a solid pipe.

> A king explains to them:

> All of you are right. The reason every one of you is telling it differently is because each one of you touched the different part of the elephant. So, actually the elephant has all the features you mentioned (Wikipedia, Jain World).

As illustrated by this parable, risk characterization and exposure assessment for nanoparticles requires the combined picture, developed by using several points of view and instrumental approaches to create multiple lines of evidence.

Exposure Assessment Considerations

The phrase *routes of exposure* describes the manner in which an environmental agent may enter or contact the body. For nanoparticles, the routes of exposure that are of most interest are inhalation, ingestion, and skin contact. The traditional methods of engineering and administrative controls lend themselves well to control of nanoparticles, if employed with an understanding of the particular material being handled.

There are not yet any occupational exposure limits for specific types of engineered nanoparticles that are mandatory or enforceable by a governmental authority in the United States. In April 2011, the National Institute of Occupational Safety and Health (NIOSH) recommended occupational exposure limits (OELs) of 2.4 mg/m^3 for fine TiO_2 and 0.3 mg/m^3 for ultrafine (including engineered nanoscale) TiO_2, as time-weighted average (TWA) concentrations for up to ten hours per day during a 40-hour work week. NIOSH has concluded that ultrafine TiO_2 is a potential human carcinogen, and therefore recommended a lower exposure limit for that form of the substance (NIOSH CIB 63, 2011).

NIOSH has released a draft *Current Intelligence Bulletin 161A on Occupational Exposure to Carbon Nanotubes and Nanofibers* in November/December 2010 for public comment and peer review. In this draft document, the following recommendation was made:

> Until improved sampling and analytical methods can be developed, and until data become available to determine if an alternative exposure metric to mass may be more biologically relevant, NIOSH is recommending a Recommended Exposure Limit (REL) of 7 μg/m^3 elemental carbon (EC) as an 8-hr TWA respirable mass airborne concentration. Occupational exposures to all types of CNT can be quantified by NIOSH Method 5040 as airborne EC. While data from animal studies with CNF are more limited …, physiochemical similarities between CNT and CNF and findings of acute pulmonary inflammation and interstitial fibrosis in animals exposed to CNF indicate the need to also control occupational exposure to CNF at the REL using Method 5040.

The mass concentration of 7μg/m^3 was selected as the upper limit of quantitation (LOQ) of Method 5040, which is an analytical technique originally developed to measure diesel particulate matter in occupational settings. Workers exposed at this mass concentration of CNT or CNF may have a greater than 10-percent excess risk of developing early-stage pulmonary fibrosis if exposed at this level over a working lifetime, based on animal risk data. Exposures to CNT or CNF should be kept lower than this level to the extent possible, according to this draft CIB.

NIOSH recommends that caution should be applied in control of the exposure to nanoparticles in general, and materials should be handled in totally enclosed systems to the extent practicable. When nanoparticle material must be taken out of total enclosure, laboratory hoods with local exhaust ventilation and HEPA filtration should be used. Personal protective equipment (PPE) recommendations have also been made by NIOSH, indicating that N95 or N100 filter respirators are expected to provide filtration of nanoparticles due to electrostatic and other filtration modalities (Shaffer and Rengasamy, 2009). Dermal protection should be sufficient using nitrile gloves (*Approaches to Safe Nanotechnology*, DHHS (NIOSH) Publication No. 2009–125).

The inhalation of airborne particulate is often the route of exposure of most concern when evaluating exposure to an aerosol of nanoparticles. The Human Respiratory Tract Model of the International Commission on Radiation Protection (ICRP) provides deposition data of inhaled particles from 1 nm to 10 μm indicating that between 20 to 50 percent of nanoscale particles reach the alveolar regions of the adult human lung. A recent review of animal studies of the inhalation of various nanoparticles indicates that 75 to 80 percent of the particles that reach the alveolar/gas exchange portion of the deep lung may be retained there for more than 48 hours (Geiser and Kreyling, 2010). Some studies suggest that translocation of engineered nanoparticles across the blood-brain barrier may occur (Sinko and Mattsson, 2010).

