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SweNanoSafe

Swedish National Platform for Nanosafety

Nanomaterials in the Environment

AN OVERVIEW OF THE CURRENT STATE OF KNOWLEDGE AND THE KNOWLEDGE GAPS TODAY

FREJA MILTON, MAJA FINNVEDEN AND ARNE WALLIN, GOODPOINT AB

Foreword by SweNanoSafe

Commissioned by the Ministry of the Environment and the Swedish Chemicals Agency, SweNanoSafe holds the role of a national platform for the safe handling of nanomaterials. The platform also works towards contributing to the environmental goal of a non-toxic environment and aims to protect human health. SweNanoSafe is commissioned to provide specific support to authorities on issues related to the safe handling and use of nanomaterials, as well as communicating the current knowledge and understanding of nanomaterials. SweNanoSafe brings together academia, authorities, industry and organizations for a joint dialogue on nanosafety. In addition to actively promoting improved nanosafety, the mission also includes identifying needs for the safe handling of nanomaterials and contributing with proposals for solutions and concrete measures that meet the current needs.

Since 2019, SweNanoSafe is hosted by the Institute of Environmental Medicine at Karolinska Institutet who run the platform activities with help from a Steering group and the Coordination team, and support from the SweNanoSafe Expert Panel, Council of Authorities, Research Network and Education Network. Activities include for example workshops and meetings, and communication via the website (www.swenanosafe.se).

At the suggestion of SweNanoSafe's Expert Panel, Nanomaterials in the Environment were identified as a priority area that needs to be investigated. SweNanoSafe commissioned Goodpoint AB to compile an overview of the available knowledge and gaps in knowledge in this field. The report Nanomaterials in the Environment describes the use of nanomaterials, emissions and accumulation in the environment, analytical methods for different matrices, dispersion and transformations, toxicological effects, and environmental risk assessments.

On November 17, 2020, SweNanoSafe arranged the digital workshop "3rd Annual Workshop of the SweNanoSafe Research Network: Nanomaterials in the Environment", where knowledge gaps were identified and with discussions that contributed to this report.

Freja Milton, Maja Finnveden and Arne Wallin at Goodpoint AB have authored this report. Klara Midander has been Project Manager and contact person at SweNanoSafe. Penny Nymark, Bengt Fadeel and Annika Hanberg also contributed with thoughts and comments.

Opinions expressed in this report are the authors' own and do not necessarily represent SweNanoSafe's views. SweNanoSafe welcomes suggestions, comments and opinions regarding nanosafety via email to swenanosafe@swenanosafe.se.

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Adobe Stock

This report can be downloaded from www.swenanosafe.se

Stockholm, May 2021

Stockholm, May 2021

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Summary

Nanomaterials are a broad group of chemical substances. In the environment, they interact with other substances and the environmental conditions. Nanomaterials have many areas of use, and their properties can be utilized in technical applications to improve the environment, and thus help achieve the sustainable development goals. The use of nanomaterials is predicted to increase in the future, as is the number of nanomaterials that end up in the environment. Nanomaterials can be released throughout their whole life cycle. Today, there is only limited information on how and to what extent nanomaterials exist in the environment. There is also a lack of understanding about the environmental impact of nanomaterials during the different phases of their life cycle.

The purpose of this assignment was to review the research available today about the impact and distribution of nanomaterials in the environment, based on the current conditions in Sweden. Subsequently, gaps in knowledge and areas where further research efforts are needed have been identified. This report focuses on manufactured nanomaterials and how they interact with the environment.

To date, just under a thousand products containing nanomaterials have been reported to the Swedish Chemicals Agency's Products Register. The most common product types containing nanomaterials are (in descending order): raw materials for plastics and rubber, paints including pigments, sealants, fillers and binders. The most common substances in nanomaterials are titanium dioxide, silicon and silica compounds, and carbon black.

The analytical methods available to detect and quantify nanomaterials in the environment are very limited and are often applied on a laboratory scale. It is important to improve and develop analytical methods that are suitable for analyzing nanomaterials in different environmental matrices. Reliable and adapted analytical methods are also fundamental to the understanding of how and to what extent nanomaterials are dispersed in different environmental matrices. It is also important for the assessment of the environmental threat posed by nanomaterial emissions, and for carrying out reliable risk assessments.

The fate, mobility, toxicity, and bioavailability of nanomaterials in the environment are dependent on the intrinsic properties of the nanomaterial, how it interacts with other materials and on environmental factors. Mainly nanomaterials with simpler structures have been evaluated from an ecotoxicity perspective today. When a nanomaterial is released in the environment, it can undergo chemical, biological or physical transformation processes that affect its fate, mobility, toxicity, and bioavailability.

Nanomaterials can have toxic effects on an organism, both acute and long-term effects. When nanomaterials accumulate in matrices such as soil and water, the risk of both acute and chronic effects increases. Furthermore, other compounds can form an environmental corona around the nanomaterial, thus increasing the bioavailability of the compound. Today, there is limited understanding of the toxicological effects of nanomaterials on different types of organisms.

Today's research is mostly investigating individual nanomaterials or areas of use, while research examining a broader perspective and complex environmental matrices is lacking. There is also a lack of consensus on the environmental effects of nanomaterials. Instead, most studies available today only provide indications of how nanomaterials can affect the environment and what effect they could have on different organisms. Current research focuses on laboratory studies. More research is needed regarding nanomaterials in the environment and organisms, as well as the effects of nanomaterials on an individual, population and ecological level.

Foreword by the authors

Today, there is limited information on how and to what extent nanomaterials exist in the environment, and there is a lack of understanding about the environmental impact of nanomaterials during the different phases of their life cycle.

Increased use of manufactured nanomaterials in various applications presents a risk of further release in the environment. There are limited studies on how nanomaterials disperse, accumulate, interact, and transform in different environmental matrices. Major challenges remain regarding methods for detecting, quantifying, and characterizing nanomaterials in the environment, as well as for developing risk assessment methods. SweNanoSafe, the national platform for nanosafety, has therefore initiated a project on nanomaterials in the environment: "Identification of gaps in knowledge and proposals for new research", which focuses on the status in Sweden. As part of this project, Goodpoint was commissioned to create an overview on the existing knowledge in the field.

The purpose of this assignment was to review the current situation and compile the research that exists today about the impact and distribution of nanomaterials in the environment, based on the conditions in Sweden. Subsequently, existing gaps in knowledge have been identified.

The report is based on a review of academically published work on nanomaterials in the environment. Grey literature and other information such as websites of government agencies have also been included in the work. Since the approach has been to identify key references as a starting point for the report, the outcome should not be considered as a systematic literature study. Broad search terms related to the report's chapters were used in Lub-search (search portal for Lund University Library), Web of Science, SciFinder and Google Scholar. The search results were filtered with the aim of identifying well-cited and relevant key references, i.e., no pre-defined method of including or excluding literature was applied. In addition, reports from Sweden, followed by the Nordic region and Europe have been used to highlight a Swedish/ Nordic perspective. For more general facts about nanomaterials, reports from other parts of the world have been used.

Input based on presentations and group discussions from a workshop with the theme "Nanomaterials in the Environment" has also been included in the report. The workshop was an annual activity for SweNanoSafe's research network and was arranged digitally on November 17, 2020. The workshop was attended by people from academia, authorities, companies, and organizations with cutting-edge expertise in nanomaterials.

The assignment is limited to the environmental field and therefore current knowledge on (human) health effects of nanomaterials has not been included. The report focuses on intentionally manufactured nanomaterials, so called engineered nanomaterials (ENM). Unintentionally formed nanomaterials have not been investigated in this study. Therefore, secondary micro- and nanoplastics are not part of this report as they are inadvertently formed nanomaterials (albeit from human-made products). Nanomaterials used to purify contaminated soil are not included. Legislation and other regulations on nanomaterials have also been excluded from this literature study.

This report is aimed at individuals in government agencies, companies, academia, and other organizations who possess a basic knowledge of nanomaterials, but who wish to get an overview of the state of the current research regarding nanomaterials in the environment.

Freja Milton, Maja Finnveden and Arne Wallin, Goodpoint AB
May 2021

goodpoint

Introduction

Nanomaterials are naturally found in the environment and are formed in different environmental matrices. Natural nanomaterials can be formed through various physical, chemical, and biological processes such as weathering of minerals, precipitation reactions, mineralization, fragmentation or by nucleation in the atmosphere. In recent years, it has become increasingly common to produce nanomaterials synthetically and modify them to possess desired properties. The "nano-era" started in the early 2000s, when more than 35 countries initiated research programs in nanotechnology. This led to a steady increase in the production of nanomaterials (so-called "engineered nanomaterials") (Zuverza-Mena et al., 2017). Today, there are just under a thousand chemical products with registered nano content on the Swedish market (personal communication with Markus Ifverberg, Swedish Chemicals Agency, December 7, 2020).

A nanosized particle has a much larger surface area relative to its weight in comparison to a larger particle, which results in a difference in properties. Many of these sepcial properties are attractive, and therefore there are numerous of applications. For example, nanomaterials can have electrical, optical, magnetic, chemical, or mechanical properties (Swedish Chemicals Agency, 2019; Kahn et al., 2017). They are used in different areas such as paint, food packaging, detergents, sports equipment, cosmetics, textiles, electronic products, agriculture, water and wastewater treatment, and medical and medical device applications (Zuverza-Mena et al., 2017; Swedish Chemicals Agency, 2019; Besha et al., 2020).

