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Evaluation of methods for assessing the release of nanomaterials from commercial, nanomaterial-containing polymer composites

Évaluation des méthodes de détermination d'émission de nanomatériaux par des polymères composites commerciaux, contenant des nanomatériaux

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Contents

Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 229, *Nanotechnologies*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

0.1 General

The use of manufactured nanomaterials (MNM) in consumer products and applications is growing as manufacturers exploit the unique properties of nanomaterials. MNMs are an increasingly common feature of a growing variety of commercial applications and consumer products — from computer chips to golf clubs. So too are concerns over what is or can be released from products containing MNMs, and the risk and potential impacts of exposure to such releases. These unique properties offer significant commercial value, enabling the manufacture of products that that offer novel characteristics. The MNM might be embedded in solids, might be suspended in fluid, or might be bound to the surface of solid products. An understanding of what is released from products containing MNMs is critical to planning and managing safe development and use of those products.

This document aims to contribute to that understanding by providing a guide to the information to be taken into account in determining the methods for identifying and evaluating releases of MNMs from matrices; providing a framework for understanding how these methods and the information they produce can support decision-making; and identifying opportunities for developing standards in this area.

This document provides practical support for decisions related to product development and use through early consideration of the potential for release of MNM and through focus on realistic use scenarios where exposures to the released MNM might occur.

The intended users of this document would include:

- those planning to develop or adapt technical specifications for MNM use in commercial products;
- risk managers, product developers, exposure measurement practitioners or other stakeholders seeking guidance on the availability and utility of methods to measure releases that could occur from uses of specific MNMs in composites;
- methods and instrumentation developers seeking to identify needs of the risk management community;
- those planning basic and applied research programs for measurement and modelling to support decisions around sustainably safe uses of MNMs.

The structured review of the information regarding the selection of MNM measurement methods provided in this document is needed because technologies to produce MNMs, their uses, and MNM measurement methods are often developing at the same time, and the development of measurement methods can in some cases lag behind product development needs. Furthermore, the need to measure particular characteristics of the released MNM might also evolve as greater understanding of what might cause toxicity for a particular kind of MNM is gained. This relationship between emerging measurement methods and emerging information about toxicity makes a structured approach to review of measurement needs even more important, so that data are assembled to support decisions using the most up-to-date and fit-to-purpose measurement methods. Finally, the selection process for choosing a particular MNM-composite for a product should include the consideration of whether the available measurement methods are feasible for the evaluating the conditions of use of that MNM-composite. This consideration is needed because many methods available for research or for controlled conditions in industrial hygiene settings are not useful for realistic measurement needs where consumers might be exposed. In some cases, those methods are too difficult to conduct outside of the laboratory, and in other cases the methods are too labour-intensive to be feasible for routine decision support.

The development of the decision-making framework presented in this document is based in large part on initial analyses that focused on releases from polyamide or epoxy polymers to which multi-wall carbon nanotubes (MWCNT) have been added. Nonetheless, the framework can be used to inform the selection of methods for identifying and evaluating the releases for a wide range of MNMs and types of matrices, as illustrated by the case studies in Annex A. The case studies have been chosen because of the availability of information and methods relevant for actual MNM-polymer composite uses.

Release from polymer nanocomposites can occur through processes such as physical, chemical, or thermal degradation of a polymer matrix, resulting in particles that might include a mixture of free MNM, free polymer, and matrix-bound MNM. This document focuses on the first release to human exposure or to an effluent pathway. While acknowledging that subsequent MNM fate and transport could follow from this initial release, the primary concern of this document is whether and where release of MNMs can occur in the context of consumer or commercial use, and the need to monitor likelihood of human exposure potential. Although other stages of the lifecycle of products containing MNMs are discussed briefly to provide context, subsequent fate and transport events are not addressed in detail.

The ultimate goal is to use the report structure of this document as a foundation for addressing releases of other MNMs from other matrices in subsequent versions of the document.

0.2 Decision-Making Framework

0.2.1 General

In developing the decision-making framework set out in this document two key concepts that have proven useful in addressing the relevant risk management issues in support of decision-making have been applied. The first is "problem formulation"[1]. This describes the purpose and context of the analysis, and the nature of the decision that the analysis aims to support. By making it clear the analysis is being conducted to support a specific decision, this approach helps to ensure the analysis remains focused on methods that have practical application in making that decision. The second key concept is "fit for purpose." In other words, the nature of the analytical approach used should be sufficient for and appropriate to addressing the specific risk management decision. This includes assuring that the depth of analysis - including consideration of the sources and potential magnitude of uncertainty – is consistent with the information needed to support the decision. In the context of this document, this means that feasibility is an important consideration in the choice of analytical methods.

0.2.2 Application of concepts

In applying these concepts to the selection of methods for identifying and evaluating releases of MNMs from matrices, the problem formulation would include an evaluation of the potential for human exposure to the component of the nano-enabled product (NEP) that contains the MNM and the potential for MNM release from that component.

To evaluate the potential for human exposure, an understanding of the product design and the potential use scenarios is required. If, for example, the component containing the MNM is fully encased within a consumer product, or is part of a machine where it is accessible only during maintenance, there are limited opportunities for human exposure as part of the release event. Description of potential use scenarios is also critical for understanding the potential nature of human exposure (e.g. direct dermal contact vs. inhalation of released MNM), as well as relevant conditions of potential wear and aging (e.g. potential and nature of abrasion, temperature, presence or absence of water and UV light).

Together, these elements of the problem formulation can aid in determining which potential release scenarios need to be tested, as well as the nature of the analytical methods needed and, thus, aid in determining whether it is feasible to evaluate the risk of a given choice of product composition without substantial investment in analytical methods development.

0.2.3 Tiered approach

In some situations, a tiered approach — such as those described in Clause 8 — can be useful. For example, if release outside of a confined structure is not expected (e.g. if the MNM is contained within a phone, and release would not result in consumer exposure), an analytical method that simply detects the MNM could be sufficient. In other cases, a qualitative description might be useful to predict the potential for further interactions with other materials, and ultimately the fate and transport of the MNM. Such information could be used, for example, in deciding between alternative designs or products

0.2.4 Quantitative risk assessment presents challenges

Finally, in some cases it could be necessary to quantitatively evaluate the MNM release in order to feed into a quantitative risk assessment. In such cases, it is important to ensure that exposure measurements are made in a way that facilitates integration with hazard data to evaluate risk. Such integration includes evaluating the MNM characteristics with regard to key determinants of toxicity (e.g. degree of aggregation and functionalization), and reporting exposure in relevant dose units. Currently completing an evaluation of this kind presents a significant challenge, as the key determinants of toxicity and appropriate dose units are still being identified in many situations.

0.2.5 Data requirements

As described in this document, key data needs to support a decision related to product development and use include:

- a description of the NEP and where in the product the MNM is found;
- a description of common use scenarios, including frequency of use and relevant populations;
- a description of potential degradation mechanisms that can lead to release under the use scenario(s) of interest;
- a description of the nanomaterial;
- a description of the composite matrix and its resistance to degradation under the use scenario(s) of interest.

Based on this information, the assessor can determine the potential for release (including the release rate) and the likely media into which the release might occur. These parameters in turn inform the nature of sampling and analytic methods that might be needed.

0.3 Document structure and use

After a brief discussion of how the topic of this document relates to Lifecycle analysis, the document addresses the structure of the polymer and the embedded MNM, and how those structures inform measurement methods needs through their effect on the release rate and the form of the release (Clause 5). Clause 6 describes how the relative resilience of the polymer matrix and the embedded MNM inform measurement methods needs through their effect on the nature of the resulting release and proposes a tiered (stepwise) decision framework for deciding if or which transformations at the release point need to be considered. Worked examples applying the decision framework outlined in 6.3 are presented in Annex A. Clause 7 addresses methods for measuring and describing the characteristics of the released material, including sampling methods in various media, methods for sample preparation and analysis, and measurement challenges. Clause 8 addresses remaining gaps and data needs, and briefly reviews several available decision frameworks to support risk managers in determining the information and sampling methods needed to support product design and development decisions.

It is anticipated that the information presented in this document will find application in assisting manufacturers and regulatory agencies to more clearly identify products and scenarios with low consumer exposure potential (e.g. where the MNM is part of a component that is fully encased) and those products and scenarios with higher exposure potential (e.g. the MNM is in continuous contact with human skin or is used under conditions subject to severe weathering). This document is also intended to aid in evaluating — at the product design stage — how variation in adducts, coatings, or MNM composition would affect MNM release rates and measurement needs.

Evaluation of methods for assessing the release of nanomaterials from commercial, nanomaterial-containing polymer composites

1 Scope

This document reviews and evaluates the utility of available methods to assess material released from commercial polymer composites in support of product use and safety decisions, and describes what revised or additional methods are needed. The document is not focused on describing methods per se; rather the goal is to describe information that is appropriate for consideration in the selection of methods to support decision-making.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO/TS 80004 (all parts), *Nanotechnologies — Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO/TS 80004 (all parts) and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at https://www.electropedia.org/

3.1
manufactured nanomaterial
MNM
nanomaterial intentionally produced to have selected properties or composition

[SOURCE: ISO/TS 80004-1:2015, 2.9]

3.2
nanocomposite
solid comprising a mixture of two or more phase-separated materials, one or more being nanophase

Note 1 to entry: Gaseous nanophases are excluded [they are covered by nanoporous material].

Note 2 to entry: Materials with nanoscale phases formed by precipitation alone are not considered to be nanocomposite materials.

[SOURCE: ISO/TS 80004-4:2011, 3.2]

3.3
carbon nanotube
CNT
nanotube composed of carbon

Note 1 to entry: Carbon nanotubes usually consist of curved graphene layers, including single-wall carbon nanotubes and multiwall carbon nanotubes.

[SOURCE: ISO/TS 80004-3:2010, 4.3]

3.4
multi-wall carbon nanotube
MWCNT
carbon nanotube composed of nested, concentric or near-concentric graphene sheets with interlayer distance similar to those of graphite

Note 1 to entry: The structure is normally considered to be many single-wall carbon nanotubes nesting each other, and would be cylindrical for small diameters but tends to have a polygonal cross-section as the diameter increases.

[SOURCE: ISO/TS 80004-3:2010, 4.6]

3.5
lifecycle
consecutive and interlinked stages of a product system, from raw material acquisition or generation from natural resources to final disposal

[SOURCE: ISO 14044:2006, 3.1, modified — the term has been modified from "life cycle" to "lifecycle".]

3.6
nano-enabled
exhibiting function or performance only possible with nanotechnology

[SOURCE: ISO/TS 80004-1:2015, 2.15]

3.7
single wall carbon nanotube
SWCNT
carbon nanotube consisting of a single cylindrical graphene layer

Note 1 to entry: The structure can be visualized as a graphene sheet rolled into a cylindrical honeycomb structure.

[SOURCE: ISO/TS 80004-3:2010, 4.4]

3.8
nano-enhanced
exhibiting function or performance intensified or improved by nanotechnology

[SOURCE: ISO/TS 80004-1:2015, 2.16]

3.9
nanoscale
length range approximately from 1 nm to 100 nm

Note 1 to entry: Properties that are not extrapolations from larger sizes are predominantly exhibited in this length range.

[SOURCE: ISO/TS 80004-1:2015, 2.1]

3.10

agglomerate

collection of weakly or medium strongly bound particles where the resulting external surface area is similar to the sum of the surface areas of the individual components

Note 1 to entry: The forces holding an agglomerate together are weak forces, for example van der Waals forces or simple physical entanglement.

Note 2 to entry: Agglomerates are also termed secondary particles and the original source particles are termed *primary particles*.

[SOURCE: ISO 26824:2013, 1.2]

3.11

graphene oxide

GO

chemically modified graphene prepared by the oxidation of graphite causing extensive oxidative modification of the basal plane

[SOURCE: ISO/TS 80004-13:2017, 3.1.2.13, modified — "and exfoliation" has been deleted.]

3.12

additive

substance added to polymers to improve or modify one or more particles

Note 1 to entry: In a narrow sense, the term additive includes only ingredients added in small amounts; in such cases the term modifier is used for an ingredient added in relatively large amounts.

[SOURCE: ISO 472:1999, Clause 2]

4 Abbreviations

AC	article category
AFM	atomic force microscopy
AUC	analytical ultracentrifugation
CRM	certified reference material
ECHA	European Chemicals Agency
EC	elemental carbon
EM	electron microscopy
ERC	environmental release category
ES	exposure scenario
ESD	emissions scenario document
ICP	inductively coupled plasma
ICP-MS	inductively coupled plasma mass spectrometry
ILS	inter-laboratory studies
LCA	Lifecycle analysis
LCS	lifecycle stage

MCE	mixed cellulose ester
NEP	nano-enabled or nano-enhanced product
PC	polycarbonate
PP	polypropylene
PROC	process category
PVC	polyvinyl chloride
RM	reference material
RTM	representative test material
SEM	scanning electron microscopy
SL	service life
SU	sector of use
TEM	transmission electron microscopy
TO	thermal optical
UDS	use descriptor system
UV	ultraviolet
UV-VIS	ultraviolet-visible spectroscopy
WWTP	waste water treatment plants

5 Understanding the nano-enabled products

5.1 Pathway analysis for the supply chain

The focus of this document is on release of the MNM in the use phase of the lifecycle, including both consumer and commercial use. However, the design of NEPs needs to consider the potential for MNM release, and ultimately MNM exposure, throughout the lifecycle. Therefore, this clause briefly discusses considerations for the broader NEP lifecycle. The first step in the identification of potential releases along the lifecycle of NEPs is to provide a comprehensive pathway analysis along and beyond their value chain. The basis of this pathway analysis will be the information available about the product and the processes the product passes through during its whole lifecycle. This information might include product composition (nanomaterial and matrix type and composition), production and use volumes for each application, knowledge on fabrication and other lifecycle processes, use profiles (market details) and disposal options. Furthermore, MNM releases in industries strongly depend on the risk mitigation measures applied for waste management and uncontrolled processes.

The estimation of the concentration of chemicals released from products and ending up in the different environmental compartments could be based on the information provided in documents such as OECD Emission Scenario Documents (ESDs). The OECD Working Party on Exposure Assessment develops ESDs in order to reflect conditions on production, use, etc., that are different between countries, and so avoiding duplicative efforts by Member countries and industry. ESDs have been widely used in national and regional contexts. For example, ECHA’s guidance document on environmental exposure estimation refers to existing ESDs developed by both OECD and the European Commission. Other OECD member countries have developed their own ESDs and the US EPA has developed several generic scenarios to be used as default release scenarios in risk assessment. The OECD describes an emission scenario as a set of conditions about sources, pathways, production processes, and uses patterns that quantify the emissions (or releases) of a chemical from production, formulation, processing, use and recovery, and disposal into water, air and solid waste. An emission rate is used to quantify releases. Default values are established in a way that reflect an average number for the whole lifecycle considering the emission rate remains constant over time. However, this is not applicable to most of the cases since the rate will decrease over time for most additives.

Furthermore, to support the identification of uses and facilitate effective communication up and down the supply chain, as well as quantification of releases, ECHA has developed a standardized description of uses in the supply chain called the use descriptor system. The UDS was based on six separate descriptors: lifecycle stage, sector of use, process category, product category, article category, and ERC. There are four basic stages in the lifecycle of a substance to which a use can be assigned: manufacture, formulation or repacking, end-use (use in industrial sites, professional use, and consumer use) and (article) SL. A brief description of the product use(s) can be obtained by using these descriptors.

— **Lifecycle stage:** Reflects the stage of the chemical/ nanomaterial in its lifecycle. It is structured in such a way that it indicates the type of organizations using the chemical (or nanomaterial) after its manufacture (e.g. formulators, industrial end users).

— **Sector of use:** Describes in which sector or market area the substance (nanomaterial) is used.

EXAMPLE 1 SU4: manufacture of textiles, leather, fur; SU11: manufacture of rubber products.

— **Process category**: Describes the application techniques or process types defined from an occupational perspective; the PROC, in combination with the operational conditions and risk management measures, is the prime determinant for the level of occupational exposure. It is a required descriptor for worker uses.

EXAMPLE 2 PROC1: Production in closed process without likelihood of exposure or processes with equivalent containment conditions; PROC5: Mixing or blending in batch processes; PROC7: Industrial spraying.

— **Chemical product category**: Describes the types of products in which a substance/ nanomaterial is used. The chemical product category in combination with the operational conditions and risk management measures primarily determines the level of consumer exposure. It is a required descriptor for consumer uses.

EXAMPLE 3 PC9a: Coatings and paints, thinners, paint removers, PC24: Lubricants, greases, release products; PC31: Polishes and wax blends.

— **AC:** Describes the type of article in which the substance/nanomaterial has been processed. The AC is only relevant and used for the lifecycle stage SL.

EXAMPLE 4 AC2b: Other machinery, mechanical appliances, electrical/electronic articles; AC8e: Paper articles: Furniture and furnishings; AC13a: Plastic articles: large surface area articles.

— **ERC:** Describes the broad conditions of use from an environmental perspective, based on those characteristics that give a first indication of the potential release of the substance to the environment. The default is to select only one ERC per use.

EXAMPLE 5 ERC2: Formulation into mixture; ERC6a: Use of intermediate; ERC8a: Widespread uses of non-reactive processing aid (no inclusion into or onto article, indoor).

Table 1 provides an example of the UDS for polymeric nanocomposites. Scenarios for each lifecycle stage are listed, along with a brief description of relevant processes and activities. The table then identifies the process, product, article, and environmental release categories, to provide an overview of uses across the supply chain.

