Exposure Control Strategies in the Carbonaceous Nanomaterial Industry

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Objective: Little is known about exposure control strategies currently being implemented to minimize exposures during the production or use of nanomaterials in the United States. Our goal was to estimate types and quantities of materials used and factors related to workplace exposure reductions among companies manufacturing or using engineered carbonaceous nanomaterials (ECNs). **Methods:** Information was collected through phone surveys on work practices and exposure control strategies from 30 participating producers and users of ECN. The participants were classified into three groups for further examination. **Results:** We report here the use of exposure control strategies. Observed patterns suggest that large-scale manufacturers report greater use of nanospecific exposure control strategies particularly for respiratory protection. **Conclusion:** Workplaces producing or using ECN generally report using engineering and administrative controls as well as personal protective equipment to control workplace employee exposure.

N anotechnology has emerged at the forefront of science research and technology development over the past decade. The nanotechnology sector has already achieved a multibillion dollar US market and is widely expected to grow to a 1 trillion dollar market in the United States by 2015.¹ As the mass production of engineered carbonaceous nanomaterials (ECNs) continues to grow, increased numbers of workers will be exposed to these materials.

Concurrent to the growth of the ECN market there is a coalescing level of evidence, which indicates that exposure to some forms of ECNs may cause adverse health effects. Although there are many active toxicology programs assessing the potential health effects of ECN, no epidemiologic studies are yet available, as they require long time periods and a sizeable workforce to be informative.² As with most particles in the workplace, inhalation is considered to be the main route by which free unbound nanomaterials can enter the bodies of workers, although data supports the possibility of dermal exposures as well.³

Studies have shown that long carbon nanotubes possess asbestos-like pathogenicity, which has raised even greater concerns about the possibility of exposures to such ECNs.^{4–6} Other animal studies have linked ECNs to possible adverse health effects, such as pulmonary inflammation, oxidative stress, onset of early interstitial fibrosis, and granulomas.^{7,8} Genotoxicity may result from ECN exposure: single-walled carbon nanotubes have been found to induce aneuploidy in human respiratory epithelial cells through interference with mitosis.⁹ Some evidence suggests that, once inhaled, nanomaterials can pass from the lungs into the bloodstream and might present

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a systemic health hazard. Inhaled carbon nanomaterials have been shown to rapidly clear rat lungs and translocate to other organs including the liver and spleen.¹⁰ Therefore, because of the current scientific evidence concerning the potential health hazards associated with nanomaterials, appropriate steps should be taken in the workplace to minimize worker exposure to ECN.

Safe occupational handling approaches and exposure control strategies for ECN, including administrative and engineering controls as well as personal protective equipment (PPE), are still developing. Nevertheless, several guidelines for working with nanomaterials have been issued by various countries^{11–15} and other guidelines from various stakeholders have been released as well.^{16,17} Nevertheless, the extent to which these exposure control strategies are being used during the manufacturing of nanomaterials in the United States has been relatively unknown.

As part of an investigation of the feasibility of industrywide exposure assessment and epidemiologic studies of ECN workers,¹⁸ the authors conducted a survey of companies manufacturing ECN in the United States, to identify types and quantities of materials produced and factors related to workplace exposure reductions. Several other studies, similar in nature to this project, have been conducted internationally^{19,20} to assess workplace health and safety and product stewardship practices for nanomaterials. The main objective of this manuscript is to describe current ECN manufacturing exposure control strategies, specifically engineering and administrative controls and PPE being used in the US ECN manufacturing industry.

METHODS

The methods used to identify companies participating in the study are described in detail elsewhere.¹⁸ Briefly, study participants were identified by using the Lux Nanotech Reports, fourth and fifth editions,^{21,22} as well as Web searches for manufacturers of ECN. The number of companies initially found totaled 139. Inclusion criteria for this study focused on companies manufacturing (or using during manufacturing) in the United States some type of ECN, which was defined as elemental carbon particles purposefully engineered to have specific properties or composition with at least one dimension less than 100 nm. Of the 139 companies originally identified from the initial list of prospective participants, 78 did not meet the inclusion criteria, because they were not handling ECN (41%), were involved solely in bench-scale research and development work (18%), had non-US carbon nanomaterials manufacturing operations only (14%), were solely repackagers (12%), or for other reasons (15%).¹

