



Aerosol Emission Monitoring and Assessment of Potential Exposure to Multi-walled Carbon Nanotubes in the Manufacture of Polymer Nanocomposites

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ABSTRACT

Recent animal studies have shown that carbon nanotubes (CNTs) may pose a significant health risk to those exposed in the workplace. To further understand this potential risk, effort must be taken to measure the occupational exposure to CNTs. Results from an assessment of potential exposure to multi-walled carbon nanotubes (MWCNTs) conducted at an industrial facility where polymer nanocomposites were manufactured by an extrusion process are presented. Exposure to MWCNTs was quantified by the thermal-optical analysis for elemental carbon (EC) of respirable dust collected by personal sampling. All personal respirable samples collected ($n = 8$) had estimated 8-h time weighted average (TWA) EC concentrations below the limit of detection for the analysis which was about one-half of the recommended exposure limit for CNTs, $1 \mu\text{g EC}/\text{m}^3$ as an 8-h TWA respirable mass concentration. Potential exposure sources were identified and characterized by direct-reading instruments and area sampling. Area samples analyzed for EC yielded quantifiable mass concentrations inside an enclosure where unbound MWCNTs were handled and near a pelletizer where nanocomposite was cut, while those analyzed by electron microscopy detected the presence of MWCNTs at six locations throughout the facility. Through size selective area sampling it was identified that the airborne MWCNTs present in the workplace were in the form of large agglomerates. This was confirmed by electron microscopy where most of the MWCNT structures observed were in the form of micrometer-sized ropey agglomerates. However, a small fraction of single, free MWCNTs was also observed. It was found that the high number concentrations of nanoparticles, $\sim 200\,000$ particles/ cm^3 , present in the manufacturing facility were likely attributable to polymer fumes produced in the extrusion process.

KEYWORDS: carbon nanotubes; exposure assessment; nanofiller; nanoparticle; polymer extrusion; polymer nanocomposite

INTRODUCTION

Since engineered carbon nanotubes (CNTs) were first brought to the attention of the scientific community in 1991 (Iijima, 1991), there has been extensive research on the unique properties of this material and their possible applications. The high strength and electrical properties of CNTs have led to their use in numerous applications, including energy storage, semiconductor devices, and conductive composite materials (Baughman *et al.*, 2002). In fact, the worldwide production capacity of CNTs was estimated to be ~5 kilotons per year in 2011, a 10-fold increase from 2004 (De Volder *et al.*, 2013).

With the proliferation of CNTs has come concern about potential hazards to human health. Recent toxicological studies have suggested that exposure to CNTs may pose a health risk. Length dependent asbestos-like pathogenicity was observed when multi-walled (MWCNTs) were injected into the abdominal cavity of mice (Poland *et al.*, 2008). Murphy *et al.* (2013) examined three CNT samples of differing lengths and found only the long CNT sample caused acute neutrophilic inflammation in bronchoalveolar lavage at 1 week. However, MWCNTs with a shorter length have also caused adverse health effects in animal studies (Mercer *et al.*, 2010, 2011; Porter *et al.*, 2013). Sargent *et al.* (2014) demonstrated that inhalation exposure to MWCNTs can promote the growth of lung adenocarcinoma. Several factors may influence the toxicity of CNTs, including the degree of agglomeration (Wick *et al.*, 2007), surface functionalization (Sayes *et al.*, 2006), metal content (Shvedova *et al.*, 2008), and surface wall defects (Muller *et al.*, 2008).

While it has been demonstrated that CNTs may elicit negative health effects, currently there are no enforceable occupational exposure limits for CNTs. In a recent current intelligence bulletin the National Institute for Occupational Safety and Health (NIOSH, 2013) has proposed a recommended exposure limit (REL) for CNTs and carbon nanofibers of $1 \mu\text{g}/\text{m}^3$ elemental carbon (EC) as an 8-h time weighted average (TWA) respirable mass concentration with the recommended analytical method being NIOSH Method 5040 (NIOSH, 2003a). For comparison, the permissible exposure limit for carbon black is 3500 times higher (CFR, 2007). The British Standards Institute has suggested a benchmark exposure limit of $0.01 \text{ fibers}/\text{cm}^3$, one-tenth of the asbestos exposure limit (BSI, 2007).

There are limited data on exposure to CNTs in the workplace. Many of the studies which have been conducted were at research facilities where CNTs were produced (Maynard *et al.*, 2004; Bello *et al.*, 2008a; Tsai *et al.*, 2009; Methner *et al.*, 2010; Ogura *et al.*, 2010) and handled (Johnson *et al.*, 2010; Methner *et al.*, 2010; R'mili *et al.*, 2010) and where advanced composites containing CNTs were produced (Cena and Peters, 2011; Fleury *et al.*, 2013) or machined (Bello *et al.*, 2008b). Additional studies have been conducted at industrial sites where CNTs or products utilizing CNTs were manufactured (Han *et al.*, 2008; Lee *et al.*, 2010, 2014, 2015; Dahm *et al.*, 2012, 2015; Wang *et al.*, 2011; Methner *et al.*, 2012; Takaya *et al.*, 2012; Fonseca *et al.*, 2014; Hedmer *et al.*, 2014; Heitbrink *et al.*, 2015; Ji *et al.*, 2015). Only two studies have employed the recommended sampling and analytical method for quantifying the CNT REL. Hedmer *et al.* (2014) measured respirable EC mass concentrations ranging from <0.08 to $7.4 \mu\text{g EC}/\text{m}^3$ from personal breathing zone (PBZ) sampling during the production, sieving, and purification of MWCNTs. Dahm *et al.* (2015) measured respirable EC PBZ concentrations ranging from <0.02 to $2.94 \mu\text{g EC}/\text{m}^3$ and an 8-h TWA concentration of $0.16 \mu\text{g EC}/\text{m}^3$ at five primary and secondary CNT manufacturers. With this lack of personal exposure measurements in primary and secondary manufacturers of CNTs, it is obvious that there is a critical need for further workplace measurements. In this study potential exposure to MWCNTs was monitored during the manufacturing of polymer nanocomposites where MWCNTs were used as nanofiller. This article will investigate the volatile nature of the nanoparticles present, address the temporal and spatial variation of particle concentrations in the facility, quantify MWCNT emissions and potential personal exposure, and characterize the morphology of airborne MWCNT structures.

METHODS

Facility and process descriptions

Potential exposure was monitored at a secondary MWCNT manufacturer which produced polymer nanocomposites by an extrusion process. The assessment was conducted April 2010–September 2010 and April 2011–August 2011. At this facility commercially available MWCNTs were used as nanofiller. These

MWCNTs produced by chemical vapor deposition processes were >95% pure carbon and contained no detectable amorphous carbon. They had 3–15 walls, a mean outer diameter of 13 nm, lengths >1 μm , and were in the form of agglomerates which could be as large as 1 mm. A cobalt impurity was known by the nanocomposite manufacturer to be present in the MWCNTs at a mass fraction of 0.0022. In the extrusion process thermoplastic polymer and MWCNT feedstock were fed into a twin screw extruder, where the polymer was melted and MWCNTs were dispersed throughout the polymer matrix. This mixture was extruded through a die, creating polymer nanocomposite strands, which were cooled in a water bath, passed through a dryer, and cut into pellets. The pellets entered a shaker for size selection and then a cyclone to remove any dust. Finally, the polymer nanocomposite pellets were packaged.

