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Measuring Nanomaterial Release from Carbon Nanotube Composites: Review of the State of the Science

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Abstract. Hazard studies of “as-produced” nanomaterials are increasingly available, yet a critical gap exists in exposure science that may impede safe development of nanomaterials. The gap is that we do not understand what is actually released because nanomaterials can change when released in ways that are not understood. We also generally do not have methods capable of quantitatively measuring what is released to support dose assessment. This review presents a case study of multi-walled carbon nanotubes (MWCNTs) for the measurement challenge to bridge this gap. As the use and value of MWCNTs increases, methods to measure what is released in ways relevant to risk evaluation are critically needed if products containing these materials are to be economically, environmentally, and socially sustainable. This review draws on the input of over 50 experts engaged in a program of workshops and technical report writing to address the release of MWCNTs from nanocomposite materials across their life cycle. The expert analyses reveals that new and sophisticated methods are required to measure and assess MWCNT exposures for realistic exposure scenarios. Furthermore, method requirements vary with the materials and conditions of release across life cycle stages of products. While review shows that the likelihood of significant release of MWCNTs appears to be low for many stages of composite life cycle, measurement methods are needed so that exposures from MWCNT-composites are understood and managed. In addition, there is an immediate need to refocus attention from study of “as-produced” nanomaterials to coordinated research on actual release scenarios.
VOCABULARY: Release – detachment of a particle or fragment from a larger whole such as a consumer product during use. Specifically in the context of this case study, when a fragment that contains MWCNTs detaches from a MWCNT-polymer composite and is nano-sized or possesses nano-characteristics, the release is considered to be a Nanorelease. Release Mechanism – a process, such as abrasion or degradation, which results in the release of fragments and discrete MWCNTs from a MWCNT-polymer composite. Release Measurement Method – generation, collection, and characterization of fragments containing MWCNT or discrete MWCNTs released from a product. Method may be for detection or quantification. Lifecycle – a time sequence depicting the life of a MWCNT-polymer composite or product, the phases of which include MWCNT-polymer composite production, product manufacture and use, and disposal, recycling, or re-purposing. Release Scenario – an event or chain of events resulting in a nanorelease during a lifecycle phase of a product as described by the release mechanism, setting (e.g., workplace, dwelling, and environment), relevant media (e.g., air, water, mixed solids, and biological matrices), and form and amount of released material. Probability of Release – the likelihood of nanorelease, as determined by a quantitative or qualitative measurement or prediction of the total number or mass concentration of released material, for a specified release scenario and time interval. Release Evaluation – a total assessment of nanorelease, including the release mechanism, form of the released entity, release scenario, probability of release, and lifecycle simulation, if relevant.

1. Introduction
Developers of practical and beneficial products containing engineered nanomaterials lack critical information for nanomaterial use that is needed to align innovation goals with sustainable, safe product development. This lack of information is causing unnecessary uncertainty regarding the safety of products using nanomaterials. To support innovative nanomaterial-based products with low life cycle risk profiles, greater information is needed on the potential hazards associated with specific exposure scenarios. Although this seems intuitive, the authors found that there are currently no standard methods to measure what is released from use of products containing nanomaterials. Furthermore, there is insufficient information to define the risk-relevant properties of nanoparticles released during stages of the life cycles of nanocomposites. As a result, it is currently challenging to complete the exposure pathway from release to environmental transport to a receptor’s exposure, and then to relate the exposure to possible health outcomes from toxicology data for a given nanomaterial in a given use.

There are many claims that engineered nanomaterials are used widely and may not be well controlled. The gap in understanding realistic nanomaterial release is sufficiently great that measuring the nanomaterial release rate from a material in a given context has rarely even been attempted compared with a growing body of studies of the potential hazards of nanomaterials. As a result, the rate of development of hazard studies has far outpaced exposure-related studies and the situation is not improving (Figure 1). This in turn is propagating an imbalance in understanding of the risk potential of nanomaterial uses. Furthermore, although advances for some types of nanomaterials have been made for some endpoints, mechanistic evaluations of nanomaterial characteristics that predict toxicity have not led to a level of understanding that allows producers and regulators to trace a released or measured nanomaterial in the environment to a risk-relevant exposure for a receptor. This relative lack of release information and the inability to link release data to exposure data have weakened the ability of producers, users, and regulators alike to address concerns about the use of nanotechnology.