Table 1 — Example of the ECHA use descriptor system of CNT in polymeric nanocomposites

LCS	ES	Short description of process or activity	PROC	SU	Product category	AC	ERC
LCS 1: CNT synthesis	Production/ synthesis of CNTs using chemical vapour deposition	Synthesis	PROC1	—	—	—	ERC1 Manufacture of the substance
		Recovery	PROC2				
		Packing	PROC9				
		Internal transport	PROC8b				
		Cleaning and maintenance	PROC8b				
		Storage and distribution	PROC8b				
	Production/ synthesis of CNT using arc-vapour	Synthesis	PROC1	—	—	—	ERC1 Manufacture of the substance
		Recovery	PROC2				
		Packing	PROC9				
		Internal transport	PROC8b				
		Cleaning and maintenance	PROC8b				
		Storage and distribution	PROC8b				
	Production/ synthesis of CNT using laser ablation	Synthesis	PROC1	—	—	—	ERC1 Manufacture of the substance
		Recovery	PROC2				
		Packing	PROC9				
		Internal transport	PROC8b				
		Cleaning and maintenance	PROC8b				
		Storage and distribution	PROC8b				
LCS 2: CNT Incorporation into products	Manufacturing of intermediate composite materials containing CNTS	Weighing, mixing, loading	PROC5	SU12 Manufacture of plastics products, including compounding and conversion	—	—	ERC1 Manufacture of the substance
		Extrusion and granulation	PROC14				
		Packing	PROC21				
		Internal transport	PROC21				
		Cleaning and maintenance	PROC8b				
		Storage and distribution	PROC21				

Table 1 *(continued)*

LCS	ES	Short description of process or activity	PROC	SU	Product category	AC	ERC
LCS 3: Manufacturing of products containing CNTs	Manufacturing of solid products with composite materials containing CNTs	Weighing, mixing and loading	PROC5	SU12 Manufacture of plastics products, including compounding and conversion	PC32 Polymer preparations and compounds	AC13 Plastic articles	ERC3 Formulation into solid matrix
		Extrusion, moulding and forming	PROC14				
		Shaping and finishing	PROC24				
		Cleaning and maintenance	PROC8b				
		Storage and distribution	PROC21				
LCS 4: Use and service life	Professional use (service life) of solid composite materials containing CNT	Cutting, shaping, drilling, sanding	PROC24	—	PC32 Polymer preparations and compounds	—	ERC11a Widespread use of articles with low release (indoor)
LCS 5: Recycling and end of life	Recycling and disposal of products containing CNTs	Sorting (mechanical, electromagnetical and manual separation)	PROC21	—	PC32 Polymer preparations and compounds	—	ERC12a Processing of articles at industrial sites with low release
		Processing (mechanical and thermal processes)	PROC24				
		Landfill	PROC21				
		Incineration	PROC2				

The descriptors for all of these categories are requested under the registration, evaluation, authorization and restriction of chemicals (REACH) regulation in Europe for the safety assessment of chemical substances (including nanomaterials) and their uses. The information from this assessment is summarized in the REACH chemical safety report (CSR). One key component of that CSR is the ES in which manufacturers or importers set out the conditions for safe use of their substance. This information is essential to many actors in the chemical supply chain in their day-to-day handling of substances (including nanomaterials). For the identification of the ESs associated with a nano-enabled product, the generation of conceptual maps for the product lifecycle is proposed (general diagram in Figure 1). This diagram links the lifecycle stages of a product with potential exposure/release scenarios (defined as those activities from which release is highly probable to occur), receptors (human, water, soil, air, biota) and technological compartments (WWTPs, incinerators, landfill sites). The five lifecycle stages considered are:

a) MNM synthesis,

b) incorporation of MNM into the product (nano-enabled product manufacturing),

c) manufacturing of products containing MNM,

d) use and service life phase, and

e) recycling and end of life.

A full description of the lifecycle, particularly potential use scenarios, can aid in focusing release testing on conditions that are potentially relevant to the product. During the use phase, intended and unintended release of MNM can occur. The unintended release of MNM typically results from non-point sources such as washed off sunscreens in the ocean water or release from other consumer products, while the intended release results from point sources such as a WWTP that uses MNM for groundwater remediation. In Figure 1, green arrows indicate releases to the environment (generally uncontrolled) and possibly resulting in human exposure (workers and consumers) and red arrows indicate MNM release pathways ending up in waste management or end-of-life treatments.

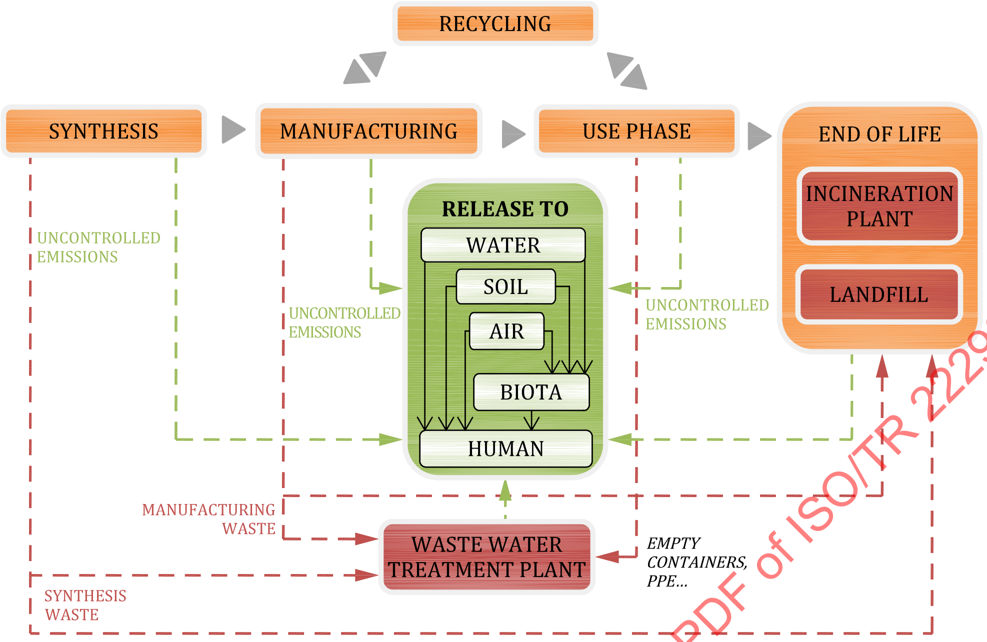


Figure 1 — Lifecycle of a nano-enabled product

5.2 Matrix and MNM characteristics affecting rate and form of release

5.2.1 General

Variations in matrix materials, and MNM types and compositions of nanocomposites can affect the likelihood of nanomaterial release, form of release (e.g. particles containing filler, free filler, degraded filler), and in general the magnitude of materials release, which in turn can each affect measurement method selection.[2] Understanding the physicochemical properties of the neat polymeric matrix material, MNM additive, and composite material is critical in understanding the release behaviour of nanocomposites in their use cases. Potential exposure is often application-specific and is highly dependent on MNM physicochemical properties, the way the MNM is incorporated into the product, and the way the product is being used. Subclause 5.2 briefly reviews key aspects of the physicochemical properties and other key characteristics of the major matrices and MNM additives relevant to nanocomposites to help frame evaluation of the effect of MNM-matrix differences on MNM release characteristics in Clause 6 and the need for particular sampling and measurement methods in Clause 7.

The key topics discussed include:

- release of mnm throughout lifecycle;
- standardized descriptors of nep use, quantification of releases;
- factors affecting MNM release:
  - mnm type,
  - structure/composition of matrix, and
  - product use.

5.2.2 Consideration of the polymer used in the composite

5.2.2.1 General

To fabricate industrial and consumer NEPs the MNM is usually integrated in a matrix. This matrix is often a designated plastic, i.e. a synthetic material made from a wide range of organic polymers. Plastics are broadly classified as thermosetting or thermoplastic polymers; the classification reflects the post-manufacturing malleability and flexibility. Thermosetting polymers are irreversibly hardened via curing by, for example, heat. Thermoplastic polymers are pliable or moldable at a certain elevated temperature and solidifies upon cooling. The thermal properties depend on the chemical structure and molecular units that form polymer chains and backbones. Thermosetting polymers are often crosslinked forming resins and rubbers (duromers). Understanding the performance differences can help making better sourcing decisions and improve product design.

5.2.2.2 Thermosetting polymers

Thermosetting polymers are made from polymer chains that cross-link together during the curing process to form a permanent chemical bond. Cross-linking that occurs during the curing process prevents movement of individual polymer chains after curing. Because of this, once cured, the structure of thermosetting polymers cannot be altered. This process prevents the product from re-melting when heat is applied, making thermosets ideal for high-heat applications like appliances and electronics. Thermosetting polymers can greatly improve the material’s mechanical properties, providing enhanced chemical resistance, heat resistance and structural integrity. Thermosetting polymers are frequently used for sealed products due to their resistance to deformation and are among some of the most impact resistant plastics available. The properties of thermosetting polymers include:

- excellent resistance to solvents and corrosives;
- resistance to high temperatures;
- high fatigue strength;
- tailored elasticity;
- excellent adhesion;
- excellent finishing (e.g. polishing, painting).

The common thermosetting polymers (and applications) include polyester (textiles, 3D printing), vinyl ester (vessels, airplanes), epoxy (adhesives), phenolics (electrical components, household laminates), and urethane (insulating foams, footwear). the most common thermosetting polymers used today is a polyester resin, followed by vinyl ester and epoxy.

5.2.2.3 Thermoplastic polymers

A thermoplastic is a polymeric material or plastic that becomes soft and formable when heated and rigid when cooled. This process can be repeated a number of times without chemically altering the material. Thermoplastic materials offer many performance benefits, such as high strength, shrink-resistance, and easy bendability. Thermoplastic polymers can serve low-stress applications such as plastic bags but are also used in high-stress mechanical parts, depending on the type of thermoplastic material. Thermoplastic materials are highly recyclable, offering aesthetically-superior finishes, high-impact resistance, remolding/reshaping capabilities, chemical resistance, hard crystalline or rubbery surface options, and eco-friendly manufacturing.

Examples of common thermoplastic polymers used today and typical consumer products manufactured from them include Polyethylene Terephthalate (PET) (water and soda bottles), Polypropylene (PP) (packaging containers, automotive parts), Polycarbonate (PC) (windshields, safety glass lenses), Polybutylene terephthalate (PBT) (generic plastic parts, including children's toys), Polyethylene (PE) (packaging, grocery bags), PVC(piping, window frames), Polyethylenimine (PEI) (airplane armrests), and Polyamide (PA) (footwear, fishery nets, 3D printing). Table 2 summarizes key features of thermoplastics and thermosetting polymers.

Table 2 — Comparison of important features of thermoplastics and thermoset plastics

Thermoplastic polymers	Thermosetting polymers
can be synthesized by addition polymerization	can be synthesized by condensation polymerization
monomer used is generally bifunctional	monomer used is tri-, tetra- or polyfunctional
long chain linear polymer with negligible cross links	three-dimensional network structure with a number of cross links
low molecular weight	high molecular weight
soft, weak, and brittle	hard, strong, and more brittle
low melting point and low tensile strength	high melting point and high tensile strength

5.2.3 Polymer degradation

All polymers will undergo some degradation during SL. The result will be a steady decline in their mechanical properties caused by changes to the molecular weight, molecular weight distribution, and composition of the polymer. Other possible changes include embrittlement (chain hardening), softening (chain scission), colour changes, and cracking and charring (mass loss). Factors causing polymer degradation include heat, mechanical energy, radiation, ozone, solvents, acids, and bases.

In general, the resistance to degradation will depend on the chemical composition of the polymer. For example, polymers such as PP, PVC, and polybutadiene (PBD) are very susceptible to thermal degradation, even at normal temperature, and can only be prevented from degradation when formulated with UV stabilizers and antioxidants; whereas polymers such as polysulfone (PSU), polyethersulfone (PES), polyetherketone (PEEK), and polysiloxanes (silicones) present excellent resistance to thermal and oxidative degradation due to the strong bonds in the long chain backbones and in the side-groups. The energy applied during processing [mechanical stresses, grinding, ultraviolet (UV) radiation] can cause breakage of bonds. Dissociation energy for the different chemical bonds in a polymer structure ranges from 65 kCal/mol to 110 kCal/mol. These factors can cause degradation of the polymer due to chains scission (by hydrolysis), crosslinking, oxidation, or via other chemical reactions. Oxidation can result in the destruction of crystalline order. Ingredients, additives, or contaminants can undergo radical formation, which then attacks the polymer. However, stabilizers are used to counter various types of degradation processes (e.g. antioxidants, light stabilizers, heat stabilizers, antiozonants).

Furthermore, some properties of the polymer could facilitate oxidation processes: for example, low degree of crystallinity, low molecular weight polymers, higher branching, presence of double bonds in the chemical structure, and the presence of additives leading to free radicals.

5.2.4 Consideration of MNM used in the composite

MNM additives used in composites can be classified based on their composition and geometry. The basic composition can be either organic (e.g. dendrimers, polymers), inorganic (e.g. metals, metal oxides, metal hydroxides), carbon (e.g. carbon nanotubes, bucky-balls), or combinations of these materials. Even more complex systems can be generated by surface functionalization.

The selection of the MNM in the production of nanocomposites depends on the desired properties for the specific application. Specific thermal, mechanical, electrical, magnetic, and optical properties can be obtained or enhanced by inclusion of different MNM into a polymeric matrix. Preparation of MNM-polymer nanocomposites might involve surface modification of MNM because it is important to obtain strong interactions between MNM and polymer to enhance structural features and optimize stable dispersion of the MNM in the nanocomposite. There have been many studies on optimizing the dispersibility of MNM additives in the polymeric matrix. It is possible to increase hydrophobicity of the MNM additives via surface modification, enhance interfacial adhesion via chain entanglement or chemical bonding.

Potential MNM additives include those based on carbon, metal oxides, and metals. The properties provided to the composites by the incorporation of these different nano additives is briefly described.

One of the most commonly used carbon-based MNM additive are CNTs. The nature of the atomic arrangements and bonding in CNTs provide these materials with exceptional mechanical properties (tensile strength, elastic modulus, and hardness), very good thermal conductivity, and structure-dependent electrical properties (metallic to semiconducting). These properties, along with low density and large aspect ratios, make CNTs attractive for many applications.[3] Additionally, the incorporation of graphene or graphene oxide in polymeric nanocomposites resulted in significant improvements not only in the mechanical, thermal and electrical activities,[4] but also improvements in the conductivities and gas barrier properties compare to the neat polymer[5].

A wide range of metal oxide-based MNM have proved to provide interesting properties: nanoclays present multiple advantages, they can be obtained from relatively cheap materials (clays). Additionally, their flat morphology makes it much easier to obtain good dispersions into the polymeric matrices[6] and therefore, provides multiple properties (flame retardancy, anticorrosion, gas barrier, increase stiffness and heat distortion temperature).[7],[8] The addition of amorphous SiO_2 into certain polymeric matrices resulted in an improvement of mechanical properties (increasing tensile, impact and strength) as well as evidences of flame-retardant properties have been found.[9],[10] Zinc oxide (ZnO) is an interesting material to be introduced into polymeric matrices due to its antibacterial properties[11],[12] and it is also used in applications such as food packaging[13] to improve food preservation in storage and in some circumstances (actively forming hydrogen bonds) can improve mechanical properties of the composite.[12] TiO_2 nanoparticles (both anatase and rutile polymorphs), which are well recognized for their photocatalytic activity,[14],[15] also are commonly incorporated into polymeric matrices, providing an increase in UV absorption to the nanocomposite, useful for multiple applications. The incorporation of TiO_2 nanoparticles in some polymers resulted in an increase in the tensile modulus, decomposition temperature, dimension stability, bending stress, impact stress and elongation break[16],[17].

Finally, considering the incorporation of metal-based MNM, Silver (Ag) is one of the most interesting MNM additives due to its unique electric, optical, catalytic and, particularly, antimicrobial properties.[18] For this reason, its incorporation into polymers have been widely studied and tested.[19] When combined with polymers, if correctly dispersed and designed, the resulting nanocomposite acquires antibacterial properties that are useful for many applications (e.g. medical devices area)[18].

The selection of MNM to use in a nanocomposite and preparation of the MNM nanocomposite might affect release sampling, sample preparation, and analytic needs as discussed in Clauses 6 and 7.

5.2.5 Polymer nanocomposites

Scientific and technological development in recent years has allowed the incorporation of different nanoscale compounds (e.g. carbon nanotubes, metal oxide nanoparticles, nanoclays) into polymer matrices. The incorporation of those additives can change some properties of the matrix, due to the large surface area to volume ratio of nanomaterials when compared to the microscale or macroscale additives. The dispersion of a MNM in the polymer matrix can introduce new physical properties and novel behaviours compared to the original matrices, effectively changing the nature of the original matrix. This can be used to produce either advanced materials with improved properties or new applications, or both.[20] These properties and applications are important to consider in terms of how they might affect release measurement needs. For example, nanocomposite rubber tires with everyday use account for more than one megaton per year of carbon black and silica production in the nanoscale range. However, degradation of rubber nanocomposite tire tread during use is a prime example of the challenge of measuring MNM release during the use phase of lifecycle.[21] Furthermore, major innovations might soon drive rapid growth of the "highly dispersible (HD)" silica additives that are replacing carbon black and so standard methods to measure MNM release must be adapted to changing properties of the tires as innovations proceed. The use of MNM in tires is also unusual because it represents a nanocomposite with very high filler content (above 40 % by weight), whereas the additive content of most other nanocomposites is in the 1 % to 5 % range.

Products that contain MWCNTs are manufactured from composite made from MWNCTs incorporated in a polymer matrix. Five polymers that are commercially relevant and represent a range of polymer characteristics are epoxy (EP), PA, polyurethane (PU), PE, and PC (see also Table 2). Composites used for final products are typically formulations of the polymer and additives designed to modify the physicochemical characteristics of the polymer, particularly its mechanical properties (strength, toughness, and wear resistance) and chemical and thermal resistance to degradation.

The development of other polymer nanocomposites is a growing area in all the industrial sectors. Over the past decade, these MNM filled compounds have attracted considerable interests in both academia and industry, owing to their outstanding variety of properties with only a small amount of MNM additives. Examples include mechanical (e.g. elastic stiffness and strength),[22],[23] physical (e.g. barrier resistance, flame retardancy or scratch resistance),[7] electrical,[24] magnetic,[25] thermal, and optical properties. These new nanocomposites enable interesting applications in most of the industrial sectors, with a particularly high incidence in the electronics, automotive, textile, and mining sectors.

Polymer nanocomposites will not only expand the performance space of traditional filled polymers but also introduce completely new combinations of properties, and thus enable new applications for plastics.[26],[27] Low volume additions (1 % to 5 %) of nanoparticles, such as layered silicates or carbon nanotubes, provide property enhancements (with respect to the neat resin) that are comparable to those achieved by conventional loadings (15 % to 40 %) of traditional fillers. The lower loadings facilitate processing and reduce component weight. Most important, though, is the added unique properties, such as reduced permeability, optical clarity, self-passivation, and increased resistance to oxidation and ablation, not normally possible with traditional additives. These characteristics have been transformed into numerous commercial successes, including automotive parts, coatings, and flame-retardants.

5.2.6 Application areas and use phase (or lifecycle) processes

The end user could be intentionally or unintentionally exposed to MNMs as a result of NEP use. During common use of the products, the end user can be subjected to various controllable and uncontrollable conditions, which might increase the potential for the release and transformation of the MNMs. Released MNMs are often different from the pristine parent material in terms of size and aggregation and agglomeration state, and they can be released either as free MNMs or together with fragments of the product matrix. The use phase will, in most cases, be the most important part of the lifecycle for consumer exposure to MNMs. The analysis of the needs for release measurement methods for each product and product category will require a separate evaluation of the use scenario that accounts for the product design, how it is used, and the resulting potential conditions of MNM release. The way a MNM is incorporated or applied in the product will have a high influence on the MNM properties and the potential for being released and subsequently leading to consumer or environmental exposure.