This production facility had the capability to operate continuously, 24 h a day. Typically this facility would handle ~5 kg of MWCNTs daily. Two employees actively worked in the manufacturing area. Each would work 12 h days with alternating 3 and 4 day workweeks. Tasks performed by the employees included the handling of unbound MWCNTs, the cleaning and maintenance of machinery, cleaning of the facility, sampling and testing of nanocomposite for quality control, and the transporting of feedstock and finished product. A large portion of the employees' time was spent at a computer console where processes were monitored and data were entered for record keeping.

The MWCNT feedstock supplied to the extruder was replenished about once every other day. The apparatus which housed the MWCNT feedstock consisted of a drum funnel with a butterfly valve at its end which was attached to the top of an opened MWCNT shipping drum with an o-ring and ring clamp. When the drum was spent the butterfly valve was closed and the apparatus was removed from atop the MWCNT feedstock feeder. The funnel was unclamped and the funnel and o-ring were taken off. The o-ring, funnel, and interior of the spent drum were cleaned by a vacuum with a high-efficiency particulate air (HEPA) filter. Then a new shipping drum was opened, the o-ring and funnel were reattached, and the funnel was clamped down. The lid from the newly opened drum was attached to the spent drum. The apparatus was then affixed to the

MWCNT feedstock hopper and the butterfly valve was opened. A HEPA vacuum was used to clean the floor in the surrounding area. The entire duration of the transferring procedure was ~5 min.

This facility had many control measures in place to prevent worker exposure. The nanocomposite production area had a ventilation system which was separate from the rest of the building. The production area was under negative pressure and underwent 15–30 air changes per hour. The area was under controlled access, with workers needing clearance to gain entry. Closed-circuit television allowed for remote monitoring of the facility. Handling of unbound MWCNTs and the cleaning and maintenance of MWCNT contaminated equipment was performed inside of strip curtain enclosures where local exhaust ventilation (LEV) was employed. All cleaning of MWCNT contaminated surfaces was done by HEPA vacuum or wet wiping methods. All waste was triple bagged and incinerated. Strip curtains also surrounded electric forklift access doors used to collect packaged nanocomposite product on the first floor and to bring in feedstock on the second floor. Alarms would sound if forklift access doors remained open for extended periods of time. There were sticky mats placed at the exit of the facility. There was a separate gowning room, degowning room, and anteroom, each with interlocked pneumatic sliding doors. The personal protective equipment required inside the manufacturing facility included Tyvek coveralls with hood, shoe covers, nitrile gloves, and full facepiece power air-purifying respirators (PAPRs) with organic vapor cartridges and P100 filters. Employees were required to wash their hands after degowning. A layout of the production facility is shown in Fig. 1.

Monitoring strategy

The monitoring strategy employed involved task and process based area sampling and measurement by direct-reading instruments, as well as PBZ sampling. Direct-reading instruments and area sampling equipment were typically positioned as close to the task being monitored as possible without disrupting the work and were generally within 1 m of the presumed emission source. The locations where area measurements were performed are labeled in parentheses in Fig. 1. Background sampling and measurements were taken for the downstairs and upstairs of the

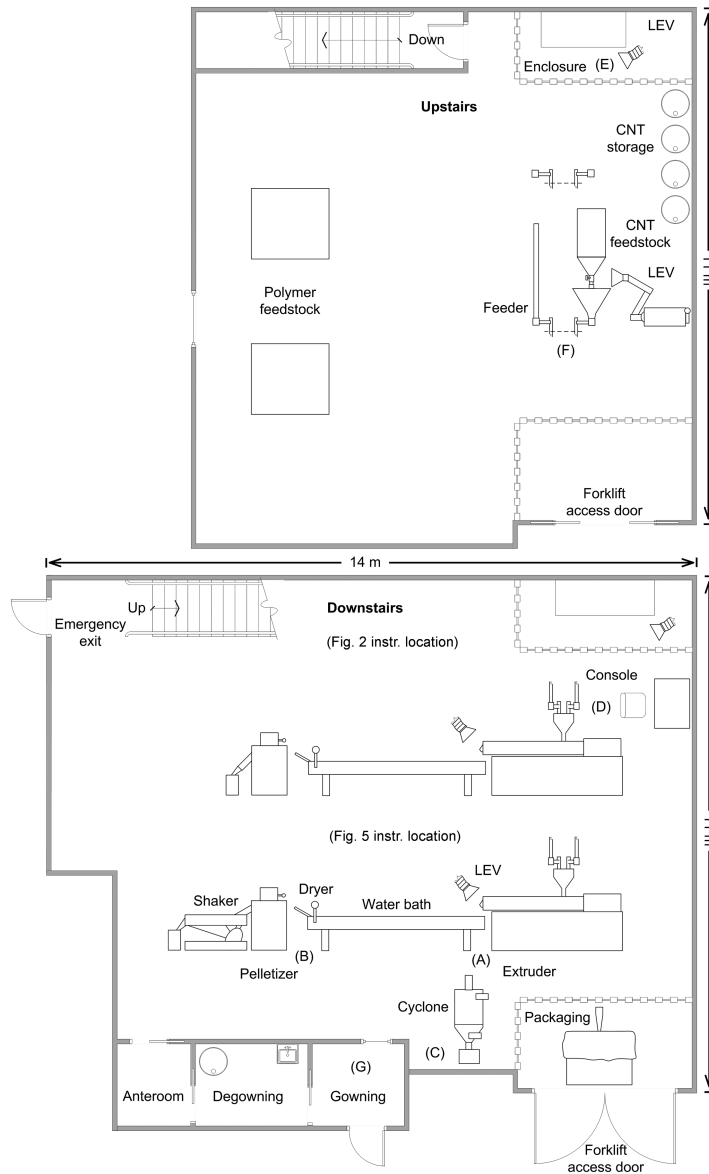


Figure 1. Schematic of polymer nanocomposite production facility with the locations of area measurements given in parentheses.

manufacturing facility at the console and in the enclosure (locations D and E, respectively, in Fig. 1) on days where no work tasks were done. The durations of the measurements by direct-reading instruments and sampling times for determining these background concentrations were 1 and 1.5 h, respectively.

