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Review

Potential release scenarios for carbon nanotubes used in composites[☆]

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ABSTRACT

The expected widespread use of carbon nanotube (CNT)-composites in consumer products calls for an assessment of the possible release and exposure to workers, consumers and the environment. Release of CNTs may occur at all steps in the life cycle of products, but to date only limited information is available about release of CNTs from actual products and articles. As a starting point for exposure assessment, exploring sources and pathways of release helps to identify relevant applications and situations where the environment and especially humans may encounter releases of CNTs. It is the aim of this review to identify various potential release scenarios for CNTs used in polymers and identify the greatest likelihood of release at the various stages throughout the life-cycle of the product. The available information on release of CNTs from products and articles is reviewed in a first part. In a second part nine relevant release scenarios are described in detail: injection molding, manufacturing, sports equipment, electronics, windmill blades, fuel system components, tires, textiles, incineration, and landfills. Release from products can potentially occur by two pathways; (a) where free CNTs are released directly, or more frequently (b) where the initial release is a particle with CNTs embedded in the matrix, potentially followed by the subsequent release of CNTs from the matrix.

The potential for release during manufacturing exists for all scenarios, however, this is also the situation when exposure can be best controlled. For most of the other life cycle stages and their corresponding release scenarios, potential release of CNTs can be considered to be low, but it cannot be excluded totally. Direct release to the environment is also considered to be very low for most scenarios except for the use of CNTs in tires where significant abrasion during use and release into the environment would occur. Also the possible future use of CNTs in textiles could result in consumer exposure. A possibility for significant release also exists during recycling operations when the polymers containing CNTs are handled together with other polymers and mainly occupational users would be exposed.

It can be concluded that in general, significant release of CNTs from products and articles is unlikely except in manufacturing and subsequent processing, tires, recycling, and potentially in textiles. However except for high energy machining processes, most likely the resulting exposure for these scenarios will be low and to a non-pristine form of CNTs. Actual exposure studies, which quantify the amount of material released should be conducted to provide further evidence for this conclusion.

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1. Introduction

The prospective widespread usage of carbon nanotubes (CNTs) in industrial applications and consumer products and articles creates the potential for release of CNTs that could result in a possible increase of human and environmental exposure to CNTs (Gottschalk and Nowack, 2011; Koehler et al., 2008). As a starting point to exposure assessment, exploring sources and pathways of release helps to identify relevant applications and situations where humans or the environment may encounter releases of CNTs. By tracking the life cycle of products, it is possible to explore whether and in which situations a release of CNTs from applications may occur (Upadhyayula et al., 2012).

The focus of this review is on release as a prerequisite for exposure. Exposure scenarios are used to describe the conditions that may result in exposure, see for example the REACH definition of an exposure scenario: “Set of conditions, including operational conditions and risk management measures, that describe how the substance is manufactured or used during its life-cycle and how the manufacturer or importer controls, or recommends downstream users to control, exposures of humans and the environment” (ECHA, 2008).

A catalogue of generic and specific exposure scenarios (ESs) has been developed for engineered nanomaterials (ENM), taking into account the release scenarios over the entire life-cycle of these materials (Brouwer et al., 2010; Clark et al., 2012). For occupational exposure scenarios, published measurement data and contextual information were collected. These were reviewed to describe and characterize occupational exposure and the available tools and models to predict occupational exposure to the ENMs. For the development of generic exposure scenario descriptions, a library for the collection of exposure scenarios according to REACH Guidance was developed. From the 57 occupational exposure scenarios (Brouwer et al., 2010), 14 are related to carbon-based nanomaterials, generating 35 contributing exposure scenarios describing some facet of occupational exposure. Most of the ESs were from the production/synthesis of carbon-based nanomaterials or from handling materials (weighting, removing, sonication, etc.); two scenarios addressed tasks related to the machining of composites containing CNT.

Based on the process of developing these ESs, several main conclusions could be drawn (Clark et al., 2012): Most studies reported had an explorative character and were focused on concentration/emission analysis. Therefore, the reports from these studies did not include most of the information necessary to build ESs, e.g. amount used and frequency of activities. Basic characterization of the products used was often not available and operational conditions were often not described. Most concentration/emission-related measurement results were task-based. An important observation was the lack of harmonization of either the measurement strategy including distinction between manufactured nanoaerosols and ‘background’ aerosols, or the analysis and reporting of measurement data.

ENM-release during synthesis is best described by an emission factor (EF), which is defined as number, surface area and/or mass (volume) per unit of time released to the environment (Fissan and Horn, 2013). The ENM-release per unit of mass of produced material is best described by a release factor (RF), defined as number, surface area and/or mass (volume) per unit of mass of nanostructured material (Fissan and Horn, 2013). This depends on nanostructured material properties and the amount and kind of energy input during the different kinds of treatments of the material. The ENM emission and release factors can be considered to be important process and material properties, since without emission and release there is no exposure and therefore no risk.

An international Technical Specification has been developed in ISO/TC 229 “Nanotechnologies” and published by ISO, ISO/TS 12025:2012 “Nanomaterials — Quantification of nano-object release from powders by generation of aerosols”. CNTs are included in the term nano-object, together with nanoparticles and nanoplatelets. This Technical Specification provides a methodology for the quantification of nano-object release from powders as a result of treatment, ranging from handling to high-energy dispersion, by measuring aerosols liberated after a defined aerosolization procedure. In addition to information in terms of mass, the aerosol is characterized for particle concentrations and size distributions. This Technical Specification provides information on factors to be considered when selecting from the available methods for powder sampling and treatment procedures and specifies minimum requirements for test sample preparation, test protocol development, measuring particle release and reporting data. In order to characterize the full size range of particles generated, the measurement of nano-objects as well as agglomerates and aggregates is recommended in this Technical Specification.

In the context of this review, we describe release scenarios as opposed to exposure scenarios. The definition of a release scenario is not unambiguous; however, for the purpose of this review a release scenario is defined as *the operational and or environmental conditions of any treatment or stress of CNTs or CNT composite material during all life-cycle phases that results into the release of CNTs/composite material into indoor environments, e.g. workplace, dwellings, and/or environmental compartments (air, water, soil and sediments), and the set of parameters to describe the type, form and magnitude of release*.