Rationale for Material Characterization

"But you gotta know the territory…" (Meredith Wilson, "Rock Island," *The Music Man*)

Since mass is a function of the cube of the diameter of a particle, the number of particles of ultrafine or nanoscale size needed to make up the same mass (i.e., micrograms per cubic meter) as larger particles of the same material increases rapidly as size gets smaller. The potential for ultrafine particles to penetrate into the deepest recesses of the lung, and the increased surface area of ultrafine particles compared to the same mass of larger particles of the same material may result in increased contact with lung tissue. Another consideration is the potential for other chemicals at the molecular scale, such as polyaromatic hydrocarbons or toxic metals, to be adsorbed to the outside of spongy particulate. Surface charge might be another characteristic of nanoparticles that could have biological relevance, although research is still continuing in this regard. The propensity of nanoscale particle to form agglomerates or aggregates is an important consideration. The American Society for Testing & Materials (ASTM) defines *agglomerate* as "a group of particles held together by relatively weak forces (for example, Van der Waals or capillary), that may break apart into smaller particles upon processing, for example," and *aggregate* as "a discrete group of particles in which the various individual components are not easily broken apart, such as is the case of primary particles that are strongly bonded together (for example, fused, sintered, or metallically bonded particles" (ASTM E2456-06). The shape of aggregates, e.g., fibrous or fractal, may also be important determinants of toxicity, as we learned with asbestos and other fibrous aerosols, some of which, such as silicon dioxide whiskers or potassium titanate whiskers, are at the cutting edge of study.

Therefore, our exposure assessment approach must take all these possibilities into account, which underscores the key foundational step of material characterization. It is essential to determine the chemical and physical properties of the nanoscale material to the extent possible before designing the exposure assessment strategy. The safety professional should request as much information as possible from the material scientists who have been developing the nanomaterial. The properties of interest for commercial development of a nanomaterial, including particle dimensions, degree of agglomeration or aggregation, electromagnetic, thermal and optical properties, may be helpful in deciding what exposure measurement techniques to use.

A recent study of the propensity for nanomaterials to form respirable dust aerosols has described the use of a novel low-mass dustiness tester, which found that, among 14 powders, ten of which were nano-sized, an amorphous silicon dioxide had a dustiness index significantly greater than all other powders tested. In general, fibrous nanopowders and those with primary particles greater than 100 nm were not as dusty as those with granular, nano scale primary particles. Half of the powders tested were not significantly as or more dusty than Arizona road dust or bentonite clay (O'Shaughnessy et al., 2012).

Particle Mass Concentration

In recent decades, most occupational exposure limits for particulates, including the NIOSH recommendations above, have been expressed as a mass concentration, usually milligrams or micrograms of substance per cubic meter of air volume, (mg/m^3 or $\mu g/m^3$). Respirable dust concentrations are measured by drawing the aerosol to be sampled through a cyclone sampler, which is designed to capture a particle-size distribution resembling the penetration of particles into the alveolar region of the deep lung. The ISO and CEN standards call for the 50-percent mass median diameter to be 4 micrometers, with progressively larger percentages of particles collected as the particle size decreases, and with less than 1 percent of particles of 10 micrometers being

selected. The aerosol passing this cyclone separator is then deposited on a filter for further examination by gravimetric, x-ray diffraction, chemical or microscopic methods.

The advantage of mass concentration measurements is that it may be compared to existing OELs for the bulk phase material; however, it may underestimate the true hazard potential of the ultrafine or nanoscale form because of the larger number of particles, surface area, and other consideration discussed above. For nanomaterials whose bulk forms are considered carcinogenic, mutagenic, asthmagenic and reproductive toxins (CMAR), the British Standards Institute (BSI) has recommended reducing the OEL for the bulk phase material by 0.1 times the bulk material's workplace exposure limit (WEL). For poorly soluble nanomaterials, BSI recommended a guideline of 0.066 times the WEL, and for soluble nanomaterials, a guideline of 0.5 times the WEL was recommended.(BSI, 2007).

Particle Count Concentration

In the early days of industrial hygiene, dust concentrations were measured by sparging the sampled air stream through water in an impinger, and then counting the number of dust particles using optical microscopy. The resulting dust concentration was expressed as "million particles per cubic foot" (mppcf). More recently, fibrous particulates have been assessed by particle number concentration. . For example, the OSHA permissible exposure limit for asbestos is 0.1 fibers per cubic centimeter of air (f/cc). In this case, the asbestos fiber concentration is assessed by capturing the particulate on a filter, which is examined through either optical or electron microscopy. BSI has recommended limiting particle number concentration to 20,000 particles per cc above the ambient background concentration (BSI, 2007).