Direct-reading instruments

An Engine Exhaust Particle Sizer Spectrometer (Model 3090, TSI Inc., USA) and Nanoparticle Surface Area

Monitor (Model 3550, TSI Inc.) were used to monitor the temporal evolution of particle size distributions from 5.6 to 560 nm every 0.1 s with a 1 s averaging interval and lung deposited surface area concentrations in the alveoli region of the lung every second, respectively, from inactivity in the manufacturing area to steady production from two extruders. A handheld condensation particle counter (CPC) (Model 8525, TSI Inc.), Aerosol Particle Sizer (APS) Spectrometer (Model 3321, TSI Inc.), DustTrak with a Dorr-Oliver

cyclone attached at its inlet (Model 8530, TSI Inc.), and AeroTrak 9000 (Model 9000, TSI Inc.) measured task and location based particle number concentrations for particles 20–1000 nm in size every second, particle number concentrations for particles 0.5–20 μm in aerodynamic diameter every 20 s, respirable particle mass concentrations every 20 s, and lung deposited surface area concentrations in the alveoli region of the lung every second, respectively. The sampling time at each location typically ranged from 1.5 to 3.5 h, except for the respirable particle mass concentration measurements at the pelletizer and enclosure which were only for 2 and 30 min, respectively, due to instrument error. To investigate the volatility of the particles present during nanocomposite extrusion, a catalytic stripper (CS) was used to condition the aerosol before it entered a scanning mobility particle sizer (SMPS) spectrometer consisting of an Electrostatic Classifier (Model 8030, TSI Inc.) with a Nano-Differential Mobility Analyzer (Model 3085, TSI Inc.) operating at a sheath to aerosol flow ratio of 5 connected to an ultrafine CPC (Model 3025A, TSI Inc.) operating in high flow mode. The CS removed the semi-volatile, typically organic carbon, fraction by passing the aerosol over an oxidation catalyst heated to 300°C (Swanson *et al.*, 2013). Four size distribution measurements, each with scanning times of 2 min, were made with and without the CS. WPS Commander (WPS Commander 3.0, MSP Corp., USA) was used for analyzing and applying fits to the particle size data.

Area and PBZ sampling

Area samples were positioned at breathing zone height (1.5 m) using tripod stands (No. 228–502, SKC Inc., USA). Closed face three-piece cassettes were used to sample total suspended particulate (TSP). For the sampling of respirable particles, aerosol collected by a sampler with a 4 μm median cut point (PM_4), the inlet of the three-piece cassette was replaced with an aluminum cyclone (No. 225-01-01, SKC Inc.) operated at a flow rate of 2.5 l/min which is specified in NIOSH Method 0600 for the sampling of respirable particles (NIOSH, 2003b). A recently developed personal nanoparticle sampler (PENS) was also employed. Through the use of a respirable cyclone and micro-orifice impactor with cutoff aerodynamic diameter of 100 nm, the PENS was able to simultaneously sample respirable particles at a flow rate of 2 l/min in

two separate size selective samples, with $\text{PM}_{0.1-4}$ collected on an impaction surface and $\text{PM}_{0.1}$ collected in an after filter housed in a two-piece polycarbonate cassette (Tsai *et al.*, 2012). Sampling in workers' PBZ was conducted as well. Workers wore a respirable particle sampler as described above housed in a filter cassette holder (No. 225-1, SKC Inc.) positioned on their chest by clipping it on to the zipper of their Tyvek coveralls. The personal sampling pump (AirChek XR5000, SKC Inc.) was attached to their belt-mounted PAPR. The sampling times for area sampling ranged from 0.28 to 24 h with an average of 6.6 h and for PBZ sampling ranged from 1.9 to 4.9 h with an average of 3.7 h. A summary of the sampling times for the area and PBZ sampling is provided in [Supplementary Table S1](#) at *Annals of Occupational Hygiene* online.

Organic carbon–elemental carbon analysis

TSP, PM_4 , $\text{PM}_{0.1-4}$, and $\text{PM}_{0.1}$ area samples ($n = 23$) and PM_4 PBZ samples ($n = 8$) were collected for organic carbon (OC) and EC analysis. Samplers were loaded with heat-treated quartz fiber filters (Tissuquartz 2500 QAT-UP, Pall Corp., USA). Three-piece 25 mm conductive cassettes (No. 225–329, SKC Inc.) were used for TSP and PM_4 sampling. Closed face sampling at a flow rate of 4 L/min was conducted for the TSP sampling. Such sampling conditions may have resulted in an uneven deposit on the filter (Miller *et al.*, 2013), invalidating the assumption made that the $\sim 1.5 \text{ cm}^2$ punch analyzed was representative of the entire filter. As a result, reported TSP concentrations for OC–EC may be overestimated. Samples were analyzed by Sunset Laboratory Inc. (Tigard, OR) using NIOSH Method 5040 (NIOSH, 2003a). Thermal-optical speciation for the quantification of carbonaceous particles has been applied in several recent exposure assessments (Kuhlbusch *et al.*, 2004; Kuhlbusch and Fissan, 2006; Methner *et al.*, 2007; Ono-Ogasawara and Myojo, 2011; Birch *et al.*, 2011; Dahm *et al.*, 2012; Takaya *et al.*, 2012; Hedmer *et al.*, 2014; Lee *et al.*, 2014; Dahm *et al.*, 2015). The limit of detection (LOD) was assumed to be 0.09 μg EC per cm^2 of filter, the value reported by NIOSH (2013) for a given as-received 25 mm quartz filter media lot. This LOD can be expressed as an air concentration when multiplied by the filter deposit area and divided by the sampled air volume and for this assessment ranged from ~ 0.1 to 1 μg EC/ m^3 . Task-based PM_4 PBZ

samples with sampling times ranging from 1.9 to 4.9 h during a 12 h shift were compared to the 8-h TWA REL using two assumptions. One, the 8-h TWA was based on the worst 8 h of exposure during the entire extended work shift as suggested by the Occupational Safety and Health Administration for the evaluation of permissible exposure limits over an extended work shift (OSHA, 1997). Two, the concentrations determined by task-based sampling were representative of the worst 8 h of exposure.

Inductively coupled mass spectrometry analysis for metals

TSP area sampling for trace metal analysis by inductively coupled mass spectrometry (ICP-MS) was carried out with 37 mm hydrophilic mixed cellulose ester (MCE) filters (GN-4 Metrical, Pall Corp.) in closed faced three-piece polycarbonate cassettes (No. M000037A0, EMD Millipore, USA) at a sampling flow rate of 5 l/min. The filter samples ($n = 5$) were leached in 10 ml of 5% nitric acid for 4 h. ICP-MS was used to estimate the mass concentration of MWCNTs by measuring the mass concentration of cobalt, an impurity present at a known mass fraction. This technique was previously utilized in a study where iron catalyst was used as a descriptor for CNTs (Maynard *et al.*, 2004). The LOD of the ICP-MS sampling method was calculated as three times the standard deviation of cobalt mass in seven media blanks. Two blanks which had cobalt masses below the instrument detection limit were incorporated by using the Kaplan–Meier method (Helsel, 2010) via the statistical software ProUCL (ProUCL 5.0.00, US Environmental Protection Agency, USA), where the blank cobalt mass was assumed to be normally distributed. The method was found to have an LOD of 2.04 μg of MWCNTs per filter which can be expressed as an air concentration when divided by the sampled air volume.

