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Fiber emission of carbon nanotube containing materials for construction applications

Candace S. J. Tsai^{a,b,c} , Nara Shin^b, and Anthony Formella^c

^aDepartment of Environmental Health Sciences, Field School of Public Health, University of California, Los Angeles, Los Angeles, California, USA; ^bDepartment of Environmental and Radiological Health Sciences, Colorado State University, Fort Collins, Colorado, USA; ^cDepartment of Chemical and Biological Engineering, Colorado State University, Fort Collins, Colorado, USA

ABSTRACT

This project aimed to assess the carbon nanotube (CNT) fiber emission and the potential exposure associated with grinding and brushing of CNT containing products for applications in construction. Specifically, we looked at applications of pre-dispersed CNT in a liquid phase, where the likelihood of exposure was evaluated. The CNT products to be evaluated were tested in two ways: As a dried-out film formed on the surfaces of concrete tiles to simulate a spill and embedded in concrete during mixing to simulate intended use. The surface film trial showed no loose and individual CNT fiber with aspect ratio higher than 3 to 1 released by the brushing motion, although larger particles containing CNT were found as airborne particles originating from the brushing of CNT containing tile surfaces. A few non-CNT straight fibers with sub-micrometer to a few micrometers in length were found from concrete cylinder grinding. This can potentially be related to the specific loading and concentration used or can be a consequence of the chemical pre-dispersion state of the liquid CNT prior to the trials taking place. According to the low number of CNT containing particles found, very trace amount of elemental carbon was contributed by CNTs. We also demonstrated the importance of confirming the presence of individual CNT and CNT containing substance using electron microscopy analysis and the efficiency of using direct sampling method as a result of comparisons among employed methods.

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Introduction

Construction workers can be classified as a high-risk group for respiratory diseases due to excessive exposure to silica (Meijer, Kromhout, and Heederik 2001; Tavakol et al. 2017). Respirable crystalline silica consists of particles smaller than sub micrometer sizes that are created when scrubbing, brushing, cutting, sawing, grinding, drilling, and crushing stone, concrete, brick, and mortar. About 2.3 million people in the U.S. are exposed to silica at work (EPA 1996) and the risk for silicosis remain similar in 2000s (Bang et al. 2015; Sauvé et al. 2013). Long-term silica dust exposure has been associated with substantially increased mortality among exposed population; the increased health risk was observed not only for deaths due to respiratory diseases and lung cancer, but also due to cardiovascular disease (Chen et al. 2012). Various activities involving concrete work have been reported to result in exposure levels many times higher than the permissible exposure limit (PEL). Grinding and

cutting concrete have been found to create a higher exposure than other activities (Flanagan et al. 2003; Park and Hwang 2017), and a high proportion of workers performing concrete grinding were overexposed to respirable crystalline silica dust (Akbar-Khanzadeh and Brillhart 2002). Environmental exposure to silica has also been reported with concerns for causing fatal disease (Bhagia 2012; EPA 1996).

Concrete reinforced with multiple-walled carbon nanotubes (MWCNTs) (“CNT concrete”), a novel advanced material, may release a mixture of MWCNT fibers and silica particles into the environment when it is processed and handled in various applications. CNT exposure has been of increasing concern because of its morphological similarities to asbestos (Donaldson et al. 2006; Donaldson et al. 2010; Donaldson et al. 2013; Maynard et al. 2006). The hazards of asbestos exposure are well-known. Recent studies have shown the potential carcinogenicity of MWCNTs, especially those known as type 7, which

CONTACT Candace S. J. Tsai  candacetsai@ucla.edu  Department of Environmental Health Sciences, Field School of Public Health, University of California, 650 Charles E. Young Drive S., MC 177220, Los Angeles, Los Angeles, CA 90095, USA.

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were classified as a 2B carcinogen in 2014 by the International Agency for Research on Cancer and the Organization for Economic Co-operation and Development (OECD) (Grosse et al. 2014; Kuempel et al. 2017; OECD 2016).

In addition, CNT toxicity has been demonstrated in a number of animal studies, suggesting that CNTs may significantly impact pulmonary cells by inducing inflammation, granulomas, and fibrotic reactions (Lam et al. 2004; Lam et al. 2006; Muller et al. 2005; Muller et al. 2009; OECD 2016; Poland et al. 2008). CNTs are respirable particles with individual fibers that have been observed to be 4 to 100 nm in diameter and 50 nm to 15 μm in length (Bateson et al. 2017; Iijima 1991; Wang et al. 2009; Yamashita et al. 2010). CNT agglomerates larger than the respirable size range have also been found in workplaces (Dahm et al. 2015; Dahm et al. 2018). The physical characteristics of CNTs give them the ability to elicit pathological responses similar to asbestos; thus, accurate characterization of exposure is imperative. The recommended exposure limit (REL) by the National Institute for Occupational Safety and Health (NIOSH) for CNTs is $1\ \mu\text{g}/\text{m}^3$ of elemental carbon using the NIOSH Manual of Analytical Method (NMAM) 5040 (NIOSH 2013, 2016). The REL employed in Europe, called the nano reference value, is $0.01\ \text{fiber}/\text{cm}^3$ using instrument readings (Social and Economic Council 2012).

CNTs are now produced in large scale and applied in various applications. Assessment is needed in these applications to evaluate the risk and any associated health effects from CNT emissions. Human's exposure to CNT concrete dust may be of particular concern because silica is a known lung carcinogen and fibrotic agent. In addition, CNTs with diameter hundredth smaller than asbestos, some like asbestos, have caused lung cancer, mesothelioma and fibrosis in laboratory animals, raising the possibility of synergistic interactions between the two materials (Kisin et al. 2011; Takagi et al. 2008).