Introductory letters explaining the purpose of the study along with data collection forms were sent to company contacts prior to contact via e-mail or mail. This allowed participants advance notice of the type of questions that would be asked as well as the data being collected. Initial contacts were made to explain the aims and goals of the study, and formal interview times with knowledgeable company personnel were arranged. Phone surveys were conducted from October 2008 to May 2009. All phone interviews were administered by a certified industrial hygienist. Company representatives participating in the interviews included environmental health and safety personnel, scientists, and managers. The certified industrial hygienist conducting the phone interview preferentially scheduled

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The findings and conclusions in this report are those of the authors and do not necessarily represent the views of the National Institute for Occupational Safety and Health.

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the phone survey with a representative of the environmental health and safety staff or, if unavailable, the chief technical officer or other knowledgeable technical contact.

Data were collected to identify facility location, types, and quantities of materials produced as well as work practices and exposure control strategies from the participating companies manufacturing ECNs at or below 100 nm. Nevertheless, data were also collected for materials in the diameter size range greater than 100 nm as long as the company produced one form of ECN under 100 nm. Information was also ascertained on the size of worker populations at each facility as well as the change in the industrywide work force size from 2006 through 2008.¹⁸ Because there was no measure for response accuracy on the collected data, responses are described as reported. Potential participants were informed at the time of contact that participation was completely voluntary, and that results would be published only in aggregate form. The information gathered from this survey is being used to evaluate the feasibility of an industrywide exposure assessment and epidemiology study for US manufacturers and users of ECN. The challenges and opportunities for designing surveillance work are further discussed in the companion paper.18

Participating respondents included companies that were selfdescribed as currently manufacturing or using ECN, companies performing pilot scale work, and companies performing research and development (R&D) activities with plans of scaling up within the next 5 years. Potential participants who were strictly involved with R&D work with no plans to scale up were excluded. The participants were then classified into three groups for further examination on the basis of trends seen in production and exposure controls methods already in place. The groups consisted of companies performing manufacturing using production-based exposure controls, companies performing manufacturing using laboratory-based exposure controls, and companies performing R&D or pilot scale work. Proportions are calculated per group use of the specific exposure control strategy found in Tables 2 through 5. Ninety-five percent confidence intervals were calculated for all proportions in SAS 9.2, using the Wilson interval for estimation of binomial proportions.23

RESULTS

Sample Characteristics

From the 61 eligible companies, 30 agreed to participate in the study, resulting in a response rate of 49.2%. The eligible participating companies consisted of 15 manufacturers, as well as 15 companies performing pilot scale or R&D type work with plans to scale up within the next 5 years. The 30 participating companies were further divided into three groups for closer examination, on the basis of trends seen in production and exposure control methods already in place for each facility. Group 1 consisted of eight companies performing manufacturing using production-based exposure controls. Group 2 was composed of seven companies performing manufacturing using laboratory-based exposure controls. The 15 pilot-scale or R&D companies composed group 3. The eight group 1 companies described systems and programs more typical of largescale manufacturing operations, such as enclosed systems, comprehensive ventilation with pollution control devices, and automated packing operations. Most of these manufacturers also provided work clothing along with change facilities to their employees. The group 2 manufacturers appeared to employ laboratory practices (nonspecific laboratory hoods, biological safety cabinets (BSC), benchtop glove boxes, or benchtop vented boxes) with some specialized modifications to contain the ECN being handled. The group 3 companies consisted of several large corporations as well as small start-up companies performing R&D or pilot scale work with ECN. Their use of controls was a mixture of laboratory- and production-based methods.

ECN Characteristics

Nearly half of all participating companies reported manufacturing more than one type of ECN (n = 11), while several companies made different variations of the same type of material (n = 4). A total of 56 different types of ECN were reportedly produced by all respondents (Table 1). The most frequently produced types of nanomaterials were multiwalled carbon nanotubes (MWCNT;n = 18, 32.1%), followed by single-walled carbon nanotubes (SWCNT; n = 17, 30.4%), graphene (n = 6, 10.7%), nanofibers (n = 5, 8.9%), fullerenes (n = 4, 7.2%), and others, which included carbon quantum dots, dendrimers, diamond like films, and nanoengineered carbon black (n = 6, 10.7%).