The aim of this review is to build release scenarios for CNTs in polymer composites. It focuses on multi-wall CNTs, which is the form of CNTs normally used in polymer composites. The general term “CNT” is used throughout the manuscript as a synonym for multi-wall CNTs. In a first part the available literature on release of CNTs is reviewed, in a second part nine relevant release scenarios are described in detail: Injection molding, manufacturing, sports equipment, electronics, non-consumer applications (windmill blades/fuel system components), tires, textiles, incineration, and landfills.

2. Release scenarios of nanomaterials in general

Release of nanomaterials from products and articles might occur throughout the product life-cycle, depending on the circumstances of manufacturing (production and processing), use of the product or article in specific environments, and its disposition at the end of life (Upadhyayula et al., 2012). Although we are defining the release and not a human or environmental exposure, it is instructive to consider the continuum of activities involved in how products are developed, used and discarded or re-used to inform the consideration of potential release scenarios. Fig. 1 shows the life-cycle of products containing CNTs from synthesis of the CNTs, over fabrication of master batch and manufacturing of final product, e.g. an article, to use and disposal of the product or article. It also emphasized that release results first in occupational (or consumer) exposure and then also in environmental exposure.

The highest likelihood for release of ENM is during the synthesis and handling of ENM, particularly during the handling of powders prior to the fabrication of the composite (Tsai et al., 2009; Yeganeh et al., 2008). In fabrication activities, post-material generation, or master batch formation, release might occur when creating applications from the composite product. For a polymer composite, mechanical processes such as drilling, cutting and sanding could generate the release of nanomaterials. Thermal and high-energy processes, that, for example, might be used to shape a composite, could destabilize the composite resulting in a release of nanomaterials. If the composite material is flexible, for example a fabric, all of the above activities and additional ones, including rolling, folding or other handling might release nanomaterials. In summary, at the fabrication phase a release of nanomaterial is possible if there are steps in which the polymer structure is modified. Kuhlbusch et al. (2011) summarized and reviewed all publications which include investigations of ENM release at workplace or simulated scenarios for use and end of life up to the year 2011 and gave a good overview of possible release scenarios, not only for polymer compounds.

During the use phases, both environmental sources of stress and human activities that stress the composite may result in releases. The media in which the composite is used affect the environmental factors: weathering is affected by moisture, salinity, pressure, temperature and light radiation (especially UV), and will vary in marine or fresh water, or with altitude and biogeochemical conditions of exposure. Specific applications — represented by a limited number of standardized processes, are useful to limit the number of possible release scenarios. Human activities at the use phase include mechanical, thermal and biochemical interactions, but conditions may differ in the environment. For example, CNT/polymer composite building materials will normally be subjected to weathering stress, and less to mechanical stress. On the other hand, a CNT/polymer composite used in a laptop computer housing will mainly be subject to mechanical stress (e.g. by scratching or cracking). Generally speaking, the likelihood that only the nanostructured material is released is small, because of the high-energy input needed. Most likely, lumps of composite material containing CNTs or nanostructured material or vaporized nanostructured materials will be released.

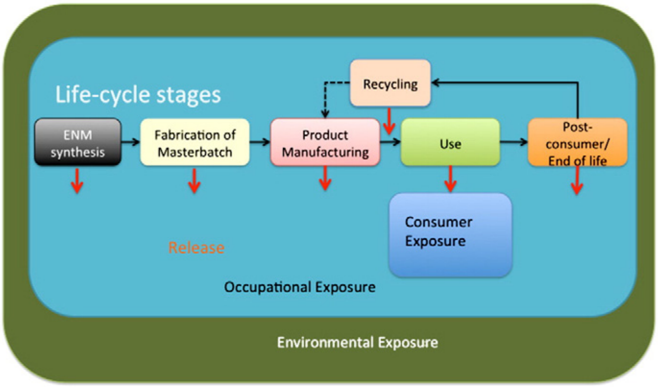

Fig. 1. Life cycle of products containing nanoparticles.

Post-use releases could result from waste treatment — landfilling, recycling or incineration. Otherwise, they are more likely to occur from environmental rather than human impacts such as weathering effects after waste treatment. If composites are landfilled, they could slowly break down (depending on their degradability) and potentially release nanomaterials to the leachate. If the landfill is not well controlled, releases could be via dust from weathered composites. Recycling of composite materials could release nanomaterials to the atmosphere during processing, or to a new mixture with an alternative use. Incineration could release nanomaterials from a composite; whether they are released to the atmosphere, or become part of fly ash or bottom ash if the incineration conditions do not determine a conversion of the ENM into a non-ENM (e.g. the conversion of CNTs at 800 °C under oxygen to CO_2) (Roes et al., 2012). If the composite was used in an application that involved washing with water, release into wastewater is possible resulting in either a land or aquatic pathway (Gottschalk et al., 2009). Post-consumer uses, including unintended uses, could create novel pathways for release. For example, fabric intended as a protective layer in a composite could be recovered from poorly managed waste handling facilities and used for clothing, in homes or in ways that result in consumer exposure.

3. Release of CNT from polymer composites

To date, few studies have focused on the potential releases of CNTs contained within advanced polymer composites. Studies have focused on several types of releases from two main scenarios: the first scenario involves release due to high energy processes during post manufacturing of the master batch, leading to potential occupational, consumer, or environmental exposures occurring from drilling, sanding, and cutting the CNT composite; the other scenario consists of potential releases of CNTs from the bound matrices due to low-energy processes, e.g. consumer use and environmental degradation from UV-light and weathering.

For the first scenario, several high-energy machining methods have been used, including wet and dry machining using a band-saw and a rotary cutting wheel and wet and dry solid core drilling (Bello et al., 2009, 2010). Both studies used similar types of CNT–carbon and CNT–alumina hybrid composites and were both conducted within a controlled laboratory setting. For both studies, a suite of direct reading instruments along with time integrated samples was used to determine potential personal breathing zone and area exposures. Several of the metrics analyzed included particle size distribution, number concentration, optically based mass measurements, and active surface area. Time integrated samples were collected for examination of particle morphology and fibers, e.g. respirable fibers, by transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

A study specifically looking at wet and dry machining operations found that dry cutting of composites generated statistically significant quantities of nanoscale and fine particles as compared to background and generated by wet sawing, regardless of the composite type (CNT–carbon, CNT–alumina, control without ENM) (Bello et al., 2009). Submicron length fibers with nanoscale diameter and larger respirable fibers were also generated. Results showed no significant difference between samples with and without CNTs with regard to the particle number concentration. Microscopy samples analyzed by SEM and TEM showed no evidence of CNTs and could not clearly identify individual CNT structures or bundles in the fibers or the particle agglomerates. Emissions resulting from wet cutting (with water) were not statistically different from background levels, except when the cutting wheel guard was damaged.