Through consumer product use, disposal, or recycling, nanocomposites encounter mechanical, thermal, and/or chemical energy inputs that could degrade the nanocomposite and result in the release of the embedded nanomaterials. Several studies cited in this section below investigated release of MNM from polymer nanocomposites in different scenarios (weathering, abrasion, sanding, incineration). From these studies, it is observed that there are generally insufficient data generated to support decision making about MNM release rates using a common and harmonized methodology. However, after analysing the methods used in each case, one could establish some parameter ranges for each process to experimentally simulate real conditions using different laboratory simulations. Laboratory simulations can lead to the following potential erroneous conclusions:

- The stresses of the laboratory simulation tests might not be representative of the stresses by the intended use or operational conditions or handling; for example, the machining tool used in the laboratory experiments might have different characteristics than the one used by the operator or consumer; or, self-ignited thermal decomposition might not reflect the conditions of waste incinerators:
  - risk: the form of release and rate of release would be incorrectly determined;
  - mitigation: recommends stressing the nanocomposite by established ISO protocols that represent real-world scenarios. For example, the NanoRelease weathering protocol uses the

established ISO 4892-3[231] for the aging of the polymer nanocomposites, before sampling and analysis. Furthermore, 5.2.6 lists characteristics of tools.

- The static emission measurements are performed; for example, aerosols from sanding might accumulate and agglomerate, or, leachates might reach saturation:
  - risk: weak correlation from sanding emission to human exposure in the breathing zone. Simulated leaching might underestimate environmental leaching.
  - mitigation: more than one concentration of nanocomposite should be tested.

One should also consider different situations such as:

- The nanocomposite might contain an MNM that is known to be hazardous:
  - risk: the field test will put either operators or the environment, or both, at risk;
  - mitigation: use the options of containment in a laboratory simulation.
- The release rates are often low:
  - risk: the industrial or environmental background might conceal the released fragments of the nanocomposite;
  - mitigation: use the options to reduce background in laboratory simulations, for example, by testing in ultrapure water or in HEPA-filtered sanding boxes.
- In early stages of research, only small amounts of the nanocomposite might be available:
  - risk: unavailability of a sufficient amount of nanocomposites;
  - mitigation: use laboratory simulation testing to require less sample material.

Further limitations of experimental conditions could be possible, depending on the specific product and potential use scenarios.

For example, Table 3 lists different methods or processes used to induce release for PA polymer nanocomposites containing MWCNT, including conditions applied in each of the scenarios studied.

NOTE All of these studies involved laboratory simulations.

Table 3 — Experimental conditions for releases from different processes

Process or cause for release	Description	References
Weathering	UV = 60 W to 480 W (in 300 nm to 400 nm wavelength intervals) for 1 000 h in an accelerated chamber, equivalent to approximately 1 year to 3 year in real conditions based on ISO 4892-3[231]	[28], [29], [30], [31], [32], [33], [34], [35], [36], [37]

Table 3 *(continued)*

Process or cause for release		**Description**	**References**
Sanding	Manual sanding	Manually sanded epoxy test sticks with sandpaper (220 grit)	[38], [39]
	Sandpaper affixed to a rotational disk plate	Three levels of sandpaper roughness (ADSLOX A290 P80, P150 and P320) were used, adhesively affixed to the surface of a disk plate fixed onto a lathe	[40], [41]
	Hand-held sanding equipment	A miniature sander (Model Dremel 400 series) with a contact force of $2{,}0 \times 10^{-1}$ N to 1,0 N, contact pressure of $1{,}0 \times 10^{4}$ to $5{,}0 \times 10^{4}$ and peripheral speed of 1,8 m/s to 24 m/s or a hand-held sanding machine (Metabo FSR200 with 22 000 oscillations/min was used	[42], [43]
	Sanding belt	A belt sander (Model 97181) with a sanding belt (10,2 cm × 91,4 cm) operating at a constant speed of 5,6 m/s with a silicon-aluminium based sandpaper having grit sizes of P150 and P320	[39], [44]
Abrasion		Taber equipment with H-18 abrasive wheel, an applied weight of 0,75 kg and a frequency of 60 c/min	[45]
Band saw		A 220 blade grit, a 1,65 mm blade width, 20 m/s blade speed and 0,2 cm/s to 0,4 cm/s rate of advance of the composites in dry and wet ambient environment	[39], [43], [46]
Rotatory cutting wheel		A 220 blade grit, a 1,65 mm blade width, 15 m/s blade speed and 0,4 cm/s rate of advance of the composites in wet condition (water flushing)	[46]
Drilling		725 rpm to 1 355 rpm drilling speed, 17 N normal load, and 1,3 mm to 3,9 mm specimen thickness, performed under dry and wet ambient conditions	[47], [48]
Scratching		Normal load of 5 N to 25 N, scratch length of 5 mm at 5 mm/min speed for a total of one to 15 scratches	[49]
Crushing		7 900 rpm to 18 750 rpm rotation speed at 108 mm crushing chamber diameter; 14 thousand total rotations	[50]
Incineration		The lab simulations of waste incineration reproduced ISO 15270, which requires a furnace temperature of at least 850 °C (1 562 °F), after overfire, air injection of at least 2 s, and oxygen concentration of 20,9 vol %. Only for hazardous waste incineration, ISO requires temperatures up to 1 200 °C (2 192 °F), but were not yet tested.	[51], [52], [53], [54]

Table 3 *(continued)*

Process or cause for release	Description	References
Food contact	Release has been observed for NEPs that were tested for contact with vinegar, alcoholic beverages, flavour extracts, and the like, simulated in food contact standards by 3 % acetic acid and 50 % to 95 % ethanol. The release was dominated by MNM dissolution inside the NEP matrix in these cases.	[55], [56], [57]

The processes or causes listed in Table 3 for release of MWCNT from PA composites describe rigorous conditions that could also be applied for other composite and MNM additive combinations. However, as noted, although the extremes of some of the test conditions reflect the relatively short test periods, further consideration of the use scenario might allow the developers of a testing program to focus on a subset of specific potential release mechanisms, under conditions that more closely mimic potential end use conditions.

6 Factors affecting release measurement method selection

6.1 General

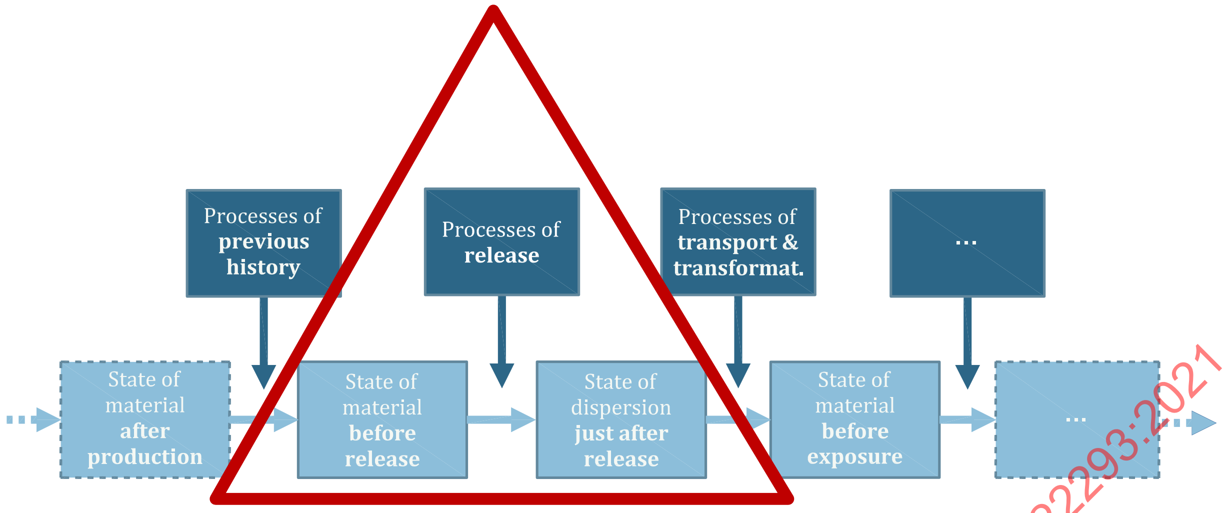
The available literature has extensively evaluated the effect of release mechanisms as described in 5.2.6 (e.g. abrasion, chemical, thermal) and conditions (e.g. temperature, pH, release media) on the forms of materials that would be released, and amounts of release materials that can occur (red triangle in Figure 2).

For the purpose of this document, release is defined as the first release of material from an MNM containing composite into exposure or effluent pathways during consumer or commercial use of the product (see Figure 2). Subsequent fate and transport and determination of resulting exposures are beyond the scope of this document. Release can occur through processes such as physical, chemical, or thermal degradation of polymer matrix resulting in particles that could include a mixture of free MNM additive, matrix-bound MNM additive, and matrix without MNM additive. Subsequent MNM additive release could follow from this first release. For example, MNM additive could eventually be released from the initially released particles as those particles degrade in the environment; however, these subsequent release events will not be addressed in detail in this document.

The sampling and measurement methods discussed in this document are targeted for the size range from few nanometres to several micrometres, as these size ranges are relevant to inhalation, dermal, or incidental ingestion exposure events.

The key topics covered include:

- size range, toxicity, form of release, mnm/matrix resilience;
- identification/evaluation of release concerns;
- relevant scenarios.



NOTE The release events covered in this document are outlined by the red triangle and do not include fate, transport, exposure, or secondary transformation of released fragments or MNM.

Figure 2 — Release events

6.2 Forms of release

The motivation for systematic consideration of the form in which MNM are released is strengthened by the link between the properties of the MNM-containing forms (as indicated in Figure 3) and their toxicity. These properties could be altered during the release process, and the potential toxicity and health impacts of the released materials can be affected by such transformations (in the cases of TiO_2, Fe_2O_3, metal-organic pigments, and CNT), resulting in reduced toxicity as compared to free MNM[43],[58]-[62] or ecotoxicity.[63] For example, the MNM can be released as particles embedded in the matrix, followed by later release (or not) of the free MNM. However, under certain conditions the presence of catalytically active MNM (e.g. catalyst in CNT during thermal decomposition in the absence of waste incinerator conditions) can also render the release products more hazardous.[52],[64] Similar processes can occur with the intrinsic transformation of materials during additive manufacturing. The form and timescale of release are critical for toxicity evaluation, and hence transformations at the release point (see Figure 2, red triangle) deserve attention in the release assessment. Subclause 6.3 describes a proposed tiered (stepwise) decision framework to aid decision makers in determining if and which transformations at the release point need to be considered.

During the literature review, it was observed that the literature tends to cluster around two different cases.

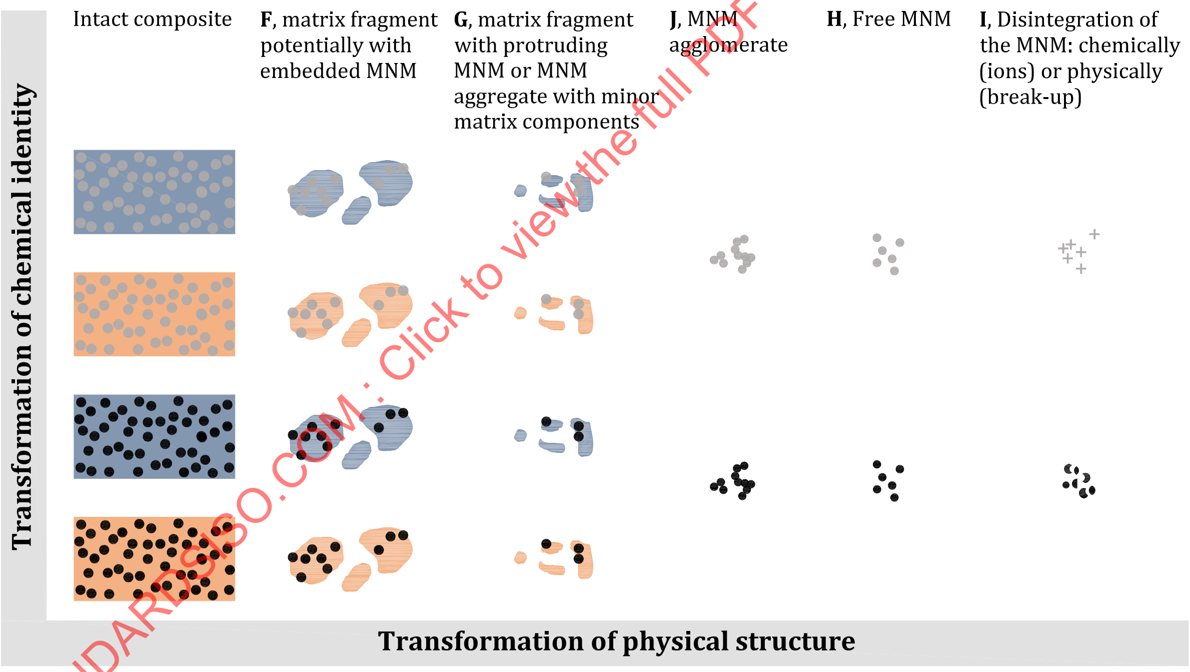
— Release scenarios where the MNM is less resilient than the matrix: examples include washing and leaching of Ag-textile, Cu-wood, and quantum dot (QD) films, because under the stresses of the specific scenarios, the degradation of the MNM is faster than the degradation of the matrix.

— Release scenarios where the matrix is less resilient than the MNM: examples include weathering of MWCNT-epoxy, of MWCNT-PA, of MWCNT-PP, of Fe_2O_3-PP, but also thermal decomposition of composites, because under the stresses of the specific scenarios, the degradation of the matrix is faster than the degradation of the MNM.

Earlier works on the release from NEPs, especially on MWCNT composites, focused on transformations of physical structures, whereas recent work on metal-containing MNM has often focused on dissolution and transformation of chemical identity (i.e. speciation, composition). Both can occur before or during release (in scope of the present document) or after release (beyond scope). With colours symbolizing the chemical identity, Figure 3 depicts hypothetical transformations before or during release leading to particle releases.

- The physical forms of release can be simplified to five generic forms that can be experimentally differentiated[65],[36]:
  - F: matrix fragment (potentially with embedded MNM);
  - G: matrix fragment with protruding MNM or MNM aggregate (with minor matrix components);
  - J: MNM agglomerate;
  - H: Free MNM;
  - I: Disintegration of the MNM: chemically (ions) or physically (break-up).

Some of the forms are hypothetical, while others have been observed in the literature and are reproduced in Figures 4 and 5 and in the case studies in Annex A. The two axes in Figure 3 represent transformation of physical structure (left is intact composite NEP, right is breakdown of NEP structure) and by the transformation of chemical identity (blue symbolizes a chemically transformed matrix, for example, polymer turned to charcoal, gray symbolizes a chemically transformed MNM, for example, metal turned to metal oxide, or to ions). Fragmentation of the MNM without chemical transformation is indicated at the bottom right corner, but has only been observed for the case of fibres that break.



Key

🟧 original matrix

🟦 transformed matrix

● original MNM

○ transformed MNM

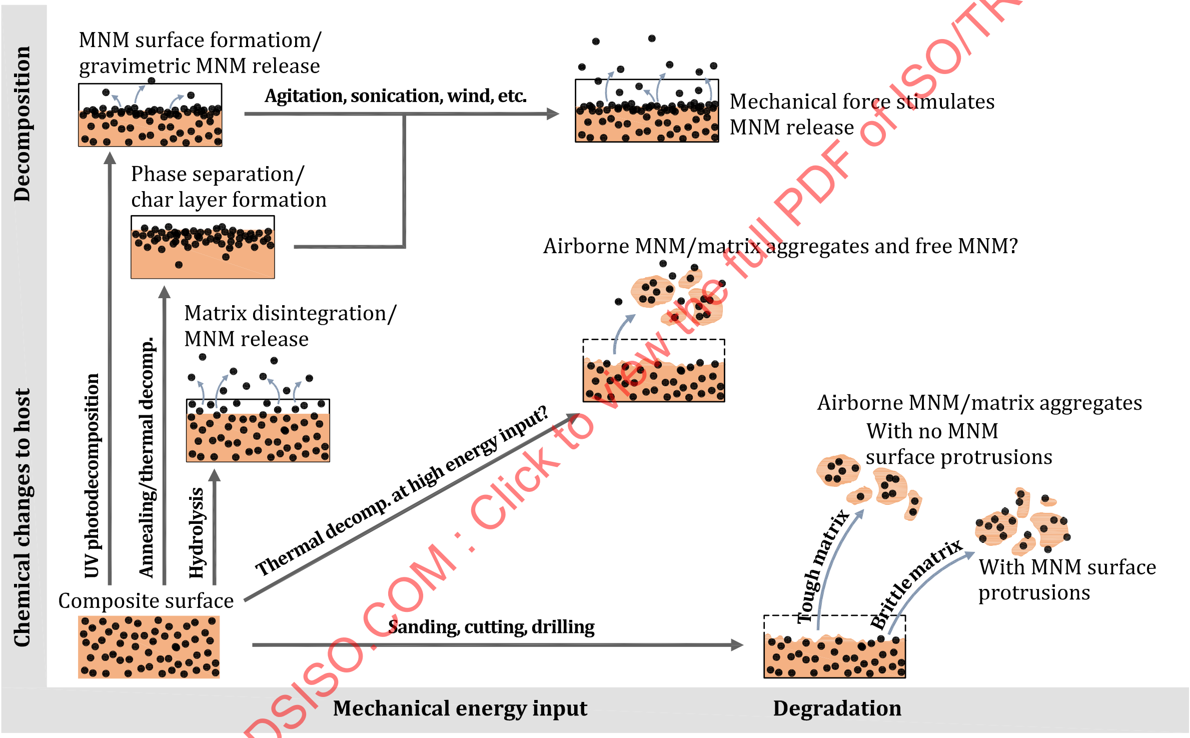
NOTE Adapted from the NanoRelease state of the science report[65].

Figure 3 — Graphical schematic of forms of release

The NanoRelease interlaboratory comparison performed release testing during controlled weathering with an analysis of the form of release by TEM.[36] The results found some remaining ambiguity between "free MNM" and "MNM agglomerate," because the operators of the image evaluation of experimental TEM images missed clear criteria to differentiate between the two forms H and J, so that an experimental assessment might categorize by their sum H^+J. However, the interlaboratory comparison achieved reproducible results for the identification of all other release forms (F, G, H^+J, I) by the methods listed in the case studies (see Annex A)[36].

Consideration of the release processes, the matrix identity, and the resulting potential forms of release are key aspects of the decision-making process (described later in this clause). By linking the release processes (step 1 of the stepwise decision-making process) with the identity of the matrix (step 2), systematic schemes from literature depict the resulting physical transformations before or during release. Figure 4 (adapted from Reference [66]) describes structural transformations of generic MNM-polymer composites, focusing on the case of MNM more resilient than matrix. For simplicity, it does not show chemical transformations (such as the thermal decomposition of a polymer matrix, symbolized by the "blue matrix" in Figure 3).