The mean quantity produced for each nanomaterial ranged from 4.1 kg for fullerenes to 5001.8 kg for nanofibers (Table 1) with cumulative production total from all participants of roughly 15,000 kg of ECN. The mean diameter for the reported nanomaterials ranged from 0.6 nm for the fullerenes to 157 nm for the nanofibers. The mean particle length for reported nanomaterials of nonspherical shape ranged from 58.4 μ m for nanofibers to 187.9 μ m for SWCNT to 773.3 μ m for MWCNT. The calculated mean aspect ratio (AR) was largest for SWCNT at 186,936, while MWCNT and nanofibers had mean ARs of 68,704 and 424, respectively. Agglomerates of ECN were reported for all types of nanomaterials surveyed with average sizes ranging from 26.5 nm for the group consisting of other types of ECN to 209.3 nm for MWCNTs. Functional groups were reported to be present on 44.6% (n = 25) of all types of ECN. Common functional groups reported by participating companies were carboxylic acids, alcohols, and amines. Metal impurities were also reported for 23 (41.1%) of the 56 different types of ECN, all of which were either SWCNT or MWCNT. The most common types of metal impurities reported were Co, Ni, Fe, Mo, Y, and Al.

Engineering Controls

All participating companies reported using some sort of engineering control to reduce worker exposure to ECN and used multiple forms of engineering controls to reduce worker exposure as well (n = 30, 100%). Overall, the most common forms of controls used to minimize workplace exposures to ECN were that of chemical fume hoods (n = 25, 83%), seen in Table 2. This trend was true for both group 3 (n = 13, 87%) and group 2 (n = 7, 100%). A total of 3 of the 25 companies which reported using fume hoods also reported having HEPA filters associated with those hoods; however, this question was not directly asked as part of the original survey and cannot be considered representative.

The most commonly used form of engineering controls set in place by the group 1 exposure control group was local exhaust ventilation (LEV; n = 8, 100%), which was often reported to be custom built for the specific process or task. Two companies (25%) from group 1 reported using LEV with a HEPA filtration system, while only one company (14%) reported using this control for group 2 and five companies (33%) from group 3 reported using LEV with a HEPA filtration system.

The least common type of engineering exposure control strategy used by all three groups was BSC (n = 2, 7%). One BSC each was reportedly used by groups 2 and 3, while none were used in group 1. Group 1 also reported using the highest percentage of ventilated enclosures and glove boxes (n = 6, 75%) closely followed by group 3 (n = 10, 67%), while group 2 used this form of control the least (n = 2, 29%). Of the 18 total companies reportedly using ventilated enclosures and glove boxes, half reported that they were designed with HEPA filters. Nevertheless, this question was not directly asked during the phone survey, and it was not included on

	Total Number Produced	Diameter/Size, mean (range) (nm)	Length, mean (range) (µm)	Mean Aspect Ratio	Mean Agglomerate Size (µm)	Mean Quantity Produced (kg)
SWCNT	17 (30.4%)	5.04 (0.5-50)	187.9 (0.5–1,000)	186,936	68.3	44.9
MWCNT	18 (32.1%)	29.3 (1.2-200)	773.3 (0.1–18,000)	68,704	209.3	21.6
Nanofibers	5 (8.9%)	157 (20-300)	58.4 (1-200)	424	100	5,001.8
Graphene	6 (10.7%)	133 (2-500)	N/A	N/A	100	10.07
Fullerene	4 (7.2%)	0.6 (0.1–1)	N/A	N/A	200	4.1
Others	6 (10.7%)	52.9 (5-100)	N/A	N/A	26.5	1,175.02

TABLE 1. Descriptive Information on ECN From Participating Responded
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MWCNT, multiwalled carbon nanotubes; N/A, not applicable; SWCNT, single-walled carbon nanotubes.

Ranges and percentages are represented in parentheses. Means calculated with values provided from survey. Mean aspect ratio was calculated by averaging the individually calculated aspect ratios.