Concrete is a porous material that can form cracks, which is a safety concern for construction. Fillers such as CNT fibers can be used to fill in the pores of the concrete and to connect the components and disperse stresses in concrete (Elkady and Hassan 2018). Fiber-reinforced concrete can reduce the pre-cracks and pores often found in hardened concrete (Gangsa, Flanders, and Landis 2015; Oesch, Landis, and Kuchma 2016). Nanometer-sized fibers such as CNT and carbon nanofibers (CNF) have been added to reinforce concrete as crack bridging (Elkady and Hassan 2018; Li et al. 2017; Vidivelli and Ashwini

2018; Yakovlev et al. 2017). Concrete as a cementitious composite is held together by a complex network of nanoparticles (NPs) known as calcium silicate hydrate (CSH). The large surface energy and number of atoms present at the nanotube surface promotes the formation of an interface with CSH and leads to strong binding for stress transfer (Elkady and Hassan 2018; Vidivelli and Ashwini 2018; Yakovlev et al. 2017). The addition of a small amount (1%) of CNT can improve mechanical properties, and MWCNTs show the best improvement (Vidivelli and Ashwini 2018). The enhanced flexibility of concrete can strengthen the tolerance of the mechanical force from environmental factors and results in a sustainable construction. It is of fundamental importance that the addition of CNT to concrete work does not increase the need for protective measures beyond what is already needed for safe handling of concrete with regard to eliminating the risk of silica particle exposure.

There is an immediate need to characterize substance emission from the practical use of MWCNT-reinforced concrete products as other products before the widespread application of the material (NIOSH 2013). This study specifically determined emerging risks related to emission level and released substance to the environment from the MWCNT concrete and explored ways in which new technologies can safely benefit society. Therefore, the objectives of this study were to study the release of airborne particles from practical activities on CNT containing surfaces and concretes; and evaluate methods which can accurately determine a trace amount of exposure from CNT concrete. Our results will aid further improvement of CNT concrete products to minimize the risk of disease development in the future and enable the society to be benefited from this emerging technology.

Materials and methods

The CNT filmed and embedded concrete products to be evaluated were tested in two ways: As a dried-out film formed on the surfaces of concrete tiles to simulate a spill of CNT admixture and embedded in concrete during mixing to simulate intended use. The CNTs contained in the studied products were MWCNTs. We referred CNTs to MWCNTs in this study. The concrete tiles with film consisted of CNT stabilized and pre-dispersed in a liquid admixture coated onto the surfaces were called tile product, and concrete cylinders embedded with the same CNT containing liquid were called cylinder product. The CNT containing products were evaluated through comparison with control

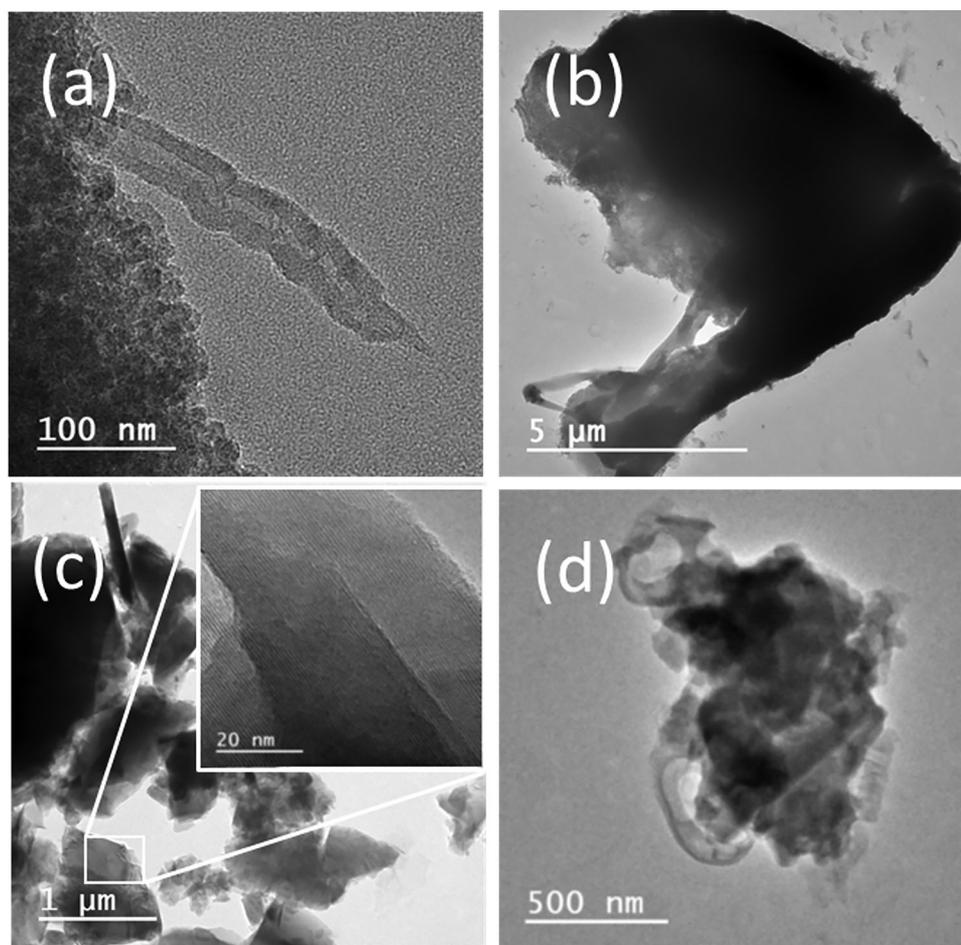


Figure 1. TEM images of particles collected and analyzed following the NMAM 7402. (a) A large agglomerate with a CNT fiber embedded from brushing CNT containing tile surface, product code A. (b) A Large amorphous particle collected from brushing non-CNT containing tile surface, product code B. (c) Particles showing lattice collected from grinding CNT containing concrete cylinder, product code C. (d) An amorphous particle collected from grinding non-CNT containing concrete cylinder, product code D.

products without CNTs. This project was performed based on the worst scenario case to evaluate the potential release of CNT fibers embedded in the product under aggressive manipulation methods. The coated concrete tile products and concrete cylinder products were made and provided by the sponsoring company. The cylinders were filled and cured according to American Society for Testing and Materials (ASTM) C192 standards (ASTM C192/C192M-19 2019). More details are available in the [online supplementary information \(SI\)](#).