Nanotechnology and nanomaterials are often used when developing technologies that are expected to be environmentally friendly, or to help solve current environmental issues. Therefore, they could help contribute to a sustainable development of the society and to achieve the sustainable development goals. By utilizing the different properties of nanomaterials, conventional materials and products can be improved or replaced with options that are more resource efficient, energy efficient or easier to recycle. The development of advanced measuring equipment with sensors based on nanomaterials can indirectly lead to environmental improvements by allowing the detection and quantification of pollutants in different environmental matrices. Nanomaterials can also be used in technical applications for water and air purification, thus directly contributing to environmental improvement (Schwirn and Völker, 2020; Kabir et al., 2018). Therefore, the development of nanomaterials is justified by several sustainability goals, such as *Clean Water and Sanitation* (6), *Affordable and Clean Energy* (7), but above all the broader goals of *Responsible Consumption and Production* (12) and *Climate Action* (13) (UN Sustainable Development Goals, n.d).

However, while nanomaterials can be of great benefit, their benefits must be weighed against the potential environmental impact. Throughout the life cycle from production, through use and waste management, there is a risk of nanomaterials leaking into the environment (Swedish Chemicals Agency, 2020a). To achieve the environmental goal "A non-toxic environment", the Swedish Chemicals Agency has published the report “Giftfritt från början” (English translation "Non-toxic from the beginning") (Swedish Chemicals Agency, 2020a). This report highlights that the understanding of the effects of nanomaterials in the environment is currently limited and needs to be urgently increased. The report highlights three key areas that must be the focus areas to achieve the goal "A non-toxic environment":

1. **Phase out hazardous substances.** Some nanomaterials have hazardous properties and should be substituted and phased out to the furthest extent possible.

2. **Non-toxic circular economy.** By avoiding the use of nanomaterials that are environmental or health hazards, products containing nanomaterials can be reused and recycled and thus contribute to a circular life cycle.
3. **Reduce overall exposure.** Ensure that nanomaterials are not released into the environment, thereby reducing exposure.

The environmental fate of a nanomaterial include different processes with the main ones being dispersion, degradation and transformation (physical, chemical and biological) and/or accumulation in air, water, soil, sediment and biota.

The development of nanotechnology and nanomaterials is expected to continue at a rapid pace (Swedish Chemicals Agency, 2020a). Researchers believe that the use of nanomaterials in both research and industry will increase in the coming years (Gottschalk et al., 2015; Schwirn and Völker, 2020). Today, there is a consensus among researchers that the increased use of nanomaterials will result in more nanomaterials in the environment (Gottschalk et al., 2015). At the same time, there are large gaps in knowledge regarding the transformation and fate of nanomaterials in the environment, as well as regarding the negative effects they may have on living organisms (Gottschalk et al., 2015). With this knowledge at hand, there is an obvious need to summarize information on nanomaterials in the environment, their life cycle, their behavior and their fate. It is important to identify risks, as well as methods for analyzing and measuring nanomaterials in the environment. This report provides an overview of the state of knowledge regarding manufactured nanomaterials (engineered nanomaterials), which from here on will be referred to as nanomaterials.

Nanomaterials

This chapter will provide an introduction to the concept of nanomaterials and how the term is used in the report. Thereafter, the different types of nanomaterials and the most common groups of nanomaterials will be presented.

Definition

There is currently no official definition of nanomaterials. In 2011, the EU adopted a recommendation for a definition of the term 'nanomaterial' (2011/696/EU), as shown in the blue box below. This is also the definition that will be used in this report.

Definition

Nanomaterial means a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm-100 nm.

Categories of nanomaterials

Nanomaterials can take on different forms, such as tubes, fibers, flakes or spheres (Swedish Chemicals Agency, 2019; Gottschalk et al., 2015). They can be divided into groups depending on their physical and chemical properties, as well as on size, shape and structure (Ijaz et al., 2020; Kahn et al., 2017). Based on these characteristics, this section provides a brief introduction to different categories of nanomaterials. Table 1 shows an overview of common structures for nanomaterials (Swedish Chemicals Agency, 2009).

Table 1. Examples of common structures for nanomaterials.

Structure	Definition
Nanomaterial	A nanomaterial is a natural, incidental, or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1-100 nm.
Nano surface	A material with one dimension that is of nanomaterial length (1-100 nm) and another dimension that is extended to flakes, thin film or coating.
Nanoporous material	The material is larger than a traditional nanomaterial but contains cavities that are nanosized.
Nano rod (nanotube, nanofiber)	A material that have two dimensions that are in the range 1-100 nm and which is extended in the third dimension.

Shown below are some of the most common groups of manufactured nanomaterials.

Carbon-based nanomaterials

Carbon-based nanomaterials are usually divided into three groups: fullerenes, carbon nanotubes and graphene (Zuverza-Mena et al., 2017), as described in Table 2.

Table 2. The three most common groups of carbon-based nanomaterials: fullerenes, carbon nanotubes and graphene and their uses.

Group	Description
Fullerene	Sphere-shaped nanomaterials containing 28-100 carbon atoms (Swedish Chemicals Agency, 2009) are called fullerenes. They are hollow, or have several cavities, making them strong, pressure resistant and light. The hollowness also makes them potentially suitable for transporting other chemicals, such as pharmaceuticals (Swedish Chemicals Agency, 2009). Fullerenes can be used as catalysts, and their electrical properties make them suitable for use in electrical applications. Other areas of use include fillers, gas adsorbents for environmental remediation and as a support medium for catalysts (Kahn et al., 2017).
Carbon nanotube (CNT)	Carbon nanotubes are tubes of carbon atoms. Their diameter is only 1 nm, but the length can be several thousand nm (Swedish Chemicals Agency, 2009). Carbon nanotubes can be packed into rods or wires. The carbon atoms can be arranged in layers that are rolled up into tubes, which subsequently can be inserted into one another. Carbon nanotubes are known for their strength and low weight as well as their electrical and heat conductive properties. Carbon nanotubes are used in many different areas and industries, for

	example in flat screens, marine paints, sports equipment such as skis, hockey sticks, baseball bats, batteries and electronics (Greenlane, 2017).
Graphene	Graphene is a nanomaterial consisting of a carbon atoms arranged in a hexagonal honeycomb lattice. Graphene has a high flexibility and a large specific surface area (Swedish Chemicals Agency, 2016), and has a strength stronger than steel. It also has excellent thermal and electrical conducting properties. The material can be used in coatings, sensors, and simpler energy storage products.

Metallic nanomaterials

Metallic nanomaterials consist of pure metals (e.g., gold (Au), platinum (Pt), silver (Ag), titanium (Ti), zinc (Zn), cerium (Ce), iron (Fe) and thallium (Tl) or their inorganic compounds (e.g., oxides, hydroxides, sulfides, phosphates, fluorides, and chlorides) (Zuverza-Mena et al., 2017). Table 3 shows an overview of some of the most common metals that exist in nanoform and their compounds. Metal nanomaterials are usually shaped like surfaces or particles and consist of for example elemental gold or silver, or metal oxides such as titanium dioxide (Swedish Chemicals Agency, 2009). Their properties are dependent on the surface-area-to-volume ratio. Many metallic nanomaterials have unique optoelectronic properties (Swedish Chemicals Agency 2009; Kahn et al., 2017). Nanomaterials of alkali or noble metals such as copper, gold and silver have a broad absorption band of the electromagnetic spectrum. Due to these optical properties, metal nanomaterials are currently used in different applications and in numerous research areas (Kahn et al., 2017). For example, titanium dioxide and zinc oxide are suitable for use in transparent sunscreens, since they reflect UV light but does not interact with visible light. Another application is nanosilver, which has antibacterial properties and can be used on textiles to avoid bad odors. Other metals and metal oxides can be used to form nanospheres or nanorods that can be used as lubricants, catalysts, or energy storage (Swedish Chemicals Agency, 2009).

Table 1. Common metals present in nanoform and examples of common inorganic compounds.

Name	Chemical symbol	Examples of compounds present in nanoform
zinc	Zn	ZnO
iron	Fe	Fe_2O_3, $FeOOH$, Fe_3O_4
copper	Cu	CuO
silver	Ag	AgO, Ag_2S
gold	Au	-
cerium	Ce	CeO_2
titanium	Ti	TiO_2

Polymeric nanomaterials

Due to their variation in functionality, polymeric nanomaterials have numerous applications (Kahn et al., 2017). They are mainly consisting of a polymeric core, on which other compounds can be adsorbed or entrapped within (Zielińska et al., 2020). These additional compounds can provide the nanomaterial with different functionalities and as well as new reaction pathways.

Polymeric nanomaterials are excellent for surface treatment (Swedish Chemicals Agency, 2009). They can also be synthesized as nanoporous materials, providing a possibility to include other materials such as pharmaceuticals or metals within them (Kahn et al., 2017; Swedish Chemicals Agency 2009). Polymeric nanomaterials can also have a fiber shape that can be used to create for example wrinkle free or stain resistant textiles.

Nanocellulose is another type of polymeric nanomaterial. It is extracted from wood fiber and has exceptional strength characteristics (Pasaoglu and Koyuncu, 2020). For example, nanocellulose can be used to reinforce paper and cardboard. It has applications in surface bonding and coating, or as a barrier material in packaging. Additionally, nanocellulose is also used as a thickening agent in food.