This review addresses these issues based on the example of multi-walled carbon nanotubes (MWCNTs) and polymer composites. MWCNTs are one of the more contentious and potentially valuable nanoscale materials to have emerged in recent years. Many current and near-term applications involve integration of MWCNTs into polymer matrices to enhance thermal, mechanical, and/or electrical properties. The electronics, defense, and energy sectors are leading in MWCNT-polymer applications, and MWCNT-polymers are increasingly being used in consumer sporting goods, textiles, and packaging.
Although MWCNTs in composites are typically tightly bound, their release through the life cycle of the nanocomposite is possible.\textsuperscript{1} Research on hazards associated with pristine MWCNTs has been previously reviewed.\textsuperscript{29} This information currently does not consider the quantity and form released to exposure pathways, yet this knowledge is critical to forming a quantifiable and actionable understanding of risk.\textsuperscript{30}

Release and transport of polymer fragments to the environment occurs on a large scale, and analogous concerns exist for microplastic particles in marine and soil systems.\textsuperscript{31,32} For example, it is known that polymeric materials can be released to the environment, degraded into small pieces (millimeters to micrometers in scale), and transported over long distances. Research has shown polymer fragments to be an important component of household dust as well as a source for human exposure to polybrominated and phosphorous-containing flame retardants.\textsuperscript{33} Some retardants were found to be transferred to dust via physical processes such as abrasion from polymers.\textsuperscript{34} It is possible that MWCNT-containing polymers in consumer products will undergo similar processes, resulting in MWCNT-containing fragments in household dust and subsequent exposure to a wide cross-section of the population. Given that global revenues for MWCNT-nanocomposites at an early stage of market penetration were on the order of $37 million in 2009,\textsuperscript{35} and new product development is continuing, a structured analysis of our current knowledge on MWCNT release from such nanocomposites was considered necessary.

Here we provide a comprehensive review of the state of scientific understanding on the potential sources and pathways of release, pointing to situations and specific applications in which humans or the environment could encounter MWCNT releases and which methods to measure such release and exposure are needed. This review also suggests integrated, systematic approaches to increase the breadth and depth of our knowledge base on nanomaterial release from composites.

2. Effects of the Product Use Life Cycle on Release Likelihood and Measurement

The potential for release of MWCNTs from composites can vary throughout the life cycle of a product depending on the production and manufacturing processes, the use/misuse of the final product, and end-of-life (EOL) treatment (Figure 2). Understanding the quantitative analysis and instrumentation needs with respect to measuring release at a particular life cycle stage will depend on factors such as proximity to receptors or the nature of the media into which release occurs. For example, evaluating a life cycle stage with high potential for consumer contact could be accomplished by a simple demonstration of a lack of physical opportunity for release (e.g., sealed components in a display screen), whereas specific
information on the magnitude and nature of long-term release from those same components may be needed to understand contributions to downstream or downwind receptors at EOL disposal.

Both physical and chemical mechanisms of release can further affect the specific release potential for nanomaterials added to composites because they can influence whether the nanomaterial remains embedded or is transformed during the release (Figure 3). Release mechanisms can be categorized based on the driving forces that can cause the release of MWCNTs throughout a product life cycle, such as mechanical stress, chemical processes (e.g., hydrolysis and photolysis), and incineration through human and environmental processes. The use of life cycle concepts combined with an understanding of the driving forces provides a framework that enables the occurrence of particular mechanisms and their potential effect on nanomaterial release to be mapped out. This type of methodology is needed if communication is to occur effectively between different actors along the value chain.