The transformations depicted in this figure were experimentally confirmed in numerous reports, and are exemplified by the Fe_2O_3-PP case study (see Table A.5).

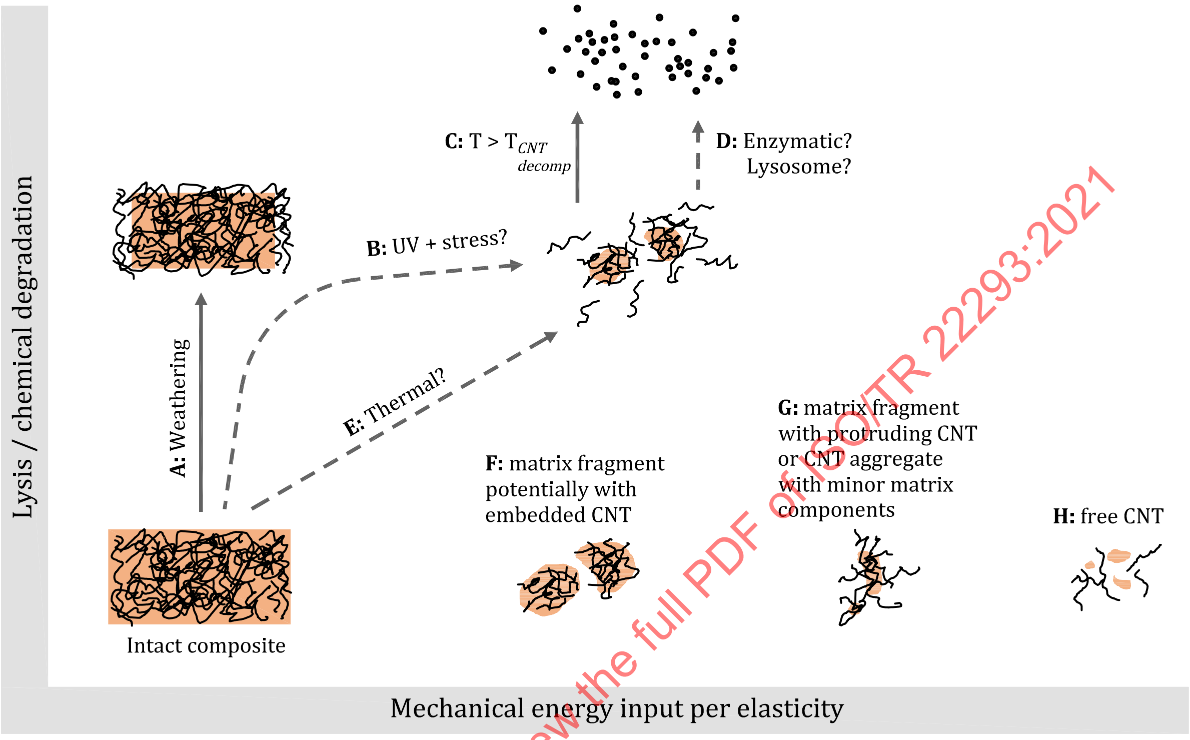


NOTE Adapted from Reference [66].

Figure 4 — Linking the forms of release (Figure 3) to release processes; transformations of generic MNM-polymer composites, focusing on the case of MNM more resilient than matrix

A transformation scheme from Reference [65] (which was based on Reference [41]) is proposed specifically for MWCNT polymer composites in Figure 5. Here, the elasticity of the polymer matrix is considered. Fragments with protruding MWCNT are less likely to form with softer polymers, and more likely with brittle polymers,[41] as a softer polymer will flow around the relatively stiffer MWCNT during mechanical disruption. The transformations F, G and H were experimentally confirmed in the interlaboratory comparison of MWCNT-polymer weathering[36] (see Figure 6) and by various sanding experiments.[67],[68] The combined results of all relevant studies are exemplified by the MWCNT-epoxy and MWCNT-PP case studies (see Annex A).

Although Figure 5 captures the transformation for many situations, there is an important difference for the incineration and thermal decomposition transformation route. After incomplete combustion (20 % oxygen, 500 °C), the majority of CNT in the NEP, if not all, remained in the residual ash. At elevated temperatures (20 % O, 800 °C), as relevant for waste combustion, residual ash was zero from CNT-based NEPs, but inorganic MNM remained concentrated in chemically transformed ash.[53] MNMs were rarely released.[53],[54],[69] Fibrous fillers such as CNTs and carbon fibres can experience further transformation during the release process, for example, the CNTs could be chopped to shorter ones (see Figure 3, form I).



NOTE The release forms F, G, H are indicated in accordance with Figure 3. Adapted from the NanoRelease state of the science report[65].

Figure 5 — Linking the forms of release (Figure 3) to release processes: Transformations of MWCNT-polymer composites

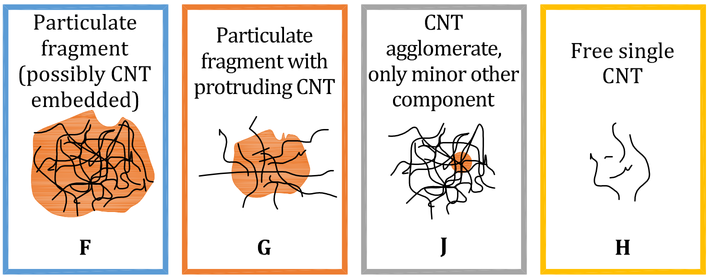
Figure 6 depicts experimental confirmation that the form of release can be reproducibly quantified by TEM analysis according to the schemes in Figure 5. The figure is adapted from the NanoRelease interlaboratory comparison,[36] with colour coding [see Figure 6, a)] of the forms of release F, G, H, J, as described above. The results represent more than 400 TEM evaluations by two analysis laboratories (see Figure 6b and 6c, respectively) on plastics aged according to ISO 4892-3[231], in four aging laboratories, each processing the two MWCNT nanocomposites (P4 and E4) and the two controls (P0 for neat polyamide and E0 for neat epoxy). The comparison included two intensities of sampling, by shaking and by sonication. The manual TEM analysis followed the rule that elongated structures were identified as MWCNTs, only if all three parameters were in line with the MWCNT positive control:

— observed hollow core;

— matching diameter (for the specific type of MWCNT: between 5 nm and 20 nm);

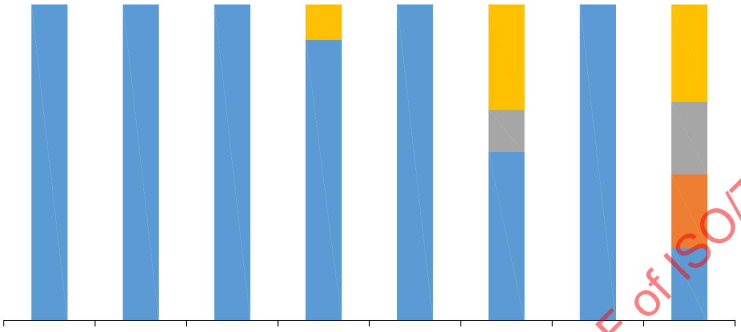
— matching length (for the specific type of MWCNT: no longer than 2 µm).

The interlaboratory comparison confirmed reproducibility.[36] Minor subjectivity remained between categories F vs. G [compare Figures 6, b) versus 6, c)].

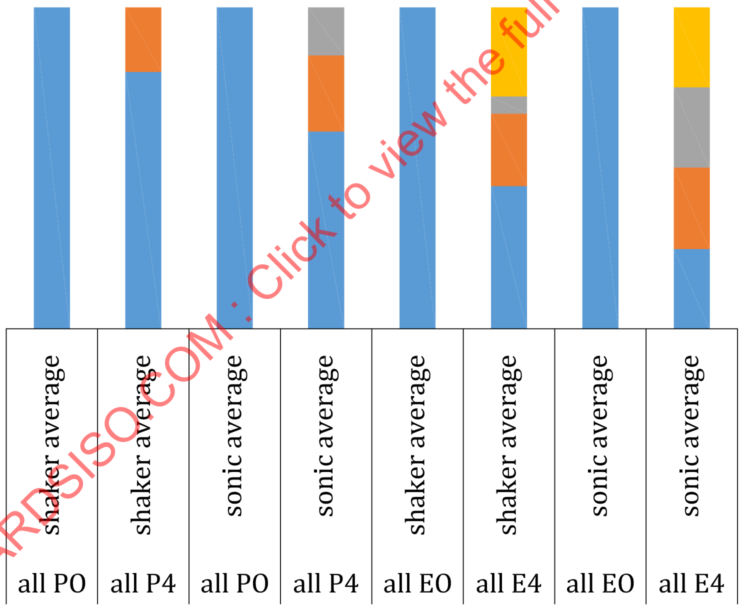


F - H as in release systematics by Harper et al. 2015

a) Colour coding forms of release



b) Interlaboratory comparison: results of lab 1



c) Interlaboratory comparison: results of lab 2

NOTE 1 Figure 6, a) explains the colour-coding of forms of release. Figure 6, b) shows the interlaboratory comparison analysis results for laboratory 1. Figure 6, c) shows the interlaboratory comparison analysis results for laboratory 2.

NOTE 2 Adapted from Reference [36].

Figure 6 — Experimental confirmation that the form of release can be reproducibly quantified by TEM analysis according to the schemes in Figure 5

For the case of MNM less resilient than matrix (depicted in Figure 3 by “gray dots in orange matrix”), no universally applicable scheme is known, because transformation at release often involves complex sequences of oxidation / dissolution / transformation / reprecipitation of MNM. The issue has been discussed for leaching of QDs from polymer[70],[55], leaching of copper from wood[71],[73] and leaching of Ag from textiles[74] as opposed to the potential migration of intact titanium nitride (TiN) from polymer, which was not actually observed.[75] An example case study on a Cu-treated wood is included to demonstrate that the decision-making process is useful also in the case of a MNM that is less resilient than the matrix (see Annex A). Thus, the primary release event could lead either to differentiation (increase of diversity) or to assimilation (increase of similarity) of release forms depending on the MNM-polymer formulations[76].

6.3 Decision support framework to determine which transformations need consideration with examples

Based on the literature review findings, a tiered (stepwise) evaluation framework was developed to aid in decisions of whether/which transformations at the release point need to be considered. Together with consideration of the specific product use scenario, this framework can aid in determining the necessary sampling and analytical methods. That is, determining the potential for exposure if release does occur is an important aspect of understanding the measurement methods needs for the specific use and release scenario. For example, the potential for such exposure might be high for an MNM embedded in a textile, but the potential for direct exposure would likely be low during commercial and consumer use for a NEP that is encased within a consumer product (although exposure in the latter case might occur during manufacture, servicing, disposal, and recycling).

Table 4 below provides a list of input parameters used to derive the corresponding decision-supporting parameters and the resulting decision support framework output.

Table 4 — Parameters for tiered framework to support decisions about if and which transformations at the release point need to be considered

Steps	Input parameters	Decision supporting parameters	Output
1	Release scenario	Release process (relevant stresses or combinations thereof, their intensity and duration)	Forms of release to be primarily sampled and analysed
2	Identity of matrix material	Resilience of matrix against relevant stresses	
3	Identity of MNM	Resilience of MNM against relevant stresses	
4	Content and compatibility of MNM in matrix, state of dispersion of MNM in matrix	Homogeneity, stability, and concentration of MNM dispersion in the components of the material that contacts the release medium	Modulations of rate and form of release (e.g. degree MNM is bound to the matrix in released particles)

Annex A describes several application-specific examples, which illustrate how the decision support framework process in Table 4 can be used to select sampling and analysis methods for identification and quantification of release of MNM from nanocomposites. These examples illustrate releases of a variety of MNM, for which there was sufficient literature.

a) Lightweight parts made of MWCNT-epoxy (e.g. in airplane applications). This example illustrates the case where the MNM is more resilient than the matrix.

b) Silver nanoparticle impregnated in textiles for anti-microbial protection. This example illustrates the case where the MNM is less resilient than the matrix.

c) Copper-based MNM impregnated into woods that are placed outdoors into soil (e.g. terrace poles). This example illustrates the case where the MNM is less resilient than the matrix. Some metrological challenges here are similar in Ag-textile scenarios, or QDs in a polymer.

d) Automotive parts made of MWCNT or Fe_2O_3 in thermoplastics (PP and PA). This example illustrates the case where both the MNM and the matrix are resilient against most stresses, but not always to the same extent. End-of-life processes can be destructive to both MNM and matrix. Metrological challenges in this case are similar to that seen with metal-oxide in paints or coatings (similar matrix degradation mechanisms, but lower metrological challenges).

e) 3D printing of MNM-containing thermoplastics illustrates MNM is more resilient than the matrix. End-of-life processes are expected to be destructive to both MNM and matrix.

All the examples follow the same structured process for each release concern; see Tables 4 and 5. The release scenarios are identified, along with the identity of the matrix and the MNM. Implications for each of these factors are then identified and described. The forms of release and methods used in the cited literature are identified. In this regard, steps 1 through 3 are essential to select the most critical protocols for aging, sampling, and analysis. Step 4 is of course quite relevant for understanding nanocomposite properties and rate of release, which might also affect protocol selection and will be critical as models using release data are more fully developed. For each of these steps one considers implications for the lifecycle stage.

Table 5 — A structured process to evaluate each release concern

Steps	Questions (input prameter)	Answer	Implications (as many as relevant for example)			
			Release concern 1	Release concern 2	...	Release concern n
1	What are the relevant release scenario(s)?					
2	What is the identity of matrix?					
3	What is the identity of MNM?					
4	What is the content and compatibility?					
	What is the dispersion state of MNM in matrix?					
		= FORMS OF RELEASE observed in literature on specific case (to what degree is the NM bound to the matrix when released? Completely, partially, pristine?)				
		Methods used in the cited literature				

It is acknowledged that one needs to have basic knowledge about the composition of MNM and matrix to use the decision support framework. If the resilience of the pure matrix or pure MNM is not known, this could be tested as an initial step, or the user could choose to go directly to release testing with very comprehensive sampling and analytics. In some cases, it might not even be known which MNM (or matrix material) is used. In this case, the decision support framework stops after step 1, and advises to perform an adequate simulation of the relevant stresses, with comprehensive sampling and analytics for all potential forms of release.

As a criterion for adequacy, good correlation of the simulation with real-life degradation of macroscopic properties (such as colour, gloss, mechanics) is recommended and the simulation of relevant stresses is ideally a validated ISO protocol used for specifying product performance in the intended use. Thus, the decision approach is best supported by targeting the testing protocol to the relevant scenarios, consistent with the problem formulation.

The resulting information of release forms is useful in supporting decisions about the relative impact of the added MNM on risk management decisions: step 4 (supported by all previous steps) is exclusively relevant for prediction or grouping approaches. To prepare long-term goals of non-testing release assessment, step 4 is included because it is anticipated that the steps 1 through 4 gather the information required for modelling approaches, but clearly such models do not exist yet. Experimental release testing is currently still required. In this regard, steps 1 through 3 are essential to select the most critical protocols for aging, sampling, and analysis.

7 Approaches to detecting and quantifying the released material associated with added manufactured nanomaterials

7.1 General

Nanocomposite materials can incorporate a wide variety of MNMs that can differ significantly in their properties and intended applications. Although the overall strategic approaches to sampling and measurement of release from composites incorporating different MNMs are broadly similar, the specific analytical and/or sample preparation methods differ depending on the MNM and polymer matrix under consideration.

As noted earlier, the problem formulation and potential ES play key roles in designing a sampling strategy. The release testing and sampling strategy needs to be relevant to the potential ES's, feasible, and statistically valid. This means that different types of sampling could be appropriate for different scenarios. For example, in some cases it could be sufficient to start with a qualitative question of whether there is release, rather than proceeding immediately to a time-intensive approach of determining the nature and number of released particles.

Unless noted otherwise, this discussion is focused on analytical quantification and sampling methods specifically relevant to the release of MWCNT and MWCNT/polymer particles. MWCNT was chosen to serve as a model system to illustrate the decision support process presented in this document, but the concepts and approach can be applied to other MNMs and matrices. Annex A provides several examples of the decision support framework for these other materials. Measurement of material released from MWCNT-polymer composites is exceptionally challenging for numerous reasons. The foremost reason is the chemical and physical complexity of the released material, which can take many different forms as illustrated in Figure 3. Clause 7 includes a review of the available methods for detection, measurement, and description of MWCNT released from composites into various media (e.g. air, water, solid and biological matrices) by different mechanisms linked to effects as a result of use.

NOTE Indirect methods that characterize the test specimen or consumer product before and after the release event can also support the release assessment. For example, when the MNM is less resilient than the matrix, specifically for antimicrobial-enhanced textiles, the total MNM content of the NEP before and after washing can be important information (a document is under development on this topic).

The key topics include:

- approaches suitable to mnms;
- factors affecting sampling method, preparation and analysis;
- measurement methods/challenges;
- detection, quantification, characterization of releases.

7.2 Methods for sampling released material

7.2.1 General

Any combination and distribution of free polymer fragments, free MNM, and polymer fragments with MNM (see Figure 3) could be released into air, water, solids (e.g., soils), and biological fluids throughout the lifecycle of an article. Hence, the choice of method(s) for sampling released materials might differ depending upon the media of interest (e.g., air versus water). Note that the choice of sampling method is not independent of an overall measurement strategy. Rather, the choice of sampling method, subsequent preparation (if any), and analysis are inter-dependent, and all these measurements steps are critical for obtaining meaningful data on material release. To date, most efforts to evaluate MNM release from composites have focused primarily on release to air. This emphasis on airborne release is, in part, because of interest in protecting workers who are often at risk of exposure early in an MNM's lifecycle (e.g. during masterbatch production or materials processing). Attention is also given to potential for ecological consequences (release into water, soils, and biological tissues) at the end of an article's lifecycle.

7.2.2 Sampling material released into air

Generally, methods for sampling aerosols can be divided into two categories: time resolved/real-time instruments and time-integrated samplers. Both types of sampling are used for evaluating potential exposures to nanomaterials.

Real-time instruments have the advantage of providing instantaneous measures of particle characteristics such as number, mass, size, or surface area concentration in air. However, all existing real-time instruments are non-specific and cannot differentiate an MNM of interest from an incidental aerosol particle (e.g. diesel soot) with nanoscale size. This limits their utility in identifying MNM released from composites, so they are not described at length in this document.

Time-integrated samplers involve collection of aerosol particles onto a substrate for subsequent off-line analysis. These sampling methods offer the advantage of permitting identification of captured MNMs by off-line analysis, but often require additional preparation steps prior to analysis.