Simulated activities

To simulate the dispersion of the dried CNT admixture on the concrete, the surfaces of the prepared tile products were brushed with an electrical brush wheel (Versa 4V Lithium ion power scrubber, Dremel, Racine, WI, USA) on a hand grinder to simulate vigorous dry sweeping after a spill. The concrete cylinder

products were abraded with a diamond wheel on a hand grinder (18 V Angle grinder, RYOBI, Fuchu, Hiroshima, Japan) to simulate grinding of the concrete products. The airborne particles released from these activities were evaluated and characterized with the methods described in the following sections. All experiments for brushing and grinding products were entirely conducted inside a glovebox equipped with an ultrafilter (with pore size $\sim 0.01 \mu\text{m}$). The ventilation system of the glovebox was kept off during the experiment, and no air exchange occurred. The glovebox was wiped clean before and after each set of experiments, and the background concentrations were monitored using real time instrument (RTI).

Assessment of airborne substances from concrete tile products

The tile products coated with dried out CNT-containing admixture and the reference admixture as control

Table 1. Mass concentrations and sampling information with five different methods.

		Tile with CNT	Tile control	Concrete with CNT	Concrete control
Sample code		A	B	C	D
NMAM 7402	Total mass (mg)	5.75 (3.40)	1.57 (1.63)	84.9 (60.0)	132 (12.1)
	Total mass conc. (mg/m ³)	57.5 (34.0)	15.7 (16.3)	1420 (1000)	2200 (202)
TDS	Total mass (mg)	6.67 (1.29)	0.57 (0.35)	18.2 (6.57)	19.4 (12.8)
	Total mass conc. (mg/m ³)	445 (88.1)	38.0 (22.0)	2030 (729)	2160 (1410)
NMAM 5040	Total mass (mg)	6.93 (2.08)	3.07 (3.34)	129 (93)	244 (13.9)
	Total mass conc. (mg/m ³)	69.3 (20.8)	30.7 (33.4)	2150 (1540)	4070 (232)
	EC mass (mg)	6.35 (6.58)	<0.7	109 (166)	31.3 (4.51)
	EC conc. (mg/m ³)	63.5 (65.8)	<7	1810 (2770)	517 (80.2)
NMAM 7500	Total mass (mg)	0.03 (0.06)	1.23 (1.10)	29.1 (26.8)	61.3 (11.9)
	Total mass conc. (mg/m ³)	314 (543)	14500 (12900)	570000 (526000)	1201000 (233000)
	Quartz (mg/sample)	<5.0	<5.0	4070 (4930)	631 (543)
	Cristobalite (mg/sample)	<5.0	<5.0	<5.0	<5.0
	Tridymite (mg/sample)	<30	<30	<30	<30
	Total silica (mg/sample)	ND	ND	4070 (4930)	631 (543)
	Silica mass conc. (mg/m ³)	NA	NA	79800 (96700)	12400 (10600)

Note:

- Standard deviation of mass or mass concentration was presented in parentheses.
- ND: Not detectable; NA: Not available.
- NMAM 7402 and 5040 collect particles at a flowrate of 2 L/min. TDS collects particles at a flowrate of 0.3 L/min. NMAM 7500 collects particles at a flowrate of 1.7 L/min. Each sampler collects tile brushing for 50 min, and concrete grinding for 30 min.

are denoted “A” and “B” as product code, respectively, followed by a number (1, 2, or 3) representing each of the three repeated experiments. All tile products were brushed, and the released particles became airborne from the surfaces of the tiles. Each experiment was performed as follows: (1) 10 min measurements of pre-experiment background concentrations, (2) 50 min measurements of 10 cycles of brushing on new areas of the tile (with 1 min of brushing and a 4 min break in one cycle), and (3) 1 h measurement of post-experiment background concentrations, thus making the total experimental time of 2 h. To simulate the worst scenario of particle release and collect the highest amount of released particles for characterization, a customized vinyl panel (cube shape with 17.8 cm/7 inch in W, L, and H) was placed on the four sides of the tile to enclose it with the top open for accessing the tile and collecting released dust. Measurements of airborne particles and collections of released substance were taken at the top side of the panel, which was 17.8 cm/7 inch vertically above the work surface of the glovebox and approximately 12.7 cm/5 inch vertically above the tile surface. The experimental set up was shown in the SI Figure S1.

Assessment of airborne substances from concrete cylinder products

The cylinder containing CNT is denoted “C,” and the cylinder not containing CNT is denoted “D,” as product code. Three experiments were performed for each cylinder and noted with numbers 1 to 3. The evaluation of particle release from the cylinder began with a 10 min pre-experiment background measurement.

Then, the concrete cylinder was ground by using a small angle grinder in a cycle of 2 min of grinding and a 3 min break for six cycles, for a total of 30 min. The post-experiment background concentration was measured immediately after the grinding cycles were finished, until the total experimental time of 2 h was reached. All measurements and collections of airborne substances were performed 12.7 cm/5 inch horizontally away from the center of the cylinder and 25.4 cm/10 inch vertically above the work surface of the glovebox, which is 5 cm/2 inch vertically above the surface of the cylinder, as shown in Figure S1.

Specific methods of sampling and analysis

This study used five sampling methods and devices to evaluate the particle release and potential exposure to CNT, silica, and other substances. The methods include (1) NIOSH Manual of Analytical Methods (NMAM) 7402 for fiber collection (NIOSH 1994), (2) the diffusion sampler (TDS), a newly designed sampling device for nanoparticles (Tsai and Theisen 2018; Tsai et al. 2018), (3) direct reading real-time instruments (RTIs) including NanoScan SMPS (model 3910, TSI, Shoreview, MN, USA) and OPS (model 3330, TSI, Shoreview, MN, USA) measuring particle mobility diameters, (4) NMAM 5040 for evaluating elemental carbon, and (5) NMAM 7500 for evaluating silica. Details of these sampling devices and processes are included in the SI. NMAM 7402 was a suggested method by NIOSH for identification of CNT fibers. In this study, we also measured the mass of deposited dust on the filter. The particle size distribution data were further analyzed with Pearson correlation