Ceramic nanomaterials

Ceramic nanomaterials are inorganic non-metallic substances synthesized via heating and subsequent cooling (Kahn, et al., 2017). Ceramic nanomaterials can be amorphous, polycrystalline, dense, porous, or hollow (Sigmund et al., 2006). Due to their variation in form, these nanomaterials have been widely used in research. Currently, they are used in applications such as catalysis and photodegradation of dyes (Kahn et al. 2017).

Lipid-based nanomaterials

Lipid-based nanomaterials are often sphere shaped materials with a solid lipid core surrounded by a matrix of lipophilic molecules. These nanomaterials are used in detergents and surfactants, as well as in biomedical applications. Currently, biomedical research is being conducted on how these particles can be used as drug carrier and for delivery of active substances, for example in cancer treatment (Kahn et al., 2017).

Semiconductor nanomaterials

Semiconductor nanomaterials such as silica possess properties between those of metals and non-metals (Kahn et al., 2017). Therefore, they have a wide range of applications, such as in photocatalysis, photo optics and in electronic devices.

Advanced nanomaterials

The development of nanomaterials is rapid. The development has moved from the so-called simple nanomaterials described in the above six examples to more complex assembly structures (Camboni, et al., 2019; Teunenbroek et al., 2017). In Swedish, these nanomaterials are referred to as complex nanomaterials or next generation nanomaterials. In English, they are usually referred to as advanced materials or advanced nanomaterials. Advanced nanomaterials are distinguished by the fact that they usually increase in complexity and may contain a variety of substances and nanomaterials.

Applications of nanomaterials

As previously mentioned, nanomaterials have a variety of applications. They are often used in coatings, such as paint and solvents, in pigments, as catalyst additives and in cosmetics and other similar products (Personal Communication, Markus Ifverberg, Swedish Chemicals Agency, 2020-12-07). Figure 1 shows an overview of areas where nanomaterials are used. Common applications for nanomaterials are surface treatments and coatings (e.g., self-cleaning surfaces and paint), adhesives, sealing and filling materials, functional materials (e.g., sporting goods, cutting tools, polymer-based articles, fibers and textiles), electronics and appliances, cosmetic and hygienic products, pharmaceuticals and alternative medicine, pigments, biocides, and in energy and chemical applications (e.g., catalysts and in solar cells). For many of the products, it is possible that nanomaterials are released to the environment in all steps of their life cycle.

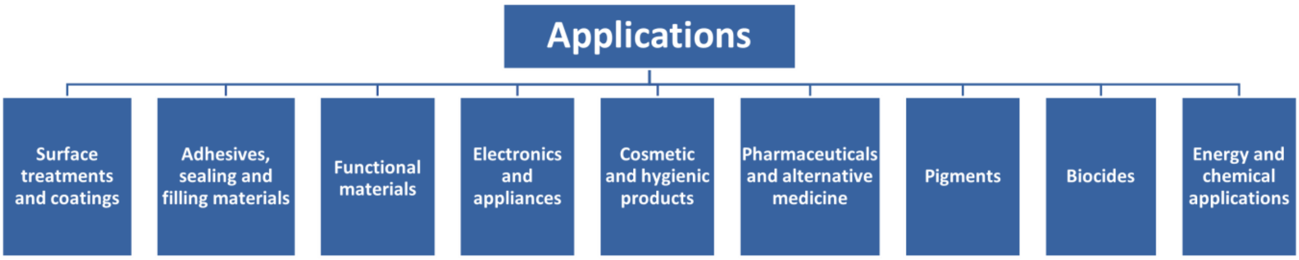

Figure 1. Different areas of use for nanomaterials.

Swedish Chemicals Agency's Products Register

Previously, no data on which chemical products that contain nanomaterials was available in Sweden. Since 2019, products containing nanomaterials that have been intentionally added to a classified chemical product must be reported to the Swedish Chemicals Agency's Products Register. The physical and chemical properties of the nanomaterial, such as function, particle size, shape, crystal structure, surface area, surface treatment and surface charge must be reported to the Products Register. To date, just under a thousand products containing nanomaterials have been registered. The most common product types containing nanomaterials are (in descending order): raw materials for plastics and rubber, paints (including pigments), sealants and fillers and binders. The most common substances are titanium dioxide, silicon, silica compounds and carbon black. An overview of products that are containing nanomaterials as reported by sector, is shown in Figure 2.

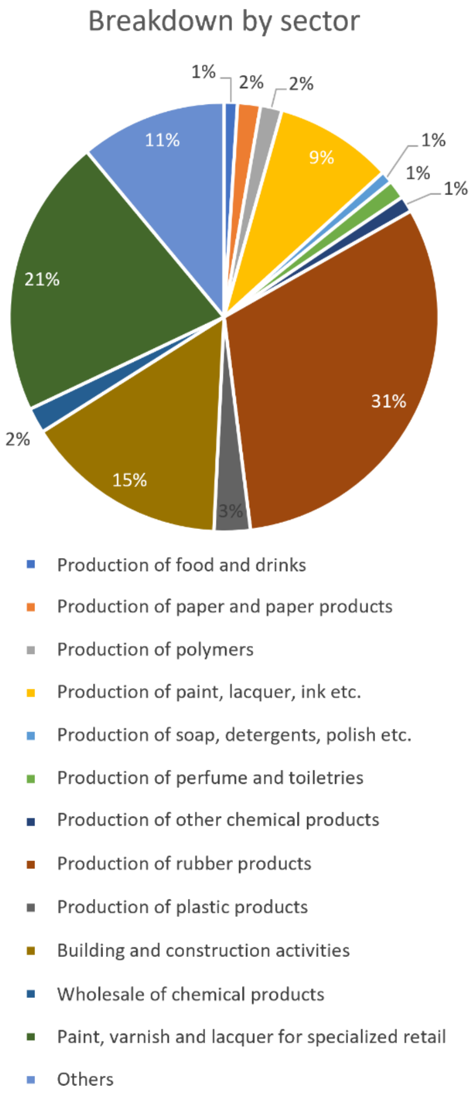

Figure 2. The distribution of chemical products with registered content of nanomaterials (N=989). (Swedish Chemicals Agency's Products Register, 2021).

Release of nanomaterials to the environment

Nanomaterial emissions can occur during the entire life cycle of the nanomaterial. This chapter addresses the sources of emissions of nanomaterials and current state of knowledge about the quantities and volumes of nanomaterials emitted to the environment. Furthermore, a description of how nanomaterials can be transported in various environmental matrices such as water, air and soil will be given as well as more detailed information on the presence of nanomaterials in different environmental matrices.

Emission sources

Sources of emission of nanomaterials to the environment may be natural sources or sources derived from human activity (Kabir et al., 2018). Nanomaterials originating from human activity can either be manufactured nanomaterials or secondary nanomaterials. Nanomaterial emissions from natural sources arise from for example forest fires, volcanic eruptions, sandstorms, or soil erosion. The release of nanomaterials from human activity can be both intentional and unintentional. Intentional emissions of manufactured nanomaterials occur due to the utilization or landfilling of products in which nanomaterials have been added to achieve specific properties. For example, this occurs when contaminated water is purified (Kabir et al., 2018; Gottschalk et al., 2015). Unintentional emission of manufactured nanomaterials can take place via technical systems such as from wastewater in treatment plants, from sewage sludge in agriculture, or leakage from landfills. Unintentional emissions of secondary nanomaterials could take place through human activities such as combustion, demolition, extraction of raw materials, or through automobile traffic (Kabir et al., 2018).

As the use of nanomaterials in products and applications is increasing, emissions to the environment are also expected to increase (Bundschuh et al., 2018). When nanomaterials are released to the environment, there is the risk of accumulation or transformation in different matrices such as soil, water, air, or sediment (Kabir et al., 2018). This is described in the section "Accumulation in different environmental matrices". The probability of a nanomaterial accumulating in the environment increases with its stability. Manufactured nanomaterials can be emitted throughout all steps of their life cycle (Figure 3). Thus, they affect the environment from the production to the waste stage (Arvidsson, 2015; Bundschuh et al., 2018).

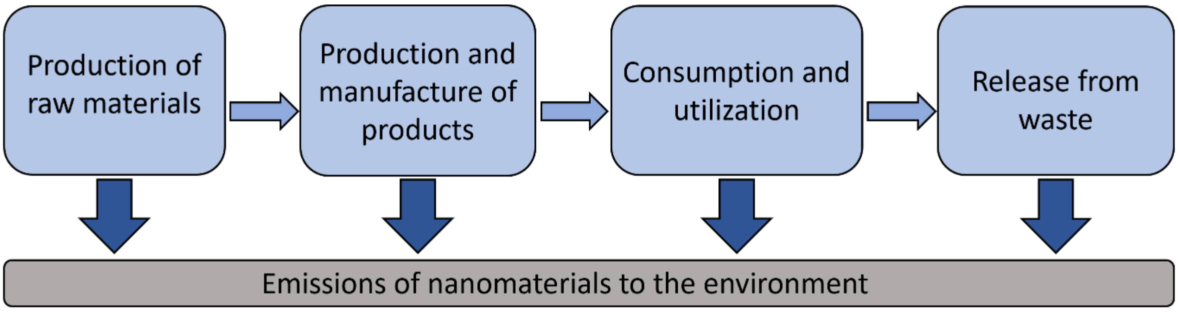

Figure 3. Overview of the different life cycle steps of a nanomaterial or product containing nanomaterials where emissions of nanomaterials can occur. Emissions of nanomaterials can occur throughout the entire life cycle.