TABLE 2.	Number, Propo	ortion (95% Confidence	e Interval) of Com	panies Using	Various Engineer	ing Control Methods for ECN

	n	LEV	LEV W/HEPA	Chemical Fume Hoods	Biological Safety Cabinets	Ventilated Enclosures/ Glove Boxes	Enclosed Production Processes	Separate Ventilation for Office
Manufacturing Type								
Group 1: production- based exposure controls	8	8 , 1.0 (.68, 1.0)	2 , .25 (.07, .59)	5, .63 (.31, .86)	0 , 0.0 (0.0, .32)	6 , .75 (.41, .93)	3 , .38 (.14, .69)	6 , .75 (.41, .93)
Group 2: laboratory- based exposure controls	7	3 , .43 (.16, .75)	1 , .14 (.03, .51)	7, 1.0 (.65, 1.0)	1 , .14 (.03, .51)	2 , .29 (.08, .64)	3 , .43 (.16, .75)	3 , .43 (.16, .75)
Group 3: pilot and R&D scale operations	15	8 , .53 (.3, .75)	5 , .33 (.15, .58)	13 , .87 (.62, .96)	1 , .07 (.01, .3)	10 , .67 (.42, .85)	5, .33 (.15, .58)	11, .73 (.48, .89)
Total	30	19, .63 (.46, .78)	8, .27 (.14, .44)	25, .83 (.66, .93)	2 , .07 (.02, .21)	18, .6 (.42, .75)	11, .37 (.22, .54)	20, .67 (.49, .81)

HEPA, high-efficiency particulate air filtration; LEV, local exhaust ventilation.

Cells report number of companies (bold) as well as proportions. Corresponding 95% confidence intervals are represented in parentheses.

the data collection forms provided to the companies and may not be representative.

Overall, a total of 11 companies (37%) reported having completely enclosed production processes. Five (33%) of the enclosed production processes came from group 3, while three each came from groups 1 (38%) and 2 (43%). Most companies (n = 20, 67%) reported the overall use of a separate ventilation system for any office space that was near or connected to the manufacturing areas of ECN.

Some respondents described specialized or modified engineering controls such as walk-in hoods for high exposure tasks, or sonicators in closed containers (in some cases, the enclosed sonicators were placed inside chemical fume hoods). Most companies that reported using a HEPA filtered ventilated hood or other ventilated enclosures indicated using these devices when the exposure potential was deemed to be the greatest.

Work Practice and Administrative Controls

Overall, most companies reported providing some form of Health and Safety (H&S) training to employees (n = 21, 70%) (Table 3). Group 2 reported providing the least amount of H&S training (n = 4, 57%), while group 1 were the most likely to provide H&S training to their employees (n = 6, 75%) closely followed by group 3 (n = 11, 73%).

A majority of respondents, overall, had a housekeeping program in place (n = 25, 83%) as well as standard operating procedures for equipment maintenance (n = 21, 70%). A majority of companies also used wet methods for clean up (n = 21, 70%) as well as using some form of restricted or isolated access during the production or handling of ECN (n = 22, 73%). Group 3 companies reported using wet methods for clean up the most (n = 13, 87%), while group 2 reported using restricted access or isolated operations to control employee exposures most frequently (n = 6, 86%). Group 3 also reported using HEPA-filtered vacuums most often to clean spills or for routine cleaning (n = 9, 60%). Group 1 reported that three (38%) of the companies used HEPA vacuums and group 2 reported using HEPA vacuums the least often (n = 2, 29%).

Overall, a minority of companies provided change facilities or laundering programs for employee work clothing respectively (n = 9, 30%; n = 13, 43%). Nevertheless, group 1 reported providing both services to employees (n = 4, 50%; n = 4, 50%) more often than do the other groups.

Many companies described specific administrative controls such as placing carbon nanotubes in solution as soon as possible to minimize employee exposure. Two companies mentioned internal policies of carbon nanotubes only being allowed out of ventilated work areas when they were in solution. A few companies mentioned placing sticky mats at all entrances and exits of any room where ECN was stored or handled to reduce possible cross contamination.