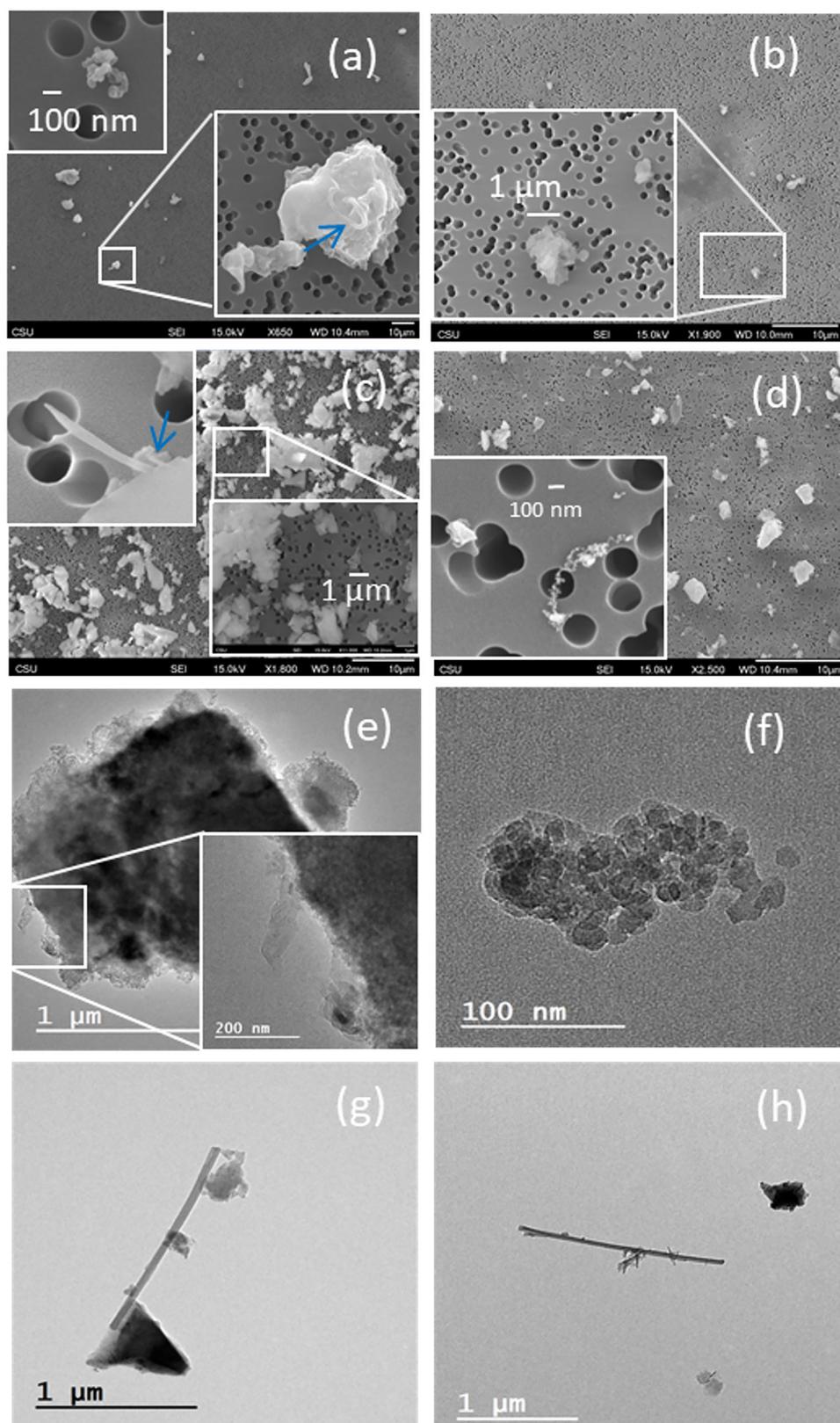


Figure 2. SEM (a)–(d) and TEM (e)–(h) images of particles collected on the polycarbonate filters and grids by TDS. (a) Images of particles on a polycarbonate filter with a stick shape particle and a CNT fiber containing particle from brushing tile A. (b) Particles from brushing tile B. (c) Particles from grinding cylinder C showing a stick shape particle and CNT fiber in the agglomerate. (d) Particles from grinding cylinder D showing a chain shape agglomerate consisting of many nanometer sized particles. (e) A CNT containing particle from tile A. (f) An agglomerated particle from tile B. (g) Particles including a stick shape particle from grinding cylinder C. (h) Particles including a stick shape particle from grinding cylinder D.

analysis using SPSS program to determine the correlation/similarity of emitted particle sizes among brushing or grinding CNT containing and non-CNT containing products.

Results and discussion

Airborne particle characterizations using microscopy analysis

Sampling following NMAM7402 from brushing tiles and grinding cylinders

Airborne particles collected during tile and cylinder tests were prepared following NMAM 7402 by a commercial vendor, Bureau Veritas. A total of 36 grids containing particles transferred from 12 mixed cellulose ester (MCE) filter samples, 3 grids per filter sample, were prepared. Among those grids, one representative grid per sample was analyzed using transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS) for morphology and elemental composition analysis of particles. Common shapes of particles found in these samples were amorphous, round or irregular as shown in [Figure 1](#). The number of microscopic images taken and the number of particle agglomerates containing CNT were listed in the SI Table S1.

A CNT containing agglomerate was found on particles collected during brushing CNT containing tile surface (code A) as seen in [Figure 1a](#), which was the only one CNT containing particle found from 21 analyzed TEM images of the sample collected and analyzed following NMAM 7402 from brushing CNT containing tile surface. Particles collected from brushing non-CNT containing tile surface (code B) showed an example in [Figure 1b](#) with a large amorphous particle and no free CNT fiber was found from all images taken and analyzed. [Figure 1c](#) showed particles collected from grinding CNT containing concrete cylinder (code C) and they were in amorphous and acicular shapes with the structure of carbon/graphene seen in the amplified image. As shown in [Figure 1d](#), particles collected from grinding non-CNT containing concrete cylinder (code D) showed an agglomerate with hollow structures. Among released airborne substances associated with grinding cylinder, we could not find CNT containing or fiber containing particle among 41 analyzed particle images, which 17 and 24 images, respectively, were particles released from grinding CNT containing concrete C and non-CNT containing concrete D. Additional images accompanied with elemental composition analysis are available in the SI.