For the second scenario (low energy processes), similar instruments and conditions were employed during a study on possible releases of CNTs during wet and dry solid core drilling with the exception of using a cascade impactor/diffusion battery combination to collect a time integrated area sample for metal analysis (Bello et al., 2010). Differences were observed in the solid core drilling when compared to the cutting operations in the size distributions, fiber concentration, particle morphology, and observation of CNT aggregates. Clusters of CNT aggregates were observed by TEM during the core drilling of CNT composites.

Lower energy sanding and abrasion of composites containing CNTs have been studied by a number of authors (Cena and Peters, 2011; Golanski et al., 2010; Gupta et al., 2006; Wohlleben et al., 2011). Manual sanding processes examined differ notably from high speed cutting and drilling and higher energy sanding in that they produce significantly lower airborne particle concentrations (Gohler et al., 2010). The parameters, which have to be specified for the testing method, are the material of the abrasion wheel, the contact force or the contact pressure, and the peripheral speed. For manual sanding the increase in number concentration was found to be negligible compared with background levels (Cena and Peters, 2011). Similar results showing limited release from low energy sanding and abrasion were obtained in a study working with CNTs embedded in polyoxymethylene polymer ($<5\%$ by wt) (Wohlleben et al., 2011).

An early study reported that CNTs stuck out of larger particles following the mechanical sanding of a 1% CNT in a composite (Gupta et al., 2006). The experiment was conducted within a glove box and no single CNT-fibers were reported as well. Cena and Peters (2011) reported that TEM showed large particles >300 nm size with CNT protruding, but no free CNTs were observed and noted that the toxicity of epoxy particles containing CNTs is unknown. Another study reported that nanoparticles were emitted, but no isolated CNTs were found (Golanski et al., 2010). The first study to report the presence of free CNTs after abrading CNT-composites has very recently been published; however, no quantitative information is given on the concentration of free CNTs (Schlagenhauf et al., 2012).

Weathering of CNTs embedded in polyoxymethylene polymer ($<5\%$ by wt) under intense UV light was studied (Wohlleben et al., 2011). For weathering, matrices were subjected to UV radiation with the acceleration factor 8 corresponding to 50° northern latitude (i.e., one year of Central European sun). Under this condition, the polymer degraded to expose, but not necessarily release, free CNTs.

Recently, a study was published which conducted an initial, task-based comparative assessment to determine the potential for release of carbon nanofibers (CNFs) during dry material handling, wet cutting, grinding, and sanding (by machine and hand) of plastic composite material containing CNFs (Methner et al., 2012). Using a combination of direct reading instruments and filter-based air sampling methods for airborne mass and TEM, concentrations were measured and characterized near sources of particle generation, in the breathing zone of the workers, and in the general work area. Tasks such as surface grinding of composite material and manually transferring dry CNFs produced substantial increases in particle number concentration. Concomitant increases in mass concentration were also associated with most tasks. Over 90%, i.e. 12 out of 13 samples taken during abrasion of CNF composites examined via TEM, indicated that releases of CNFs do occur, mainly as agglomerated CNF, and that the potential for exposure exists, although exposure levels were not quantified.

Degradation of the polymer/CNT matrix potentially provides key step(s) in the release of CNTs in all phases of the life cycle including manufacturing, product or article life/usage and end of life. Several other recent papers have provided useful discussions of polymer nanocomposite degradation, including polymer CNT composites (Nguyen et al., 2011; Petersen et al., 2011; Wohlleben et al., 2011).

The potentially important role of abrasion in the release of nanoparticles from polymer matrices has been discussed by Wohlleben and coworkers (Wohlleben et al., 2011). Abrasion increases exposure to polymer-CNT simply by enhancing surface area to mass. In addition to these direct effects, the creation of much smaller particles also enhances dispersion by atmospheric and aquatic routes. Degradation generally decreases the tensile strength of the polymer matrix thus increasing its susceptibility to abrasion and breakdown to small particles, i.e. referred to as the “chalking” phenomenon in some cases (Wohlleben et al., 2011). Fragmentation to smaller particles can in turn increase exposure to light and hydrolytic and/or microbial breakdown. However, current results have shown that nanoparticles remain associated with the debris that results from sanding of polyoxymethylene and polyamide with embedded inorganic nanoparticles (Wohlleben et al., 2011).

4. Existing release scenarios for CNTs from polymer composites

So far, one generic release scenario for CNTs in composites has been published (Nowack et al., 2012). These authors have evaluated how different environmental conditions affect the alteration of the composite material, as well as the transformation of the CNTs once they are released from the composite. This generic release and alteration scenario is very simplistic and was formulated to highlight the possible transformation that the CNTs can undergo over the whole life cycle. It did not evaluate in any detail the release mechanisms. The main conclusions from that work are as follows (Nowack et al., 2012): The release of CNTs from products or articles containing CNT-composites may occur over a long time scale and thus this material will probably alter at a slow rate. It was considered that CNTs can be released upon photochemical degradation of CNT-containing composites. These released CNTs can be transported to wastewater treatment plants (WWTP) or be directly deposited into environmental compartments where they would undergo transformation by photochemistry, oxidation, adsorption of natural organic matter and other organic colloids, biotransformation, and continued abrasive forces. These transformation processes are thought to change CNT aggregation, dispersibility, and interaction with biota in the environmental compartment.

The disposal methods, i.e., incineration, WWTPs, and landfill disposal apply to both the CNT composite as well as released CNTs. The incineration of CNT composites subjects them to high temperatures that might result in the airborne release of CNTs if the CNTs survive at low temperature for a short time. Theoretically CNTs should be burned and mineralized during incineration, as the temperature (around 1000 °C) is higher than the ignition temperature of CNTs (normally below 600 °C) (Sobek and Bucheli, 2009) and the waste is incinerated in the presence of oxygen. However, poorly controlled incineration might result in lower temperatures that would not destroy the CNTs. Disposal of CNT composites in landfills could lead to degradation or transformation of the polymers, resulting in possible release of CNTs, depending on the presence and efficiency of landfill liners.