	n	H&S Training Training	House Keeping Program	Wet Method for Clean up	HEPA Filtered Vacuum	Restricted/ Isolated Operations	Equipment Maintenance SOPs	Change Facilities	Uniforms Supplied/ Laundered
Manufacturing Type									
Production-based	8	6, .75	7, .88	4, .5	3 , .38	6 , .75	7, .88	4, .5	4, .5
exposure controls		(.41, .93)	(.53, .98)	(.22, .78)	(.14, .69)	(.41, .93)	(.53, .98)	(.22, .78)	(.22,.78)
Laboratory-based	7	4, .57	6 , .86	4, .57	2 , .29	6 , .86	4, .57	0 , 0.0	2 , .29
exposure controls		(.25, .84)	(.49, .97)	(.25, .84)	(.08, .64)	(.49, .97)	(.25, .84)	(0.0, .35)	(.08, .64)
Pilot and R&D Scale	15	11, .73	12, .8	13, .87	9, .6	10, .67	10, .67	5, .33	7, .47
Operations		(.48, .89)	(.55, .93)	(.62, .96)	(.36, .8)	(.42, .85)	(.42, .85)	(.15, .58)	(.25, .7)
Total	30	21, .7	25, .83	21, .7	14, .47	22 , .73	21, .7	9, .3	13, .43
		(.52, .83)	(.66, .93)	(.52, .83)	(.3, .64)	(.56, .86)	(.52, .83)	(.17, .48)	(.27, .61)

TABLE 3. Number, Proportion (95% Confidence Interval) of Companies Using Various Work Practice and Administrative Exposure Control Methods for ECN

H&S, health and safety; HEPA, high-efficiency particulate air filtration; SOP, standard operating procedures.

Cells report number of companies (bold) as well as proportions. Corresponding 95% confidence intervals are represented in parentheses.

Also, several companies reported that the weighing and transferring operations for dry powders occurred in isolated or restricted access areas and workers who entered these areas were required to complete nanospecific hazard training.

Two manufacturers and two R&D/pilot scale operations reported performing routine monitoring for airborne particulates. Nonspecific, total particulate counters were reported as the instruments employed. These questions were not directly asked as part of data collection efforts so may not be representative of the numbers of participating manufacturers performing air monitoring.

PPE Controls. Every company surveyed reported using some form of PPE to minimize worker exposure to ECN (Table 4). The most common form of protective clothing reported was the use of gloves (n = 29, 97%), which was reported by all of the companies in groups 1 and 2 (100%) and by 14 companies in group 3 (93%). The next most common form of protective clothing reported was the use of aprons (n = 14, 47%), which was most often reported by group 3 (n = 8, 53%). Full Tyvek suits were reportedly used most often by group 1 (n = 7, 88%), while group 2 used this form the least (n = 1, 14%). Nearly all surveyed companies reported using safety glasses (n = 28, 93%), while companies reportedly provided footwear and boot covers to employees less often (n = 12, 40%).

Respiratory Protection

A majority of companies reported providing some kind of respiratory protection to employees when working with ECN as well (n = 23, 77%) (Table 5). Most of the companies that reported using respiratory protection stated using either a half face negative pressure respirator (n = 13, 43%) with P100 or N100 cartridges and P100 or N95 filtering facepieces (n = 6, 20%). Several companies, mostly in group 1, reported providing multiple types of respiratory protection depending on the possibility and level of exposure. Three companies (10%), overall, reported the use of some type of respirator but did not specify the type. One company each from groups 2 (14%) and 3 (7%) reported using only nuisance dust masks. For this study's purpose those, two companies were counted as not using respirators because dust masks do not provide adequate respiratory protection for nanoparticles.^{14,24} A total of seven companies (23%), six from group 3 (40%) and one from group 2 (14%) reported not using any type of respiratory protection. One of the seven companies that reported not using respiratory protection stated the reason was due to the advanced ventilation controls in place at the facility. Two of the seven companies that did not use respiratory protection during ECN production or use reported having enclosed production processes.

Only one company mentioned an OSHA 29 CFR Part 1910.134 compliant fit-test program, although the question was not directly asked as part of the survey given to participating companies.

DISCUSSION

The results of the survey generally indicate that use of exposure control strategies, including engineering and administrative controls as well as personal protective equipment, in US industry is being reported by US manufacturers and end users of ECN. Most of the participating companies from this survey employed some type of airborne particulate control method such as the use of HEPA-filtered hoods, custom designed LEV systems, or enclosed production processes to control work place exposures to ECN. Also, technical contacts at all manufacturing, pilot plant, and R&D scale operations expressed awareness of the importance of controlling exposures to airborne carbon nanomaterials through the use of administrative controls and PPE. Nevertheless, room for improvement exists in areas such as respirator selection as well as engineering control selections.