The mass concentrations and related sampling parameters of all airborne dust samples collected using NMAM 7402, TDS, NMAM 5040 and NMAM 7500 were listed in [Table 1](#). Using NMAM 7402, the average concentrations of total mass on collected airborne particles were 57.5 mg/m^3 for product A, 15.7 mg/m^3 for product B, $1,415 \text{ mg/m}^3$ for product C, and $2,200 \text{ mg/m}^3$ for product D.

Sampling using TDS from brushing tile and grinding cylinder

Particles collected using TDS during brushing tile surface and grinding concrete cylinder were imaged using scanning electron microscope (SEM) and TEM. Particles deposited on the polycarbonate filter and the TEM grid with representative images were shown in [Figure 2](#).

SEM and TEM images were presented with analysis at low and high magnifications, depending on the quantity, distribution, and size of the particles on the filter or grid. [Figures 2a–d](#) showed representative images of particles on the polycarbonate filters. These particles released from brushing the coated layer at the tile surfaces were found heavily dispersed on the filter as seen in [Figures 2a and b](#) for both CNT containing product A and non-CNT containing product B. Most particles were round individual or agglomerates with sizes ranged from a few hundred nm to a few μm . The primary size of the particles in the agglomerate was less than 100 nm as seen on one of the high magnified images in [Figure 2a](#). A particle containing one CNT fiber on the surface was shown with arrow mark on the magnified image in [Figure 2a](#). We found 3 CNT containing agglomerates similar to those seen in [Figure 2a](#) among 42 SEM images of collected particles during the brushing on the CNT containing tile surface. We could not find any fiber containing particles among 46 SEM images of collected particles during the brushing on the non-CNT containing tile product.

The particles deposited on the filter from grinding CNT containing cylinder C and non-CNT containing cylinder D were shown in [Figures 2c and d](#), respectively. Unlike brushing method, particles from grinding concrete cylinder are highly dispersed on the polycarbonate filters. Those particles contain relatively various morphologies. Due to the operation with a stronger mechanical force, the grinding released high amounts of airborne agglomerates with many down-broken particles in sizes of a few μm and smaller. Particles released from grinding CNT containing concrete cylinder C showed a straight stick particle less

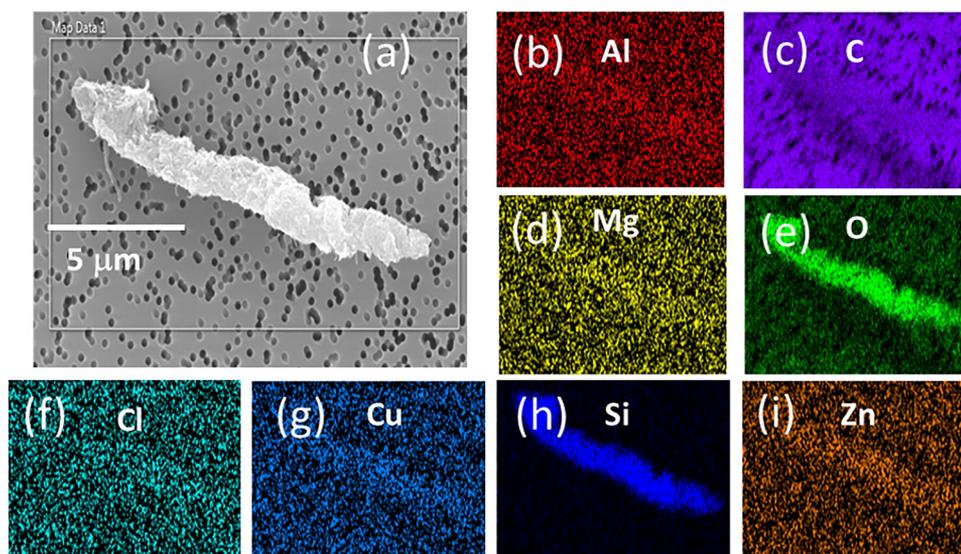


Figure 3. EDS with SEM analysis result of particles released from CNT containing tile A collected by TDS. (a) A SEM image of particle on the polycarbonate filter showing CNT fiber containing (b)–(i) colorimetric elemental intensity of particles showing for each element.

than a μm in length pointing out from an agglomerate as seen on the magnified image at the left top corner (no arrow mark) of Figure 2c. These similar stick shape particles in sizes above sub-micrometer, which unlikely were CNT or CNT containing, were found on some agglomerates released from grinding cylinders C and D. However, there was one short fiber marked with an arrow next to the stick shape particle (Figure 2c), which could be a CNT fiber embedded in the agglomerate. This CNT containing agglomerate was the only one found among 47 SEM images of product C. We could not find CNT containing particles among 40 SEM images of product D.

The particles collected on TEM grids using TDS were analyzed directly under TEM after removing the grids from the filter substrate. Figures 2e to h presented the TEM images of particles released from brushing tile surfaces (Figures 2e and f) and grinding concrete cylinders (Figures 2g and h). There was a short CNT fiber pointing out from the edge of the agglomerate seen in Figure 2e with particles released during brushing of the CNT containing tile surface A. An agglomerate consisting of with many small particles was a typical agglomerate released during brushing non-CNT containing tile surface B as seen in Figure 2f. Using TDS method, six CNT containing particles were found among 57 TEM images of particles released during brushing CNT containing tile surfaces A; and one needle like particle (not CNT) was found among 56 TEM images of particles released during brushing non-CNT containing tile surfaces B. We also found straight stick shape, silica containing

particles (Figures 2g and h) on the TEM grids from grinding concrete cylinders C and D. We found four CNT containing particles among 63 TEM images of particles released during grinding concrete cylinder C, and one straight stick shape particle among 60 TEM images of particles associated with grinding cylinder D.