The main conclusion from this generic release scenario is that after release of CNTs to the environment a multitude of reactions can affect the form of the CNTs and result either in complete destruction or change of properties.

5. Formulation of the release scenarios

The potential release scenarios that are formulated in this review begin with formation of the solid product (master batch) and move through its life-cycle as a product and article, ending with the article's reuse or disposal. Exposure scenarios during formation of the master batch as presented by (Fleury et al., in press) are therefore not part of our analysis. The synthesis of CNTs and the making of the master batch (extrusion) are not included in the evaluation. The pelletizing of the master batch is the first process considered. The life-cycle may roughly be broken into three stages:

- Manufacturing of CNT/matrix, i.e. the introduction of CNTs into the matrix, and the ultimate product, e.g. a master batch or paint, or article made from/with the CNT/matrix.
- Normal/consumer/commercial use of product or article throughout life-cycle; including any anticipated but unintended uses of the article where release might occur.
- Post-consumer/end of life/disposal issues (weathering/degradation; repair/refurbishing/mechanical alteration of the article; disposal/demolition/reuse/resale of used article (landfill, incineration, sewage treatment, recycling)).

The characterization of release scenarios will, if possible, take into account:

- Site of potential release; for manufacturing, this includes release to workplace air and environmental release associated with the manufacturing process; for product life/usage, this includes general population/consumers and workplace exposures; for end of life/disposal, this includes potential environmental, general population and workplace exposures.
- Populations potentially exposed — for manufacture, workers; for product life/usage general public (if product is in a public building/space) workers or specific consumers (who buy the product or article).
- Underlying mechanisms of release: This paper considers that the release of CNTs to be both; (a) direct release of free CNTs, or (b) release of particles with CNTs embedded in the matrix.
- Environmental conditions that cause (influence/facilitate) release, e.g., UV intensity, humidity, abrasion conditions.
- Qualitative assessment of the magnitude of release.
- Material properties of the matrix that define release.
- Estimates of frequency/duration of release.

The type of CNT, how it is embedded in the matrix and in which form it is released could not be evaluated due to missing data.

Different release scenarios are formulated for the manufacturing of products and articles (2 occupational scenarios), the use phase of articles (5 consumer scenarios) and the end-of-life phase (2 worker and general public scenarios). The chosen scenarios are representative for the uses of CNT composites today: sporting goods and consumer electronics containing CNTs are on the market today, see the Woodrow Wilson Database (http://www.nanotechproject.org/inventories/consumer). Also uses in cars (small components in various parts) and as large-scale structures (e.g. airplanes, windmill blades) have been described (Dahm et al., 2012). The use of CNTs in rubber for tires has been patented (Kim, 2003). Several possible uses of CNTs in textiles have been described (Goncalves et al., 2012; Koehler et al., 2008; Liu et al., 2008; Panhuis et al., 2007). A flame retardant CNT formulation called Thermocyl© is being marketed in part for use with textiles but no other products are on the market.

The scenarios chosen for this work are summarized in Table 1. In addition to the use-phase scenarios of products on the market or near-market, two scenarios cover the production and manufacturing of the composites. Two additional scenarios look in detail at release during waste incineration and in landfills, because these two life-cycle steps will be common to many applications.

6. Description of release scenarios

6.1. Release scenario 1: manufacturing of products or articles (injection molding)

Injection molding is one of the most common plastic manufacturing method used to mass-produce parts of the same type. It is advantageous to use this method as it is a low cost option to mass produce parts with low tolerance variability, minimal after process activities such as grinding, cutting and sanding, high production yields and the ability to use multiple material types. The injection molding manufacturing process begins with a CNT master batch thermoplastic or thermoset pellet feed into a hopper. The pellets are screw fed into a heated barrel, where the material is melted. This process is enclosed, preventing any potential release of CNTs to the workplace. The temperature of the melt process is dependent upon the melt point of the plastic used in the process. A plunger mechanism forces the melted plastic material into the part mold. The plastic returns to its solid format inside the mold and once the part has completely solidified, the part is removed from the mold and finished. The final preparation of master batches involves cutting the long strings of extruded composite into pellets. This process is done after the extruded composite cools to room temperature. These strings are then passed through a knifing process to cut the pellets.

Table 1
Release scenarios covered in this work. "x" denotes a life cycle stage was considered in the scenario.

	Release scenario	Professional user	Consumer	Environment	Recycling
1	Injection molding	x	–	x	–
2	Manufacturing	x	–	x	–
3	Sports equipment	(x)[1]	x	x	x
4	Electronics	(x)[1]	x	x	x
5	Windmill blades/fuel system parts	(x)[1]	x	x	x
6	Tires	(x)[1]	x	x	x
7	Textiles	(x)[1]	x	x	x
8	Incineration		–	x	–
9	Landfill	–	–	x	–

[1] During recycling activities.

The majority of the injection molding manufacturing process occurs within an enclosed system thus minimizing the exposure of employees to the plastic and CNT materials. It is unlikely that any CNT release occurs during the actual mold process due to emissions from solvents released later during the solidification/curing process. Scrap and/or off-spec materials from the production processes will cause the generation of a solid waste stream and create potential for dermal exposures by those who handle them. Maintenance of injection molding material may also potentially generate a waste product of wipe cloths and/CNT containing particulates. Currently these two waste streams are mainly treated using incineration.

6.2. Release scenario 2: processing of nanocomposites (cutting, sawing, drilling and sanding of raw nanocomposites)

The injection-molded parts described in scenario 1 may require finishing steps before incorporation into the final product. The final finishing process may include sanding, grinding, drilling and/or burnishing. Machining operations like sanding, cutting and drilling are based on high energy input and may lead in each case to a considerable generation of nanoparticles in workplaces as described in the "Release of CNT from polymer composites" section (Bello et al., 2009, 2010; Cena and Peters, 2011; Golanski et al., 2010; Gupta et al., 2006; Wohlleben et al., 2011). During weak, but long-term abrasion processes, relevant for the use-phase, only a slight release of coarse particles containing embedded nano-objects was observed (Cena and Peters, 2011; Golanski et al., 2010; Gupta et al., 2006; Wohlleben et al., 2011). However, more data with composites that have a wide range of tensile strengths need to be obtained to support this conclusion. Especially data from real-world situations need to be provided, preferably in the form of well-described exposure scenarios (Clark et al., 2012).