Gravimetric mass analysis

Gravimetric measurements were also conducted to determine mass concentrations of area samples ($n = 4$). Polytetrafluoroethylene filters with a polymethylpentene support ring and diameter of 37 mm (Teflo, Pall Corp.) were utilized in three-piece polycarbonate cassettes with the inlet of the cassette replaced with an aluminum cyclone and in the after filter of the PENs

for PM_4 and $\text{PM}_{0.1}$ sampling, respectively. Silicone impaction surface spray (No. 0100-96-0559A-X, MSP Corp.) coated aluminum foil was used as the impaction surface for $\text{PM}_{0.1-4}$. After 24 h of conditioning in a temperature and humidity controlled environment, samples were weighed on a microbalance accurate to 1 μg (C-31 Microbalance, Cahn Instruments, Inc., USA).

Scanning electron microscopy analysis

Sampling of the TSP size fraction was conducted at roughly 2.5 l/min for subsequent analysis by scanning electron microscope (SEM) for the identification and morphological characterization of MWCNT structures. Closed faced, conductive, three-piece cassettes with extended cowls (No. 4376, Pall Corp.) suitable for asbestos monitoring were used. Track-etched polycarbonate filters with 0.1 μm pore size and 25 mm diameter (Isopore, EMD Millipore) backed with 5 μm pore size MCE filters (No. SMWP02500, EMD Millipore) and MCE support pads (No. 66238, Pall Corp.) were housed inside the cassettes. Roughly 3 mm by 3 mm sections were removed from the center of the filter samples ($n = 11$) by scalpel, adhered to SEM sample stubs with carbon conductive tape, and then coated with 5 nm of carbon applied by ion-beam sputtering. Samples were observed with a field emission gun SEM (JSM-6500F, JEOL, Japan) where the samples were manually scanned in a serpentine fashion at a magnification of $\sim 10\text{--}20$ nm/pixel to search for MWCNT structures. Identified MWCNT structures were then imaged at higher magnifications (2–20 nm/pixel) and the micrographs with resolution of 1280×964 pixels were analyzed by the image processing software ImageJ (ImageJ 1.43u, US National Institutes of Health, USA) to calculate equivalent projected area diameters, d_{PA} , and Feret diameters of the structures.

RESULTS AND DISCUSSION

Direct-reading instruments

The temporal evolution of particle number concentration, lung deposited surface area concentration, and particle size distribution from the 3.5 h of monitoring of particle emissions during nanocomposite production on 8 April 2010 is shown in Fig. 2. During inactivity (period i in Fig. 2), when the facility was

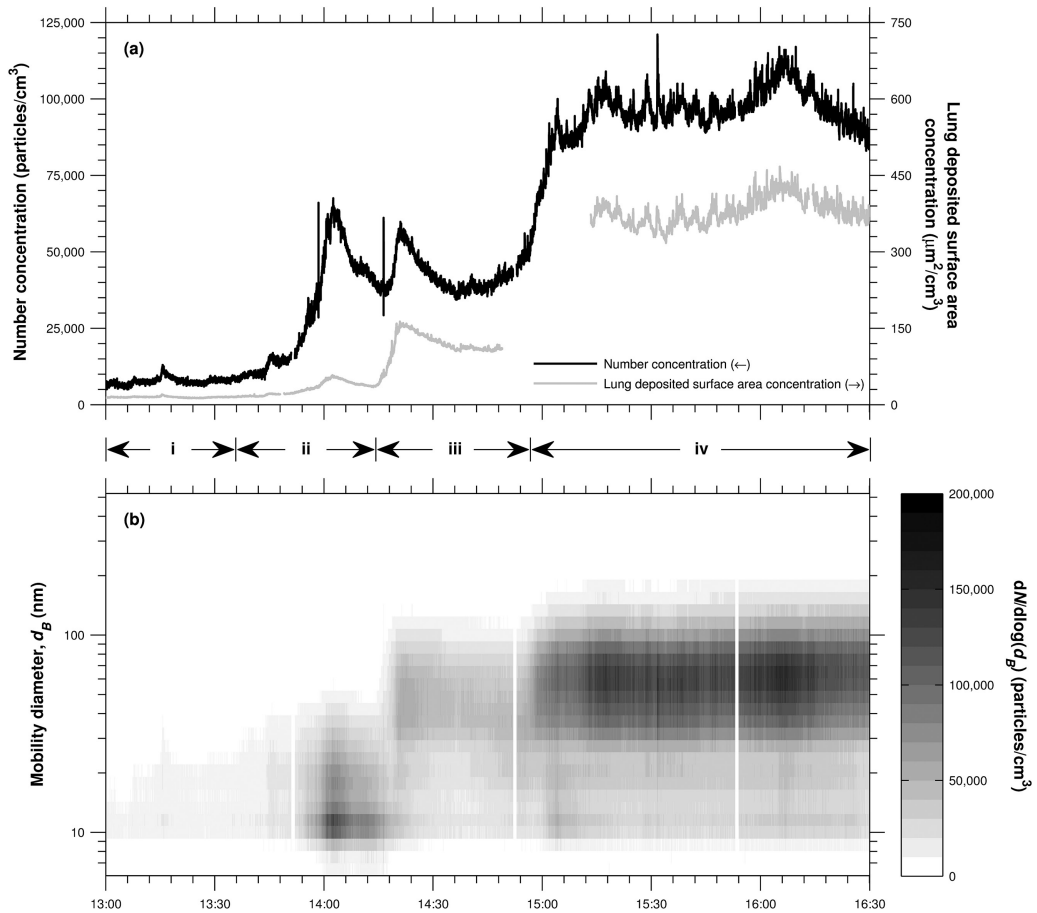


Figure 2. Real-time particle measurements during the production of polymer nanocomposites on 8 April 2010 where time periods (i)–(iv) represent (i) inactivity, (ii) equipment warm-up, (iii) operation of one extruder, and (iv) operation of two extruders. (a) Time series of particle number and lung deposited surface area concentrations. (b) Time series of particle size distributions. Reproduced from Wang *et al.* (2011) with kind permission from Springer Science and Business Media.

unoccupied, the particle number and lung deposited surface area concentrations were $\sim 10\,000$ particles/cm³ and $15\ \mu\text{m}^2/\text{cm}^3$, respectively. When the manufacturing equipment was being warmed-up (period ii in Fig. 2) 10–20 nm nanoparticles were generated at number and lung deposited surface area concentrations of around $50\,000$ particles/cm³ and $50\ \mu\text{m}^2/\text{cm}^3$, respectively. When one extruder was operating (period iii in Fig. 2) the particle number and lung deposited surface area concentrations were $\sim 50\,000$ particles/cm³ and $150\ \mu\text{m}^2/\text{cm}^3$, respectively, and the mode size observed was ~ 50 nm. When two extruders were in operation (period iv in Fig. 2) nanoparticles with a mode size of ~ 60 nm and number and lung deposited surface area concentrations of $\sim 100\,000$ particles/cm³ and

$400\ \mu\text{m}^2/\text{cm}^3$, respectively, were measured. The nanoparticles measured were thought to have been generated by the condensation of polymer fumes produced in this manufacturing process (Wang *et al.*, 2011). Similar concentrations and size distributions were observed in the production of CNT-polymer nanocomposites by melt-molding (Fleury *et al.*, 2013) and in the compounding of nanocomposites using nanoalumina as fillers (Tsai *et al.*, 2008), where in both studies it was suggested that polymer fume particles were the major nanoparticle source. Zhang *et al.* (2012) and Kuo *et al.* (2014) characterized the chemical composition of nanoparticles from thermal cutting of polystyrene foams and showed that the particles were formed by condensing chemical vapors from the high-temperature process.