The most important finding was that nearly one in four companies surveyed manufacturing or using ECN in the United States reported not using any type of respiratory protection or reported using an ineffective form of protection such as a dust mask. One of the seven companies not using respiratory protection stated that it was not needed due to the operations being fully enclosed, and one other company reported having enclosed production processes but did not state that this was their reason for not using respirators. Similar trends on respirator usage have been seen in previous international surveys on exposure control strategies and PPE uses.^{19,20} NIOSH has recently recommended that respirator use be considered even for enclosed processes if measurement data indicate that nanomaterial exposure is not well controlled.¹⁴ As recommended exposure limits become available for airborne nanoparticles, it will be possible to use the traditional NIOSH respirator selection logic to select respiratory protection with an assigned protection factor that is sufficient to provide protection against the actual airborne concentration of nanoparticles in the workplace.²⁵ In January 2011, NIOSH posted on its Web site for public comment, a recommended exposure limit for carbon nanotubes and carbon nanofibers of 7 μ g/m³ as an 8-hour time weighed average.26

It is difficult to generalize about what types of exposure control strategies are appropriate for each individual company. Factors that influence selection of engineering controls and other exposure control strategies include the physical form of the nanomaterial, task duration, frequency, and quantity of ECN being handled. Nevertheless,

	n	Aprons	Tyvek Suits	Work Boots/Boot Covers	Safety Glasses	Gloves	Respirators
Manufacturing Type							
Production-based exposure controls	8	3 , .38 (.14, .69)	7, .88 (.53, .98)	3 , .38 (.14, .69)	7, .88 (.53, .98)	8 , 1.0 (.68, 1.0)	8 , 1.0 (.68, 1.0)
Laboratory-based exposure controls	7	3 , .43 (.16, .75)	1 , .14 (.03, .51)	3 , .43 (.16, .75)	7, 1.0 (.65, 1.0)	7, 1.0 (.65, 1.0)	6 , .86 (.49, .97)
Pilot and R&D scale operations	15	8 , .53 (.3, .75)	5 , .33 (.15, .58)	6 , .4 (.2, .64)	14, .93 (.7, .99)	14, .93 (.7, .99)	9 , .6 (.36, .8)
Total	30	14, .47 (.3, .64)	13, .43 (.27, .61)	12, .4 (.25, .58)	28 , .93 (.79, .98)	29 , .97 (.83, .99)	23, .77 (.59, .88)

TABLE 4.	Number, Proportior	n (95% Confidence Interval) of Companie	es Using Personal Prote	ective Equipment for ECN

TABLE 5. Number, Proportion (95% Confidence Interval) of Companies Using Respirator for ECN

	n	Dust Mask	Filtering Facepiece	Half Face	Full Face	PAPR	Did Not Specify	None
Manufacturing Type								
Production-based exposure controls	8	0 , 0.0 (0.0, .32)	2 , .25 (.07, .59)	5, .63 (.31, .86)	1, .13 (.02, .47)	2 , .25 (.07, .59)	0 , 0.0 (0.0, .32)	0 , 0.0 (0.0, .32)
Laboratory-based exposure controls	7	1 , .14 (.03, .51)	1, .14 (.03, .51)	4 , .57 (.25, .84)	0 , 0.0 (0.0, .35)	0 , 0.0 (0.0, .35)	1 , .14 (.03, .51)	1, .14 (.03, .51)
Pilot and R&D scale operations	15	1 , .07 (.01, .3)	3 , .2 (.07, .45)	4 , .27 (.11, .52)	0 , 0.0 (0.0, .2)	1, .07 (.01, .3)	2 , .13 (.04, .38)	6 , .4 (.2, .64)
Total	30	2, .07 (.02, .21)	6, .2 (.1, .37)	13, .43 (.27, .61)	1, .03 (.01, .17)	3, .1 (.03, .26)	3, .1 (.03, .26)	7, .23 (.12, .41)

Cells report number of companies (bold) as well as proportions. Corresponding 95% confidence intervals are represented in parentheses.

given the limited information about the human health risks associated with occupational exposure to ECN, appropriate steps should be taken to minimize the risk of worker exposure through the implementation of risk management programs.^{13,27} When controlling potential exposures within a workplace, NIOSH has recommended a hierarchical approach to reduce worker exposures.²⁸ The basis for the hierarchy of controls is to eliminate the hazard when possible by substituting it with a less hazardous material or, if not feasible, control the hazard at or as close to the source as possible through engineering controls. If those measures are not successful, then administrative controls and PPE, respectively, should be used as last efforts.