Figure 2. Life cycle of a nanocomposite. (A) Relevance for exposure of professionals or consumers, and environmental emission from nanofiller production to end of life/recycling. (B) Specific life cycle map of sports equipment made of MWCNT-polymer composite, detailing release processes that must be considered with the anticipated relative release probability indicated by the thickness of arrows. Reprinted (with modification) from Nowack et al., with permission from Elsevier.
Specific release information is particularly important for those cases in which release mechanisms may increase hazard and risk, because the knowledge of the nanomaterial content and type in a product usually decreases along the value chain of a product. Consideration of the whole life cycle of nanoproducst should ensure that possible effects on humans and the environment can be systematically identified and thoroughly assessed. For instance, combinations of polymer types and additives that affect performance at one life cycle phase may lead to instabilities in the MWCNT-polymer at another life cycle phase, complicating measurement of released MWCNTs for the life cycle of the material use. Thus, systematic evaluations of release mechanisms and potentials are critical to life cycle risk assessment that informs product development.

3. Specific Evaluation of Life Cycles for MWCNT-Polymer Composites
Considering the beginning of a MWCNT product life cycle, the synthesis and handling of MWCNT powders prior to formation of composites present conditions that may lead to high likelihood for release if not appropriately addressed. However, standard industrial hygiene measures can limit exposure of professional users and the environment to a great extent. In addition, during masterbatch production in which high-concentration composites are created and during manufacturing of the final product in occupational settings, conditions for release can also be controlled and exposure of professional users to material can be minimized. At increased temperatures during subsequent processing involving injection molding and extrusion, polymer can vaporize and re-condense into airborne particles (polymer fumes).
Particles released from melt processing of nanocomposites could represent a complex mixture of polymer fume particles, individual and agglomerated nanofillers, and perhaps other particles. However, a sampling analysis of such processes did not reveal isolated MWCNTs. Subsequent mechanical processes such as cutting, drilling, and sanding during manufacture or installation (e.g., in construction) could additionally create particles that contain MWCNTs, as below and in Table 1.

During the industrial and consumer use phases of the life cycle, environmental conditions and human activities can alter the MWCNT-polymer product. The use, characteristics, and magnitude of MWCNT-related release in response to these conditions depend strongly on the type of product and how much energy is applied to it. Again, the release potential for particles can range from zero or near-zero release due to physical barriers, to possibly significant release in applications with consistent high energy input (e.g., tires). Whether such particle release constitutes release of added nanomaterial in the “as added” form is subject to case-by-case evaluation. However, it is clear that for many applications currently on the market (e.g., sports equipment, consumer electronics), consideration of the physical opportunity for release during use leads to the conclusion that release magnitude is anticipated to be very low.

Continuing the evaluation along the life cycle of the material, there is very little direct information to inform the behavior of MWCNT-composites, including those currently used in commerce as well as those in the disposal or recycling phase. Established recycling schemes are available for some of the intended consumer uses of MWCNT-composites (e.g., electronics waste recycling). Recycling or controlled disposal of large-scale structures, such as windmill blades or aircraft, is also likely. Release of MWCNTs from the matrix is again possible because recycling frequently involves high-energy process such as shredding, yet this is currently a largely unevaluated release scenario.

In contrast, release during waste incineration can be considered to be low given that MWCNTs should combust if incinerated at a sufficiently high temperature and provided sufficient oxygen during the process. By well-ventilated incineration at temperatures above 1000°C, the carbon nanofibers present in a composite were effectively destroyed in the flames, and the same is expected from the known decomposition temperatures of MWCNTs. If the MWCNTs should survive the incineration process, they would typically end up either in bottom ash and be landfilled, or would be carried away with the flue gas. An industrial-scale study on nanomaterials in municipal waste demonstrated that flue gas can be effectively filtered to be clear of nanoparticles; therefore, remaining MWCNTs would end up in the filter ash, which is also landfilled. Landfills in industrialized countries are not expected to release MWCNTs to the environment because current landfills are operated in a way that release of leachates to the environment is minimized.