Direct-reading instruments were unable to detect a MWCNT release in the replenishment of the MWCNT feedstock when unbounded MWCNTs were handled and a HEPA vacuum was used to clean MWCNT contaminated surfaces. In addition, direct-reading instruments did not distinguish a MWCNT release in the servicing and cleaning of MWCNT contaminated manufacturing equipment. The average particle number concentrations for particles 20–1000 nm in size, particle number concentrations for particles 0.5–20 μm in aerodynamic diameter, respirable particle mass concentrations, and lung deposited surface area concentrations during steady, continuous nanocomposite production, where the respective background concentrations measured during inactivity has been subtracted, at several locations in the production facility are given in Fig. 3. It can be seen that the number concentrations measured by CPC and lung deposited surface area concentrations were higher downstairs than upstairs with concentrations downstairs highest near the extruder. This suggests that the extruder was the major source of nanoparticle emissions. During production the number concentrations measured by APS and mass concentrations at all locations were mostly similar, except for near the cyclone. It is possible that some of the coarse dust which was removed from the surface of nanocomposite pellets by the cyclone was emitted.

The number concentration measured by CPC and lung deposited surface area concentration showed a linear correlation, while the APS measured number concentration correlated linearly with the respirable mass concentration, as shown in Fig. 4. This was because both the CPC and AeroTrak 9000 and the APS and DustTrak operate in similar size ranges. While the AeroTrak 9000 and DustTrak measure concentrations weighted by particle size, lung deposited surface area and respirable mass concentrations, respectively, spatial and temporal variations in particle size distributions likely were not great enough to affect this correlation. The Pearson correlation coefficient for the number concentration measured by CPC and lung deposited surface area was $r = 0.91$ and for the number concentration measured by APS and respirable mass concentration it was $r = 0.97$. In contrast, the Pearson correlation coefficients for all other instrument combinations were in the range of $r = -0.27$ to -0.08 (Supplementary Fig. S1 is available at *Annals of Occupational Hygiene* online). These results are similar to those reported by Heitbrink *et al.* (2009) who found that active surface area concentrations correlated strongly with fine particle number concentrations and weakly with respirable mass in the presence of high concentrations of ultrafine particles at an engine machining and assembly facility. Similarly, Park *et al.* (2010) found that the exposure

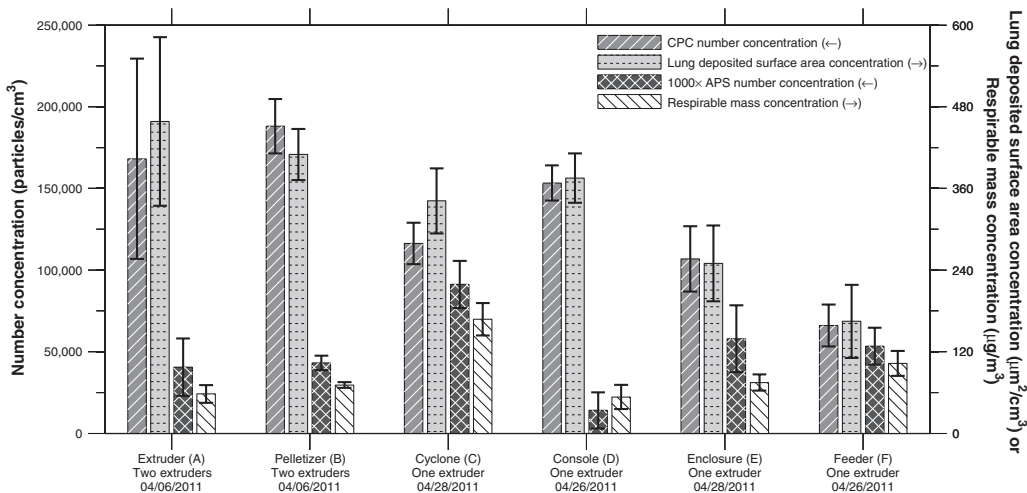


Figure 3. Average particle number concentrations measured by CPC, lung deposited surface area concentrations, particle number concentrations measured by APS, and respirable mass concentrations during steady, continuous nanocomposite production at selected locations in the facility. Error bars represent the standard deviation of concentrations.