There were several limitations to this study that are worth mentioning. One limitation is the possibility of a selection bias, which could have occurred for the survey responses from participating companies. This bias could not be avoided because all contributing participants of the survey provided information on a voluntary basis. Companies that chose to participate might have been more aware of the health and safety issues with ECN. If this were true, it still provides some perspective into the differences between the various types of manufacturing groups because of the varying range of responses received regarding the exposure control strategies already in place across all three groups.

In addition, the survey was conducted through the months of October 2008 to May 2009 during a severe economic recession, which may have affected the participation rates of companies receiving the survey. It should also be noted that the number of companies were most likely underestimated because of the exclusion of repackagers, as well as bench scale research and development companies that did not express a plan to move to at least pilot scale in the next 5 years. Also, there was no way to verify survey results from respondents. Nevertheless, given the assurance that data would be published only in aggregate form, there was little motivation for or any indication of dishonest responses, as company answers seemed generally consistent across the two groups of manufacturers and the R&D/pilot scale operations group as well. Still, it is unknown to what extent the reported engineering controls and PPE were adequately deployed within the work environment. Nevertheless, since this original survey, we have conducted several site visits at participating companies to assess possible exposures in the workplace to carbon nanotubes and nanofibers. This has allowed direct, visual confirmation of the reported survey results for the uses of exposure control strategies.

Although there have been several best practice guidelines for managing the risks of nanomaterials published, there are no widely accepted exposure limits for ECN, and there are no readily available and cost-effective instrumentation to assess workplace exposures. Much of this has to do with the diversity of ECNs being produced and their varying sizes, shapes, and compositions, which makes it difficult to develop any standard exposure limits. Another significant step to overcome is that the scientific community is still searching for the most relevant aspect of airborne nanomaterials that should be measured: number, surface area, mass concentration, or a combination of these.²⁹

For the most part, this survey indicates that the current controls used are still relatively underdeveloped or in the process of being developed by some companies manufacturing or using ECN in the United States. This is likely because of the fact that organizations worldwide have not come to a consensus regarding the existence of risks or accepted exposure limits. This unique situation can make it difficult for industry to justify reducing exposures and thus might slow the adoption and dissemination of best practice exposure control strategies. Nevertheless, until widely accepted exposure limits with validated air monitoring procedures become readily available, the general best practice guidelines provided by trusted organizations should be followed to control workplace exposures to ECN.

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REFERENCES

- Aitken R, Chaudhry M, Boxall A, Hull M. Manufacture and use of nanomaterials: current status in the UK and global trends. *Occupat Med.* 2006;56:300– 306.
- Schulte PA, Schubauer-Berigan MK, Mayweather C, et al. Issues in the development of epidemiologic studies of workers exposed to engineered nanoparticles. J Occup Environ Med. 2009;51:323–335.
- Ryman-Rasmussen J, Riviere J, Monteiro-Riviere N. Penetration of intact skin by quantum dots with diverse physicochemical properties. *Toxicol Sci.* 2006;91:159–165.
- Shvedova A, Kisin E, Mercer R, et al. Unusual inflammatory and fibrogenic pulmonary responses to single-walled carbon nanotubes in mice. *Am J Physiol: Lung Cell Mol Physiol.* 2005;289:698–708.
- Poland CA, Duffin R, Kinloch I, et al. Carbon nanotubes introduced into the abdominal cavity of mice show asbestos-like pathogenicity in a pilot study. *Nat Nanotechnol.* 2008;3:423–428.
- Pacurari M, Yin X, Zhao J, et al. Raw single-wall carbon nanotubes induce oxidative stress and activate MAPKs, AP-1, NF-κB, and Akt in normal and malignant human mesothelial cells. *Environ Health Perspect*. 2008;116:1211– 1217.
- Donaldson K, Aitken R, Tran L, et al. Carbon nanotubes: a review of their properties in relation to pulmonary toxicology and workplace safety. *Toxicol Sci.* 2006;92:5–22.
- Porter D, Hubbs A, Mercer R, et al. Mouse pulmonary dose- and time courseresponses induced by exposure to multi-walled carbon nanotubes. *Toxicology*. 2010;269:136–147.
- Sargent LM, Shvedova AA, Hubbs AF, et al. Induction of aneuploidy by single-walled carbon nanotubes. *Environ Mol Mutagen*. 2009;50:708–717.
- Oberdörster G, Sharp Z, Atudorei V, et al. Extrapulmonary translocation of ultrafine carbon particles following whole-body inhalation exposure to rats. *J Toxicol Environ Health PT A*. 2002;65:1531–1543.
- 11. Bundesanstalt für Arbeitsshutz und Arbeitsmedicin (Federal Institute for Occupational Safety and Health). Exposure to nanomaterials in Germany: results of the corporate survey of the Federal Institute for Occupational Safety and Health (BAuA) and the Association of the Chemical Industry (VCI) using questionnaires. 2008. Available at: http://www.baua.de/en/