There are numerous commercially available instrumental methods for counting particles in the nanoscale range, most of which are research instruments suited for the laboratory. For example, a Scanning Mobility Particle Sizer (SMPS) is a research-grade, highly accurate benchtop instrument, but since it is not field portable, it is of limited use measuring worker exposures in typical safety and health workplace studies (Ramachandran et al., 2011). Similarly, inertial particle cascade impactors have been developed in recent years with cut-point as small as 10 nm, but in the author's opinion, they are best suited to area or duct sampling, as the devices may weigh up to 30 pounds and require a flow rate of 10 liters per minute (MSP Corp., 2008). These modern cascade impactors, known as Multi-Orifice Uniform Deposit Impactors, or MOUDI^{TM}, have been used, along with direct reading instruments, in laboratory settings to estimate particle generation rates, and to collect samples for further electron microscope and chemical analysis (Raynor et al., 2012).

Several manufacturers have recently developed hand-held, battery-operated, real-time particle counters for field use. The two commonly used types are optical particle counters (OPCs) and condensation particle counters (CPCs). OPCs use a laser to scatter light off the particles in an air stream drawn into the instrument by a built-in sampling pump. The optics and associated software are designed to use the nature of the forward scattered light beam to estimate the number of particles in various size ranges, typically from 300 nm to 10 or 20 um. The OPC generally has an upper concentration range of 70 particles/cm^3 (2 million particles/ft^3) (Keady, 2000).

CPCs pass the aerosol sample through an atmosphere saturated with an alcohol, typically isopropanol or butanol, which adsorbs particles as small as 10 or 20 nm to make them "visible" to the laser counting optics and software. CPCs cannot grade the particles into size bins, but they can count smaller particles than OPCs. The use of a CPC, together with an OPC, allows an estimation of the number of particles between 10 or 20 nm and 300 nm, and then differential

counts of particles in user-selected size ranges up to 10 to 20 um. The CPC generally has an upper concentration range of 500,000 particles/cm^3 (1.5 x 10^{10} particles/ft^3) (Keady, 2000).

<u>Examination by Light and Electron Microscopy</u>
The use of both optical and electron microscopy to assess exposure potential is commonplace in the analysis of asbestos and similar fibrous particulate. The NIOSH 7400 method used for counting asbestos fibers requires the use of an optical phase contrast microscope with a special graticule, which divides the image into various fields for counting. The method does not specifically identify asbestos, but requires fibers with a diameter less than 3 micrometers (µm) and longer than 5 um with a length to width ratio of 3:1 to be counted. At least 20 fields, each representing an area of 0.00785 mm^2, up to 100 fields, must be examined, and fibers are selected for counting based on a set of rules specified in the method. A transmission electron microscope (TEM) method, NIOSH 7402, can provide positive identification, shape and structure of asbestos and was designed to be used with the 7400 optical method.

Due to their small size, individual or *primary* nanoparticles can only be directly observed using high-resolution techniques, either field-emission scanning electron microscopy (FE-SEM) or transmission electron microscopy (TEM). In special cases, polarized light optical microscopy can be used for "screening" large numbers of fields to assist in selection of fields for electron microscopy. The high magnifications available with electron microscopy means that the area of the "field" being observed is extremely small, and therefore, a very large number of fields would need to be examined to characterize the sample collected on a typical 37 mm or 25 mm filter. Thus, the number of fields that must be examined to "count" nano-scale particles by electron microscopy is prohibitive for most budgets and time schedules. However, electron microscopy provides unique benefits to characterize the shape, surface texture and degree of agglomeration or aggregation of particulate. A SEM "scans" the surface of the particle with an electron beam while the TEM "shoots" the electron beam through the particle. These techniques are complementary; they provide a more complete picture of the particle than either technique alone. The SEM can be paired with energy dispersive x-ray spectrometry to perform chemical elemental analysis of nanoparticles and associated catalyst metals, and Raman spectroscopy to explore molecular vibrational frequencies for "fingerprinting" specific materials. The TEM can provide a higher resolution, akin to a higher "magnification" than an SEM, and gives a better picture of the interior of an object.