Accumulation in environmental matrices

The fate of a nanomaterial in the environment includes different processes, with the main ones being dispersion, degradation (chemical, physical or biological), transformation and/or accumulation in different environmental matrices such as air, water, soil, and sediment. Figure 4 shows an overview of how nanomaterials are dispersed and transported in the environment.

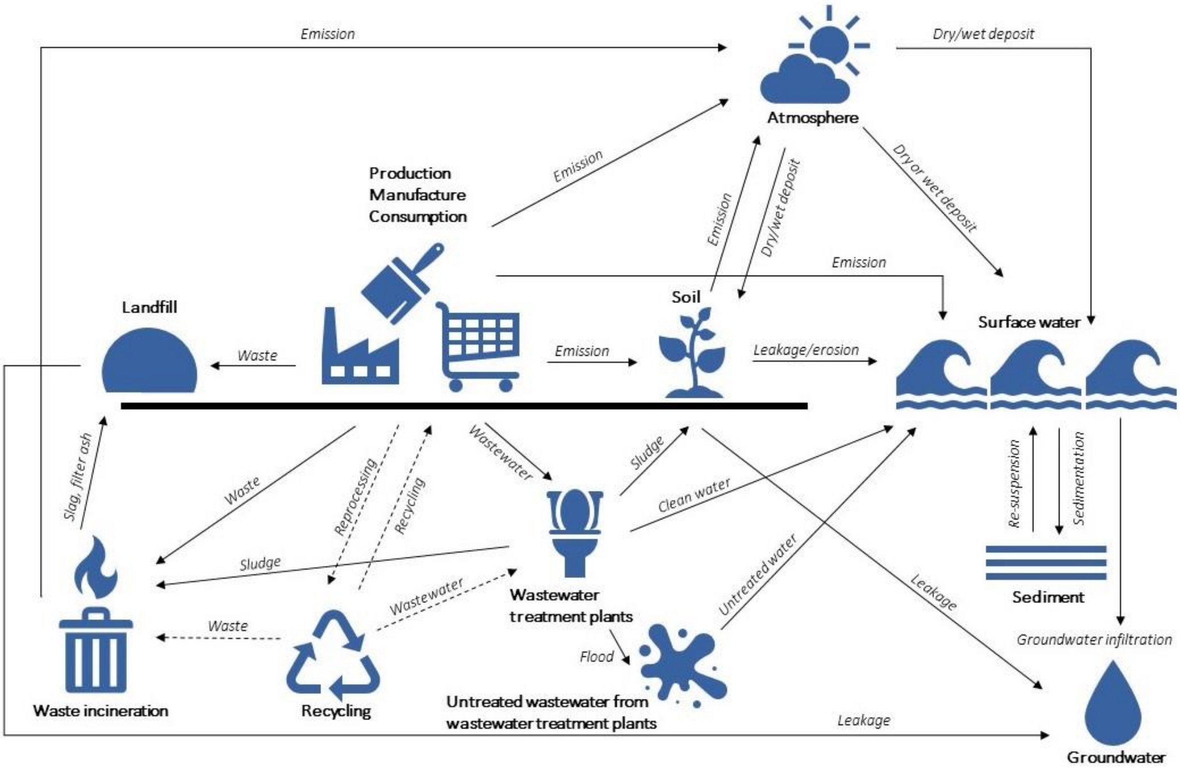

Figure 4. Overview of the flow of nanomaterials in different environmental matrices. The arrows show how nanomaterials are transported between matrices and possible pathways based on their properties and environmental conditions. From the steps production, manufacture, and consumption in the middle of the figure, nanomaterials can be emitted into air, soil, surface water, wastewater or deposited as waste. From the air, nanomaterials can be deposited by dry or wet deposit on soil or surface water. If the nanomaterial ends up in surface water, it can sediment, or accumulate in the groundwater. If a nanomaterial reaches the ground, it can be absorbed by plants or reach the sediment or groundwater by seepage or erosion. If a nanomaterial ends up in wastewater, it reaches wastewater treatment plants. Through that pathway, it can be transported to various matrices such as soil, surface water, or to waste incineration. The figure is a compilation from several sources i.e. Batley et al., 2013, Shrivastava et al., 2019 and Gottschalk et al., 2015.

Water

A few examples of sources of nanomaterials in the aquatic environment are industrial emissions and dumping of wastewater. Furthermore, runoff from soil, from construction materials or from asphalt and similar surfaces can also be sources of nanomaterials (Kabir et al., 2018). Release of purified water from wastewater treatment plants have previously been identified as one of the major sources of nanomaterials in the environment (Schwirn and Völker, 2016). However, studies of wastewater treatment plants show that less than ten percent of the nanomaterials that pass through the treatment plant reach the recipient, in this case bodies of surface water (Schwirn and Völker, 2016).

The fate of nanomaterials that end up in water is influenced by different factors, such as aggregation, accumulation, diffusion, interaction with other compounds (and aquatic organisms) and biodegradation (e.g., aerobic, anaerobic, photolysis and hydrolysis) (Abbas et al., 2020).

Most commonly, nanomaterials in water aggregate with other substances depending on several factors (Kabir et al., 2018). On one hand, aggregation depends on properties of the particles (size, type, and surface properties), and on the other hand on the matrix (ionic strength, pH and dissolved organic carbon content). When nanomaterials aggregate, it can lead to reduced reactivity. The reason is that the surface area, and therefore bioavailability, decreases. This can lead to changes in toxicity. Generally, a reduced surface area will lead to a reduced toxicity.

Previous studies have reported several adverse effects in aquatic organisms (e.g., DNA damage, mortality, oxidative stress and growth reduction) due to exposure of nanomaterials. However, these studies were performed as acute laboratory exposure tests and do not reflect the complex conditions in a real ecosystem. Organisms in ecosystems are continuously exposed to several different nanomaterials (Kabir et al., 2018). More details on the effects on living organisms are described in the section Ecotoxicological Effects.

Earth

Nanomaterials accumulate in soil from various sources and through different exposure routes, such as from fertilizers, sewage water, sludge effluents or floodplains (Kabir et al., 2018). Soil is a complex matrix consisting of several layers of components. For example, it contains various organisms, as well as organic and inorganic substances that can exist in gaseous, solid, or liquid state. Studies conducted at wastewater treatment plants show that 90 percent of the nanomaterial accumulates in the sludge (Schwirn and Völker, 2016). In Sweden, 34 percent of all sewage sludge is used in agriculture (SOU 2020:3). The sludge released to agricultural systems is a potential source of emitted nanomaterials (Besha et al., 2020).

Carbon and metal nanomaterials can accumulate in sediments and biosolids in agricultural soil (Zuverza-Mena et al., 2016). Commonly known as aggregation, nanomaterials pass through the pores of the soil and attach to soil particles with large surface areas. Large aggregates of nanomaterials can be immobilized due to their size when filtered through the soil (Kabir et al., 2018). The mobility in soil depends on several variables, such as physical and chemical properties, how they interact with other substances in the soil, soil properties and ambient environmental conditions. Previous studies have reported that plants can absorb nanomaterials from the soil. This can affect growth and photosynthesis, among other things (Schwirn and Völker, 2016; Zuverza-Mena et al., 2017). The fact that nanomaterials are absorbed by plants allows them to enter the food chain (Shivastava et al., 2019). Studies have also shown adverse effects on the biodiversity of terrestrial organisms caused by nanomaterials (Kabir et al., 2018; Schwirn and Völker, 2016).

Air

Throughout the whole life cycle from production, processing, transport, handling and application to the final phase of a nanomaterial, emissions to the surrounding air can take place (Kabir et al., 2018). The most observed metals in air include sodium, calcium, potassium, aluminum, iron, chromium, nickel, titanium, and zinc (Sanderson et al., 2014).

Emission of nanomaterials during incineration in waste facilities depends mainly on the group to which the nanomaterial belongs (Kabir et al., 2018). It is known that metals such as antimony, cadmium and lead are emitted at combustion plants, and these three metals have therefore previously been used as markers for emissions (Sanderson et al., 2014). Organic nanomaterials are usually completely incinerated (Kabir et al., 2018).

However, a Danish study from 2015 showed that there is no evidence that manufactured nanomaterials are emitted during combustion. The reason is that the purification of flue gases today is very well developed (Gottschalk et al., 2015). There are studies on how nanomaterials such as CeO_2 and TiO_2 behave in a waste incineration plant. This data indicated that the nanomaterials that are not completely incinerated mainly accumulate in the slag and fly ash (Walser et al., 2012). Only negligible amounts are released into the air (Schwirn and Völker, 2016).

Exposure to UV radiation likely contributes to airborne nanomaterials undergoing photochemical changes (Kabir et al., 2018). When nanomaterials are released into the air, they are exposed to sunlight and UV radiation to a greater extent than nanomaterials emitted to other matrices (Kabir et al., 2018). UV radiation affects how the nanomaterial is transformed in the atmosphere. Nanomaterials can undergo various types of transformations in the atmosphere. Compounds with low volatility can condense, while other nanomaterials can increase in size by adsorbing water or other volatile substances.

Sources of emission of nanomaterials

Table 4 presents sources of nanomaterials in the environment. For each source, the type of nanomaterial, where it can be found, the exposure pathway and potential impact on the environment is described.