One fiber-like CNT containing agglomerate in micrometer size associated with brushing CNT containing tile product A was presented in Figure 3 with the SEM image in Figure 3a and EDS analysis results in Figures 3b–i. We identified various elements (Figure 3) including Al, C, Cl, Cu, Mg, O, Si, and Zn in which Si and O were identified mostly on the fiber. The full EDS analyses were presented in SI Figures S6–S13.

The total mass concentrations of filter samples collected by TDS were 445 mg/m^3 for tile product A, 38 mg/m^3 for tile product B, $2,026\text{ mg/m}^3$ for cylinder product C, and $2,157\text{ mg/m}^3$ for cylinder product D as listed in Table 1.

Size-fractionated measurements of airborne particles using real time instruments

Measurements taken using RTIs provided size-fractionated number concentrations of airborne particles corresponding to brushing or grinding activities. The background concentrations, defined as the time period before brushing or grinding could start were lower than $200\text{ particles/cm}^3$ of a total number concentration as monitored with NanoScan SMPS. Particle total number concentrations measured during the entire

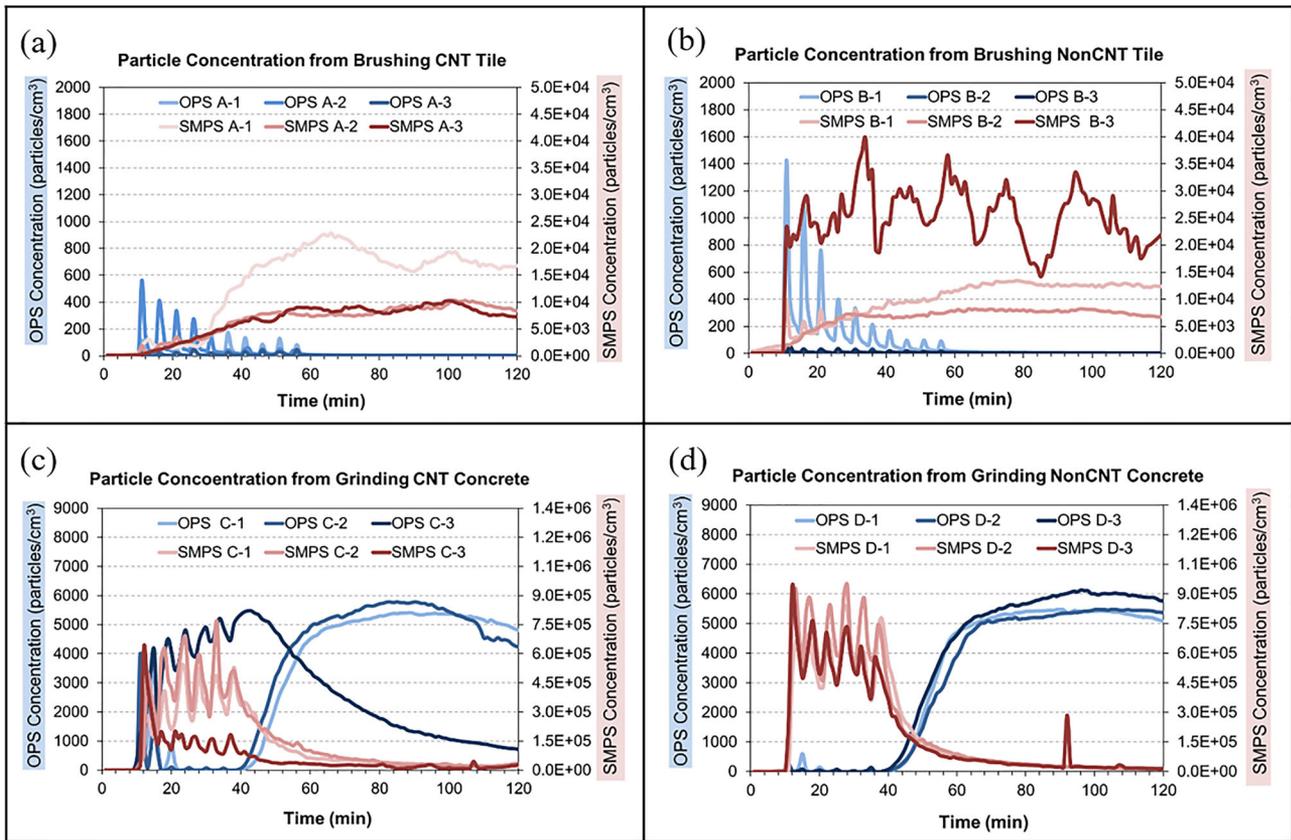


Figure 4. Particle total number concentration during the entire experiment duration. (a) Brushing CNT containing tile surface, with sample code A, (b) brushing non-CNT containing tile surface, with sample code B, (c) grinding CNT containing concrete cylinder, with sample code C, and (d) grinding non-CNT containing concrete cylinder, with sample code D.

experiment with two RTIs for brushing and grinding activities were presented in Figure 4.

Each graph in Figure 4 showed three repetitions of each product test, and the concentration changes corresponded to the timeline of activities. As shown in Figures 4a and b, the concentration changes during brushing activity on both products A and B presented similar patterns on OPS measurements with particles larger than $0.3\ \mu\text{m}$ in size that corresponded with the brushing time interval as seen showing multiple peaks of concentration following the brushing activities. Particles in the sub-micrometer and smaller sizes (particle mobility diameter) accumulated throughout the experiment as seen the concentrations measured by NanoScan SMPS gradually increased throughout the brushing activity period (Figure 4a). An exception seen on the B-3 experiment measured with NanoScan SMPS was related to the wearing of the brushing tool causing the instability and difficulty to use the tool at the constant brushing speed. These small particles emitted during brushing were suspended and accumulated in the air during the entire period of measurement including the time period after the completion of brushing.