Material to be examined can be collected on media suitable for transfer to either optical slides or electron microscope substrates, such as polyethylene film, for surface wipe samples and polycarbonate membrane filters for air samples.

Case Study Using Multiple Lines of Evidence for Exposure Assessment

The potential exposure of workers was assessed by the author during the decommissioning and decontamination of a single-walled carbon nanotube (SWCNT) manufacturing facility and the associated laboratories. Three manufacturing process units were dismantled, which included a four-story high furnace and reactor and a two-story high reactor, both of which used a chemical vapor deposition (CVD) process and a floor-level pilot unit using a high-pressure carbon monoxide (HipCO) process. The four-story tall unit used an iron/manganese/molybdenum catalyst, while the other two units used a very pure, fine iron catalyst generated from iron pentacarbonyl. All three manufacturing units were in the pilot plant area of a petroleum refining

research and development technology center. Due to the likely presence of other forms of elemental carbon from the petroleum-related processes, the method that NIOSH recommended for CNT was not expected to be determinative for the graphitic form of carbon present in CNT. Therefore, airborne mass concentration was assessed by personal breathing zone respirable dust samples, which were subjected to x-ray diffraction analysis for synthetic graphite if sufficient material was collected. Area air samples were collected on open-faced 25 mm 0.8 um silver membrane filters in conductive cowls to allow x-ray diffraction analysis for graphite at low-dust loadings. This is a modification of the standard method for collecting graphite samples, where the aerosol is collected directly onto the silver membrane filter used in the x-ray diffraction instrument to avoid the loss of some of the sample that may occur from re-depositing the material collected on a standard PVC filter to the silver membrane. Airborne presence of SWCNT was also measured by personal breathing zone and area samples on 25 mm 0.8 um polycarbonate membrane filters in conductive plastic cassettes to be examined by optical and electron microscopy. Particle number concentrations were assessed at the same time using a hand-held condensation particle counter and optical particle counter. These instruments were held as close as possible the breathing zone of the workers who were opening vessels or process lines. These real-time, direct reading particle counters were useful for identifying tasks that presented higher particle concentrations and for determining whether flange blanks and double taping of cut ends of tubing and lines had been completely sealed off. The specific tasks of opening vessels, flanges and cutting tubing and opening pipes were of short duration, typically less than an hour, so the opportunity to collect a sufficient mass of sample for gravimetric and x-ray diffraction analysis using standard flow rates of 1.5 to 2.5 liters per minute on personal air sampling pumps was limited. Area samples were collected for several hours' duration after the activities potentially releasing CNT were over, to collect as much sample material as possible for analysis. Particle counts were also spot checked during this time to compare to background particle concentrations in other parts of the building and outdoors.

The decommissioning and refurbishment of the laboratories presented a different set of challenges for exposure assessment. The owner of the technology center wished to ensure that a laboratory was deemed "cleared" of CNT before the next phase of work, typically mold remediation and/or abatement of asbestos vinyl floor tile, could be performed. Therefore, a rapid means of screening for the presence of CNT was needed so that contractors could work expeditiously without long delays waiting for lab results. A method was developed, which relied on information from the material characterization phase. Prior to starting the project, health and safety management representatives of the CNT manufacturer and the technology center owner designated seven areas that appeared visually to be "dirty" or "extensively" contaminated by black CNT material, seven areas that appeared to be clean or have "limited" presence of CNT, and seven other areas that were in between, having a "moderate" amount of CNT. Wipe samples of 100 square centimeters area were collected with a double-zipper polyethylene sandwich bag turned inside out in each of the 21 areas. The wipe samples were submitted to a microscopy laboratory with experience in examination of CNT. The samples were initially screened by optical polarized light microscopy for visual resemblance to a sample of reference CNT material provided by the manufacturer, and the samples were then observed by field emission SEM and TEM to determine if CNT morphology was present. The reference material was also analyzed by energy dispersive X-ray spectroscopy to determine if any rarely found metals in the catalyst could be used as definitive markers of CNT material by chemical analysis. Unfortunately, most of the catalyst found was iron, which. like carbon. would be ubiquitous in this pilot plant and laboratory environment.