Topics-from-A-to-Z/Hazardous-Substances/Nanotechnology/pdf/survey.pdf? __blob=publicationFile&v=2. Accessed April 19, 2011.

- British Standards Institute. Nanotechnologies—part 1: good practice guide for specifying manufactured nanomaterials. 2008:PD 6699-1:2007.
- British Standards Institute. Nanotechnologies—part 2: guide to safe handling and disposal of manufactured nanomaterials. 2008:PD 6699-2:2007.
- 14. National Institute for Occupational Safety and Health. Approaches to Safe Nanotechnology: Managing the Health and Safety Concerns Associated with Engineered Nanomaterials. Cincinnati, OH: US Department of Health and Human Services, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 2009-125: 2009.
- Institut de recherché Robert-Sauvé en santé et en sécurité du travial. Best practice guide to synthetic nanoparticle risk management. 2009: Report R599.
- National Research Council. Review of the Federal Strategy for Nanotechnology-Related Environmental, Health, and Safety Research. Atlanta, GA: National Academies Press; 2009.
- International Council on Nanotechnology (ICON). GoodNanoGuide. Available at: http://www.goodnanoguide.org/tiki-index.php?page=HomePage. Accessed February 2010.
- Schubauer-Berigan MK, Dahm MM, Yencken MS. Engineered carbonaceous nanomaterials manufacturers in the United States: workforce size, characteristics, and feasibility of epidemiologic studies. *J Occup Environ Med.* 2011;53(6 Supp):S62–S67.
- Conti J, Killpack K, Gerritzen G, et al. Health and safety practices in the nanomaterials workplace: results from an international survey. *Environ Sci Technol.* 2008;42:3155–3162.
- Balas F, Arruebo M, Urrutia J, Santamaria J. Reported nanosafety practices in research laboratories worldwide. *Nat Nanotechnol.* 2010;5:93–96.
- Lux Research, Inc. The Nanotech Report 4. Investment Overview and Market Research for Nanotechnology. Bostan, MA: Lux Research, Inc; 2006:207.
- Lux Research, Inc. The Nanotech Report 5. Investment Overview and Market Research for Nanotechnology. Bostan, MA: Lux Research, Inc; 2007:246.
- Agresti A, Coull B. Approximate is better than "Exact" for interval estimation of binomial proportions. *Am Statist.* 1998;52:119–126.
- Rengasamy S, Eimer B, Shaffer RE. Nanoparticle filtration performance of commercially available dust masks. J Int Soc Res Prot. 2008;25:27–41.
- 25. National Institute for Occupational Safety and Health. *Respirator Selection Logic*. Cincinnati, OH: US Department of Health and Human Services, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 2005-100; 2004.
- 26. National Institute for Occupational Safety and Health. Draft Current Intelligence Bulletin Occupational Exposure to Carbon Nanotubes and Nanofibers. Cincinnati, OH: US Department of Health and Human Services, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH), NIOSH Docket Number: NIOSH 161-A; 2010. Available at: http://www.cdc.gov/niosh/docket/review/docket161A/. Accessed February 2011.
- Schulte P, Geraci C, Zumwalde R, Hoover M, Kuempel E. Occupational risk management of engineered nanoparticles. *J Occup Environ Hyg.* 2008;5:239– 249.
- 28. National Institute for Occupational Safety and Health. NIOSH Testimony on the Occupational Safety and Health Administration Proposed Rule on Health Standards: Methods of Compliance. Cincinnati, OH: US Department of Health and Human Services, Centers for Disease Control, National Institute for Occupational Safety and Health; 1990.
- Maynard A, Aitken R, Butz T, et al. Safe handling of nanotechnology. *Nature* 2006:444:267–269.