Source	Examples	Biota	Possible exposure pathway	Potential environmental problems
Loss during the production of nanomaterials [a]	Metal, metal oxide, carbon-based nanomaterials etc.	Aquatic and terrestrial organisms.	Emissions to air and through wastewater. Through the air, the nanomaterial reaches soil and surface water. The wastewater can be transferred to an external treatment plant or taken care of in the industry's own treatment plant.	Transfer of wastewater to a municipal treatment plant can affect the nitrogen cycle in the wastewater treatment plant.
Sludge incineration [a]	Nanomaterials in the form of ash and slag (e.g., nano CeO_2, TiO_2, SiO_2 and CNT)	Aquatic and terrestrial organisms.	Transport of slag or ash. Emission of nanomaterials to the atmosphere, which subsequently are deposited in water and soil.	If the nanomaterial ends up in soil, it can affect soil bacteria. Environmental issues arise if the slag is used for e.g., road construction (i.e., potential leaching).
Sludge dispersion in fields/biosolids (organic soil improver) [a]	Nano Ag, ZnO, TiO_2, etc.	Aquatic and terrestrial organisms.	Via use of biosolids for agricultural purposes, nanomaterials can reach the soil and be absorbed by plants. In	Negative effect on the diversity of bacterial communities, reduced activity of soil bacteria and growth of crops. As

			addition, nanomaterials can seep into groundwater.	crops grow, they can absorb nanomaterials and potentially pollute the food chain for both humans and animals. However, Ag is often found as Ag_2S and ZnO as ZnS in sludge, which are less toxic forms. Nanomaterials can accumulate in the soil which reduces their mobility.
Nano-agricultural chemicals (e.g., nanofertilizers, nanobiocides and nanopesticides) [a]	Kitosan, Ag, nanocapsules, ZnO, Fe etc.	Terrestrial and aquatic organisms.	Nanomaterials can disperse during spraying with nano-agrochemicals. In case of rain, nanofertilizers can be washed away to surface water or leached to the groundwater.	Nano-agrochemicals can be absorbed by plants and have harmful effects on growth, such as affecting the roots of the plant.
Incoming wastewater [a]	TiO_2, ZnO, CeO_2, Ag, fullerenes etc.	Micro-organisms.	Personal care products such as skincare and cosmetics, detergents and other cleaning products, textiles during washing, surface run-off of spilled lubricants, oils fuels and emissions from paints.	Laboratory-scale experiments have shown that nanomaterials affect different processes in wastewater treatment plants, such as the nitrogen cycle and the removal of phosphorus.
Outgoing wastewater [a]	TiO_2, ZnO, CeO_2, fullerenes etc.	Aquatic organisms.	After treatment, wastewater is released to the surface water.	If nanomaterials reach watercourses, they can affect aquatic animals. Indirectly, they can also have harmful effects on terrestrial animals.
Airborne nanomaterials [a]	TiO_2, ZnO, CeO_2, Ag, Au etc.	Atmospheric organisms. Indirect impact on terrestrial and aquatic animals.	For example, nanomaterials can leak from industries or from ash from burning fossil fuels. Aerosols can contain nanomaterials can that are transported when sprayed indoors.	Airborne nanomaterials can be inhaled or end up in watercourses and subsequently affect fish and microorganisms.

Cosmetics and hygiene articles [(a), (c)]	TiO_2, ZnO etc. All products containing nanomaterials.	Mainly aquatic organisms, but also airborne and terrestrial organisms.	For example, hygiene products and cosmetic cleansers can leak into wastewater and watercourses etc. When using sunscreen, nanomaterials can be released in seas and watercourses, especially close to beaches.	Treated and untreated waste adversely affects both humans and ecological systems (fish, wildlife). UV filters containing nanomaterials can cause birth defects and affect hormone levels. They are non-biodegradable and can accumulate in food chains.
Industrial wastewater [b]	TiO_2, ZnO, CeO_2, fullerenes etc.	Terrestrial and aquatic organisms.	At production plants for paints and varnishes, nanomaterials can end up in the production's internal wastewater treatment system. In the first stage of sewage treatment where flocculation/ settling takes place, nanomaterials are precipitated and end up in the sewage sludge, which thereafter often is incinerated. Nanomaterials that do not end up in the sludge will be transferred to the municipal treatment plant or released to the recipient.	If nanomaterials reach watercourses, they can affect aquatic animals. Indirectly, they can also have harmful effects on terrestrial animals.

[a] Besha et al., 2020

[b] Gottschalk et al., 2015

[c] Labille et al., 2020

Quantities

Estimation of emissions and evaluation of volume of nanomaterials (mainly nanoparticles) in the aquatic environment has so far been impeded by the lack of appropriate analytical techniques. This is described in more detail below in the section "Analytical methods" (Bundschuh et al., 2018). In the absence of practical analytical methods for estimating the quantity of nanomaterials in the environment, computational modeling is often used. Material flow models depend on information about the life cycle and production volumes of nanomaterials. Detailed information on this is not always available, which leads to limitations in the calculations and models (Bundschuh et al., 2018).

Emissions and concentrations of nanomaterials in the environment have been calculated with the use of material flow modelling for the whole life cycle of a nanomaterial. By using the production volume of specific nanomaterials, it is possible to make a reasonable assumption on how much of a specific nanomaterial is released to the environment (Bundschuh et al., 2018). Emissions of nanomaterials have been estimated globally based on production volumes. This estimate indicates that landfills receive the largest share of emissions from production volumes (63-91%), followed by soil (8-28%). Aquatic systems receive nanomaterial emissions corresponding to 7% of emissions from production volumes and air receives emissions corresponding to 1.5% (Bundschuh et al., 2018). In Sweden, however, landfilling is an unusual as well as undesirable method for final disposal of waste and most of the Swedish waste is incinerated (Swedish Environmental Protection Agency, 2019). A negligible part of the nanomaterial incinerated is expected to be released to the air (Gottschalk et al., 2015). Most of it ends up in the slag/ash, which later is deposited or used as a filler (Walser et al., 2012).

Of the published material flow model, a large number are static models and do not include time-dependent processes regarding the use and release of nanomaterials (Gottschalk et al., 2015). Existing models only include the production, manufacture and consumption of products containing nanomaterials over one year. Thereafter, the quantities are distributed across the whole the system over the relevant year. They also assume that all nanomaterials produced and emitted into waste streams and released in environmental matrices do so in the same year as they enter the system. No form of storage or accumulation is considered. With these two simplifications, the models are not representative of real conditions. The production of nanomaterials is increasing and storage takes place during the use phase, resulting in flawed models. With the models being static, they do not take concentration sinks in soil or sediment into account. More realistic models of the flows of nanomaterials in the environment are required. The models also need to consider that the environment can be dynamic. As long as it is not possible to quantify nanomaterials at natural concentrations and distinguish them from the natural (background) particles, modeling is the only available method of gaining information on exposure (Sun et al., 2016).

Knowledge Gaps

- Many academic publications concern toxicity, mobility and transformation of nanomaterials in the aquatic environment. There are also several publications on nanomaterials in soil. However, publications examining toxicity, mobility or transformation in air are rare. As nanomaterials occur as an air pollutant, more research is needed in this area.
- Nanomaterials used in products that become waste end up in our waste system. There is a lack of data on nanomaterial-containing products in Sweden and on how nanomaterials flow affect the end-use phase. Research is needed on what happens to nanomaterials in the final handling phase and when emissions to the environment from nanomaterial-containing waste takes place.
- Today, there is an estimate of actual or potential sources, emission pathways and processes that lead to environmental exposure. However, many are based on assumptions, rather than scientific evidence. More research on actual conditions is needed. Analytical methods are also required to map actual concentrations of nanomaterials in the environment to verify the accuracy of the models.
- Emissions and concentrations in the environment are currently estimated using material flow models based on assumptions of the life cycle of a nanomaterial. Differences between the models used make comparisons difficult. For increased reliability, better statistics from material flow models and estimated emission quantities of nanomaterials to the environment are required. A uniform way of modelling quantities and flows needs to be developed.
- Nanomaterials can be used in a variety of goods and chemical products. There is limited knowledge on how much nanomaterials our society uses, and in which products they are used. More data is required on which products contain nanomaterials, and on the volumes of nanomaterials circulating in society. This will assist in developing reliable models that can estimate concentrations of nanomaterials in different environmental matrices.

Analytical methods

Analysis, that is being able to detect and quantify nanomaterials in different environmental matrices, presents a major challenge (Shrivastava et al., 2019). In this chapter, we review the current challenges for analysis of nanomaterials in environmental matrices.

Despite the technological development, analytical methods to detect and quantify nanomaterials in environmental matrices are very limited (Baysal och Saygin, 2020). The methods available have mostly been used in laboratory or bench scale setting (Zhang et al., 2019; Abdolahpur et al., 2019). It is important to improve and develop analytical methods that are able to analyzenanomaterials in different environmental matrices. Suitable and reliable analytical methods are also fundamental to the understanding of how and to what extent nanomaterials are dispersed in the environment. Furthermore, it is a requirement for assessing the threat of nanomaterial emissions to the environment. Several scientific review articles have outlined the analytical methods for nanomaterial analysis (for example Zhang et al., 2019; Shrivastava et al., 2019; Rauscher et al., 2019 and Rasmussen et al., 2019). Figure 5 shows an overview of areas where analytical methods are needed for detection of nanomaterials in the forms they occur in the environment. Some of the challenges related to analysis of nanomaterials in the environment are described in the following.