Numerous time-integrated samplers are available for aerosol collection and some are capable of separating particles by size (e.g. aerodynamic, thermodynamic) while others are not. In general, time-integrated samplers collect particles with sizes well above the nanoscale. However, it is widely recognized that many MNMs form micrometre-scale agglomerates in air or might be adhered to, or contained in, larger particles that become airborne (e.g. polymer fragments), making time-integrated methods appropriate for exposure assessment. Size-selective aerosol samplers include dichotomous and multi-stage samplers. Dichotomous samplers such as the respirable cyclone have traditionally been used for occupational exposure assessment because they separate particles into two fractions, respirable and non-respirable. In these samplers, the respirable fraction is deposited onto a filter for subsequent off-line analysis. The respirable aerosol fraction includes particles with size small enough to permit penetration and deposition into the alveolar (gas exchange) region of the lung. Therefore, this fraction is of interest for chronic lung disease and is often used to sample for airborne MNMs[46],[77]-[83]. Analogous samplers developed for environmental monitoring of ambient particulate matter (PM) include PM_{10}, $PM_{2.5}$, and PM_1 samplers that collect particles with aerodynamic diameters of less than 10 µm, 2,5 µm and 1 µm, respectively[54],[78],[84]-[86]. Multi-stage aerosol samplers are capable of separating particles into multiple size fractions and include low-pressure impactors such as the Berner sampler (eight size fractions from 16 000 nm to 60 nm) and electrical low-pressure impactor (12 size fractions from 6 800 nm to 30 nm) [43],[45],[87],[88]; wide-range aerosol sampling system (12 size fractions from 20 000 nm to 2 nm)[47],[78]; micro-orifice uniform deposit impactor (10 size fractions from > 18 000 nm to 56 nm)[79],[80],[82],[89]; and Sioutas cascade impactor (five size fractions from 10 000 nm to 250 nm).[80],[90] For evaluation of consumer exposures, both the particle size distribution and morphology are characterized.

Time-integrated samplers that are not particle size-specific but are still frequently used to collect airborne MNMs include plastic cassette samplers and conductive cowl samplers[38]-[41],[46],[47],[77],[80],[81],[90]-[99]. Plastic cassette samplers can be operated using a 'close-faced' configuration in which air is drawn into the sampler through a 4 mm inlet or in an 'open-faced' configuration where the top section of the cassette with the inlet has been removed. Conductive cowl samplers utilize an open-faced configuration and were originally developed for sampling asbestos fibres. However, they are now being used to collect high aspect ratio MNMs such as MWCNTs and carbon fibres.

Regardless of the type of the filter-based time integrated sampler, the choice of filter used as collection substrate is a critical consideration because it has to be amenable to the desired analytical technique (discussed below). For example: track-etched PC filters have a smooth surface appearance and are used to collect particles for subsequent EM analysis; poly(tetrafluoroethylene) filters have good weight stability and are used to collect particles for gravimetric determination of mass; mixed cellulose ester and polyvinyl chloride filters are easily digested in acids and are used to collect particles for determination of elemental mass by atomic spectroscopy and gravimetric analysis, and particle count, morphology, and chemical composition by TEM analysis; and quartz fibre filters possess good stability at elevated temperatures and are used to collect carbonaceous nanomaterials such as MWCNTs for thermal optical (TO) transmittance analysis (organic/elemental carbon).

Additionally, sufficient sample must be collected onto a filter or collection substrate to meet analytical detection limits. Several options exist for increasing material collection. For example, in laboratory studies of MWCNT release from composites, investigators could construct a chamber or enclosure around an experimental system to concentrate the emitted aerosol for sampling[40]-[42],[44],[45],[61],[86],[89],[100]-[107]. Another method to increase collection is to increase the sampling time. For example, when collecting worker exposure to aerosol, typical measurements are based on shift durations and can be as long as 8 h.[108] When assessing consumer exposure to aerosol,[109] sampling time is shorter than a typical work place sampling duration since the consumer exposure is not based on shift schedule. However, if necessary, sufficient sample can be collected by combining multiple sampling runs. For samplers such as cassettes and asbestos cowls, typical sample collection rates are one to two litres of air per minute when performing full work shift sampling but these flow rates can be increased to tens of litres per minute to increase collection. However, it should be noted that increasing the air collection flow rate for samplers that separate particles by size will alter the performance of the sampler; i.e. increasing flow rate will lower the aerodynamic size cut-offs of impactor stages or might require different type of filter media or pore size filters to accommodate increased flow rate[110].

Another type of time-integrated sampler is a precipitator. There are two main types of precipitators: electrostatic precipitator (ESP) and thermophoretic precipitator (TP). Both types are frequently used to sample for airborne MNMs[42],[44]-[47],[61],[77],[78],[101]-[106],[111]-[115]. Precipitators have an important advantage over samplers that use filters because they collect particles directly onto grids (for TEM analysis) or flat substrates (for SEM or AFM analysis), thereby eliminating the need for any subsequent sample preparation. With an ESP, aerosol is pulled through the sampler and particles are simultaneously charged in a very high voltage electrical field and collected using a flat surface onto which a sampling substrate (grid) has been mounted as the cathode. For a TP, air is drawn between two parallel plates possessing a temperature differential; particles move by diffusion away from the hot plate and are collected onto a grid located on the cold plate.[116] A variation to the direct particle-to-grid sampling approach of precipitators is to tape an EM grid to a filter held in a cassette sampler[38],[80],[117]-[119]; however, the performance characteristics of such a sampling approach are unknown.

7.2.3 Sampling material released into water, solids, and biological fluids

Studies of MWCNT release from composites into water are limited and no information is available for release into solids or biological fluids. Busquets-Fité et al.[29] subjected ethyl vinyl acetate-, polypropylene- and PA-MWCNT composites to accelerated aging (UV light) and weathering (simulated rain episodes) in a chamber using ISO 4892-3[231]. Following exposures, analysis of the rain water using TEM identified composite fragments, but not MWCNTs. Fernandez-Rosas[30] measured release of MWCNTs from PA6 composites after wet aging using a combination of gravimetric and thermogravimetric analysis. Although this method was rapid and reasonably simple, the authors pointed out that for complete impact assessments, the released material should be collected and analysed to determine its form and other physicochemical characteristics.

Although only a few studies have investigated MWCNTs released into liquids, relevant sampling and analytical methods can be inferred from release studies concerning other types of embedded particles. For instance, Bott et al.[120] investigated release of carbon black from low density polyethylene food packaging composites using asymmetric flow field flow fractionation (AF4) (for sample preparation and particle separation) coupled to multi-angle light scattering (for detection); they observed no release of carbonaceous nanoparticles under the conditions tested, with a detection limit of 12 µg/kg. This method should be adaptable to analysis of MWCNT release, given that MWCNTs and carbon black have a similar elemental makeup. In addition, many studies have investigated release of metallic, semiconductor, or metal oxide particles (see Reference [55] for an overview of this literature) into environmental liquids or food simulants. Most of these studies directly sampled the liquid media using ICP-MS or equivalent for nanoparticle mass quantitation, sometimes using front-end separation techniques or time-resolution modes for separation of particles from dissolve fractions. Some of these studies were strictly passive release scenarios,[36],[121] whereas others (e.g. Reference [45]) simulated more aggressive weathering by applying abrasion conditions; for example, those specified in ISO 11998[232]. This device pumps an aqueous abrasive solution onto a coated surface and the abrasive buffer is linearly rubbed on the sample to generate dynamic friction and released particles are collected in the liquid, where they can be analysed by conventional analytical techniques. Although it should be noted that ICP-MS-based sampling techniques are not directly applicable to detection of released MWCNTs, since they are nominally carbon-based, quantification of MWCNTs in liquid media using ICP-MS has been shown to be possible via detection of trace metals residual from the MWCNT manufacturing process (e.g. see Reference [122]).

Studies on the fate of MWCNTs in water,[123]-[125] solids,[126,127] and biological tissues and fluids[126]-[128] have been published and provide additional useful insights for sample collection in composite release scenarios. These studies have demonstrated that MWCNTs dispersed in waters containing natural organic matter (NOM) remain well dispersed.[123]-[125] In contrast, Holbrook et al.[124], demonstrated that the presence of kaolin and alginates in waters promoted MWCNT coagulation and Zhang et al.[125] reported that sediments in hard water or seawater readily sorbed MWCNTs. Hence, the presence of certain water constituents in release scenarios has important implications for sample collection. Specifically, if only NOM is present, MWCNTs will likely be well dispersed in the suspension and a representative sample could be drawn from anywhere in the water. In contrast, if kaolin or alginates are present (fresh water) or sediments (seawater), the MWCNTs will coagulate or sorb to sediment particles which might require sample collection from the bottom of the water and/or additional sample preparation steps (e.g. centrifugation to separate solids from liquids). With regard to solids, Petersen et al.[126], fortified river sediment containing peat with MWCNTs and by tumbling were able to disperse the tubes homogeneously throughout the matrix. A similar protocol was used in a subsequent study by Petersen et al.[127], to homogeneously disperse MWCNTs in soil. Studies of MWCNT uptake to tissues, for example, by fish,[128] aquatic worms,[126] and earthworms,[127] simply involves harvesting the organisms from the media using a net or sieve.

7.3 Methods for preparing samples of released material for subsequent analysis

7.3.1 General

Sample preparation is the second step of an overall measurement strategy. The preparation method will depend on the analytical technique to be employed. As with collection, it is critical that the sample preparation step preserve the properties of the MWCNTs in the same state as in the matrix into which they were released.

7.3.2 Preparation and analysis of air samples

Collection of aerosol particles directly onto microscopy grids or flat substrates (e.g. mica, Si wafers) using precipitators does not require any sample preparation. The substrate is simply removed from the sampling device and placed in the TEM, SEM, or AFM instrument sample holder. Hence, this clause only addresses manipulation of filter samples for off-line analyses.

The most common sample preparation steps described for filters were for subsequent analysis using TEM or SEM. For EM, sample preparation is relatively simple as long as the sample is vacuum compatible and the sample surface is electrically conductive[67],[114],[129]. For SEM substrates with a smooth surface (e.g. PC filters or aluminium foils), a piece is sectioned using a scalpel, mounted on a stub using double sided carbon tape or other conductive adhesive, and sputter coated with a conductive material such as carbon, platinum, gold, and/or palladium[33],[40],[41],[43],[47],[60],[61],[87],[92],[96],[98],[105],[130],[131]. In TEM, electrons are transmitted through a specimen to generate high-resolution images. Therefore, TEM samples must be thin enough (100 nm or less) to be electron transparent. If the substrate has a thick uneven surface, such as MCE filters, additional preparation steps (collapsing and clearing) are necessary because particles can deposit and become hidden from view in the furrows and pores. Most collapsing and clearing procedures for MCE filters are a variation of NIOSH Method 7402 — Asbestos by TEM — and are used to prepare samples for TEM analysis (though SEM can also be used if the sample is coated with a conductive material).[99] In this procedure, a section of the MCE filter is placed on a standard 3 mm TEM grid and collapsed and made translucent using acetone[39],[81],[97],[95], chloroform,[92] or 50 % of water/ 35 % of dimethylformamide/ 15 % of glacial acetic acid[132] vapour. Another method reported to prepare samples for TEM analysis was to immerse PC filters in acetone, disperse the particles by ultrasonic agitation, and either dip a microscopy grid into the suspension[40] or deposit a drop of the suspension onto a grid[41].

Elemental carbon/organic carbon (EC/OC) analysis is another common filter analysis technique for measuring organic carbon and elemental carbon content. In EC/OC analysis, particles that were collected on quartz fibre filters (QFF) are incrementally heated to oxidize the carbon constituents. In this technique, the EC fraction is used as a marker for MWCNTs based on the assumption that CNTs have negligible OC content[39],[80],[81],[90],[95],[133]-[137]. Most EC/OC analyses are variations of NIOSH Method 5040 — *Diesel particulate matter (as elemental carbon)*[139] which uses thermal-optical (TO) analysis technique. In these methods, typically a 1,5 cm^2 section of a filter is removed for analysis; however, if the particles were not evenly distributed across the filter surface during collection, multiple sections of the filter or the entire filter should be analysed to accurately determine EC content[80].

If a weight-stable filter was used to collect a sample, it can be pre- and post-weighed under identical temperature- and humidity-controlled conditions to determine the total mass of particles captured during a release test. The composite sample itself can also be pre- and post-weighed in this same manner to determine the mass of material that was released during a test[31],[61],[60]. Subsequent analysis of filter samples by atomic spectroscopy is a sensitive method for determination of low levels of metals in aerosols[47],[78]-[80],[82],[95]. Atomic spectroscopy has been used to quantify masses of airborne nanoparticles (e.g. Cu, see Reference [83]) or masses of residual catalyst contamination (e.g. nickel or cobalt) as a marker of MWCNTs. Prior to quantification of metals, the entire mixed cellulose ester or polyvinyl chloride filter sample is subject to dissolution using acids and/or thermal treatment such as a hotblock or microwave. The exact choice of acids and/or thermal treatment is specific to the metal of interest, though commonly used standard methods include US EPA Method 3051 – *Microwave assisted acid digestion of sediments, sludges, soils, and oils*,[140] NIOSH Method 7300 – *Elements by ICP (nitric/perchloric acid ashing)*,[138] and NIOSH Method 7303 – *Elements by ICP (hot block/HCl/HNO$_3$ digestion)*.[141] For composite release scenarios, if MWCNTs could be tagged with a unique metal, analysis of air filters could be used as a qualitative indicator of release.

The filter preparation procedures outlined above are used for direct analysis of material collected on the substrate. However, with additional processing, material can be analysed by analytical techniques including colloid counting and AUC. For example, a filter can be placed in an appropriate liquid and subjected to ultrasonic agitation to remove particles (fragments and free MWCNTs) from the substrate and disperse them in the liquid for subsequent sizing by laser diffraction or AUC[61,60] or Ultraviolet-Visible (UV-Vis) spectroscopy[142].

In some cases, the masses of fragments released to air can be relatively high (e.g. sanding) or occur over such a long period of time (e.g. UV weathering), such that collection of particles without size selectivity (for respirable or inhalable fraction) onto a substrate is not feasible. In these cases, investigators have recovered materials from the surfaces of the enclosure surrounding a sample[61],[60] or used settling plates.[31] When sufficient quantities of released material are available, the loose powder can be pressed into a sample holder for analysis using X-ray photoelectron spectroscopy (XPS) to discriminate MWCNT protrusions from polymer background using the shift in C(1s) spectra of tubes[143],[41],[48].

7.3.3 Preparation and analysis of waters, solids and biological fluid samples

With appropriate sample preparation, many of the same analytical techniques used to analyse air samples are also applicable to waters, solids, and biological fluids. For EM analysis of materials released into water, an aliquot of the suspension is directly pipetted onto a substrate such as an SEM stub[142],[124],[88],[29] or a TEM grid[29],[123],[144],[145] and allowed to dry in air or in an oven. If an aqueous sample contains a wide range of particle sizes, additional sample preparation might be necessary before depositing the suspension onto a substrate. For example, Kaegi et al.[145], used a two-step centrifugation process to isolate silver nanoparticles in rainwater. First, an aliquot of water was centrifuged at a low *g*-force to remove large particles followed by a second centrifugation at a higher *g*-force to collect nanoparticles onto TEM grids placed in the bottom of the centrifuge tube. Alternatively, Tagmatarchis et al.[144], separated MWCNTs from amorphous material in a buffered suspension by flow field-flow fractionation and used the eluted MWCNT suspension to prepare a grid samples for TEM analysis. Numerous other techniques exist for pre-fractionation of nanoparticle from large particles in aqueous suspensions, soils, and biological (e.g. milk) fluids using capillary electrophoresis and variations of chromatography (e.g. hydrodynamic, ion exchange, size exclusion). These pre-fractionation techniques can be used in tandem with analytical methods such as ultraviolet-visible spectroscopy and atomic spectroscopy, and the reader is referred to the review articles by Bandyopadhyay et al.,[146] Tiede et al.,[147] and Duncan and Singh[148] for more information on these procedures. Finally, if it is desired to analyse wet samples, specialized sample holders[147] and variable pressure SEMs[149] could be used for measurement of MWCNTs in water and biological fluids and tissues.

TO-transmittance is a robust method that can be used to detect EC in not only air, but also water, soil, and biological fluids[60],[123],[135]. In a methods development study, Doudrick et al.[135], prepared suspensions of MWCNT in waters (surface, municipal tap, waste), solids (river sediment), and biological fluids and tissues (lyophilized bacteria, synthetic urine, human serum, lung tissue, and commercially available cow's milk), deposited the materials onto QFF, dried, and successfully used TO-transmittance analysis (along with Raman spectroscopy) to quantify masses of EC in samples.

Atomic spectroscopy is also amenable to analysis of waters, soils, and biological fluids.[145] As with air filters, samples should first be digested using various chemical and thermal treatments, though there are many standard methods available for this purpose (e.g. EPA 3051[140]). As with air samples, the applicability of atomic spectroscopy to detection of MWCNTs, either tagged with a metal or containing residual catalysts, in waters, soils, and biological fluids will be limited to qualitative information. An alternative to metals analysis by atomic spectroscopy is scintillation counting of radiolabelled MWCNTs. Several publications[125]-[128] have demonstrated the sensitivity and utility of scintillation counting for detection and quantification of labelled MWCNTs in waters, soils (sediment, peat), and biological fluids (earthworm gut contents), and tissues (fish, earthworms, aquatic worms). For waters, sample preparation consists of diluting the specimen with scintillation cocktail before counting. For solids and biologicals, samples were freeze-dried, combusted in a biological oxidizer, and mixed with scintillation cocktail before counting. While scintillation counting is a robust method that is applicable to a wide range of matrices, a potential disadvantage of this approach is the use of radioactive materials and the generation of radioactive waste from testing.

7.4 Measurement challenges

7.4.1 General

Based upon existing data, it is reasonable to assume that the sample of interest from a given release scenario is a collection of many entities (fragments, unbound MNMs, or both) as opposed to a single fragment or MNMs. There is a plethora of possible characteristics of a sample that could be measured (e.g. size distribution). Consideration of the problem formulation and the key determinants of toxicity can help to focus the analysis strategy on the critical elements. In addition to the complexity of the released sample, there are several challenges associated specifically with measurement of MNMs in complex matrices and these are discussed below. Finally, more conventional analytical hurdles such as repeatability and method validation, the availability of suitable RMs, difficulty of identifying control materials or processes, and resource management issues (cost and expertise) are also commonly encountered in nanomaterials analysis. Although these issues will not be described further in this document, their consideration in the context of the problem formulation is critical in determining the appropriate analysis strategy.

7.4.2 Surface functionalization and transformations

The large surface area and reactivity of the various MWCNT chirality types can promote adsorption of contaminants from the surrounding media following release. Such surface functionalization can result in physical and chemical transformations that affect measurements. The type of functionalization and resultant transformations will vary depending on the phase of the product lifecycle. For example, it is widely recognized that surfaces of MWCNTs are hydrophobic, so they are frequently functionalized (e.g. with carboxylic acid functional groups) to promote dispersion in masterbatches of polymer during production. If released to air during use, MWCNTs (individually or protruding from polymer fragments) can be oxidized, thereby changing surface reactivity. If released to aqueous matrices during the end-of-life phase of the lifecycle, the presence of organic matter or other water constituents will alter the surface chemistry and the behaviour of MWCNTs in suspension[123]-[125],[150].