The wipe samples were collected in each designated area, and digital photographs were taken of each sampling location, along with the sample identification number. The samples were sent to the microscopy laboratory on a blind basis, except for the reference material, which was labeled as such. At the laboratory, an optical microscopist extensively studied the reference material and described it as "clumps or mats with individual nanotubes or nanoropes apparent…the greatest majority similar to the reference material had filaments of CNT attached to clumps or mats of larger particles…free individual CNT not extensively present and are probably rare." If the optical microscopist observed material similar to the reference material, it was further examined by SEM and/or TEM for confirmation. In some cases, the sample was subjected to two different mounting techniques for SEM to confirm that the soluble gum used to transfer particulate was not obscuring features of interest. In one case, the sample appeared to contain an extensive amount of carbonaceous material with catalyst particles present similar to the reference material, but was largely devoid of nanotube or nano rope structures under SEM. Under TEM, only one or two small fragments of nanotubes were observed; however, as a precaution, this sample was classified as an extensive result. In another case, a moderate amount of black material was found, but no nanotube structure was observed by SEM in most of the sample, with the exception of one small area, and no nano rope structure was observed anywhere. In this case, the sample was classified as moderate.

Once each wipe sample had been examined and classified by microscopy, the results were plotted on a contingency table. Chi-squared statistical analysis determined that the visual determination of the initial classification of each sample was in statistically significant (i.e., $p < 0.025$) agreement with the microscopic determination. Exhibits 1 and 2 depict the optical and electron microscopic appearance of the reference material and sampled material confirmed to be CNT.
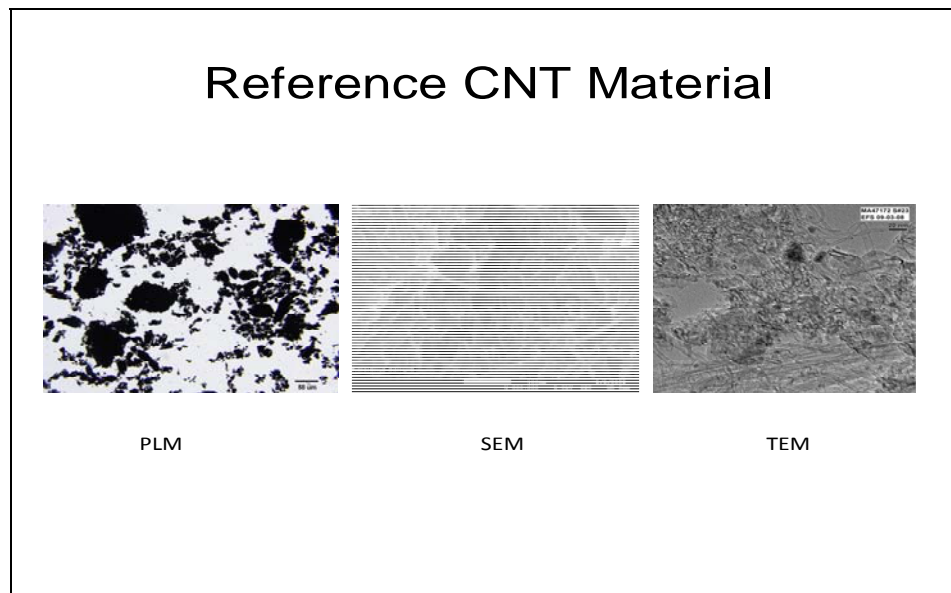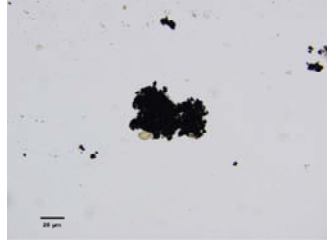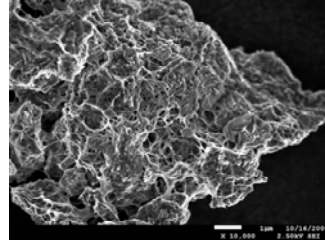

Exhibit 1. This is how the reference material appeared under PLM, SEM and TEM.