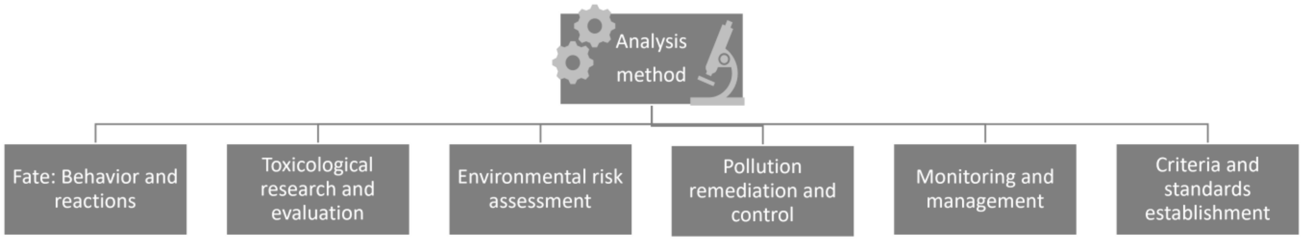

Figure 5. Overview of areas that require analytical methods. Image modified from Zhang et al., 2019.

Challenges in analyzing nanomaterials in the environment

As both size and concentration of nanomaterials often are below the detection limit of many methods, there are apparent limitations to the existing techniques (Zhang et al., 2019). Different techniques may need to be used to concentrate nanomaterials prior to analysis, for example through extraction, sedimentation or filtration. When using these techniques, it is important to remember that nanomaterials often coexist with other components in matrices, such as organic matter, colloids, or particles. Both organic and inorganic pollutants can interfere with the analysis of the nanomaterial. Sometimes, chemical agents are used to concentrate the nanomaterial in the sample. If chemical agents are added prior to nanomaterial analysis, the chemicals could change the surface chemistry of the nanomaterial, which subsequently could affect the outcome (Zhang et al., 2019).

Even if a nanomaterial is detected in the environment, there are difficulties in distinguishing naturally occurring nanomaterials from manufactured nanomaterials (Schwirn and Völker, 2016; Yi et al. 2020). One of the most common nanomaterials is TiO_2, which is often used in engineered nanomaterials (e.g., 1-100 nm) and as pigments (e.g., 100-300 nm) (Wang et al., 2020). One challenge in determining concentrations of TiO_2 nanomaterials in environmental matrices is the complexity in distinguishing natural from manufactured TiO_2 nanomaterials. However, there are methods to determine the origin of the nanomaterial. For example, engineered TiO_2 particles can be identified by mass balance calculations based on shifts in elementary concentration ratios, or by transmission electron microscopy coupled with energy dispersive spectroscopy (Wang et al., 2020).

In 2019, Zhang et al. published an overview article on the status and the challenges associated with the detection of nanomaterials in water. The article concludes that there are no reliable methods for measuring nanomaterials at potential emission sites (Zhang et al., 2019). Analytical methods need to be improved to adapt to real aquatic environments, such as freshwater, sewage and industrial wastewater. These environments have different compositions of background compounds, pH and ionic strength among other factors that need to be considered (Zhang et al., 2019).

Since the size and shape of the nanomaterial largely determine its toxicological properties, analytical methods to identify the physiological properties and their distribution in matrices are important. Today, a range of analytical technologies are used for the characterization of nanomaterials and their toxicological and ecotoxicological properties. However, there is a demand for technologies that can determine both physical and chemical properties of nanomaterials in soil, plants and living organisms simultaneously.

One report that outlines the difficulties in quantifying nanomaterials in solid samples such as soil and sediment was published by Schwirn and Völker in 2016. In most cases, nanomaterials are not directly detectable using existing analytical methods. This is due to the very low concentration. Additionally, even if detected, it is difficult to distinguish engineered nanomaterials from naturally occurring nanomaterials (Schwirn and Völker, 2016).

UV radiation can be an effective way to promote degradation of organic materials in soil. These substances could otherwise interfere with the analysis of nanomaterials (Gao et al., 2020). Gao et al. (2020) has developed an SP-ICP-MS based method for extracting gold nanomaterial (AuNP) from soil and sediment. UV radiation was used to degrade organic materials to improve the recovery of AuNP. It is otherwise difficult to extract nanomaterials from soil and a prerequisite is that the nanomaterial itself does not decompose or transform in the extraction process.

An article by Abdolahpur et al. from 2019 describes difficulties in measuring and tracking nanomaterials in living organisms (Abdolahpur et al., 2019). The tracking of nanomaterials is a requirement to understand the fate and behavior in living organisms.

Air

There are analytical methods that can quantify particles in air. These methods can in some cases detect fractions of nanomaterials. These fractions must be processed before the type of nanomaterials can be determined (Baysal and Saygin, 2020). Even when nanomaterials are detected in air, there are challenges in distinguishing manufactured nanomaterials from natural nanomaterials (Schwirn and Völker, 2016). Today, there are technologies for identifying nanomaterials in air. However, many of these are still at laboratory stage and cannot be used in the field. An overview is shown below. For more information about each technology, see Baysal and Saygin (2020).

- Spectroscopy and spectrometry can be used to identify properties of the nanomaterial, such as size and composition. Examples of analytical methods are ICP (Inductively coupled plasma), X-ray and laser.
- Microscopy can be used to identify shape, size, concentration, and composition. Common methods are TEM (Transmission electron microscopy), SEM (Scanning electron microscopy), HRTEM (High-resolution transmission electron microscopy), SPrM (Scanning proton microscopy) and AFM (Atomic force microscopy).
- Light scattering can be used to detect different nanomaterials or large numbers of nanoparticles in a sample. The light scatter detection technology is suitable for determining size, surface properties and particle size distribution in the sample. Analytical methods for this are Dynamic light scattering (DLS), Static light scattering (SLS), Nanoparticle tracking analysis (NTA).

- Different methods are used to detect nanomaterials in air or heterogeneous environments. This is a true challenge and there is a need to develop sensitive and selective analyses to detect nanomaterials in heterogeneous environmental matrices. Today, mainly mass spectrometry (MS) is used, which can be used for analyzing both organic and inorganic materials.
- Electroanalytical technologies are a complementary to existing technologies such as spectrometry and microscopy. This technology is cost effective and can be used to characterize and detect nanomaterials in air. The method is suitable for the detection of nanomaterials of metals, metal oxides or quantum dots. For example, voltammetry of nanoparticles, voltammetry of immobilized nanoparticles or particle collision coulometer are common techniques.
- Sensors that measure nanomaterials can be grouped into either the transducing mechanism (e.g., optical, electrical, thermal) or the recognition principle (e.g., biological, enzymatic, molecular). Chemical sensors and biosensors are good for detecting toxins and chemical markers.

Research is currently underway to develop new methods for measuring nanomaterials in air. The focus is on developing electroanalytical based sensors and sample preparation methods based on mass techniques (Baysal and Saygin, 2020).

Knowledge Gaps

- There is a lack of standardized analytical methods for all environmental matrices. This makes it difficult to estimate the amount of nanomaterials in the environment and to compare different studies. The lack of reliable and standardized methods limit the possibilities of conducting relevant studies on nanomaterials in the environment.
- Due to their low concentration, nanomaterials are often not detectable in soil and sediment. In cases where we know that nanomaterials are in the matrix, standardized methods for determining concentration of nanomaterials are required.
- Today, it is not possible to distinguish engineered nanomaterials from natural nanomaterials in a matrix. This makes it difficult to analyze and quantify engineered nanomaterials in environmental matrices. There is a need to develop technologies to determine differences between natural and engineered nanomaterials.
- During sample preparation and analysis, it is difficult to retain the material in the form in which it is present in the matrix. It is desirable to determine both physical and chemical properties at the same time. Methods for analyzing primary nanomaterials are needed.

Fate and transformation processes

The fate of a nanomaterial in the environment depends on how the material interacts with other matter, as well as environmental factors (Schwirn and Völker, 2016). The intrinsic properties such as chemical composition, size, geometry, crystalline structure and surface properties (charge or surface chemistry) all play a role in determining the fate, bioavailability and toxicity of the nanomaterial (Schwirn and Völker, 2016; Abbas et al., 2020). Furthermore, abiotic factors such as pH, salinity, temperature, ionic strength, UV light and organic matter content are also important factors. If the nanomaterial is exposed to chemical, biological, or mechanical wear, the surface of it may change. All these factors affect how the nanomaterial interacts with the environment, as well as its mobility, bioavailability and ecotoxicity (Schwirn and Völker, 2016; Mortimer and Holden 2019).

This chapter describes the fate of nanomaterials in different environmental matrices. Thereafter, viable transformation processes are described in detail. The chapter also addresses several other factors that affect the fate and toxicity of nanomaterials in the environment.

Mobility of nanomaterials in environmental matrices

Mobility

The mobility and fate of nanomaterials in the environment depend on environmental factors such as ionic strength and concentration, pH and type as well as presence and concentration of natural organic matter in soil (Bundschuh et al., 2018). In porous media, water saturation also plays a role in the mobility and fate of nanomaterials.

The mobility of nanomaterials in ionic form is dependent on the ionic strength of the medium (Bundschuh et al., 2018). In porous media, the deposition rate of nanomaterials increases with increasing ionic strength of the pore water in the soil. When a nanomaterial aggregates or agglomerates, the nanomaterial forms larger particles. This usually results in a decrease in mobility. In general, larger and bulkier nanomaterials result in a reduced mobility. Therefore, nanomaterials that aggregate have lower mobility than when they occur freely or in ionic form. In soils containing aggregates of colloids, smaller nanomaterials have a higher mobility than larger nanomaterials, as the colloids allows for smaller nanomaterials to pass through. Furthermore, electrostatic attraction and repulsion from natural organic matter affect the mobility of nanomaterials. Depending on their charge, the mobility will increase or decrease. If pH decreases, the mobility of nanomaterials will generally decrease in porous media (Bundschuh et al., 2018).