4. The Significance of MWCNT Physical Form Variation at Point of Release

The simplest and perhaps most widely held conception of MWCNT release is that free nanotubes would be released upon wear, abrasion, or degradation of a product with MWCNTs. However, a finding by many laboratories is that release of free MWCNTs is a rarity for the MWCNT-composite materials thus far evaluated. The more frequently reported released entity is MWCNTs embedded in particles of the composite matrix. In fact, the nature of the MWCNT release expected for a life cycle stage can be explored by contrasting findings from studies of MWCNTs in epoxy (the most commonly studied composite) with other composites to identify emerging structure–activity relationships (SARs); in this case, “activity” refers to the probability to release fragments of different types, as highlighted in Table 1.

The systematic SAR is spanned by the chemical and mechanical axes, as shown in Figure 2. Such evaluation indicates that, unlike carbon fibers, the interfacial shear strength and length of MWCNTs predicts that they should not break under tensile stress but instead should either be pulled out from the matrix or pull the matrix along, resulting in protrusions of MWCNTs emerging from polymer fragments. The tensile strength and bonding properties of the MWCNT would therefore tend to create a high likelihood of composite-MWCNT fragments as the dominant released moieties from MWCNT-composites studied to date. Indeed, as such qualitative SARs would predict, particles with protrusions are observed after sanding of matrices with less than 10% elongation at the break. This is true of epoxy or cement, but not the majority of thermoplastics.
TABLE 1. Areas for detection and identification before selective quantification can begin

<table>
<thead>
<tr>
<th>Release Scenario (Anticipated Degradation Mechanism)</th>
<th>Release Pathway</th>
<th>Method to Simulate the Life Cycle to Induce, Detect, and Quantify Release</th>
<th>Morphology of Typical Released Fragments</th>
<th>Key Findings and Research Needs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outdoor use (UV degradation, hydrolysis, and weak mechanical forces)</td>
<td>A</td>
<td>Accelerated dry or wet weathering (ISO4892), followed by immersion to induce release into water, detected by AUC, TEM, EDX, LD, XPS</td>
<td>[Image of morphology]</td>
<td>Nguyen et al. found a collapsed layer of MWCNTs on MWCNT-epoxy after UV irradiation\textsuperscript{15}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Weathering tests are highly standardized for plastics and coatings, but the MWCNT network formed on the composite essentially eliminates the release of MWCNT\textsuperscript{15}. Methods to induce a release during or after degradation are exploratory, and miss selective quantification. By synergy of degradation and stress a key release scenario.</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>Hirth et al. performed wet and dry weathering of MWCNT-polyurethane followed by immersion and shaking: release of polymer-MWCNT fragments, but free MWCNTs only by sonication\textsuperscript{7}</td>
<td>[Image of morphology]</td>
<td></td>
</tr>
</tbody>
</table>
Machining by sanding, bandsaw, abrasion, rotary cutting wheel, wet saw cutting, wet drilling, grinding. (moderate temperature + moderate to strong mechanical stress: energy input per test by sanding estimated is 10-fold higher than by sawing)

F-H

No standard simulation machines: monitoring by APS, CPC, SMPS, ESP, FMPS, LDPSA, NSAM, OPC, and sampling for characterization by SEM/TEM, EDX, AUC, LD, XPS

Fragments from MWCNT-epoxy were submicrons in diameter and carried protrusions of MWCNTs that were pulled out from the matrix.

Many laboratory studies on different MWCNT-polymer and nanoparticle-polymer composites found no release of free nanofillers, with exceptions linked to agglomerates in the polymer. Protrusions of MWCNTs were not observed for tough thermoplastics, which can elongate during machining and keep MWCNTs embedded.

Fragments from MWCNT-polyoxymethylene measured microns in diameter with no protrusions.

No standard simulation machines. Detect aerosols around machines by APS, CPC, Dust Trak™, ESP, FMPS, TP, TSI.

Polymorph aerosol sampled during dry drilling of a graphite-epoxy prepreg with aligned carbon fibers and aligned MWCNTs.