Regarding the aggressive grinding on concrete cylinder, the results in the emitted particles which reflected the grinding cycles were different to those emitted from brushing tiles. We found great increases of sub-micrometer sized ($10\text{--}420\ \text{nm}$) particles during the first 30 mins, the level of concentration obviously followed the grinding activities as presented in Figures 4c and d. Also, particle concentrations in this range were notably decreased soon after finishing grinding. Toward to the end of the experiment, particles in the larger size range ($0.3\text{--}10\ \mu\text{m}$) showed great increases of concentration, which were consistently seen on three repetitions of grinding cylinder products C and D. The increase and accumulation of larger sizes of particles were not seen in the brushing tile activities.

We further analyzed the sizes of emitted airborne particles and the particle size distributions, and the size-fractionated concentrations were presented in Figures S14a–d for brushing tile products A and B and in Figures S14e–h for grinding cylinder products C and D. The dots above and below the averaged data line in Figure S14 represented the original data points measured by the RTIs of three repetitions during the entire period of brushing or grinding activities.

The size-fractionated particle number concentrations of 10–420 nm showed many particles at sizes less than 100 nm in the level of 10^4 to 10^6 particles/cm³ including brushing and grinding activities; while particles in the larger size range (0.3–10 μ m) were much lower in the level of 10^3 particles/cm³. Brushing tile, products A and B generated airborne particles mostly in the sizes less than 100 nm with the peak concentrations above 10^4 particles/cm³ at 27 nm as seen in Figures S14a and c. The particles with sizes of 0.3–10 μ m emitted during brushing tile products were in the concentration mostly less than 1000 particles/cm³ as seen in Figures S14b and d. Sub-micrometer sized particles emitted during grinding concrete cylinder products C and D showed bimodal distribution with the mode sizes (with the highest concentration) at 27 nm and 154 nm as seen in Figures S14e and g; and the concentrations were approximately two orders higher than the particles emitted during brushing tile products. The size-fractionated particle number concentrations measured at 0.3–10 μ m sizes during grinding cylinder products showed multi-mode size distributions as presented in Figures S14f and Sh; and the concentrations were multiple times higher than the brushing activities.

Statistical analysis

The results were listed in SI Table S2 with descriptions. In summary, the Figure S14 statistical analysis results have shown that the emitted particle size distributions were similar and highly correlated between CNT-containing and non-CNT containing products including both brushing tile and grinding concrete cylinder with the significance of p -value < 0.005 at 2-tailed test. The analysis between brushing and grinding activities showed that emitted particle size distributions were not or limited correlated, but the correlations were not statistically significant. That indicated the sizes of particles emitted from brushing and grinding activities were mostly different but with high variations.

Analysis of particle mass concentrations using standard methods

Elemental carbon analysis

The mass concentrations of EC and silica in the emitted airborne particles and the total mass were listed in Table 1. The total mass of each filter sample collected following NMAM 5040 were in the range of 4.6–8.6 mg (with total mass concentrations of 46–86 mg/m³) for CNT containing products and

0.8–6.9 mg (with total mass concentrations of 8–69 mg/m³) for non-CNT containing products. The EC values for brushing sampling A-1 and A-2, respectively, were 1.7 μ g (with a concentration of 17 μ g/m³) and 11 μ g (with a concentration of 110 μ g/m³). The A-3 sample was lost due to an instrument error. Samples B-1, B-2 and B-3 were all below the limits of detection, <0.7 μ g of the EC and <7.0 μ g/m³ of the EC concentration. These results indicated the presence of EC in the particles collected during brushing CNT-containing tile A product; however, CNT fibers or fibrous particles were not observed in the results of NMAM 7402 analysis.

The total mass of particles released from grinding of a cylinder were in the range of 51.9 to 231.7 mg for CNT containing products and 229.0 to 256.1 mg for the non-CNT containing control products. The variations in the amounts of released particles in each experiment were related to the reduction of the grinder's battery life from the first to the third grinding. The EC values were in the range of 8.9 to 300 μ g (with concentrations of 150 to 5000 μ g/m³) for CNT containing products and 27 to 36 μ g (with concentrations of 440 to 600 μ g/m³) for control products. The average EC was 109 μ g for CNT containing cylinder C and 31 μ g for non-CNT containing cylinder D. The difference in EC between the CNT-containing concrete cylinder C and the non-CNT containing cylinder D was 78 μ g. The average EC concentration was 1,810 μ g/m³ for cylinder C and 517 μ g/m³ for cylinder D, and the difference was 1,293 μ g/m³. Notably, the EC concentrations measured in this study represented the worst case of particle release measured within few inches of distance from the releasing/grinding source in a glovebox without air exchange. According to the number of CNT containing particles we found, very trace amount of EC was contributed by CNTs.

Evaluation of silica contents

Both A and B tile air samples showed silica content that was either below the limit of detection or non-detectable. The average silica mass concentration for product C was 79,804 μ g/m³, and that for product D was 12,380 μ g/m³. The silica concentrations measured in this study represented the worst case of dust release measured within few inches of distance at the releasing source in a glovebox without air exchange.

Based on all 306 TEM images and 175 SEM images of airborne particles analyzed from both tile and cylinder products, we found no free CNT and a few CNT containing particles (1 by NMAM7402, 3 by TDS SEM, 6 by TDS TEM) from brushing tile A, and

1 fiber containing particle (not CNT) from brushing tile B. For saw-cutting concrete cylinders, we found less CNT containing particles than on the tiles. The results have indicated that the CNT materials applied onto the surface of the concrete tile intending to simulate the cleanup of spills on a concrete floor manages to arrest individual CNTs during the dry out process and eliminate the release of free single CNTs. However, it was found that the dried out liquid admixture releases larger CNT containing airborne substances during the cleanup with the dry brushing method. Although CNT containing particles were also found in the released airborne substance of cylinders, the CNT materials embedded with the concrete mix showed a lower number of airborne CNT containing substance under dry grinding, which simulated a common task that would be performed by a person on the construction structure made of concrete. The absence of free individual CNT seen during sawing was likely a consequence of how the chemistry of the pre-dispersion of the CNT in the liquid admixture assisted in forming and bonding the crystal structure of the concrete. This was likely achieved by the CNT surface facilitating and guiding the early CSH crystal formation, that would effectively encapsulate the CNTs in the strongest, best built part of the concrete matrix.