Fate of nanomaterials in the atmosphere

Nanomaterials are often short-lived in atmosphere. Once there, they will undergo physical and chemical transformations. The transformation process that a nanomaterial undergoes determines the fate of the nanomaterial when it precipitates and is deposited in soil or water. In air, homo- and heteroaggregation of nanomaterials take place. Heteroaggregation is most common. Nanomaterials can also react with inorganic compounds such as sulphate, nitrite, and ammonia, or reactive organic materials. The concentration and particle size of nanomaterials in the atmosphere are affected by environmental factors such as temperature, pH, humidity, and wind. As a result, the fate is also affected. In the atmosphere, photochemical reactions can occur. They are mainly promoted by free radicals and UV radiation, which subsequently affects the transformation process of the nanomaterial. By adsorption of substances, the nanomaterial can grow and form large aggregates. Once the aggregates reach a certain size (100-2500 nm), they can remain suspended in the atmosphere for days to weeks. During this time, they can be transported long distances, such as from the Sahara to Europe (Abbas et al., 2020). Thus, the atmosphere can be seen as an important transportation pathway for nanomaterials.

From the atmosphere, nanomaterials are deposited in soil and water matrices through wet or dry deposition. The rate of dry deposition depends on several environmental factors. For example, the Brownian motion of particles in air and transfer between atmospheric interfaces governs the deposition. It is also affected by gravity and particle size. Studies from urban areas in Denmark have estimated the rate of dry deposition to be 20 hours for particle sizes of 40-50 nm. Other studies on particles in the range 100-1000 nm showed a deposition rate from a few hours to several days. Wet deposition through precipitation is an effective way for removal of nanomaterials to soil or water. The deposition rate is determined by the rate and type of precipitation, as well as the properties of the nanomaterial. The time scale for wet deposition by precipitation ranges from a few minutes to several hours (Abbas et al., 2020).

Once the nanomaterial has reached the earth's surface via deposition from the atmosphere, it can be returned to the atmosphere via wind. This occurs if the deposition takes place on an impermeable surface (such as a roof, rock, hardened surface such as asphalt or similar surface). Furthermore, nanomaterials can be washed away with rainwater and thus reach watercourses or soil. In soil and water, nanomaterials can subsequently be further transformed (Abbas et al., 2020).

Fate of nanomaterials in soil and water

When nanomaterials are released into soil or water, they can undergo various transformations. Possible transformation pathways could be homo- or heteroaggregation, dissolution, sedimentation, adsorption, oxidation, reduction, sulfidation, or photochemical and biological reactions. Their transformation affects their mobility, fate, and bioavailability for organisms.

Environmental factors such as acidic water or acidic soil can, depending on the surrounding environment, contribute to an increased release of ions from the nanomaterial. If a large amount of dissolved organic matter is present in an aquatic system containing nanomaterials, the dissolved organic material can create a coating on the nanomaterial. This can make the particle more stable, reducing the ecotoxicological potential as the reactive surface of the nanomaterial decreases. The same applies to nanomaterials that via heteroaggregation bind to particles such as organic matter, polyvinylpyrrolidone, rubber or citrate. This results in a reduced risk of the nanomaterial emitting ions and therefore, the bioavailability is reduced.

Transformation processes

Nanomaterials can undergo chemical, physical or biological transformation processes throughout their lifetime. In the environment, nanomaterials in their pristine form are often transformed when they end up in the environment (Abbas et al., 2020). Via what process they are transformed is determined partly by the properties of the nanomaterial and partly by the ambient environmental conditions (Mortimer and Holden 2019), see Figure 6. For many types of nanomaterials, it is difficult to predict their behavior in the environment. For example, silver can undergo different types of transformation processes. Silver nanomaterials can for example oxidize and emit ions, react with sulfur and form an insoluble coating or react with other complexes (Liu et al., 2010). After a nanomaterial has undergone a transformation process, the final product (e.g., silver nanomaterials in oxidized, sulfidized or complex form) determines the bioavailability and therefore also the toxicity (Ribeiro et al., 2014). For silver, it has been observed that the dissolution of nanomaterials and the release of silver ions are believed to be what leads to the highest toxicity (Ribeiro et al., 2014).

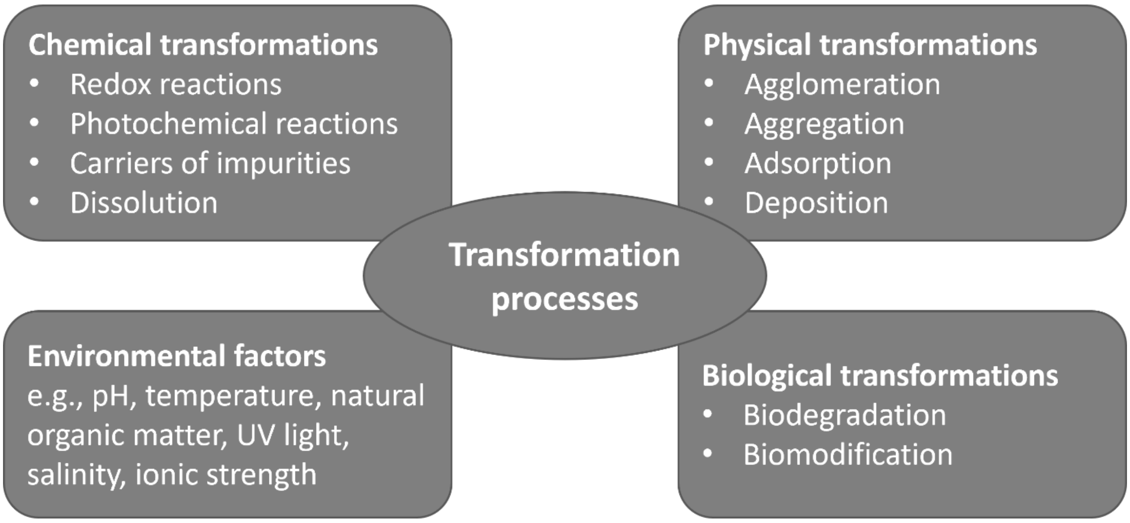

Figure 6. Different types of transformation processes that a nanomaterial can undergo in the environment and examples of environmental factors that affect the type of transformation process that will take place.

Chemical transformation

A nanomaterial can be chemically transformed via oxidation and reduction processes (redox reactions), dissolution, complexation, degradation, and photochemical reactions (Abbas et al., 2020).

Redox reactions

In the environment, nanomaterials can react through a redox reaction where electrons are gained or lost (Bundschuh et al., 2018). The rate and the probability of redox reactions taking place are determined by environmental factors such as pH and presence of redox active substances (Abbas et al., 2020). In well drained soils, the oxidation process is predominant while the reduction process is predominant in oxygen-poor environments such as groundwater and sediment. In some cases, an inert coating is formed around the nanomaterial (Abbas et al., 2020).

Dissolution and release of ions

When dissolution of nanomaterials in aquatic systems takes place, ions or molecules are released (Abbas et al., 2020). The solubility of nanomaterials differs. The nanomaterials with the highest solubility in water include silver/silver oxide, gold, copper/copper oxide, iron oxide, zinc/zinc oxide. Among nanomaterials with the lowest solubility in water are CeO_2 and TiO_2. Some nanomaterials are highly insoluble under natural conditions, such as CNTs, graphene and fullerenes. The rate of dissolution depends on solvent and concentration of the nanomaterial. Also the properties of the nanomaterial such as chemical composition, coating, geometry, size and surface area play a role. Furthermore, the properties of the environmental matrix such as pH, temperature and access to natural organic matter contribute to solubility. Natural organic matter react through complex reactions with metal ions. Low concentrations of natural organic matter induce disagglomeration and promote the dissolution of the nanomaterial.

Interactions with other chemical compounds

Ions released from the nanomaterial can be adsorbed on the surface of soil particles or form complexes with water. They can also form complexes with sulfides through a so-called sulfidation (Abbas et al., 2020). The interactions affect the toxicity and bioavailability of the nanomaterial. Sulfidation is common for nanomaterials such as nanoparticles of silver, ZnO and CuO (Bundschuh et al., 2018). When sulfidation occurs, the sulfide reacts with the nanomaterial leading to the formation of a core-shell around the nanomaterial by oxidative dissolution or oxysulfidation. The outcome is a hollow structure. Sulfidized metal nanomaterials have been identified in wastewater, aerobic and anaerobic sewage sludge and in wetlands and sediments (Abbas et al., 2020). When sulfidation of nanomaterials occurs, an almost completely inert surface of the nanomaterial is formed which reduces the reactivity and toxicity. However, sulfidized nanomaterials may still be toxic to microorganisms (Kraas et al., 2017).

Nanomaterials as carriers of impurities, the Trojan Horse

It seems that the presence of nanomaterials may affect the bioavailability and toxicity of other contaminants present in the environment (Abbas et al., 2020). Nanomaterials can act as carriers of other contaminants, leading to an increase in bioavailability and toxicity. Contaminants that due to low bioavailability were not available for uptake by organisms can now be transported into the organism using the nanomaterial. This phenomenon is referred to as the "Trojan Horse effect". Nanomaterials can act as carriers of organic and inorganic contaminants. Different types of contaminants such as radioactive elements, polychlorinated compounds, and pesticides can adhere to the surface of the nanomaterial and subsequently be co-transferred. Nanomaterials with contaminants adsorbed on the surface have been found in sediment, soil and water (Abbas et al., 2020). One example is the herbicide Diuron, which has been observed to have a higher toxicity when carbon-based nanomaterials are present. The same applies to the insecticide Bifenthrin, which in the presence of fullerenes have a higher acute toxicity. However, the chronic effects were not affected (Bundschuh et al., 2018).