By synergy of degradation and stress, machining with local overheating is a key release scenario.
Compounding by hot melt extrusion and Combustion (thermal degradation)

Commercial twin-screw extruders, monitored by CPC, SMPS, sampled for TEM/SEM, or TGA (ISO 11358) with off-gases monitored and sampled

Fleury et al. conducted extrusion of MWCNT-acrylonitrile-butadiene-styrene: complex polymer fumes, no free MWCNT

Bouillard et al. found that low-temperature (400°C) combustion of the same composite can release MWCNT in flue gases

Nyden et al. showed that fire smoke from carbon-nanofiber-polyurethanes is soot with no remaining fibers

At elevated temperatures, polymer vaporizes and recondenses. Release of free MWCNTs was observed for thermal decomposition by TGA and for dry-core drilling of MWCNT-epoxy composites but not for extrusion of MWCNT-polymer.

Capacity to simulate real-world scenarios needs to be validated

Abbreviations: APS, aerodynamic particle sizer; AUC, analytical ultracentrifugation; CPC, condensation particle counter; DLS, dynamic light scattering; EDX, energy dispersive X-ray analysis; ELPI, electrical low pressure impactor; ESP, electrostatic precipitator; FE-SEM, field emission scanning electron microscope; FMPS, fast mobility particle sizer; FTIR, Fourier transform infrared spectroscopy; ICP-MS, inductively coupled plasma mass spectrometry; LIBS, laser-induced breakdown spectroscopy; NAS, nano-aerosol sampler; OPC, optical particle counter; PAS, photoelectric aerosol sensor; PSSD, particle surface sensitive device (e.g., NSAM, DiscMini, Nanocheck); SEM, scanning electron microscopy; SMPS, scanning mobility particle sizer; TEM, transmission electron microscopy; TGA, thermogravimetric analyzer; TOF-SIMS, time-of-flight secondary ion mass spectrometry; TP, thermophoretic precipitator; UNPA, universal nano-particle analyzer; WRASS, wide-range aerosol particle sampling system; XPS, X-ray photoemission spectroscopy.

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One issue to address in evaluation of the data regarding presence or absence of free MWCNTs in released material is that detection may be made difficult by the extreme polydispersity of particles, with typical particle sizes ranging from tens of micrometers for an elastic material such as polyurethane to around 100 nm for epoxies or acrylic coatings. However, visual inspection of multiple scanning electron microscopy images typically reveals no free MWCNTs from machining of epoxy. This is in contrast to detection for stiffer, longer fillers (carbon nanofiber) and MWCNT agglomerates in epoxy composites sampled on filtered air grids. The examination of released material from composites with two- and three-dimensional nanofillers (clays, pigments) began with similar expectations of a relationship between nanoparticle size, shear force, and bonding to composite. Again, no evidence of significant free particulate nanofillers has been reported. Therefore, the available studies indicate that mechanical forces applied to MWCNT-composite materials tend to release matrix particles containing MWCNTs, with rare occurrence of unbound MWCNTs. The entity to which exposure occurs is thus expected to be a heterogeneous mixture of particles with embedded or protruding MWCNTs, for which very few toxicity studies have been conducted.

Conditions that may cause the release of free MWCNTs have been observed. Airborne clusters of unbound MWCNTs, for example, were observed during machining of MWCNT-epoxy with dry solid-core drilling accompanied (or caused) by thermal degradation of the matrix material, which highlights the need for additional studies of synergistic stresses. Among the purely chemical degradation processes, the rate of matrix removal — and thus the potential rate of liberation of embedded MWCNTs — increases in the order of photolysis, hydrolysis (outdoor weathering), thermal degradation, combustion (accidental fires), and incineration (municipal waste treatment). Again, complete oxidation and destruction of MWCNTs is expected for incineration.

Conditions that lead to apparent potential for release of free MWCNTs were confirmed for weathering, in which the matrix is hydrolyzed or oxidized from the top few hundred nanometers, leaving behind an entangled network of MWCNTs. However, further research regarding life cycle release is also indicated by the finding that the same matt of fibers may act as an ultraviolet-protective layer that slows down the further polymer degradation and release. It appears that, in contrast to particulate nanofillers that are releasable by run-off waters (e.g., TiO₂ or SiO₂), high aspect ratio MWCNTs collapse to an entangled network that minimizes their release unless ultrasonic shear forces overcome van der Waals forces. However, the effects of solvents, acids, and bases such as those relevant for food contact or landfilling have not been studied.