6.3. Release scenario 3: CNT-composites used in sports equipment

During the use-phase, release by consumer influence is possible, either chemically, induced by sweat, saliva, or mechanically, by breakage (into environment) or during maintenance/repair. These releases are likely to be quite small, but cannot be totally excluded. Release may also be dependent on the type of sports equipment. With a tennis racket or golf club the consumer can have a direct contact with the CNT-composite material if it is not covered with other materials. A bicycle frame, on the other hand, is most probably coated, so no direct contact will occur. Repair operations might result in highest release, but these operations are highly unlikely for this type of sports equipment. High-end sports equipment containing CNTs (e.g. bicycle parts and golf club shafts) is sometimes customized for use, e.g. cut to size or lengthened, and thus some of these modifications, e.g. those involving cutting, might involve release. As an overall assessment we can estimate that there is only very low likelihood of release for most situations.

Release by environmental processes such as weathering by UV/water is possible (e.g. bicycle), but only relevant if material is degraded and not covered with paint/other material. The coating of the material may also degrade with time, thus even if not initially damaged, this coating may only delay the environmental release.

In the post-consumer phase smaller equipment most likely ends up in household waste (incineration, landfill, depending on region). Larger equipment such as a bicycle will probably first go back to the dealer, then probably also into normal waste (incineration, landfill). There is a low potential for these materials to be used for unintended purposes in the post-consumer phase, for example as components of art work or as structural supports in less affluent economies.

6.4. Release scenario 4: CNT-composites used in electronics

Many new electronic devices such as laptops, cell phones and computer tablets are small and are frequently contacted by the consumer. These devices may be positioned on the body during use such as a laptop, or held in the hand(s) for prolonged periods of time (e.g. cell phones). These devices will contain flame retardant chemicals in the plastic casing that come in contact with the consumer. Carbon nanotubes could be used as flame retardants (FRs) in plastic composites (Chattopadhyay and Webster, 2009) although there is limited evidence of their current use. Consumer contact may be extensive and in addition to abrasion from the manual contact with the device, skin contact and chemically induced release may also occur. Polymer fragments were detected in household dust and were found to be transferred to the dust via physical processes such as abrasion from polymers (Webster et al., 2009). Given the greater contact between consumers and electronics that may contain CNTs, the potential exposures should be explored. Routes of exposure and uptake such as through ingestion or the skin, induced by sweat/saliva, may be more likely due to the changes in electronics and use patterns. The particles may also be released into the air from where they can be inhaled directly, or they accumulate in household dust from where they may be inhaled or picked up by small children and ingested through hand-to-mouth activity.

Release by environmental processes is not expected under normal operation. In the post-consumer phase, the fate of the CNTs depends on the recycling schemes that are implemented in a region/country. Without recycling, the equipment will end up in household waste (see scenarios 8 and 9 on incineration or landfilling). If e-waste recycling is implemented and functioning recycling schemes are available, the equipment enters the e-waste recycling stream. Issues that need to be answered here are in which fraction the CNT-composite ends up or if the CNT-composite is removed before shredding.

6.5. Release scenario 5: CNT-composites used in larger non-consumer use applications, i.e. non-abrasive outdoor applications, e.g. windmill blades, and small CNT-composite parts within larger structures, e.g. fuel system components in cars

During the windmill blade use phase consumers will not be exposed to any CNTs. Release by environmental processes is possible: Weathering by UV, rain, temperature could lead to direct release to the environment (air, soil), but this is unlikely as the blades are painted and CNTs are therefore not directly exposed on the surface.

Recycling is likely for these large structures. The issues raised in scenarios 1–4 also apply here: exposure by occupational handlers is possible and depends on the processes implemented during recycling (Fig. 2).

During the automotive use-phase the consumer is not exposed to any CNTs. Release by environmental processes is also not likely because the CNT-containing parts are hidden inside the car. In the post-consumer-phase separate recycling of the small parts is not likely. The composites will therefore end up in a metal- or plastic containing fraction. Release of CNTs during handling/disposal of this fraction is possible, and is hard to control due to lack of knowledge that CNTs are present in the mixture.

6.6. Release scenario 6: CNT-rubber composites used in tires

Emissions of nanoparticles from tires are expected during use, recycling and disposal (Würth, 2007). The emissions during use are mainly due to abrasion of tire tread, consisting of rubber blend which may contain CNTs. The degree of abrasion depends primarily not only on vehicle speed, whereby abrasion increases with increasing speed, but also on tire composition and nature of the pavement. Abraded particles are probably released to air, then either deposited on road-side soils or washed into the storm-water collection system with rain water. Direct release into the environment is therefore possible.

The end-of life treatment of tires varies from country to country. In the following, the situation in Switzerland is presented (data from Würth (2007)). The most important disposal routes are the use as alternative fuel in cement works, retreading, material recycling, and the disposal in waste incineration plants. Disposal of tires in landfills is forbidden in Switzerland, and will soon be forbidden in the European Union as well (Council Directive 1999/31/EC). Especially for highly used heavy duty tires re-treading is a common practice. For tire retreading the old rubber material is removed first and small defects in the carcass are sanded, producing rubber scraps of 1 to 5 mm. These scraps are sucked off and supplied to material recycling, e.g. for rubber mats, sports fields or pavement. A large fraction of tires are used as fuel in cement works (21,000 t/a in Switzerland). Emissions from cement works are not expected because of the high temperatures (1450 °C) during sintering. The dust generated during the combustion process is mixed with the raw mix and is sintered. Approximately 2000 tonnes of old tires is combusted per year in Switzerland in waste incineration plants (see release scenario 8 for details); a further 7000 to 10,000 t/a of discarded tires is not accounted for. A part of that unaccounted material will be recycled to rubber granulate and powder, another part is used in agriculture to cover plastic sheets and silos. Occupational exposures are possible during recycling. The secondary exposures from reused rubber would include several types of consumer exposures, from cement degradation, use of mats, and from agricultural uses.