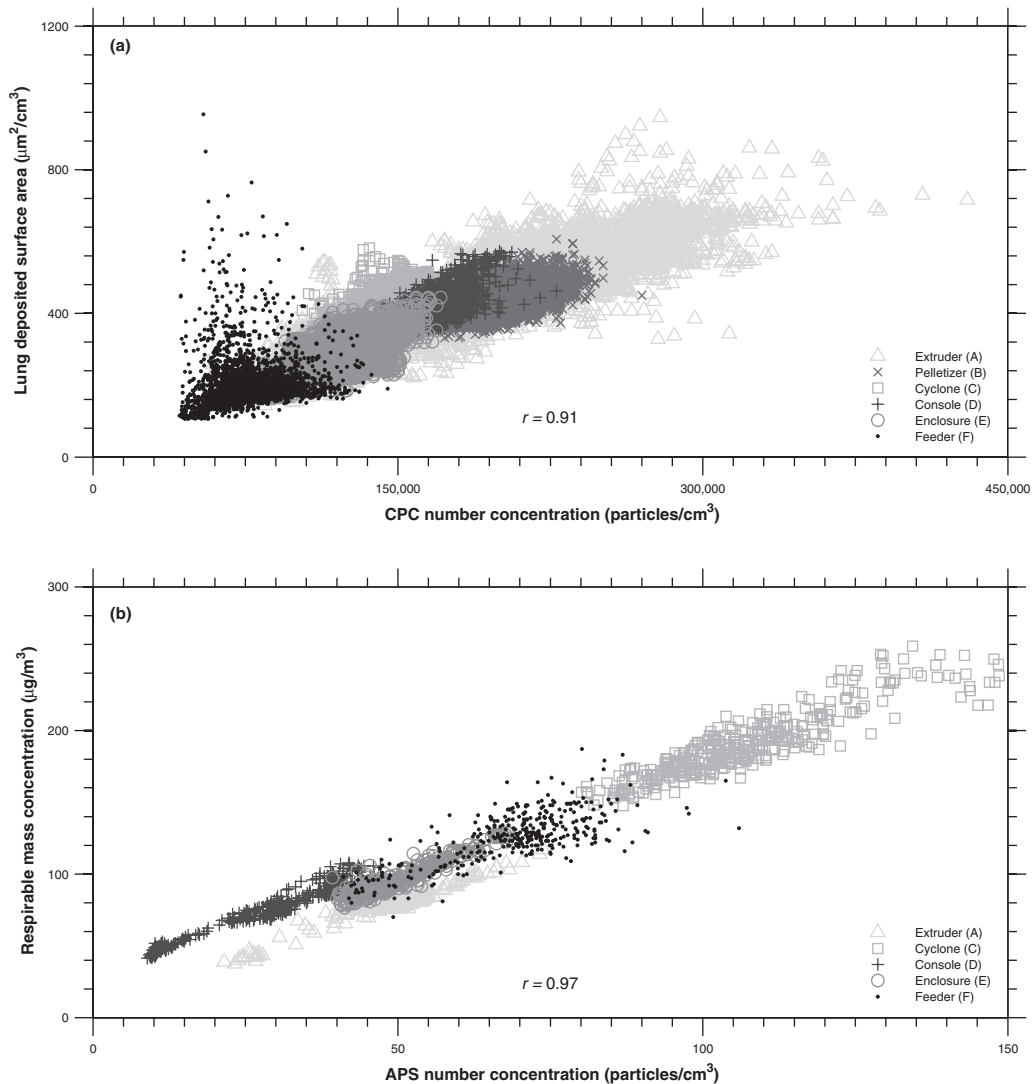


Figure 4. Correlation of (a) particle number concentrations measured by CPC and lung deposited surface area concentrations and (b) particle number concentrations measured by APS and respirable mass concentrations during steady, continuous nanocomposite production at selected locations in the facility.

metrics of surface area concentration and fine particle number concentration, rather than mass concentrations or coarse particle number concentration, agreed with incidental nanoparticle sources and distribution throughout a restaurant and die casting factory.

In Fig. 5 the size distributions measured on 27 May 2010 by an SMPS during polymer nanocomposite extrusion with and without a CS at its inlet are shown. Without the CS the size distribution was found to be lognormal with a geometric mean, μ_g , of 47 nm, a geometric standard deviation, σ_g , of 1.7 and a coefficient of determination,

R^2 , of 0.99. When this aerosol was conditioned by the CS, this mode was no longer present. While the measurement results were not corrected to account for the losses in the CS due to diffusion and thermophoresis, losses alone do not explain the difference in size distributions, as solid particle penetration was found to be 50% for 10 nm and ~80% for particles larger than 50 nm for a CS of similar design (Swanson *et al.*, 2013). These results further support the supposition that the major source of nanoparticle emissions in this facility were polymer fume particles, which would be volatilized in the CS.

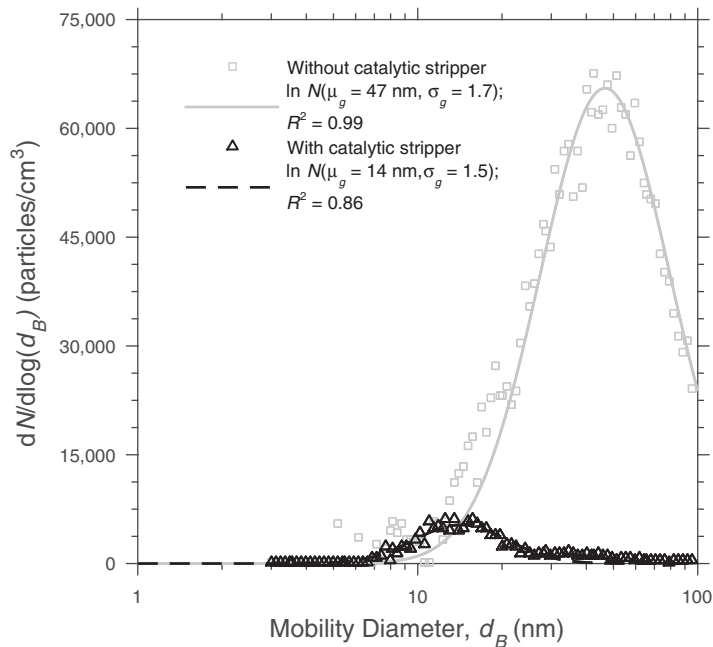


Figure 5. Size distributions measured by SMPS on 27 May 2010 with and without a CS connected to its inlet.

Area and PBZ sampling

In Table 1 an overview of the results from area and PBZ sampling by location and size fraction sampled is given. In this table the EC and OC mass concentrations determined by NIOSH Method 5040, the estimated MWCNT mass concentration calculated from measured cobalt mass concentration determined by ICP-MS, total dust mass concentration determined by gravimetric analysis, and whether or not MWCNTs were found by SEM are given for area sampling of the TSP, PM_{4} , $PM_{0.1-4}$, and $PM_{0.1}$ size fractions and for PBZ sampling of the PM_{4} size fraction. A summary of all monitoring events and their corresponding area and PBZ samples is provided in Supplementary Table S2 at *Annals of Occupational Hygiene* online. A more detailed discussion of these results is presented in the subsequent sections.

OC–EC analysis

Before reviewing OC results, it should be noted that no corrections were made for artifacts caused by adsorbed organic vapor (Birch, 2004). Although tandem quartz filters were used, the bottom filter was not analyzed for the correction of adsorbed OC vapors due to cost. The highest OC mass concentration collected by TSP area samplers was measured near the

extruder, $61 \mu\text{g OC}/\text{m}^3$. It can be seen that concentrations collected by the TSP samples were similar to those collected by PM_{4} area samples. This would indicate the OC particles and adsorbed organic vapor present in the workplace were respirable.

The EC results may have been adversely affected by OC loading which was relatively higher than the EC loading, potentially causing a bias in the EC results (NIOSH, 2013). While adsorbed OC vapor should be accounted for by the analysis of tandem filters (Birch, 2004), which was not done in this study, particulate OC should be accounted for by thermal analysis of the specific particulate OC in question to determine onset of oxidation and confirm complete oxidation (NIOSH, 2013). It was believed that there were two major types of particulate OC at the workplace: coarse particles mechanically generated by the cutting of nanocomposite at the pelletizer and fine particles formed from the evaporation and subsequent condensation of polymer during the extrusion of nanocomposite. Due to the nondisclosure agreement signed with the nanocomposite manufacturer it was not possible to account for the effect of the mechanically generated particulate OC on the EC results by thermal analysis of the bulk materials which constitute the nanocomposite or the nanocomposite as whole, as

Zhao (2013) found that in certain polymer nanocomposites the presence of CNTs can result in a decomposition temperature lower than that of the bulk polymer. The chemical composition of the fine particles which were generated by condensing polymer vapors likely differed from that of the bulk polymer, as was demonstrated in recent work on the thermal cutting of polystyrene foams (Zhang *et al.*, 2012; Kuo *et al.*, 2014).

The impact of adsorbed OC vapor and fine particulate OC from condensed OC vapor on EC results appeared to be minimal since no correlation was observed between measured OC and EC concentrations for the 31 area and PBZ samples (Supplementary Fig. S2 is available at *Annals of Occupational Hygiene* online). The extent of influence that the mechanically generated nanocomposite particles had on EC results was unclear through examination of the sample set, but the effect should be localized to sampling done near the pelletizer. Due to OC overload and/or polymer pyrolysis, it may not be possible to quantify CNT concentrations by thermal-optical analysis if they are incorporated in a polymer matrix (NIOSH, 2013). Polymer which does not fully evolve or pyrolyze in the inert atmosphere during thermal-optical analysis would result in a positive bias on EC (Conny *et al.*, 2003). The co-evolution of EC and pyrolyzed carbon formed from the charring of polymer would result in a positive or negative bias on EC depending on the light absorption coefficients of the EC and char (Yang and Yu, 2002).