The dry brushing and grinding methods employed in this study presented the worst scenario to better identify the possibility of CNT emission. Working on concrete, the wet cutting can reduce the respirable dust concentration by 85% compared to dry cutting (Shepherd and Woskie 2013). Although concrete cutting is typically a short-term task, sampling results from dry cutting often generated silica exposures exceeding the OSHA PEL (Shepherd et al. 2009; Shepherd and Woskie 2013). Wet method has been strongly recommended on working with concrete structures due to exposure to airborne silica particles which is a human carcinogen (Guha, Straif, and Benbrahim-Tallaa 2011). However, wet cutting still created respirable dust exposures exceeding the current PEL (Echt et al. 2002). Similar wet method would also be strongly recommended to reduce the possible exposure to airborne substances containing CNT, however, using a wet method could not eliminate the potential exposure. Small solid particles such as those in sub micrometer sizes would become airborne through the evaporation of mixed water droplets during the drying. Nevertheless, the subsequent exposure from CNT liquid suspension discharged into the environment is of concern for the environmental impacts and the environmental justice issues for the neighboring communities. Containment techniques to be applied for managing the

release of CNT containing substances will be a more sustainable approach in considering of potential impacts to human and the environment.

Our results showed no release of free CNT and a limited number of particles with visible fibers in the airborne samples which were collected involving brushing or grinding CNT containing products, but high EC concentrations were found. EC measurement was suggested as an indication of possible presence of CNT. According to the guidance provided by U.S. NIOSH for assessing exposure to CNT, a multi-tiered exposure measurement strategy is recommended for determining worker exposure to CNT and carbon nanofiber (CNF) (NIOSH 2013). It was suggested by NIOSH that in workplaces where exposure to other types of EC (e.g., diesel soot, carbon black) may occur, the initial evaluation of exposure should include the simultaneous collection of a personal respirable EC sample and a personal sample for electron microscopy analysis (e.g., TEM and SEM). Electron microscopy analysis, in conjunction with energy dispersive x-ray spectroscopy (EDS), can be used for CNT and CNF identification (NIOSH 2013). As a result of our study with the EC measured in a high concentration that was mostly contributed by aerosolized concrete materials, could not represent the existence or content of CNTs. We also demonstrated the importance of confirming the presence of individual CNT and CNT containing substance using electron microscopy analysis and direct sampling method such as TDS.

Additionally, our results showed that the variation among different methods for collecting and analyzing airborne particles was an influencing factor, that would impact the evaluation of the risk level to CNT fibers. We did not find CNT containing particles using NMAM7402 on particles released from grinding both cylinder C and D. Using TDS method, we found 5 CNT containing particles (1 from SEM, 4 from TEM) on particles released by grinding cylinder C, and 2 fiber containing particles (1 from SEM, 1 from TEM) from grinding cylinder D. We did not find loose and/or individual CNT fiber (an aspect ratio higher than 3 to 1) from particle images of CNT containing products A and C. We found a few straight non-CNT fibers with sub-micrometer to a few micrometers' lengths from concrete cylinders. The difference of results provided between NMAM 7402 and TDS methods was the quantity of fiber containing particles. We found a higher number of particles collected by TDS method, a direct sampling for analysis, than NMAM 7402. This result was consistent to a previous study, which has reported a higher efficiency

of collecting sub-micrometer sized fibrous particles of raw CNT airborne fibers using TDS method than the NMAM 7402 (Khattak, Theisen, and Tsai 2019).

The grinding activity on concrete cylinder was obviously more energetic than the brushing activity, and during the dry out on just tile, the CNTs did not have the ability to chemically imbed themselves in the crystal structure of the hardening concrete. This resulted in two orders higher of particle number concentrations in the sub-micrometer sizes, and multiple times higher of number concentrations in the micrometer sizes. We also observed that the airborne particles appeared to have different distributions of sizes from brushing tile surface compared with grinding concrete cylinder activities. The level of concentration and the proportions of different particle sizes have created a dynamic and complicated aerosol field where various sizes of particles would simultaneously performing Brownian motion, agglomeration, deagglomeration, and settling (Hinds 1999). The fluctuating pattern of number concentrations following the cycle of brushing or grinding activities appeared to be different that was the evident outcome presenting what has happened within the dynamic aerosol field.

For the scenario of brushing tile surface, the brushing cycle was responded with the fluctuation in number concentration of micrometer sized particles that indicated these particles were primarily generated from brushing. In the meantime, the sub-micrometer sized particles were also emitted into the air and they remained suspended for an extended time contributing to the accumulation over time. Because small/sub-micrometer particles would gradually agglomerate when the number of particles in a certain space got higher and resulted in a higher chance of particles bouncing to each other by random movement of Brownian motion; agglomerated particles would also be bounced and deagglomerated at the same time. By the time when particles were not generated from the activity, the dynamic aerosol behavior would approach steady state as seen showing a stable concentration soon after the brushing or grinding has ended as shown in Figure 4. After this stage, agglomerated particles would continue to form larger agglomerates then initiated the settlement when the gravity force overcame particles' mobility in the air. Further discussion regarding the dynamic aerosol behavior is presented in SI.

Conclusions

Although a few fiber or CNT containing particles were found in the airborne substances released from

brushing or grinding CNT containing products, individual free CNT fibers were not found. The results presented that were achieved using different methods show great variation. Thus, our study demonstrated the importance of considering a comprehensive direct sampling and a comprehensive analytical method in the CNT release assessment that is related to the practical use of nanotechnology-enabled products. In this study, all products were made with the specific content of CNT and tested within a few weeks after production. Therefore, the results of this study do not represent the potential ability of release of products with different CNT loadings, such as if the CNT had been added by other means, specifically as dry CNT vs the studied pre-dispersed wet CNT in liquid admixture, or had been degraded after weathering or long-term use.

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Competing financial interests

The other authors declare they have no actual or potential competing financial interests.

ORCID

Candace S. J. Tsai  <http://orcid.org/0000-0002-7296-8278>

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