6.7. Release scenario 7: release from textiles

Release of CNTs from textiles is possible during all life cycle stages (Koehler et al., 2008), however, there is currently no product on the market. A recent study has evaluated releases of CNTs by washing of cotton and polyester textiles (Goncalves et al., 2012). The release of inorganic nanomaterials from textiles during washing has been reported in several papers (Benn and Westerhoff, 2008; Geranio et al., 2009; Lorenz et al., 2012; Windler et al., 2012). Most studies were carried out with nano-Ag and found significant release into the washwater both as dissolved and particulate Ag (Benn and Westerhoff, 2008; Geranio et al., 2009; Lorenz et al., 2012). However, washing out of Ag can involve dissolution of $Ag+$ and precipitation as silver salts or re-formation of AgNPs by reduction of $Ag+$ (Yin et al., 2012), processes not possible for CNTs and therefore the transferability of the Ag-results

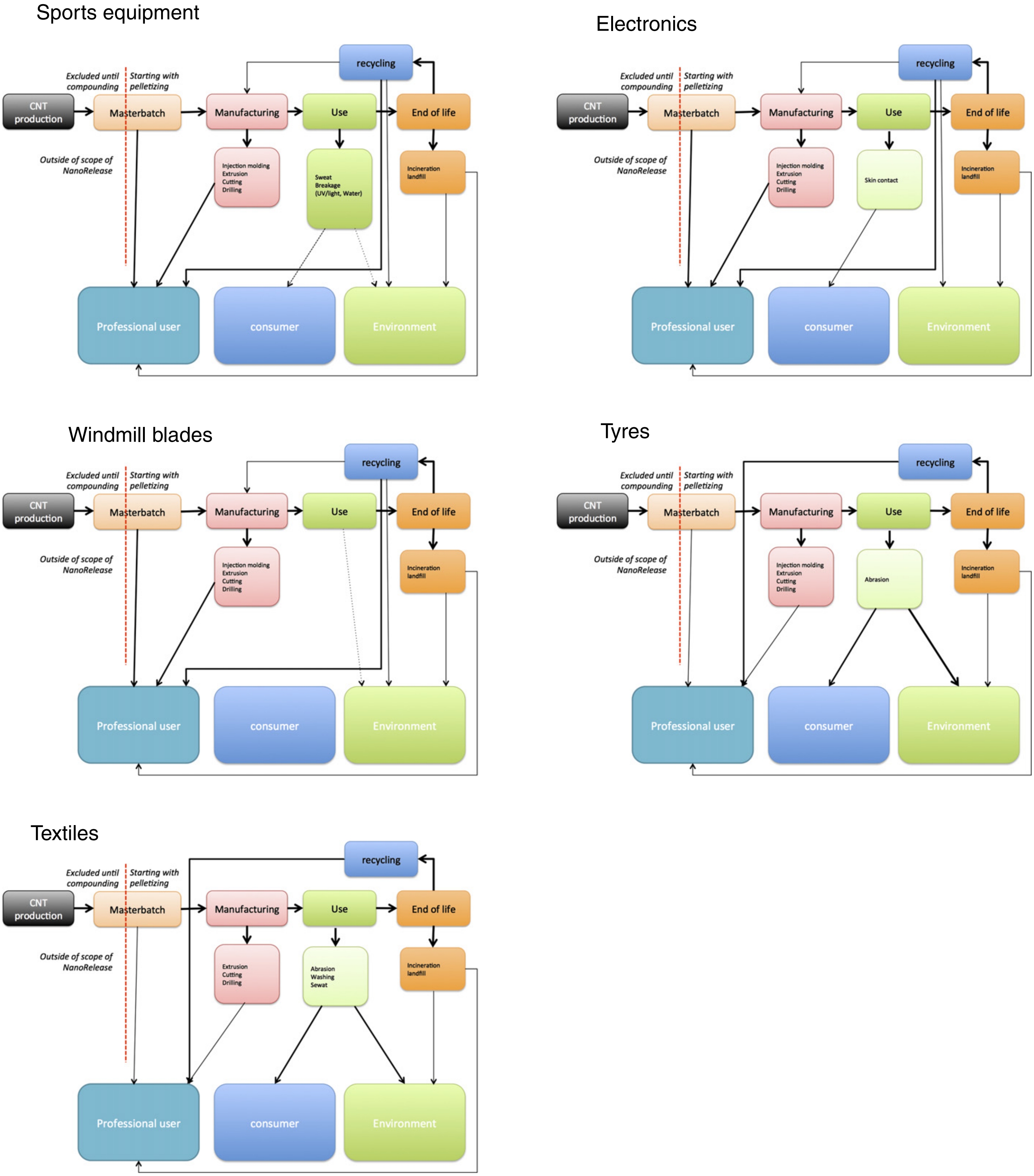

Fig. 2. Life cycle diagrams of six release scenarios (scenarios 3–7). The thickness of the lines corresponds to the estimated magnitude of release.

to CNTs may be limited. Most of the silver-textiles were also made using a finishing process and therefore the nano-Ag was only bound to the fiber surface and thus susceptible to release whereas fibers with nano-Ag embedded in the fiber released much lower amounts (Geranio et al., 2009). One study looked at releases of nano-TiO_2, which is mainly incorporated into the fibers, therefore similar to a CNT-fiber composite, and it was found that only very low amounts of TiO_2 were released into washwater (Windler et al., 2012). We can therefore expect that release of CNTs from composite fibers will be relatively low, with some fraction released into washwater and therefore wastewater treatment plants. However, in washing liquid high concentrations of surfactants are present which are known to stabilize CNTs in suspension (Bouchard et al., 2012; Schwyzer et al., 2011).

Release of materials from nano-textiles can also occur during wearing the textiles and therefore consumer exposure is possible. Only two studies looking at consumer exposure to nano-Ag textiles are available so far, however, they showed that mainly dissolution of nano-Ag occurred and the results are therefore not transferable to CNT-textiles (Kulthong et al., 2010; Yan et al., 2012). Abrasion of CNTs during use by mechanical stress has however to be expected as textiles may lose up to 10% of their weight during use (Koehler et al., 2008). Normal ironing would not be expected to result in fiber release, however accidental burning by ironing may cause thermal degradation of the textile leaving an ash cake which contains free CNTs. Depending on the country, different percentages of textiles are collected and recycled, exported or disposed. A majority of the textiles are re-used or recycled (Koehler et al., 2008) creating potential occupational, consumer and environmental exposures.