All but two of the TSP area samples had EC concentrations below the LOD, which was generally $\sim 0.6 \mu\text{g EC}/\text{m}^3$. The samples taken during production near the pelletizer and inside the curtained enclosure upstairs on 30 June 2011 had EC mass concentrations of 2.6 and $12 \mu\text{g EC}/\text{m}^3$, respectively. The EC measured near the pelletizer may have originated from the cutting of polymer nanocomposite strands which occurred at this piece of equipment. A number of studies have reported protruding CNTs from polymer particles after the cutting, sanding, or abrading of nanocomposites (Cena and Peters, 2011; Hellmann *et al.*, 2012; Huang *et al.*, 2012; Schlagenhauf *et al.*, 2012; Ogura *et al.*, 2013). In addition, a couple of studies have observed the release of free individual CNTs and agglomerated CNTs (Huang *et al.*, 2012; Schlagenhauf *et al.*, 2012; Dahm *et al.*, 2015). However, NIOSH Method 5040 would not distinguish between free

MWCNTs and MWCNTs in a polymer matrix. The other possible explanation is that this EC was entirely a result of polymer charring during analysis.

Additional area samples were collected at the pelletizer and the curtained enclosure where MWCNTs were handled using size selective samplers and larger sampling volumes. No detectable EC concentrations were found on the $\text{PM}_{0.1}$ samples, where the LOD was $<1 \mu\text{g EC}/\text{m}^3$. Quantifiable $\text{PM}_{0.1-4}$ EC concentrations of 0.58 and $0.11 \mu\text{g EC}/\text{m}^3$ were measured near the pelletizer on 11 July 2011 and 15 August 2011, respectively. The collocated PM_4 sample on 11 July 2011 was $0.52 \mu\text{g EC}/\text{m}^3$, above the LOD but below the limit of quantification (LOQ), and only differed from the quantifiable $\text{PM}_{0.1-4}$ EC concentration by 10%, suggesting that the PM_4 EC mass that was sampled consisted of respirable particles larger than 100 nm. All other PM_4 EC concentrations were below the LOD, which was typically $<1 \mu\text{g EC}/\text{m}^3$. That all quantifiable $\text{PM}_{0.1-4}$ EC concentrations sampled were less than one quarter of the quantifiable TSP EC concentrations sampled indicated that the TSP samples likely consisted of non-respirable MWCNT agglomerates or non-respirable polymer particles charred during analysis.

Personal respirable samples were analyzed by NIOSH Method 5040. The personal sampling was performed during nanocomposite production, the transferring of unbound MWCNTs, the changing of HEPA and shop vacuum cleaner bags, and the cleaning of machinery. All task-based PBZ PM_4 samples yielded EC concentrations below the LOD, which was typically $<1 \mu\text{g EC}/\text{m}^3$. Using the assumptions that for extended work shifts the REL for CNTs should be based on the worst 8 h of exposure and that the task-based samples were representative of the worst 8 h of exposure, it follows that the estimated 8-h TWA was also typically less than $1 \mu\text{g EC}/\text{m}^3$, the REL for CNTs. PBZ PM_4 OC concentrations were comparable to those measured in area sampling.

Micrometer-sized agglomerates of MWCNTs with outer diameters $<20 \text{ nm}$, similar to those used in the present study, oxidize at 700°C (Takaya *et al.*, 2012; Ono-Ogasawara and Myojo, 2013). Examination of the carbon masses detected at each oxidation temperature for NIOSH Method 5040 for the four samples with quantifiable EC concentrations revealed that the two TSP samples had highest EC masses at EC3 and the two $\text{PM}_{0.1-4}$ had highest EC masses at

EC5 (Supplementary Fig. S3 is available at *Annals of Occupational Hygiene* online). EC3 and EC5 are associated with temperatures of 700°C and 890°C, respectively (Khan *et al.*, 2011). Even though ambient particulate matter contains EC3 (Ono-Ogasawara and Myojo, 2013), it was believed that this EC3 in the quantifiable TSP area samples was indeed a signature of the MWCNTs used in this workplace due to the fact that both the area TSP sample located near the extruder and the PBZ PM₄ sample collected simultaneously yielded EC concentrations of <0.27 and <0.55 µg EC/m³, respectively. The ratios of EC to total carbon for the TSP samples taken near the pelletizer and in the enclosure were 0.22 and 0.058, respectively, while the ratios for the two PM_{0.1-4} samples collected near the pelletizer on 11 July 2011 and 15 August 2011 were 0.025 and 0.0044, respectively. Because of the low EC to total carbon ratios, the predominance of EC5 in the PM_{0.1-4} samples may not be due to actual airborne EC. Instead, the high relative OC content, likely mechanically generated polymer particles, may have caused a positive bias in the EC results (NIOSH, 2013).

The PENS was found to be an effective device for sampling MWCNTs in the workplace with improved sensitivity. Because the PENS collected PM_{0.1-4} using a micro-orifice impactor with a nozzle array with a diameter of 6.8 mm, the deposition area is greatly reduced compared to that of 25 or 37 mm filter cassettes (Tsai *et al.*, 2012). The LOD of NIOSH Method 5040 is given in µg EC per cm² of filter. By concentrating the mass sampled onto the area of one filter punch, sensitivity is increased. Likewise, although a 37 mm filter was used in the current study, a 25 mm filter could be employed as the after filter of the PENS to reduce the LOD for the PM_{0.1} sample. If one were to use a filter punch which was the same size as the impactor deposition area and a 25 mm after filter, the PENS would be capable of simultaneously detecting concentrations of 0.034 µg EC/m³ in the PM_{0.1-4} size range and 0.36 µg EC/m³ in the PM_{0.1} size in a worker's PBZ over an 8-h workday. It must be noted that although the sum of the PM_{0.1-4} and PM_{0.1} fractions is the health based fraction PM₄, the individual fractions PM_{0.1-4} and PM_{0.1} are strictly technical definitions and not health based fractions.

ICP-MS analysis for metals

The ICP-MS analysis of area TSP samples did not yield detectable quantities of cobalt. This method for

detecting CNTs was found to be difficult to implement for higher purity MWCNTs, even with the increased sensitivities offered by ICP-MS analysis. All analyzed samples had estimated MWCNTs concentrations below the LOD of ~3 µg/m³. This was roughly five times the LOD of collocated TSP EC samples.

Gravimetric analysis

When the OC mass concentrations were compared to the respirable gravimetric mass concentrations, it was seen that the mass sampled consisted largely of OC particulate matter and adsorbed vapor. This further suggested that incidental organic nanoparticles were the major nanoparticle source in this facility.