7.4.3 Sample collection artefacts

Proper choice of a sampling device and the collection conditions is the first opportunity in a measurement strategy for ensuring that a representative sample is obtained for analysis. For example, if the measurement goal is to obtain information about particle physical dimensions using EM, then the area of the filter sectioned and mounted for analysis must be representative of the whole filter. Sampling bias is possible when sectioning if the particles were not uniformly deposited across the filter. One approach to obtaining a representative filter section is to use a conductive cowl sampler that is designed to promote uniform deposition across the filter surface.

7.4.4 Applicability of a measurement method for a given release media

MNM-polymer composites and material released from composites will contact various media throughout their lifecycle. Such media could be: environmental (e.g. air, water, and mixed solids such as soil); biological (e.g. saliva, blood, and tissue); or man-made (e.g. chemicals and other products in landfills). The release scenario will determine the media. For example, in the case of grinding or sanding of MNM-polymer composites to manufacture a product, material will most likely be released into air. In the case of "weathering" of a product, optical (UV radiation) as well as chemical (water) driving forces can result in polymer degradation and subsequent release of MNMs, most likely into surrounding water or soil. It is essential that the chosen analytical method does not alter the properties of the MNM or matrix from their state at the time of sample collection. For example, TEM uses a high energy electron beam to interrogate a specimen and the beam itself can cause changes in nanoparticle properties such as size, for example by beam-induced swelling.[151] Likewise, preparation of soil samples for ICP-MS analysis will require matrix digestion to be compatible with instrumentation hardware, which almost certainly will destroy information about particles as they exist naturally in the soil.

7.4.5 Sample preparation artefacts

Proper sample preparation is critical for ensuring meaningful measurement results. Unfortunately, sample preparation is often not described in sufficient detail in existing reports. When preparing samples for EM from aqueous suspensions, drying artefacts can occur if the surface tension of the water droplet pulls the particles into contact as the liquid evaporates. To avoid this problem, TEM and SEM substrates can be functionalized with a charged coating (positive or negative) opposite to the surface charge of the particles of interest. The charged coating on the substrate will hold the oppositely charged particles in place, which helps to reduce drying artefacts and promotes well-dispersed samples for analysis. Another example is preparation of particles that were collected onto a filter for colloidal counting. Often, a filter is immersed in a liquid and subjected to ultrasonic agitation to dislodge the particles; however, bias is likely with this dispersion method if particle removal efficiency from the filter is not the same for all sizes of particles. An alternative approach could be to collect the particles directly into the analytical medium using an impinger or similar device.

7.4.6 Capability of a measurement method

For each property of interest, there are multiple possible measurement methods applicable to MNMs and each method has unique advantages and disadvantages. The use of multiple complimentary and confirmatory measurement methods is recommended to ensure a robust data set. For example, the size of fragments released from MNM-polymer composites could vary from hundreds of nanometres to hundreds of micrometres, which is very large compared to the diameters of individual MNMs (e.g. on the order of a few nanometres). Few techniques can accurately measure across such a wide range of size scales. In one study, Wohlleben et al.[61], reported the use of laser diffraction to measure the size distribution of abraded material released from a composite. This technique is not sensitive below 200 nm so a second complimentary technique, AUC (range 0,5 nm to 10 000 nm, ISO 13318-1[152]), was used to measure the size distribution of particles below 200 nm. The detection of free MWCNT (form H in Figure 5) in the presence of manifold higher background concentration of polymer fragments (form F in Figure 5) was later confirmed experimentally.[41]

NOTE If the MNM particles are encased in a polymer fragment or are protruding from the fragment surface, measurement by surface-based methods such as microscopy will not detect all the MNM in a fragment. If unbound MNM are released, it is likely that MNM will possess varying morphological characteristics including aspect ratios, making it difficult to describe the population in a sample using a single technique. In this case, pre-fractionation of samples using size exclusion chromatography or field flow fractionation in tandem with EM analysis might be required, though such approaches are time consuming. The specific measurement methods chosen should be based on the information needs for supporting the decision and will depend upon the knowledge of the specific nanomaterial.

7.4.7 Representativeness of measurements

The chosen measurement method should provide representative information on the sample that is being interrogated. The importance of this concept can be highlighted in the use of SEM for analysis of released particles. Although SEM is extensively used for particle analysis, SEM can only interrogate a thin layer of material near the particle surface and cannot detect MNM particles buried far beneath the surface of polymer fragment. This means it is often challenging to discriminate fragments that contain MNM from fragments that consist of polymer only. More recently, investigators have made progress in the use of electric force microscopy to detect and visualize MWCNTs below the surface of composites.[153],[154] Another limitation of EM techniques is obtaining sufficient measurements to ensure robust counting statistics. There are multiple particle collection parameters such as filter pore size, airflow, and sampling duration that will affect the sample.[155] For example, a standard 37-mm filter has about 960 mm^2 of available collection surface area. Typically, a 3 mm^2 to 5 mm^2 piece of filter is sectioned for analysis, which represents only 0,3 % to 0,5 % of the available collection surface. In turn, typically a few fields of view, each on the order of 10 µm^2, are imaged in the electron microscope, which corresponds to an area of about 10^{-6} % of the original sample. None of papers reviewed reported number of fields viewed or sufficiently described counting statistics from EM analysis. These issues raise challenges for the use of such data in decision making, as further discussed in Clause 8.

7.4.8 Composition measurements

The composition of the MNM and polymer might influence the utility of available methods. For example, both MWCNTs and polymers are carbon-based. Additionally, MWCNTs added to polymers also likely include a non-negligible portion of other forms of carbon nanomaterials, including cups, horns, etc. As noted previously, TO-transmittance is commonly used for the analysis of released particles and the EC fraction is used as a marker for MWCNTs. To date, studies have not sufficiently evaluated the ability of this technique to distinguish among MWCNTs, cups, horns, and polymer matrices. Further complicating measurements is the fact that polymers contain additives and stabilizers that could interfere with analyses.

7.4.9 Polymer stability

Each type of polymer possesses unique properties that make it attractive for an application, although these same properties can lead to instabilities (e.g. dissolution or degradation) of a polymer matrix that vary with the phase of the product lifecycle, thus complicating measurement of released MNM. This variation in polymer stability is especially important where the released or potentially released material is likely in the form of unbound MNM particles. Most composites are unlikely to be exposed to strong acids, bases, or solvents during use; however, at the end of its useful life, a product could contact liquids that degrade the polymer matrix in landfills, etc., or be exposed to other conditions (e.g. UV radiation) that make the polymers more susceptible to degradation from milder agents.

7.4.10 Commercial practices

As with any emerging nanotechnology, competitive advantages are to be gained by those who can understand how to effectively disperse MNM in a polymer matrix and control reproducibility of manufacturing procedures. Hence, intellectual property issues will present challenges for sharing measurement data. Additionally, the dynamic nature of the field of nanotechnology is such that products are continuously being improved. A polymer matrix used today might be obsolete in six months or a year because of changes in polymer formulations, processing methods, etc. This makes it difficult to identify a ‘representative’ composite for release testing and risk assessment.

7.5 Considerations for detection, quantification, and determination of properties of released materials

The problem formulation and associated decision needs determine the necessary nature of the analysis, whether detection, quantification, determining the characteristics of the MNM, or some combination of the three method types is needed. Detection is a qualitative method simply defined as the presence—yes or no—of MNM released from MNM-polymer composites as free MNMs or in polymer fragments. The detectability limit in terms of number or mass concentration of MNMs will vary from method-to-method, and it needs to be determined for each method using control samples[156] with appropriate MNM concentrations. A critical data need for evaluating release in many product use scenarios is information of detectability limits. As an example, when performing gravimetric air measurements, typically, the sensitivity of the analytical balance defines the detection limit. The limit of detection (LOD) will be calculated from blank filters used in the same conditions as sample filters and will be weight several times as would filter samples to determine the LOD. The detection limit and quantification for the counting of fibres for air exposure measurement would depend on the analytical sensitivity (e.g. dependent of the microscope, set up and magnification), the number of fibres counted, the surface of the filter investigated, and the sample volume of air taken. Then consideration needs to be taken of the background count levels on sample filters and blanks.

The US. CPSC[157] compiled information on a wide range of analytical methods for different MNM characteristics, including data on the method sensitivity (limit of detection) and whether the method had been validated, based on information in a range of technical reports and guidance documents. However, this compilation has not been published in the peer-reviewed literature. In addition, many of the published methods did not include information on detectability limits, the compilation did not distinguish methods appropriate for a research setting from those appropriate to support decision making, and none of the reviewed methods reported rates. That is, a method might measure mass or surface area, but not amount released per unit time.

Quantification concerns the number or mass concentration of MNMs in or released from MNM-polymer composites per unit volume, mass, or surface area of polymer matrix. Quantification of released MNMs, particularly those in polymer fragments, is challenging for the reasons described in the previous clauses; hence, many methods such as EM can only yield an estimate of concentration.

If release is detected, it might be important to determine the nature of the released material, depending on the problem formulation. Understanding the nature of the released material is also important for ensuring that the toxicity measurements are related to the measured material, although this might not require an in-depth characterization of particles in all cases. It is well-documented that the physicochemical characteristics and properties of MNMs determine the toxicity and fate of MNMs in humans and the environment; see, for example References [158] to [162]. However, description of the released material can also be the most complex step in the measurement hierarchy. This clause addresses four characteristics or properties of MNMs of importance in released material: size, i.e. MNM length, diameter; size distribution, both unbound and within polymer fragments; MNM surface chemistry; and spatial distribution of MNMs in polymer fragments.

It is important to note that measurement methods can be qualitative, that is, measurements that provide a result ranging from “the sample does or does not contain MNMs” to “the sample contains about 50 % MNMs” per unit area or volume examined. For qualitative methods, the relative uncertainty in the result is large or cannot be defined adequately because all sources of error are not known or quantifiable. In contrast, a quantitative measurement produces a numerical result such as “the diameter of individual MWCNTs ranges from 100 nm to 200 nm” with knowledge of the sources of error that contribute to relative uncertainty for the MWCNT population. The relative uncertainty in a numerical result obtained from a quantitative measurement is much smaller than that obtained from a qualitative measurement.

7.6 Applicable measurement methods

Comprehensive review articles[163]-[165] describe, in detail, measurement methods to determine the physicochemical characteristics of MNMs. The information in these articles includes spatial resolution, detection limit, advantages, disadvantages, and measurable characteristics and properties for over 40 methods. Most of the measurement methods in published release studies on MWCNT-polymer composites are included in these review articles; additionally, the articles include methods of potential applicability for release studies. Regarding measurement and counting of airborne particles in air, there are a few publications and documents published on the measurement and counting of CNTs from workplace samples (e.g. References [166] to [169]). In addition, a review article by Petersen et al.[159], focuses solely on methods to detect, quantify, and determine the characteristics of MWCNTs in environmental media. Several additional review articles provide MNM measurement and test methods relevant to a variety of application areas such as ecotoxicity assessment, foods, and food contact material[170]-[174].

8 Identification of needs for standards, methods, instrumentation, decision frameworks, and research

8.1 General

The preceding clauses reviewed the properties of MNM-polymer composites, described scenarios and driving forces that influence release, and reviewed available methods to collect, prepare, and analyse samples of materials released to environmental and biological media throughout the lifecycle of a NEP. Progress has been made in the last decade to understand the nature of particles that contain MNM that are released from composites, and the potential for hazard if people are exposed to released MNM particles. However, it is critical to address several essential gaps in order to better understand whether and where risk to human health might exceed safe levels. Addressing these might also enable innovation using nanomaterials in ways that present little or no risk. Improved (or new) measurement methods, ILS of release in relevant scenarios, development of test protocols, and standardization of methods are needed. As summarized in the bullets below this clause addresses these, and briefly reviews available decision frameworks to aid risk managers in determining the information and sampling methods needed to support product design and development decisions.

The key topics include:

- addressing knowledge gaps:
  - electron microscopy, and
  - reference materials in inter-laboratory studies;
- protocols;
- standardization approaches/challenges;
- selected decision frameworks: focus, purpose, application.

8.2 Potential improved/new methods

As new analytical methods are developed and decision frameworks are refined, it is important for the exposure measurements to be coordinated with the needs and approach of toxicologists, so that the data can be interpreted in the context of the implications for human health. For example, it might be useful to develop “counting rules” and guidance on the relevant size range for size selective samplers.

EM methods have most often been used to interrogate samples of released materials because these instruments can provide information on the presence of MNMs and/or information on their characteristics of these tubes. However, to obtain quantitative information on specific properties (e.g. size distribution) with these techniques is time-consuming and expensive. Even when the EM resources are available, quantitative analyses of released MNM using current EM methods rely heavily on many hours of manual efforts. There is a critical need for automated microscopy-based methods (SEM, TEM, and AFM) for detection, quantification, and determining the characteristics of MNM in polymer fragments to greatly accelerate measurements. Automated methods are particularly important for quantitative MWCNT size distribution and number concentration measurements. Such innovations will help in achieving an overall goal of low-cost methods for quantifying and characterizing released MNM.

Figure 2 describes this document's focus on the primary release of polymer fragments as opposed to secondary release of polymer fragments. These primary release fragments can consist of any combination of MNMs that are fully encased or protruding from the polymer surface as well as fragments that consist of polymer only (see Figure 3). Discrimination of polymer fragments that contain fully encased MNMs from polymer-only fragments is of interest for several reasons. First, the aerodynamic size of a particle strongly influences its regional deposition in the lung. For example, the incorporation of MWCNTs can alter the release fragment/particle size distribution curves, potentially influencing deposition patterns secondarily[40,44,107] Additionally, if the sizes of fragments with encased MNM represent only a portion of all released fragments, then their lung deposition pattern will differ from that predicted from the overall size distribution. Secondly, the presence of polymer only fragments that have the same appearance in the electron microscope as fragments with encased MNM increases background 'noise' and precludes accurate assessment of exposure potential. Hence, a sample preparation procedure or pre-separation technique that yields a higher purity sample (fewer polymer only fragments) would decrease analysis time and improve measurement accuracy.

8.3 Inter-laboratory studies

An ILS is a testing scheme that involves multiple laboratories wherein samples from the same batch are measured by the participants and the results are analysed with the goal of providing a precision (uncertainty) statement. There are numerous purposes for conducting an ILS, among them is to establish the effectiveness of new test methods.[175][176] In the context of MNM-polymer composites, new test methods could be procedures to reproducibly generate materials for a release scenario, protocols for sample preparation, and procedures for analytical measurements. The results of an ILS are often used to support development of a standard method.

RMs are a means to ensure or improve measurement quality and are a critical tool in any ILS scheme. Generally, RMs are produced as CRMs or as non-certified RMs. An RM is a material that is sufficiently homogeneous and stable with respect to one (or more) properties which has been established to be acceptable for its intended measurement use.[177] RMs can be used as benchmark materials for ILS studies of new test methods or protocols. A sub-set of RMs is CRMs whose properties are certified and are metrologically traceable, i.e. to a specified reference system and accompanied by an uncertainty value derived from an uncertainty budget covering all significant uncertainty contributions.[177] CRMs are used for calibration purposes or for method testing. A third class of materials that are relevant for development of test methods is RTMs which is defined as a material from a single batch which is sufficiently homogeneous and stable with respect to one (or more) specified properties and is assumed to be fit for its intended use.[178] It is important to note the differences among these types of materials and their appropriate uses in the development of test methods. For example, a RTM does not carry an uncertainty budget so it is inappropriate to use as a calibration standard but it could be adequate for testing a protocol to generate materials during a release scenario. At the opposite extreme, a CRM carries a full uncertainty budget which is necessary for instrument calibration to ensure accuracy and precision of measurement data but unnecessary for testing a protocol to generate materials during a release scenario.

In the NanoRelease pilot inter-laboratory comparison, MWCNT-epoxy was proposed as RTM with high release rates both by mechanical stresses and by weathering stresses, and with a known share of forms of release (see Figure 6) that includes free MWCNT (form H in Figure 5). MWCNT-PA was proposed as RTM with low release rates by weathering stresses. The nanoGRAVUR pilot inter-laboratory comparison of sanding processes has successfully used epoxy as RTM to calibrate the rates of sanding aerosol releases across three laboratories with differing sanding setups, achieving predictive ranking for a wide range of materials (thermosets, thermoplastics, acrylic coatings, cements).

Another concept related to measurement quality that is important for ILS is measurement validation. Validation of a measurement is defined in the Vocabulary of Metrology[179] as verification wherein the specified requirements are adequate for an intended use. Validation is a provision of objective evidence that a given item fulfils specified requirements. There are several examples of a validated measurement result. One example is the case wherein results on a given sample measured by more than one method are consistent. Another example is measurement validation through the use of a model that incorporates actual data.

Prior to conducting an ILS, a protocol should be developed that outlines the purpose and scope of the procedure and the desired outcome (e.g. a measurement result). Experience with gold nanoparticle RMs sized by dynamic light scattering, TEM, SEM, and AFM[180] and testing haemolysis[181] and cytotoxicity[182] protocols indicates that it is good practice to perform a pilot study with a modest number of organizations on the intended sample to refine a protocol before conducting a full ILS.[183] A pilot evaluation of a protocol permits identification of steps that might be confusing to participants, opportunities for improvement, and allows participants to practice the procedure.

NOTE A video demonstration of the protocol might also be helpful to participants. Once a protocol is agreed upon, a full-scale ILS can be conducted in accordance with recognized standards[119],[176].

8.4 Protocols and assays

The absence of standardized test methods for generation, collection, and analysis of fragments released from MNM-polymer composites is a major barrier to release testing (see 8.5). As recommended in Clause 6, the method to apply the stress should have a good correlation of the simulation with real-life degradation of macroscopic properties (e.g. such as colour, gloss, mechanics). This is, in general, fulfilled best by validated ISO protocols that are used for specifying product performance in the intended use.

Researchers have taken methods that were originally developed for some other purpose and adapted them to evaluate MNM release from composites. One common example is the use of a Taber abraser, which is a well-established method to quantify wear resistance of polymer coatings and paints and is specified in ISO 5470-1[184] and ASTM D4060-95[185] to evaluate MNM release from composites. The adaptation of other standards essentially results in the development of a test protocol (defined here as a list of the steps to be followed in the test). It is important to note that a test protocol prescribes a procedure but does not carry the same level of confidence as a standard method. In the early phases of research, such as with MNM release studies, test protocols are an invaluable means to begin to address critical measurement approaches and serve as starting points for evaluation of these approaches.