6.8. Release scenario 8: release during incineration

The end of life (EOL) scenario of products and articles will vary, depending on the consumer use. The potential recyclability of CNT-containing plastic parts is not as straightforward as other plastics not containing carbon nanomaterials. All CNT-containing plastic parts are black in color. With present recycling technology, it is not possible for plastic recyclers to separate different types of black plastics by plastic type. This inability to differentiate between black plastics creates a "down-cycling" or no recycle option where all black plastics are grouped together into one batch and shredded to create post-consumer black plastics, potentially diluting the beneficial mechanical and electromagnetic properties of the material. It would also expand, albeit diluted, the number of post-consumer products containing nanomaterials. Depending on the products, occupational or consumer exposure is possible.

With the advances in technology, it may be possible to design a "trigger" material into the manufacture of CNT products that can be used to separate CNT-containing black plastics from non-CNT products. This would allow the segregation of these plastics for potential "up-cycling" opportunities. The other option to fully benefit from the recycling of CNT-containing materials is the implementation of a post-consumer "take-back" program. A "take-back" program may be feasible for higher end products such as electronics, automotive, aerospace and solar receivers but would not be feasible for the toy and packaging market sectors. The lower end markets would likely end up in a landfill or be incinerated thus generating another environmental exposure scenario to include release due to UV exposure, in stormwater and/or burn. If these releases do occur, then the environment transport of these releases would need to be studied.

At the end of the life of a product it is either recycled or thrown away. Depending on the country and region, if thrown away, the waste is either incinerated or landfilled. So far only one study has been published that investigated the behavior of nanoparticles during full-scale waste incineration (Walser et al., 2012). Because this work used CeO_2 which does not undergo any changes during the incineration process the results from this study cannot be used to make conclusions about CNT-composites.

Release of CNTs during waste incineration was modeled by Gottschalk et al. (2009, 2010). These authors suggested that in Switzerland the majority of all CNTs will end up in waste incineration. Of the total flow of 0.8–2.7 t/a CNTs that was predicted to reach the waste incineration plants of Switzerland, 0.5–1.8 t/a was modeled to be eliminated, the remaining fraction was attributed to filter ash (0.1–0.4 t/a) and slag (0.16–0.55 t/a), which were either exported or landfilled.

The first data about incineration of CNT-composites are available. One study evaluated the products of the combustion of various composites under well-ventilated and under-ventilated conditions (Calogine et al., 2011) (5% CNTs in PMMA). The fraction of soot measured in the exhaust gas was a maximum of about 20 mg/g, so the majority of the composites were completely mineralized to CO_2 or other gases. The soot-fraction is likely to contain also CNTs, however, this fraction was much less than 1% of the original mass. Petersen et al. (2011) stated in their review that the CNTs present in nanocomposites would most likely not be aerosolized during incineration because incineration facilities are designed to ensure that off-gases and aerosolized particulates have long residence times at high temperatures (1000 to 1100 °C) that have been shown to be almost completely destroyed. However, incinerator ash may contain non-combusted CNTs.

6.9. Release scenario 9: release from landfills

Landfills represent the dominant option for waste disposal around the world. In general, this reliance on landfills is driven by cost considerations, particularly in developing economies (Brunner and Fellner, 2007). Nevertheless, even some highly industrialized countries such as the US, Australia, the UK, and Finland largely depend on landfilling. For example, in the US, 54% of waste generated was landfilled in 2010, with recycling and composting accounting for about 34% of municipal solid waste (MSW) management (US EPA, 2011). In Australia, about 70% of MSW has been directed to landfills without pre-treatment in 2002 (Chattopadhyay and Webster, 2009). In Japan, direct disposal of MSW accounted for less than 30% of MSW generation in 2000 with high incineration rates during the last decades due to the historic scarcity of land (Tanaka et al., 2005). Greece, the UK, and Finland are some of the most dependent on direct landfilling among the EU member states. The fraction of solid waste landfilled in 2008 was 77% in Greece, 55% in the UK, and 51% in Finland (European Commission, 2010). In contrast, landfilling accounted for less than 5% of MSW management in 2008 in Germany, The Netherlands, Sweden, Denmark, and Austria (European Commission, 2010).

Plastic waste constitutes a large and growing component of the waste placed in landfills. The longevity of plastics and therefore the release of CNTs from plastic composites under landfill conditions are not well defined but they almost certainly will depend on the biodegradability of the plastic and the range of options that currently apply to landfill management (Panhuis et al., 2007).

Given the widespread general use of landfills for waste disposal, it is reasonable to assume that landfills are also a major end-of-life (EOL) fate for nanomaterials. A recent study attempted to quantify the various EOL scenarios for nanomaterials (Asmatulu et al., 2012). This analysis concluded that the top three fates of nanomaterials at EOL were recycling, release into wastewater and landfilling and/or landfilling of burned products. The modeling of the material flow for CNTs in the US shows that the flow to the landfill likely constitutes the major flow (Gottschalk et al., 2009).

Here the possible fate of CNT/polymer composites is considered for landfills during the operational period. It is worth noting that closed landfills in almost all industrialized countries will continue to require some level of management to insure that human health and the environment is not adversely affected. Plastics likely will be among the most long-lived constituents of landfills.

The basic design elements of modern engineered landfills include several features: a waste containment liner system to separate waste from the subsurface environment, systems for the collection and management of leachate and gas, and placement of a final cover after waste deposition is complete. After loads are deposited, compactors and bulldozers are used to spread and compact the waste on the working face. Waste compacting includes the process of using a steel wheeled/drum landfill compactor to shred, tear and press together various items in the waste stream so they consume a minimal volume of landfill airspace. The higher the compaction rate, the more trash the landfill can receive and store. This will also reduce landslides, cave-ins and minimize the risk of fire. The compacted waste is covered with soil daily. In some landfills a complex multi-layer system that includes synthetic materials is used as a cover. The cover is added to minimize percolation and runoff of leachate from the landfill. Such landfills are sometimes referred to as "dry tomb" systems. Much of the waste introduced to the landfill is biologically labile. As it is covered and compacted in a dry tomb landfill, microbial oxidation of this waste rapidly depletes the oxygen and the system becomes anaerobic. Methanotrophic bacteria are abundant and methane gas is commonly produced. Processes that may lead to release of CNTs from polymers under conditions that prevail in dry tomb landfills include abrasion by the compacting processes to smaller particles. Degradation of the polymer matrix, especially in the case of non-hydrolyzable polymers, and release of CNTs are likely to be extremely slow. For example, polyethylene is so stable under landfill conditions that it has often been chosen as the liner system for the landfills. These conditions represent highly managed landfills. The situation in developing nations is less controlled and could lead to greater post-consumer and environmental releases of discarded CNT composites.