SEM analysis

Area TSP filter samples were inspected by SEM for the identification of MWCNT structures and the characterization of MWCNT structure morphology. MWCNTs were found on 10 of the 11 samples collected at 6 different locations. Locations and tasks where MWCNTs were detected by SEM include the extruder, console, feeder, cyclone, and pelletizer during nanocomposite production, as well as on samples taken in the curtained enclosure both during production activities and inactivity. This is in contrast to the OC-EC results where EC was only detected in 6 of the 23 area samples collected, those sampled near the pelletizer and in the enclosure, with the caveat that some of those EC results may have been positively biased by the charring of OC particles in analysis. Of the six area samples analyzed by OC-EC which were collocated with five TSP area samples with MWCNTs detected by SEM, all four TSP samples were below the EC LOD of 0.54–0.57 µg EC/m³ while the collocated PM₄ and PM_{0.1-4} samples had detectable EC concentrations of 0.52 and 0.58 µg EC/m³, respectively. These qualitative results which suggest that electron microscopy would offer more sensitivity and selectivity in the measurement of CNT exposure than EC analysis are substantiated by the studies of Dahm *et al.* (2012, 2015) and Hedmer *et al.* (2014) who quantified CNT number concentrations via electron microscopy on samples collected in parallel with samples whose EC concentrations were below the LOD.

One filter sample collected in the curtained enclosure on 28 April 2011, when unbound MWCNTs

were handled and vacuum bags used in the cleaning of MWCNT contaminated surfaces were changed, was found to have more MWCNT structures than the other samples. Consequently, a more detailed morphological analysis of the MWCNT structures found on this sample was conducted. Micrographs of representative MWCNT structures found on this sample are shown in Fig. 6a–d. Approximately 60% of the MWCNT structures observed were loose, ropey agglomerates. About 10% of the structures appeared to be denser, more compact agglomerates. Another 20% were either free individual MWCNTs or loose agglomerates where individual MWCNTs were discernible. The remaining 10% were some combination either amongst the types of MWCNT structures previously described or with other particulate matter. Free individual MWCNTs had a geometric mean Feret diameter of $1.8 \mu\text{m}$ with a geometric standard deviation of 1.8. Release of free individual CNTs and agglomerated CNTs was also observed in the abrasion of nanocomposite in other studies (Huang *et al.*, 2012; Schlagenhauf *et al.*, 2012). A histogram obtained from a total of 81 MWCNT structures found on this one filter sample is given in Fig. 6e. The particle size distribution was found to be lognormal in nature with

a geometric mean projected area diameter of $1.8 \mu\text{m}$ ($\sigma_g = 2.5$ and $R^2 = 0.99$). Chen *et al.* (2012) characterized MWCNTs aerosolized using an acoustic dispersion system for use in animal exposure studies and categorized the MWCNT structures into two fractions, fibrous particles and isometric particles which were MWCNT agglomerates having an aspect ratio of <3 . While in their case the fibrous particles were more numerous than agglomerates (60–80% vs. 20–40%), their reported size distributions, with fibrous particles having a geometric mean length of $3.0 \mu\text{m}$ with geometric standard deviation of 2.2 and isometric particles having a geometric mean diameter of $0.9 \mu\text{m}$ with geometric standard deviation of 2.0, were fairly representative of the MWCNTs observed in this exposure assessment.

CONCLUSIONS

All eight of the PM_{10} PBZ samples had estimated 8-h TWA EC concentrations below the LOD, which was typically less than the REL for CNTs. Analysis of area TSP samples by SEM found MWCNTs on 10 of the 11 samples collected at the extruder, console, feeder, cyclone, pelletizer, and in the curtained enclosure. While some free individual MWCNTs were found,

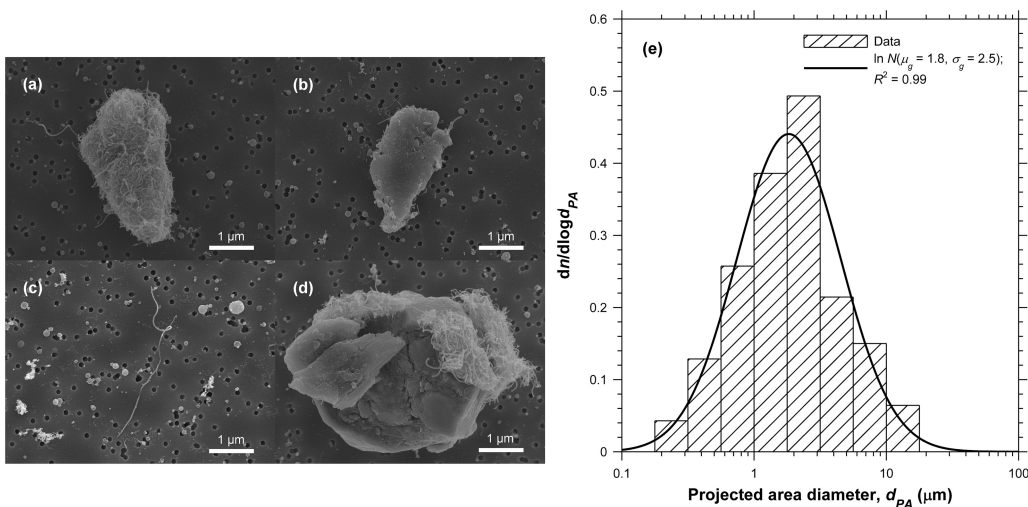


Figure 6. (a–d) Scanning electron micrographs of representative MWCNT structures collected on one filter sample in the enclosure during the transferring of unbound MWCNTs, the changing of bags from vacuums used for cleaning, and the operation of one extruder on 28 April 2011. (a) Approximately 60% were ropey agglomerates. (b) About 10% appeared to be denser, more compact agglomerates. (c) 20% were either free individual MWCNTs or loose agglomerates where individual MWCNTs were discernible. (d) 10% were some combination either amongst the types of MWCNT structures previously described or other particulate matter. (e) Histogram and calculated lognormal distribution obtained from the projected area diameters, d_{PA} , of MWCNT structures on this sample.

most of the MWCNT structures observed were in the form of ropey, micrometer-sized agglomerates. Nonetheless, it should be noted that the extent to which CNT agglomerates are dispersed once deposited in the lung is presently unknown and that diluted alveolar lining fluid was shown to effectively disperse single-walled CNTs in a biological medium (Wang *et al.*, 2010). Area TSP sampling measured quantifiable EC concentrations indicative of MWCNTs inside the enclosure where unbound MWCNTs were handled and near the pelletizer. However, the TSP EC concentration measured near the pelletizer may potentially be attributable to polymer charring. Area PM_{0.1-4} samples collected near the pelletizer yielded quantifiable EC concentrations, but this too may be due to polymer charring or the high relative OC content which may have caused a positive bias in the EC result.

It was found that nanoparticle number concentrations were elevated, exceeding 200 000 particles/cm³, on the manufacturing floor during nanocomposite production. From the results of the OC and gravimetric analyses, as well as the use of a CS at the inlet of an SMPS, it is believed that these nanoparticles consisted largely of organic material and were produced by the heating of the polymer in the extruder. Because of the high OC concentrations measured in this facility, the monitoring of organic vapor concentrations with sorbent tubes may be pertinent for fully characterizing worker exposure, as potential health effects may be additive or synergistic with co-exposures (Birch, 2011).

SUPPLEMENTARY DATA

Supplementary data can be found at <http://annhyg.oxfordjournals.org/>.

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