5. Quantifying the Dose or Released Material Associated with Added Nanomaterial

The observations that a polydisperse mixture of embedded, free, and composite particles (Figure 2) is released and that the nature of the proportions among these types of release varies with release conditions raise the question of what should be measured and reported during the sustainable design and use of materials. What should be measured to assure that a “risk-relevant” release has not occurred? What should be measured to quantify dose in an exposure pathway relevant to the added nanomaterial at any point in the manufacture of the composite? Again, there is a limited amount of quantitative data available on release rates and mass flows relevant to evaluating materials of toxicological or epidemiological interest for modeling of exposure pathways. Moreover, even the very first stages of problem formulation for risk assessment are made difficult due to the expected heterogeneity, other than for cases in which release can be physically precluded. It seems clear that a first step toward understanding what to measure will depend on a standardized description of release processes and released materials for scenarios of interest. Only then can standard methods be developed to measure the releases in those scenarios.

On an empirical level with the current state of research, the understanding of nanomaterial-specific release is also hindered by a paucity of attempts to quantitatively compare material released from nanomaterial composites to material released from nanomaterial-free composites. For example, for MWCNT-polymer composites, few studies have attempted to develop quantitative data about
MWCNT release that go further than particle size distributions and examples of morphology seen through relatively few electron microscope grids. These data are not sufficient to estimate the dose of the MWCNT-specific addition. Furthermore, methods that seem applicable to nanomaterial-specific dose estimation would require tremendous effort to sample and evaluate morphology and composition of released particles. Without methodology to quantify differential dose for the addition of the nanomaterial, we cannot estimate the added risk of using the nanomaterial. We also cannot match toxicity data for the pristine nanomaterial to what is released in ways that inform needs for further toxicity data.

Risk management is still possible if the release can be characterized within worst-case boundaries relevant to exposure. For example, release scenarios in which there is a very low physical expectation of release could be verified through evaluation of the total mass of carbon released compared to reference standards for pure MWCNTs. For this reason, the highest near-term practical priority for methods would be semi-quantitative release detection to provide upper bounds on the magnitude of release to assure sustainable development of many promising nanomaterial uses.

6. Required Research, Methods Development, and Standardization
While risk management based on surrogate measures and physical limits to exposure is possible, practical, quantitative measurement methods that would allow full risk assessment of uses of nanomaterial composites do not exist. Such methods must address the complexities of morphology, composition, and matrix-nanomaterial interactions, as well as the media into which release occurs in relation to those characteristics of the nanomaterials that are biologically deleterious. In addition to variations in polymer formulations such as antioxidants and UV stabilizers, MWCNT formulations are often optimized for a specific polymer matrix through the modification or addition of functional groups on the nanotube surface. The multivariate sequences between nanomaterial addition and release create a formidable challenge for prioritizing efforts to address these methods requirements. Critical challenges include the following: i) filling vast knowledge gaps around nanocomposites and their potential degradation routes over life cycles that allow for nanomaterial release; ii) identifying a representative set of homogeneous and well-characterized materials that can serve as reasonable surrogates or reference materials of known degradation processes; iii) validating processes to develop composites that are also representative of systems in use; iv) establishing validated and eventually standardized methods and broadly available and applicable instrumentation for sampling, detection, and characterization of MWCNT release; and v) leveraging informatics and computational methodologies to allow for prediction of MWCNT release in the absence of empirical data.

For MWCNT measurement alone, there is a lack of validated, quantitative, and statistically relevant methods for measuring and reporting the characteristics of MWCNTs that are known to affect toxicity, such as MWCNT size and size distribution, morphology, surface functionalization, purity, tube alignment of the MWCNTs, and detection of the presence of different carbon allotropes. The most widely reported techniques for detecting CNTs and determining their morphology and size are scanning electron microscopy and transmission electron microscopy; however, these methods are semi-quantitative at best and cannot be used to provide representative results needed for science-based risk assessment. With regard to other key characteristics such as surface functionalization, methods such as X-ray photoelectron spectroscopy, Raman spectroscopy, and inductively coupled plasma mass spectrometry are sensitive analytic techniques that can elucidate specific elemental composition and physical structure; however, these techniques are not currently widely utilized apart from specific application evaluations.