8.5 Opportunities for standardization of methods

The development of consensus-based standard test methods (i.e. protocols that produce a measurement result) for quantification or determining the characteristics of MNM by a standards organization such as ISO or ASTM International is predicated on the availability of a well-defined, validated protocol for the method of interest. As noted above, a goal of an ILS is to provide data to calculate a precision (uncertainty) statement. ASTM requires that all test methods be accompanied by a precision and bias statement, but ISO does not. Given the current state-of-the-science, it might not be possible to develop standard test methods for quantification or determining the characteristics of most, if not all, MNM-polymer materials released from composites at this time. For example, review of the literature for MWCNTs indicates that such methods are not possible for some aspects of quantification for characteristics needed to support an understanding of dose per unit time of release. However, it might be possible to develop standards in the form of guides, technical reports, and specifications (i.e. protocols that do not produce a measurement result) for sample preparation approaches for analysis techniques such as SEM, TEM, or AFM. Such procedures would be an essential precursor to the eventual development of standard test methods. For example, there are several ISO documents on nanotechnologies on specific methods to measure and describe the characteristics of free SWCNTs. There is only one document related to free MWCNTs: ISO/TR 10929.[186] However, it should be noted that ISO/TR 10929[186] relates primarily to characterization of MWCNT samples prepared for use under laboratory conditions and so might not apply to release conditions addressed in this technical report. ISO/TC 229 has established a study group to explore the feasibility of developing a standard for the determination of MWCNT size by TEM.

The available reports and specifications provide guidance on how to measure free MWCNT characteristics and properties; however, there are no standard test methods that yield a numerical result with an uncertainty determination. Further work is needed, including pilot studies across laboratories to identify sources of variation in sampling, sample preparation and analytic methods, then leading to more extensive ILS to inform development of a standard.

8.6 Decision frameworks

There are many factors to consider about MNM when evaluating what measurement methods should be used to support decisions about MNM release and potential for exposure from that release. Factors include physical and chemical properties of the MNM, potential uses, environmental release considerations, the potential for toxicity, and the feasibility of measurement methods for application to resulting ES's. Decision frameworks are tools that are designed to guide a user through the process of choosing methods for correctly measuring and describing MNM, based on a number of factors which are often determined by the user. In some cases, the methods might be experimental, as might be used in product development, and in other cases the methods might need to be standardized, as in support of safety in a regulatory context. Decision frameworks can aid in evaluation of methods-utility elements (material characteristics, sampling methods, analytic methods choices, MNM characteristics affecting biological interaction) so that the evaluation refers to and is bounded by realistic decision needs. Decision frameworks can also be used to identify critical gaps in the current ability to measure MNM release rates in a form useful for evaluating the presence or absence of potential toxicity and risk. These gaps might indicate critical barriers to product development, where it might not be possible to evaluate safety, or safety issues might arise.

There are many decision frameworks available and each has different considerations for selection of tests for the measurement and description of MNM.[187] Several of the available decision frameworks are presented in Table 6. Each of these has a unique focus and differs somewhat in purpose and application.

Table 6 — Decision frameworks with considerations for selection of experimental tests for the measurement and description of MNM

Decision framework	Short description
NanoGRID	Multi-tiered testing framework that guides the user through process of determining the physical properties, potential for nanoscale material release and environmental health and safety implications of nano-enabled products.
GUIDEnano	Web-based guidance tool aimed primarily at guiding industry in assessing the potential risks associated to nano-enabled product designing and applying the most appropriate risk assessment and mitigation strategies for a specific product.
SUNDS	The SUNDS software system can estimate occupational, consumer and environmental risks from MNM in industrial products along their lifecycle. In situations when the risks are not acceptable, SUNDS proposes suitable risk management measures, including information about their costs compared to the benefits of the nanotechnologies.
DF4nanoGrouping	Three-tiered framework for the grouping and testing of nanomaterials, including considerations of lifecycle releases[188],[190].
MARINA risk assessment framework	Combines four themes of materials, exposure, hazard, and risk assessment and management of nanomaterials into a risk management toolbox[191].
ECHA/JRC/RIVM	A read-across approach focuses on grouping and read across method of analysing nanomaterials[192].
nanoGRAVUR	Three-tiered framework that groups materials for their occupational, consumer, and environmental risks based on a harmonized set of materials properties[189].

The first three decision frameworks listed in Table 6 are described in further detail below.

The Nano Guidance for Risk Informed Deployment (NanoGRID) is a multi-tiered framework and tool that provides general guidance for ranking and selecting relevant test methods to determine the environmental fate and effects of nanomaterials and nano-enabled technologies. The tiered framework guides the user through a process of determining the physical properties of MNMs, potential for nanoscale material release, and environmental health and safety implications of NEPs. The framework also connects the user with appropriate definitions, publications, and regulation documents.

NanoGRID is constructed of five tiers and allows the user to use only the tiers necessary for test selection. Tier 1 guides the user through the screening criteria for the MNM that is based on material amount, size, properties, technology categories and use. Tier 1 helps compile baseline information with a focus on lifecycle, description, and categorization of the nanomaterial. Tier 2 focuses on release of potential MNMs from the nano-enabled material. In Tier 2, rankings are assigned for potential release pathways, potential use, and storage of the nanomaterial. Rankings of zero to five (five being most conservative assumption) are assigned by the user by answering a series of questions about the physical and chemical properties of the MNM and the potential environmental interaction. Release study methods are then ranked in order of importance by the NanoGRID framework for the selected MNM based on the answers provided by the user about the interactions of the MNM with the environment. Duration, cost, expertise needed, and importance of tests are incorporated into the ranking of testing method guidance. Tiers 3 and 4 focus on the fate and hazard of the MNM. Values from the testing can be entered into the tool for use in a Tier 5 report. Case studies with free nanomaterials have been analysed using NanoGRID and presented in Kennedy et al.[193].

SUNDS is another example decision framework. It is a web-based software system that has been designed to estimate occupational, consumer, public health, and environmental risks from nanomaterials in real industrial products along their lifecycles. In situations where the risks are not controlled SUNDS proposes suitable risk management measures, including information about their costs versus the benefits of the technologies. The system can simultaneously assess risks in different lifecycle stages, targets, activities, and routes of exposure based on *in vivo* toxicity data and ES's. The integration of lifecycle and release information in the SUNDS has been demonstrated in the copper case study in Annex A.[194] It was found that along the lifecycles of these formulations, used in antibacterial and antifungal wood coatings and impregnations, the risk analysis revealed inhalation risks from CuO in ES's involving workers handling dry powders and performing sanding operations as well as potential ingestion risks for children exposed to nano $Cu^2(OH)_2CO_3$ in a scenario involving hand-to-mouth transfer of the substance released from impregnated wood.

Another example is GUIDEnano, a web-based tool, which guides any potential user, including NEP developers (mainly industry) into the design and application of the most appropriate risk assessment and risk mitigation strategies for a specific product. The tool incorporates innovative methodologies to evaluate and manage human and environmental health risks of NEPs, considering the whole product lifecycle: synthesis of MNM, manufacturing of NEPs, use, and end-of-life phase. The correct implementation of this guidance ensures that the risks associated with a NEP, throughout its whole lifecycle and value chain, have been appropriately evaluated and mitigated to an acceptable level, according to the most recent knowledge at the time of implementation. The evaluation of a NEP using this tool is also useful for risk communication to regulators, insurance companies, and society.

More specifically, the exposure module of GUIDEnano includes an activity card library in which the release rates for the different processes that take place at all life-cycle stages of the NEPs are captured. There are two generic ways to determine the exposure in the tool: via release data converted into exposure data by using a dispersion model, or via input of exposure data from existing exposure models. For the exposure modelling, the exposure scenario library (ESL) developed within the MARINA project is linked to the GUIDEnano Tool (44 additional scenarios are included based on measurements in exposure chambers and at the workplace). For cases in which the user has no activity card and therefore no release/exposure data are available for the assessment scenario (AS), guidance is given to determine the similarity, relevance, and quality of a data source for comparable scenarios found in the literature. Therefore, release data generated or collected following the recommendations in this document will enrich the GUIDEnano activity card library with high quality and valuable exposure data for risk assessment purposes.

The variety of decision frameworks differ in the details of their approaches and in the specifics of their applications, but all are designed to support a decision: identifying fit-for-purpose sampling and analytical methods, or supporting a risk management decision. Efficient resource use requires that the sampling method be connected to the scenario and the risk management decision that needs to be made. For each framework, the analysis is done in the context of a specific problem formulation, which describes the exposure and use scenario, the MNM, the surrounding matrix, and the NEP. Proper application of these frameworks requires that the results be considered in the context of the specific problem formulation.

Annex A
(informative)

Example case studies

A.1 General

Several worked examples of the tiered decision support framework are presented in this Annex. The intent of this use of the decision support framework is to clarify sampling and method analysis needs. The conclusions and citation selections are provided here for illustration purposes only.

As mentioned in 6.3, five application specific case studies are detailed. Case studies included were selected based on the availability of sufficient literature to address various aspects of the framework.

a) Lightweight parts made of MWCNT-epoxy (e.g. in airplane applications). This example illustrates the case where the MNM is more resilient than the matrix.

b) Silver nanoparticle impregnated textile. This example illustrates the case where the MNM is less resilient than matrix.

c) Copper-based MNM impregnated into woods that are placed outdoors into soil (e.g. terrace poles). This example illustrates the case where the MNM is less resilient than the matrix. Some metrological challenges here are similar in Ag-textile scenarios, or QDs in a polymer.

d) Automotive parts made of MWCNT or Fe_2O_3 in thermoplastics (PP and PA). This example illustrates the case where both the MNM and the matrix are resilient against most stresses, but not always to the same extent. End-of-life processes cam be destructive to both MNM and matrix. Metrological challenges in this case are similar to that seen with metal-oxide in paints or coatings (similar matrix degradation mechanisms, but lower metrological challenges).

e) 3D printing of MWCNT-containing thermoplastics. This example illustrates MNM is more resilient than matrix. End-of-life processes are expected to be destructive to both MNM and matrix.

The examples follow the same structured process for each release concern: the release scenarios are identified, along with the identity of the matrix and the MNM. Implications for each of these factors are then identified and described, as appropriate. The forms of release and methods used in the cited literature are identified. Additional steps capture information on the MNM content (e.g. percentage), information regarding compatibility with the matrix and dispersion within the matrix. For each of these steps one identifies implications for the relevant lifecycle stage. Table 5 illustrates the structure used for each of the examples.

All examples in this Annex follow the same structured process given in Table 5.

To use the framework, work from top to bottom and left to right: First use step (1) to identify release scenarios, then proceed to step (2) to identity of the matrix, step (3) to identify the MNM. For each line, state the question, gather the answer, and consider the implications. The implications focus on release and differentiate the four main phases of the lifecycle, where the manufacturing and/or assembly phase raise primarily occupational concerns, the use phase primarily consumer and environmental concerns, and the end-of-life phase primarily environmental concerns. Additional implications can be included to reflect the situation. Each cell provides the evidence from the literature specific to the example. Step 4 is optional and captures information on the MNM content (e.g. percentage), information regarding compatibility with the matrix, and dispersion within the matrix. For each of these steps one also considers implications for the lifecycle stage. The final two rows address the forms of release and methods used to measure the release (as cited in the literature). The form(s) of released fragments, that is, the degree to which the MNM is bound to the matrix in the released fragments (completely, partially, pristine), are represented by the appropriate schematics as pictured in Figure 3.

A.2 Lightweight parts made of MWCNT-epoxy

Table A.2 illustrates the use of the decision support framework using data on lightweight MWCNT-epoxy composite parts used in airplane applications. In this example, the MNM is more resilient than the matrix. End-of-life processes are expected to be destructive to both MNM and the matrix.

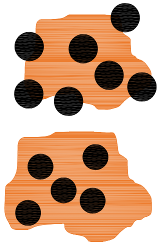
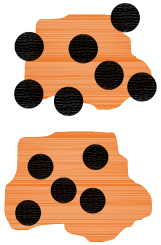
Table A.2 — Illustration of the decision support framework for lightweight parts in airplane applications made of MWCNT-epoxy

	Question	Answer	Release measurement implications				
			Manufacturing steps	**Assembly phase**	**Use phase**	**End of life**	
1	**Release scenario(s)**	Lightweight parts in airplane applications made of epoxy composites Epoxy-based composites have been used in commercial airplane frame structures, due to their high specific strength and stiffness, low weight and absence of corrosion[195],[196].	Mixing into resin (three roll milling) limited thermal stress (curing: 120 °C, 4 h)[105] Preparation of glass fibre reinforced laminate, carbon fibre, or MWCNT reinforced laminates forming final composites[38] MWCNT/polymer nanocomposites by the extrusion process[113],[197] Remark: in the assembly and use phase the final composites (i.e. epoxy +MWCNT + macroscopic glass/carbon fibres) will be looked at	During assembly in airplane: mechanical processes, machining (drilling, sawing, sanding), winding, curing[195] (relative velocities on the order of m/s, with a duration of seconds)	Composites usually covered (paint, other materials), thus no chemical degradation by e.g. weathering Mechanical cycling due to different loads might lead to material alterations (local cracking?) Local cracks can appear in carbon-epoxy composites used in spacecraft structures[195] Within use phase accidental release (very rare) and possibly repairs (see assembly) Use (accidents, repairs) and end of life (recycling): mechanical stress (relative velocities on the order of m /s, for seconds)	**Deconstruction of larger parts:**	**Final treatment in incineration plant:**
						Mechanical stress including sawing, shredding, etc. (relative velocity on the order of m/s for seconds)	Intense thermal stress during incineration: 850 °C, min for min. 2 s (mandatory conditions for incineration plants) [1948]
2	**Identity of matrix**	Epoxy	Emissions of vapours during mixing of resin and hardener. Polymer fume was released in the extrusion process[197]		Thermosetting polymers are chemically very resilient, no thermal stress (elevated temperatures) expected Epoxy resins display excellent properties such as high thermal and mechanical stability and good chemical resistance[199]	Elongation at break above 5 % to 6 %, expected to fragment into relatively larger fragments (>> 100 nm) under mechanical stress.	Ignition point < 600 °C Decompose above 500 °C.

Table A.2 *(continued)*

	Question	Answer	Release measurement implications				
			Manufacturing steps	**Assembly phase**	**Use phase**	**End of life**	
3	**Identity of MNM**	MWCNT	MWCNT are chemically resilient against limited thermal stress during curing of epoxy. The three roll milling process could reduce the MWCNT lengths from 1 µm to 10 µm to about 0,7 µm ± 0,2 µm[200].	MWCNT can rupture/break under mechanical tension, although pull-out is more probable. Protruding MWCNTs from polymer fragments after mechanical machining have been observed by many studies[38],[40],[41],[105],[68] The released MWCNTs might be shortened during the abrasion process compared to the embedded ones[105]	Besides repairs (see assembly) no change due to aging expected. A number of UV degradation studies showed that the epoxy-rich surface layer of the nanocomposite was removed relatively rapidly, leaving a surface covered almost completely with a network of MWCNTs[31],[33],[41],[201]. The integrity was not damaged.	MWCNT can rupture/break under mechanical tension, although pull-out is more probable	MWCNT decompose above 600 °C in air[53]. Pang et al.[202], studied the oxidation of MWCNTs by thermogravimetric analysis (TGA) in air. The maximum rate of weight loss took place at 695 °C at a heating rate of 1 °C /min. The oxidative stability of MWCNTs is dependent on the defects and tube diameter[203]. MWCNTs have high thermal stability and might be exposed after thermal treatment of the composites and still keep their structural integrity[204]. A release of MWCNTs was not observed by thermal decomposition of MWCNT/epoxy composites in a tube furnace[69].

Table A.2 *(continued)*

	Question	Answer	Release measurement implications				
			Manufacturing steps	**Assembly phase**	**Use phase**	**End of life**	
4	Content and compatibility of MNM in matrix, state of dispersion of MNM in matrix		Poor dispersion of MWCNTs in epoxy has been reported at 4 %[40].				Residual ash might contain unburned MWCNT[205]
		= Forms of release observed in literature for the specific case	No MWCNT emissions	Observed fragments with embedded MWCNT, occasionally protruding MWCNT, no free MWCNT [44],[46],[47],[206].  Very low amount of free standing single and agglomerated MWCNTs were released from epoxy composite by abrasion[68],[105] and sanding with 4 % MWCNTs[40]	For repairs, etc. observed fragments with embedded MWCNT, occasionally protruding MWCNT, no free MWCNT[44],[206]. 	Sawing leads to fragments with embedded MWCNT, occasionally protruding MWCNT, no free MWCNT[46]. 	MWCNT decompose above 600 °C in air[53]
		Methods used in the cited literature		Sanding, abrasion, wet and try drilling, sawing, grinding, brushing as stress simulation[207] Real time sampling of aerosol, For particles NAS/filter samples analysis by means of FMPS, SMPS, CPC, SEM NIOSH method 5040[139] NanoRelease Project[208]	UV degradation, exposure to humidity and water bath as stress simulation and combination with machining[65] For repairs: see assembly phase	Real time sampling of aerosol, For particles filter samples analysis by means of FMPS, SMPS, CPC, TEM, SEM[46]	Real time sampling of aerosol, For particles NAS/filter samples analysis by means of FMPS, SMPS, CPC, SEM Analysis of residual ash by SEM/TXRF[205]

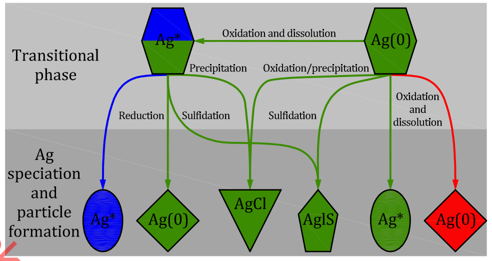
A.3 Silver nanoparticle impregnated textiles

Table A.3 illustrates the use of the decision support framework using data on Ag nanoparticles in textile for antimicrobial applications. This example illustrates silver nanoparticle incorporation into cotton/polyester textiles for clothing with antibacterial purposes and illustrates a case where the MNM is less resilient than the matrix. Two end of life processes have been considered: textile disposal in a landfill and incineration.