7. Discussion

The release of CNTs may occur as; (a) free CNTs or CNT agglomerates/aggregates or more frequently, (b) as particles of CNTs embedded in the matrix, where CNTs may be released from the matrix subsequently. The toxicity of free CNTs has been examined in detail (Wick et al., 2011), however there is limited information on the biopersistence and toxicity of matrix particles with CNTs embedded. Ecotoxicological effects of CNTs in soils and sediments appear to be very small and only occur at very high exposure concentrations, e.g. g/kg (Petersen et al., 2011). Toxic effects in the aqueous phase have been observed at mg/l-concentrations. This suggests that CNT sedimentation and transfer to sediments may reduce their potential toxic effects, while other processes such as bioturbation may increase the potential risks (Petersen et al., 2011). In considering the release scenarios, it is noted that there is a limited amount of quantitative data available on release levels. It was therefore difficult to build release scenarios combining different information sources due to the heterogeneity in the level and quality of the description of the situation (differences related to material characteristics, processes, quantities handled, control systems, etc.) and in the exposure evaluation (the absence of standards addressing different measurement strategies, equipment and data treatment). There is clearly a need for both a description of standard release processes and standardization of the reporting of release and exposure processes.

For different stress situations (mechanical, thermal, chemical and may be more energy input) processes have to be identified, which can be standardized and allow at least a release risk banding under defined conditions. The starting point could be already existing standardized processes for other purposes adjusted to the risk parameters of CNTs. As an example for thermal stress the thermal-gravimetric analysis (TGA) could be considered. The needed conditions for CNT-analysis have to be defined and the released CNT, if at all mainly included in the left over material after heating the CNT-containing material to different temperatures, has to be identified (Fissan and Horn, 2013).

The information presented here describes plausible scenarios in which CNTs can be released from products and articles. It should be emphasized that data are lacking with respect of release magnitude for many scenarios. However, Table 2 gives an overview of the estimated magnitude of release for the nine addressed release scenarios.

We can identify three distinct categories:

1) A first category where CNT release is unlikely, for example in painted structures. A potential for release during manufacturing of products and articles exists for all scenarios; however, this is also the situation when release can be best controlled e.g. by use of engineering controls.
2) In a second category the extent of CNT release is unclear or unknown — for example in the handling/disposal/recycling of waste and in new products such as the potential use as flame retardants. There are some scenarios (windmill blades and fuel system components) where exposure of consumers is non-existent because consumers cannot come into contact with these products. Release to the environment in all scenarios is not only possible at some stage of the life cycle, but is also considered to be low for most scenarios. Release during recycling operations when the polymers containing CNTs are handled together with other polymers, e.g. shredded, is possible and mainly professional users would be exposed and risk management practices can easily be employed in industrialized countries. However, we also have to consider that many recycling activities (e.g. e-waste) take place in Africa or Asia where recycling is carried out in backyards without any occupational safety measures. The actual exposure would be determined by the type of recycling operations, especially if the CNT-composites are recycled separately or mixed with conventional plastics. In infrequent cases public users could be exposed during "do-it yourself" maintenance or repair of coated car body parts, made from polymer composites.
3) In the third category CNT release can be expected — for example the use in tires or other products where abrasion is a dominant process. Consumers, i.e. the general population, could then be exposed to CNTs through air or road dust. The exposure could be not only in the form of small particles of CNT composites but also in the form of free CNTs. It has been reported that free carbon black particles can be released from conventional tires during driving (Dahl et al., 2006). Manufacturing that involves high energy machining processes (e.g. cutting, grinding or drilling) will give rise to significant release levels. Also the use of CNTs in textiles would likely result in exposure of consumers due to the close contact between textile and consumer and the mechanical stress that textiles are exposed to. While widespread use of CNTs in textiles has not been confirmed, the wearing of CNT-textiles will result in direct skin contact with CNTs. If CNTs are released into air by mechanical stress, this would constitute the greatest exposure concern (Wick et al., 2011).

In general, it can be concluded that the expected release of CNTs from products and articles is unlikely except for in manufacturing and subsequent processing, tires, textiles and in recycling operations. However except for high energy machining processes, most likely the resulting

Table 2
Summary of the likelihood of release for the 9 release scenarios investigated in this work.

	Release scenario	Professional user	Consumer	Environment	Recycling
1	Injection molding	unlikely	–	Unlikely	–
2	Manufacturing	Very likely	–	Unlikely	–
3	Sports equipment	–	Unlikely	Very unlikely	Likely
4	Electronics	–	Unlikely	Unlikely	Likely
5	Windmill blades/fuel system parts	–	Very unlikely	Unlikely	Likely
6	Tires	–	Very likely (through environment)	Very likely	Likely
7	Textiles		Very likely	Very likely (through wastewater)	Likely
8	Incineration	–	–	Unlikely	–
9	Landfill	–	–	Unlikely	–

–: not applicable (life cycle stage not considered in scenario).

exposure for these scenarios will be low and to a non-pristine form of CNTs. Actual release and exposure studies should be conducted to provide evidence for this conclusion. In this context the development of exposure scenarios can be a powerful tool for understanding the conditions under which exposure occurs (e.g. operational conditions, amounts used and risk management measures), as long as exposure has been assessed using high-quality exposure measurement methods (Clark et al., 2012). These authors also stated that significantly more research is needed before comprehensive exposure scenarios and associated exposure estimates for nanomaterials can be developed. A major hurdle is clearly that analytical methods are missing so far that could specifically and quantitatively identify and characterize the released CNTs under real-world conditions (von der Kammer et al., 2012). However, recent developments of novel analytical methods for CNTs may enable such measurements (Plata et al., 2012) and allow researchers to quantify the release of CNT from actual products.

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