For innovation to proceed with regard to safety for these valuable materials, there is an immediate need for the scientific community to adopt a systematic strategy for evaluating the critical determinants of release as well as a set of reference materials, sampling methods, and MWCNT-composites that can be used as a first step toward informing the release potential of nanotubes from MWCNT-nanocomposites. Testing materials and polymer systems selected as study systems should be as commercially relevant as possible and should preferably cover a representative range of
characteristics for that material class. Laboratory testing strategies should strive to incorporate the multiple forms in which the MWCNT is found throughout the life cycle, including the pristine MWCNT (as synthesized), the formulated MWCNT (embedded in composite), and the transformed MWCNT (affected by environmental processes). As a result of the NanoRelease initiative, draft protocols to conduct sanding and weathering of nanofiller-polymer composites were presented to ISO TC/229 for consideration at the November 2013 meeting in Belo Horizonte, Brazil. Comparative testing by these harmonized protocols applied to a single batch of MWCNT polymer nanocomposites was initiated in November 2014 in laboratories across Europe, North America and Asia.

7. Conclusions
This state-of-the-science review for MWCNTs in polymers highlights the disconnect between as-produced MWCNTs with much studied hazards and the more realistic polydisperse fragments released from nano-enabled products made of MWCNT-composites. While releases do not necessarily correlate to the quantity of exposure because there may be other mitigating factors, the quantity and characteristics of the materials released from matrices containing nanomaterials do need to be addressed during risk assessment and risk management, including assessment of the mechanism of release for each phase of the product life cycle. Specifically, two scenarios were previously classified as having a greater possibility of release: i) use of MWCNTs in tires and ii) recycling operations.

Despite a lack of best practices, and thus harmonization in measurements, measurement strategies, analysis, and reporting of measurement data, we were able to identify unifying principles across polymer classes. For most materials, degradation of the polymer matrix is associated with the greatest potential for release, with degradation and release rates dependent on the specific characteristics of the polymer, MWCNT, and environment. MWCNT-nanocomposites, as well as their susceptibility to degradation, may transform throughout the product life cycle. Release during designed consumer use is projected to be quite low and composed of polydisperse fragments with only a small fraction of free MWCNTs. Direct handling of products containing nanomaterials could result in exposure; however, laboratory simulation of mechanical handling has demonstrated very low probability of release. Environmental releases of MWCNTs will undergo various reactions that could result in their destruction or alteration. In addition, misuse of products may expose MWCNT-nanocomposites to chemical environments that could alter rates of degradation. As such, we expected that thermolysis would represent a low potential for release given the increased thermal stability of many polymers with the addition of MWCNTs into the matrix, but available studies report divergent results.

We have identified an immediate need to use realistic release scenarios as the basis for coordinated research on nanotoxicology, occupational health and safety, and exposure assessments. A qualitative life cycle analysis or similar approach should be implemented to support sustainable nanotechnologies and inform risk management decisions. Tiered approaches based on releases measured by validated methods may provide practical ways to manage risk, with a relatively short timeline to reach predictive knowledge about nanomaterial release from composites. A benefit of these efforts may be the generation of data that inform improved design of products containing nanomaterials from performance, safety, and sustainability perspectives.

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state of the science evaluation considers publications and active MWCNT release measurement projects known to the authors as of November 2013. We especially thank Lyubov Tsytsikova, Center for Risk Science Innovation and Application of ILSI Research Foundation, for her contributions to this work under the NanoRelease project, and Christina West, for editorial assistance in completing this manuscript. This article has been reviewed in accordance with the US EPA’s peer and administrative review policies and approved for publication. Mention of trade names or commercial products does not constitute an endorsement or recommendation for use by the US EPA. S. H. acknowledges support from the National Institute of Environmental Health Sciences (Grants ES017552-01A2, P30ES03850, and ES0166896-01) and the Air Force Research Laboratory (Grant FA8650-05-1-15041).

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