Wipe Sample Micrographs of CNT

PLM: Suspected CNT aggregate

SEM: confirmed CNT structure

Exhibit 2. This wipe sample was judged similar to the reference material under SEM.

The hallways providing access to the laboratories were closed off with temporary floor-to ceiling-plywood barricades and padlocked shut. The areas outside the barricaded hallways were monitored with open-faced polycarbonate filters for microscopic examination to confirm that airborne CNT was not present during the remediation work. Each laboratory had an individual HVAC system, which was shut off during the work, and an air lock enclosure was built around the entrance to each laboratory similar to those used for asbestos abatement. A HEPA-filtered air scrubber was operated continuously in each room for 24 hours a day until clearance could be confirmed. The remediation workers were monitored for personal breathing-zone respirable synthetic graphite mass concentrations and CNT open-faced samples for microscopic examination. Real-time particle number concentrations were determined, using both a condensation particle counter and an optical particle counter. Unlike the manufacturing unit dismantling, where potential exposure to CNT material was limited to short-term, well-defined tasks, the laboratory decontamination required the workers to be potentially exposed to CNT material for most of the work shift while they were removing lab benches and hoods, and HEPA vacuuming and wiping down walls, floors, and other surfaces. Acoustic ceiling tiles were assumed contaminated, and the first remediation task in each lab was to remove them, HEPA vacuum and wipe the grid, and replace them with new tiles.

The results of the monitoring for the workers who dismantled the manufacturing process units indicated that, during the dismantling of the four-story high unit, only two of seven personal air samples had quantifiable amounts of respirable dust or respirable synthetic graphite, and those two samples averaged 0.11 mg/m^3. Only one of six area samples for respirable dust/synthetic graphite had a measured amount above the limit of quantitation of 0.056 mg/m^3. However, SEM examination found CNT in four of five area air samples collected for CNT, and CNT was detected in one of three wipe samples. For the two-story high and ground level units, none of the eight personal air samples for respirable dust/synthetic graphite had quantifiable amounts of material. No CNT was detected in any of the 11 area air samples. During the decommissioning of the four-story high and two-story high units, the CPC generally counted 50 to 250 times more

particles in the 20 nm to 1 um size range than the OPC counted in the 300 nm to 1 um size range, averaging 138 times more ultrafine particles. Pilot plant background averaged 100 times ultrafine than larger particles. However, while unfastening a union from the heat exchanger lines and draining the condensate from the iron pentacarbonyl container for the ground level unit, the CPC registered from 800 to 2400 times more ultrafine particles than the OPC. Any review of the manufacturing unit decommissioning monitoring results must take into account the short task durations, from 32 to 145 minutes, and the fact that the process units had been purged with steam and nitrogen flows for many hours prior to opening any vessels or lines.

The results of the monitoring for the laboratory decontamination indicated that 31 personal air samples for respirable dust/synthetic graphite averaged 0.41 mg/m^3, ranging from <0.074 to 1.5 mg/m^3. Of 18 area air samples for respirable dust/synthetic graphite, the average was 0.17 mg/m^3, ranging from to <0.075 to 0.25 mg/m^3, but CNT were confirmed by SEM or TEM in eight of nine personal air samples and in one of three area air samples. The CPC generally recorded more ultrafine particles compared to the OPC in the laboratory work, averaging 384 times more ultrafine particles than particles greater than 300 nm. The longer task durations, usually around eight hours per day, and closer contact with potentially loose CNT material and contaminated surfaces may have contributed to elevated mass and particle number concentrations and greater prevalence of CNT material found by SEM/TEM in the laboratory decontamination compared to the manufacturing unit decommissioning.

Conclusion

In conclusion, multiple lines of evidence, when taken together, provide a more complete view of exposure potential. Mass concentrations are of limited use due to the relatively small amount of mass contributed to the total gravimetric result by ultrafine and nanoscale particles. Particle number concentrations, taken in real time with direct reading condensation particle counters and optical particle counters, indicate potential exposure sources and the need for additional exposure control. Polarized light microscopy was useful for rapid screening to SEM and TEM for this particular CNT aggregate material. Finally, material characterization of the general nature and physico-chemical characteristics of the substance of interest is essential for developing a rational and objective sampling strategy when dealing with nanomaterials.

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