Table A.3 — Illustration of the decision support framework for Ag nanoparticles in textile applications

	Questions	Answer	Release measurement implication			
			Manufacturing steps	Use phase	End of life	
					Landfill	Incineration
1	**Release scenario(s)**	Antimicrobial textiles used for clothing (e.g. socks, t-shirts, trousers).	Ag nanoparticles are usually incorporated into textiles through padding process[209] Since Ag nanoparticles are in a dispersion (wet chemistry) release to air is not likely to occur. However, if impregnation solution or water used to clean the recipients is not disposed properly, Ag nanoparticles could arrive to WWTP after being disposed in the sewage system.	Release during use phase can occur mainly due to household washings, from where release waters would go to the sewage system, WWTP and later to the environment[210],[211] In textiles for clothing, mechanical abrasion and sweat produced when the textile is worn could also produce release[212],[213]	Textiles are usually disposed to the landfill from where nanoparticles leaching to the soil could occur[214],[215]	Final treatment in incineration plant: intense thermal stress during incineration, e.g. the EU has the following mandatory conditions for such plants: 850 °C, min for min. 2 s[198]
2	**Identity of matrix**	Most commonly treated textiles are cotton and polyester	Release of textiles during manufacturing process (e.g. padding) are likely to be limited.	Releases of textiles during use stage are likely to be limited.	Cotton is biodegradable. Polyester residues take around 200 years to decompose.	Cotton decomposes above 150 °C Polyester decomposes above 500 °C.
3	**Identity of MNM**	Ag nanoparticles	Generally, Ag nanoparticles are used in dispersion (wet chemistry), which is not likely to be released. When it is used as a powder, an occupational exposure can occur due to release to air.	Evidence of silver modification under sunlight has been found[211].	Silver presents two main forms: Ag^0 (nanoparticle) and Ag^+ (dissolved ion)[215]	Ag melts above 962 °C.
4	**Content and compatibility of MNM in matrix, state of dispersion of MNM in matrix**	Ag content ranged from 18 mg Ag/kg to 2 925 mg Ag/kg textile in a study including seven commercial Ag containing textiles[216]	Ag nanoparticles dispersions usually include dispersing agents and binders to improve the nanoparticles attachment to the textiles. Particles have been observed to easily bind to the rougher surface of natural fibres than to the smooth surface of synthetic fibres[217]			Residual ash might contain Ag.

Table A.3 *(continued)*

	Questions	Answer	Release measurement implication			
			Manufacturing steps	**Use phase**	**End of life**	
		= Forms of release observed in literature for the specific case	If Ag is released from an inappropriate disposal of impregnation solution, Ag nanoparticles will be released together with binders and wetting agents.	After textile washing, Ag is released in ionic form (dissolution) or as a nanoparticle (physical process). Then, multiple transformations can occur:  [218]	Mainly freely released nanoparticles, although dissolved silver (Ag^+) is also generated[214]	Ag melts above 962 °C.
		Methods used in the cited literature	Padding process[214]	ISO standard 105-C06, colour fastness to domestic and commercial laundering (sp)ICP-MS[214] ICP-OES; TSEM and STEM coupled to EDX[216] Antimicrobial efficacy of the fabrics was tested according to a slight modification of AATCC test method 100–2004[210]	EPA Standard Method 1311: Toxicity Characteristic Leaching Procedure[214] ICP-MS, Zetasizer[214]	

A.4 Copper-based MNM impregnated into woods that are placed outdoors into soil

Table A.4 illustrates the use of the decision support framework using data on copper-based MNM impregnated into woods that are placed outdoors into soil (e.g. terrace poles). The MNM and matrix function as a controlled Cu ion release vehicle to prevent fungal biodegradation at the wood surface. This example illustrates the case where the MNM is not persistent (it is less resilient than the wood matrix). Some metrological challenges here are similar in Ag-textile scenarios, or QDs in a polymer.

Table A.4 — Micronized copper-treated wood

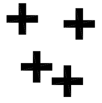
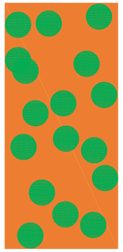
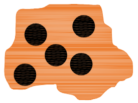
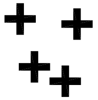
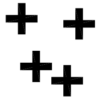
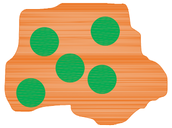
Question	Answer	Release measurement implications			
		Manufacture	Intended Use	Incidental Use	End of Life
Release scenario(s)	Outdoor/indoor (ground contact, structural) Playgrounds, dock pilings, board walks, etc.	Pressure infusion, Twelve classifications for different applications (AWPA) [219] 80 % market value of pressure-treated wood is southern pine with micronized copper azole[72]	Pressure-treated wood resists outdoor weathering (UV, rain, salt water, ground moisture and fungal biodegradation)	Initial: sawing, sanding, mechanical and human abrasion Deconstruction in open (yard) burning	Commercial incineration or land fill weathering conditions
Identity of matrix	Typically, southern yellow pine (AWPA)	Lumber processing releases wood dust which can be a health hazard	Wood is relatively resilient against weathering, except for biodegradation	Same as above	Same as above
Identity of MNM	Micronized copper carbonate cuboid particles 50 nm to 100 nm Approximately 60 % by number are < 100 nm[72],[73]	Micronized copper carbonate is protected in wood matrix Free and organically complexed copper ion is released at the wood surface 	Controlled release of copper ion inhibits mould and fungal growth and subsequent biodegradation Approximately same effectiveness by wood impregnated with micronized copper carbonate as impregnated with conventional (non-particulate) copper.	Wood fragments from pre-weathered wood released by sanding contain micronized copper carbonate particles[72] Post-weathered mechanical abrasion or human contact releases cellulose fragments which might contain organically complexed copper ion but are not likely to contain copper carbonate nanoparticles[220] Although burning of micronized Cu wood has not been reported, open burning of CCA-treated wood results in vaporization of As while Cu and Cr remain in the ash[222].	Although incineration of micronized Cu wood has not been reported, incineration of CCA-treated wood results in vaporization of As while Cu and Cr remain in the ash[223].
Content and compatibility of MNM in matrix, state of dispersion of MNM in matrix	Matrix loading of micronized Cu wood is between 0,06 lbs/ft^3 to 0,31 lbs/ft^3 depending on the intended use of the wood[219]	Wood is infused with proprietary micronized copper carbonate-azole formulations in a pressurized tank. 	Wood is typically dried and excess surface Cu carbonate removed. From personal experience at retail outlets, residual Cu carbonate from improperly dried “wet wood” can form an easily transferred paste-like coating on the wood.	NA	NA

Table A.4 *(continued)*

Question	Answer	Release measurement implications			
		Manufacture	**Intended Use**	**Incidental Use**	**End of Life**
	Forms of release observed in literature for the specific case	Cu released during the manufacturing process has not been reported.	Cu was released from as purchased and weathered wood during simulated dermal exposure wipe tests[72] and mechanical abrasion[83].  Environmental leaching or the NanoRelease weathering protocol observed Cu being released predominantly in ionic  form[73].	Cu ion leached from sawdust and sanding dust in forms similar to solid wood[220]   Open burning of CCA-treated wood results in vaporization of As, while Cu and Cr remain in the ash as $CuCr_2O_4$ and $CuCrO_2$[222].	Incineration of CCA-treated wood at temperatures of 872 K to 1 673 K results in vaporization of As while Cu and Cr remain in the ash[223].
	Methods used in the cited literature	Modified NIST and CPSC wipe methods have not been applied to the workplace. Analytical methods for air and surfaces include: APS, SMPS, DMA, CPC ICP-MS, XRD, SEM, ...	Wipe, sampling, abrasion, aerosol analysis methods include APS, SMPS, DMA, CPC, SEM, and ICPMS[83] Leaching tests used EN 84 or the NanoRelease weathering protocol, analysis by single-particle-ICPMS, AUC, UVVis, TEM, ICPMS[73].		Methods used for aerosol analysis in open burn and commercial incineration models include: MOUDI sampling, ICP-MS, SEM, WD-XRF, XRD[222],[223].

A.5 Automotive parts made of MWCNT or Fe_2O_3 in thermosetting polymers (PP and PA)

Table A.5 illustrates the use of the decision support framework using data on automotive parts made of MWCNT or Fe_2O_3 in thermoplastics (PP and PA). This example illustrates the case where both the MNM and the matrix are resilient against most stresses, but not always to the same extent. End-of-life processes can be destructive to both MNM and matrix. Metrological challenges in this case are similar to that seen with metal oxide in paints or coatings (similar matrix degradation mechanisms, but lower metrological challenges).

Table A.5 — Automotive parts made of MWCNT or Fe2O3 in thermoplastics (PP and PA): both MNM and matrix are resilient against most stresses, but end-of-life processes might be destructive to both MNM and matrix

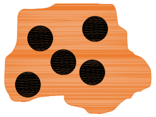
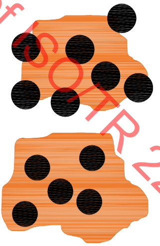
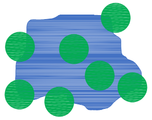
	Question	Answer	Release measurement implications			
			Manufacturing	Use	End of life	
1	**Release scenario(s)**	Automotive parts made of thermoplastic nanocomposites	limited thermal stress (injection moulding: 230 °C, 10 s)	chemical degradation (weathering, for years)	**Deconstruction of larger parts:** Mechanical stress (relative velocities on the order of m/s, for seconds)	**Final treatment in incineration plant:** Intense thermal stress during (waste incineration: 850 °C, 2 s)
2	**Identity of matrix**	PP or PA	resilient against limited thermal stress (no significant chemical degradation, but polymer fumes might be emitted)	relatively resilient against weathering (µm thin surface layer degrades)	elongation at break above 10 %, expected to fragment into relatively larger fragments (>> 100 nm) under mechanical stress.	decompose above 600 °C.
3	**Identity of MNM**	MWCNT or Fe_2O_3	MWCNT and Fe_2O_3 are chemically resilient against limited thermal stress.	MWCNT and Fe_2O_3 are chemically resilient against weathering.	MWCNT might rupture under mechanical tension, although pull-out is more probable Fe_2O_3 particles are resilient against mechanical stress	MWCNT decompose above 600 °C in air[53]. Fe_2O_3particles are persistent at 850 °C, but might transform crystallinity[53].
4	**Content and compatibility of MNM in matrix, state of dispersion of MNM in matrix**	Below 5 % compatibility, dispersion unknown		Parameters anticipated to be required for future models or groupings	Parameters anticipated to be required for future models or groupings	Trace levels of MWCNTs and Fe_2O_3 nanoparticles in the released aerosol. No MWCNT detected in aerosol. Residual ash (when Fe_2O_3 is MNM filler) consists mostly of MNM additive[53],[54].
		Forms of release observed in literature for the specific case	Observed organic aerosols (polymer fumes, chemically identified with matrix) [224],[225] 	Observed fragments with embedded MNM, no free MNM[44],[206] 	Observed fragments with embedded MNM, occasionally protruding MNM, no free MNM [36],[221] 	Agglomerated nanopowder as residual ash (in case of Fe_2O_3 MNM additive used)[53]  Potential transformation of released matrix due to the presence of MNM additive (e.g. increased PAH content) [52] 

Table A.5 *(continued)*

	Question	Answer	Release measurement implications			
			Manufacturing	Use	End of life	
		Methods used in the cited literature	Sampling of aerosol at real-world manufacturing; analysis by SEM, EDX, CPC	Stress simulation = sanding sampling = aerosol; analysis = CPC, SEM (= the best available approximation of real-world stresses);	Stress simulation = ISO 4892-3[231] up to 535 MJ/m^2; sampling = immersion fluids + sonication analysis = ICPMS, TEM, UVVis, AUC/FFF. (= NanoRelease weathering protocol)	Sampling of aerosol in real time and size-fractionated by the compact cascade impactor. *In situ* real time size measurements by aerosol particle sizer and scanning mobility particle sizer. Sampling of residual ash. *In situ* TGA-FTIR to identify off gases. Both released aerosol and residual ash examined by ICP-MS (elemental composition), GS-MS (elemental versus organic carbon quantification), EM with EDX (morphology and chemical composition), NMR (chemical composition), XRD (crystal phase analysis)[54],[53],[226]

A.6 3D printing of MNM-containing thermoplastics

A.6.1 General

Table A.6 illustrates the use of the decision support framework using data on 3D printing of MNM (MWCNT)-containing thermoplastics. This example uses two release scenarios (home and school) that are each assessed for

a) melt-processing by consumer,

b) consumer use of the product, and

c) disposal.

This example illustrates a case where the MNM is more resilient than the matrix, but end-of-life processes are expected to be destructive to both MNM and matrix.

A.6.2 Release scenario 1

A.6.2.1 Manufacturing steps and assembly

A 3D printer is used in home using an ABS filament with MWCNT to print out a coffee mug at 230 °C for 6 h (assumed values). The 3D printer is located in the basement, and the home has an HVAC system with no other engineering controls. The concern during this phase is the release of free MWCNT or ABS particles with MWCNT protruding from the matrix.

A.6.2.2 Use phase

The coffee mug is mouthed and handled by the user.

A.6.2.3 End of life

The coffee mug is disposed of in a trash can.

A.6.3 Release Scenario 2

A.6.3.1 Manufacturing steps and assembly

A 3D printer is used in an elementary school classroom. The 3D printer uses an ABS filament with MWCNT to print out a toy at 230 °C for 6 h. The children are in the classroom during the entire day and time of assembly. The concern during this phase is the release of free MWCNT or ABS particles with MWCNT protruding from the matrix.

A.6.3.2 Use phase

The toy is a check or checker piece that is used by the children on a daily basis. Children will handle and potentially mouth the pieces. Fragments of the material might accumulate in the classroom as dust.

A.6.3.3 End of life

The checker pieces are disposed of in a trash can.

Table A.6 — 3D printing of MNM-containing thermoplastics

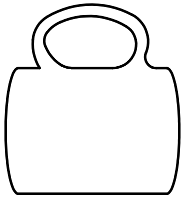
	Question	Answer	Release measurement implications				
			Manufacturing steps	Assembly phase	Use phase	End of life	
1	**Release scenario(s)**	3D printing of parts using consumer grade fused filament fabrication (FFF) marketed for consumers Wide variety of thermoplastic filaments can be used. Also, different filler materials are used to lend special properties to the filaments Custom mixing of filaments are readily available using consumer level extruders. ABS-based composites have been used in toys, small tools, and gadgets due to their high thermal stability and strength. ABS composite filaments are used for any parts that are handled in a rough manner or will be exposed high temperatures (in a hot car, for example). Cell phone cases, handles, phone mounts, jewellery (rings and bracelets), class project at school	Purchase commercially available MWCNT composite ABS filaments Purchase ABS pellets and mix MWCNTs or other MNMs using commercially available filament extruders MWCNT/polymer nanocomposites by the extrusion process[113,197] 3D printing is largely extrusion process plus heating of parts (heated stage) and abrasion for finishing step – removing burrs, smoothing the surface, etc. Home use is likely to be done in a basement, garage, or home office with HVAC and no other engineering control. School or library use is likely to be done in a larger area with better ventilation.	Might or might not require assembly. Will require some kind of finishing process since the surface will be rough. Abrasion, scratching, cutting	Might be handled frequently Exposed to high temperature Could be dropped Mouthing is possible depending on the application and the user age. Local cracking and scratching are likely Fragments can accumulate in the classroom. 	Landfill:	Final treatment in incineration plant:
						Parts will be discarded as trash. Probably small enough to not be subject to shredding type scenario Could be in landfill.	Intense thermal stress during incineration: 850 °C, min for min. 2 s (mandatory conditions for incineration plants)[198].

Table A.6 *(continued)*

	Question	Answer	Release measurement implications				
			Manufacturing steps	**Assembly phase**	**Use phase**	**End of life**	
2	**Identity of matrix**	ABS	Emissions of vapors during extrusion. Polymer fume was released in the filament extrusion process. Polymer fume and particles are released in the 3D printing process. Filament storage condition can affect print quality and release. Printing temperature settings can affect release process.	ABS is used due to its good mechanical properties such as impact resistance, toughness, and thermal stability. It does degrade under UV exposure[227]	Thermosetting polymers are chemically very resilient, no thermal stress (elevated temperatures) expected		Decomposes above 500 °C.

Table A.6 *(continued)*

	Question	Answer	Release measurement implications				
			Manufacturing steps	Assembly phase	Use phase	End of life	
3	**Identity of MNM**	MWCNT	Extrusion temperature is relatively low so not likely to cause chemical transformation in MWCNTs. Extrusion process might break MWCNTs into shorter tubes or break apart agglomerates.	MWCNT might rupture/break under mechanical tension, although pull-out is more probable. Protruding MWCNTs from polymer fragments after mechanical machining have been observed by many studies[38,40,41,105,68] The released MWCNTs might be shortened during the abrasion process compared to the embedded ones[105].	Besides repairs (see assembly) no change due to aging expected. A number of UV degradation studies showed that the epoxy-rich surface layer of the nanocomposite was removed relatively rapidly, leaving a surface covered almost completely with a network of MWCNTs. [31,33,41,201] The integrity was not damaged. The potential implications of release during mouthing behaviours of children should be considered.	MWCNT might rupture/break under mechanical tension, although pull-out is more probable	MWCNT decomposes above 600 °C in air[53]. Pang et al.[194], studied the oxidation of MWCNTs by thermogravimetric analysis (TGA) in air. The maximum rate of weight loss took place at 695 °C at a heating rate of 1 °C /min. The oxidative stability of MWCNTs is dependent on the defects and tube diameter[203]. MWCNTs have high thermal stability and might be exposed after thermal treatment of the composites and still keep their structural integrity[204]. A release of MWCNTs was not observed by thermal decomposition of MWCNT/epoxy composites in a tube furnace[69].
4	**Content and compatibility of MNM in matrix, state of dispersion of MNM in matrix**		Commercially available ABS MWCNT composites have good dispersion. Ranges from 0 % to 5 %. MWCNTs might require additional surface treatment.				Residual ash might contain unburned MWCNT[205].

Table A.6 *(continued)*

	Question	Answer	Release measurement implications				
			Manufacturing steps	**Assembly phase**	**Use phase**	**End of life**	
		= FORMS OF RELEASE observed in literature for the <u>specific</u> case	Emissions of vapors during extrusion. Emissions of ABS/MWCNT composite particles during extrusion. [228,229]	Observed fragments with embedded MWCNT, occasionally protruding MWCNT, no free MWCNT[206,44,46,47]. No bare MWCNTs during 3D printing process[230] Larger particles of ABS with embedded and protruding MWCNTs released during 3D printing[230]	Breakage, wear, impact, rough handling observed fragments with embedded MWCNT, occasionally protruding MWCNT, no free MWCNT 	Sawing leads to fragments with embedded MWCNT, occasionally protruding MWCNT, no free MWCNT[46].	MWCNT decompose above 600 °C in air[53].
		Methods used in the cited literature	CPC, DMA, OPC, PID (Photoionization detector)	Sanding, abrasion, wet and try drilling, sawing, grinding, brushing as stress simulation[207]) Real time sampling of aerosol, For particles NAS/filter samples analysis by means of FMPS, SMPS, CPC, SEM NIOSH method 5040[139] NanoRelease Project[208]	UV degradation, exposure to humidity and water bath as stress simulation and combination with machining[65]	Real time sampling of aerosol, For particles filter samples analysis by means of FMPS, SMPS, CPC, TEM, SEM[46].	Real time sampling of aerosol, For particles NAS/filter samples analysis by means of FMPS, SMPS, CPC, SEM Analysis of residual ash by SEM/TXRF[205]