Photochemically induced reactions

Photochemically induced reactions can affect the coating, oxidation state, production of free radicals and the persistence in the environment of nanomaterials (Abbas et al., 2020). Due to their photochemical activity, nanomaterials such as CNTs, fullerenes, TiO_2 and ZnO are often found in self-cleaning paints. These nanomaterials are also used in cosmetics and as UV blockers in sunscreen (Labille et al., 2020).

Physical transformation processes

Nanomaterials can undergo physical transformation processes such as agglomeration, aggregation, deposition, sedimentation, and adsorption (Abbas et al., 2020). Agglomeration can be described as assemblies of particles, aggregates, or mixtures that are held together by weak chemical bonds (van der Waals forces). Aggregation is when particles bind to each other with strong chemical bonds (covalent bonds) or through complex physical folds. The surface area of the aggregate is often significantly smaller compared to the surface area of the constituent particles.

Agglomeration, sedimentation and deposition

In the environment, only a small part of nanomaterials occur in their pristine form or as individual particles (Abbas et al., 2020). The reason is that they have a large specific surface area and therefore are prone to interact with other compounds. Nanomaterials interact with compounds such as clay, minerals, metals, oxides, or organic matter. When nanomaterials agglomerate or flock, the agglomerates increase in size and until they become too heavy and sediment or deposit. When the nanomaterial is deposited or sedimented, the concentration in soil or in an aqueous solution decrease. As a result of agglomeration, reactivity, bioavailability and toxicity of nanomaterials also decrease as their reactive surface becoming smaller and/or sterically hindered. The agglomeration is influenced by pH, ionic strength and by the size, shape, and coating of the nanomaterial.

Homo- and heteroaggregation

Homo- and heteroaggregation are examples of common fates for nanomaterials in the environment. Homoaggregation occurs when the same type of nanomaterials form aggregates (Bundschuh et al., 2018; Mortimer and Holden 2019). Heteroaggregation occurs when nanomaterials interact with other types of nanomaterials to form aggregates. Nanomaterials can also form heteroagglomerates with natural colloids such as montmorillonite, maghemite, kaolinite but also microorganisms, algae, and proteins. Since natural colloids are common in the environment, heteroaggregation is a common process. Heteroaggregation can be seen as an important process for removing nanomaterials from aquatic environments. Through this process, the steric hinderance of the nanomaterial increase, which decreases the toxicity. Furthermore, the size and weight cause sedimentation to a greater extent. Many nanomaterials sediment over time, and sedimentation is especially common for nanomaterials in aggregate structures (Bundschuh et al., 2018; Mortimer and Holden, 2019)

The proportion of nanomaterials that homoaggregate increases with the concentration of nanomaterials in the environmental matrix. This type of aggregation is less common in natural matrices. The reason is that the concentration of nanomaterials in the environment is rather low (Bundschuh et al., 2018). The rate of aggregation increases with the ionic strength of the medium, but it is also affected by environmental factors such as pH.

Adsorption

In soil, it has been observed that nanomaterials (inorganic and organic) can be adsorbed by microorganisms and form complex bio-geochemical surfaces (Bundschuh et al., 2018). This affects the toxicity and fate of the nanomaterial. However, the scientific basis is poor and only laboratory studies exist.

Biological transformation processes

Biodegradation and biotransformation are two common fates for nanomaterials in the environment. Biotransformation can be described as nanomaterials interacting with, or adsorbing macromolecules, forming an environmental corona around the nanomaterial (Abbas et al., 2020).

Biodegradation

The surface and core of the nanomaterial can be degraded by biodegradation. This is especially common for carbon-based nanomaterials such as fullerenes and CNTs (Abbas et al., 2020). When carbon-based nanomaterials undergo biodegradation, their length and diameter decrease and carboxyl groups are added. There is evidence that fungi that cause white rot (white-rot basidiomycete fungi) can enzymatically degrade the hydroxylated fullerol $C_{60}(OH)_{19\text{-}24}$. This happens through oxidation and mineralization to carbon dioxide (Schreiner et al., 2019). When carbon-based nanomaterials undergo biodegradation, the environmental hazard of the nanomaterial in ecosystems decreases. When a nanomaterial's coating undergoes biodegradation, agglomeration is induced. This leads to deposition of air-borne nanomaterials or sedimentation in aquatic systems.

Environmental corona

In aquatic systems, macromolecules can adsorb onto nanomaterials and form a so-called environmental corona. Macromolecules are biological compounds produced by flora and fauna (Abbas et al., 2020). A study by Xu et al., from 2020 divides macromolecules that can adsorb onto nanomaterials to form an environmental corona into four main groups:

1. Natural organic matter
2. Extracellular polymeric substances
3. Proteins
4. Surfactants, such as tensides

Adsorption of biomolecules can occur when nanomaterials come into contact with natural organic matter, i.e., plant and animal parts that are degrading (Xu et al., 2020). Nanomaterials can also come into contact with extracellular molecules secreted by microbes and plankton. These can subsequently be adsorbed onto the surface of the nanomaterial. Compounds that nanomaterials in aquatic environments interact with come mainly from bodily fluids from living organisms such as fish, or are surfactants from wastewater.

The environmental corona interacts with the surrounding environment and affects the bioavailability and toxicity of the nanomaterial to aquatic organisms (Spurgeon et al., 2020; Xu et al., 2020). The environmental corona can be described as a dynamic unit as its macromolecules exchanges over time and subsequently change the properties of the corona (Senapeti et al., 2017). The interaction of a nanomaterial with macromolecules will determine how quickly the environmental corona is formed and its effects, stability, or toxicity (Abbas et al., 2020).

An environmental corona made of natural organic matter or extracellular polymeric substances has been shown to mitigate the ecotoxicological effects due to the increase in stability (Xu et al., 2020). However, an environmental corona of proteins can result in a higher toxicity since the proteins can interact with other proteins and molecular functions in an organism. Surfactants can potentially cause a higher toxicity because of their often inherent toxic properties. However, the current understanding of environmental coronas on nanomaterials and how they affect the fate and behavior of nanomaterials in aquatic systems remains insufficient (Xu et al., 2020).

Knowledge Gaps

- When a nanoparticle enters the environment, it can interact and react with other substances in the environment. It can undergo various transformation processes. The transformation process affects the fate, bioavailability and toxicity of the nanomaterial. Knowledge of these transformation processes is insufficient. Qualitative and quantitative studies should focus on examining the fate of nanomaterials under natural environmental conditions, their reaction times and how long the nanomaterial is expected to remain in environmental matrices.

- The environment can be seen as a dynamic system where environmental conditions change over time. Knowledge is lacking about reversible processes once nanomaterials have been transformed. Aggregated nanomaterials appear to be able to fragment if environmental conditions change. Further research is required on how nanomaterials behave when environmental factors change.

- Plants can absorb nanomaterials through the roots or stoma. Today, there is limited knowledge of the potentially harmful effects linked to nanomaterials absorbed by plants. More research is needed on the translocation, biotransformation, and accumulation of nanomaterials in tissues, as well as on the effects of nanomaterials in the food chain.

- Nanomaterials that end up in soil can undergo a variety of transformation processes. Little is known about how nanomaterials are transformed and about their bioavailability and toxic properties in soil. More studies are required on the life cycle of nanomaterials in soil. However, this requires specialized analytical techniques.

- An environmental corona is formed when substances are adsorbed onto the surface of a nanomaterial. We know that the process changes the properties of the nanomaterial, but more research is needed on exactly how the coating changes and how this affects the fate, toxicity, and bioavailability of the nanomaterial.

- Nanomaterials can adsorb contaminants. The contaminant can be co-transferred with the nanomaterial and be absorbed by different organisms. There is limited knowledge on how nanomaterials can act as carriers of contaminants and how this affects the bioavailability and toxicity of the contaminant. More research is needed on what contaminants can be adsorbed onto nanomaterials and the negative effects this can have on humans and the environment.

- Each life cycle step of a nanomaterial, from production, use and final handling, can lead to emissions to ambient air. Nanomaterials that enter the air are more exposed to sunlight and UV radiation and are therefore more likely to undergo photochemical transformations. There are only few studies on this process.

Ecotoxicological effects

Today, mainly nanomaterials with simple structures have been evaluated from an ecotoxicity perspective (Schwirn and Völker, 2016). Nanomaterials can have both acute and long-term toxic effects on an organism. When nanomaterials accumulate in matrices such as soil and water, the risk of both acute and chronic effects increases (Kabir et al., 2018). Nanomaterials can also increase the bioavailability of other substances by acting as carriers for contaminants.

In this chapter, some of the acute and chronic effects of nanomaterials on different organisms will be described. Thereafter, a brief overview of the impact of nanomaterials on different organisms reported in the literature will be given.

Acute toxicological effects

Since nanomaterials are a diverse group of chemical substances, the effects, or mechanisms of toxicity cannot be considered to be generic (Bundschuh et al., 2018). All endpoints and mechanisms of toxicity known today are likely relevant. A couple of mechanisms of toxicity are frequently reported in the literature. These are oxidative stress, ion release, internalization and biological surface coating, as shown in Figure 7 (Bundschuh et al., 2018).

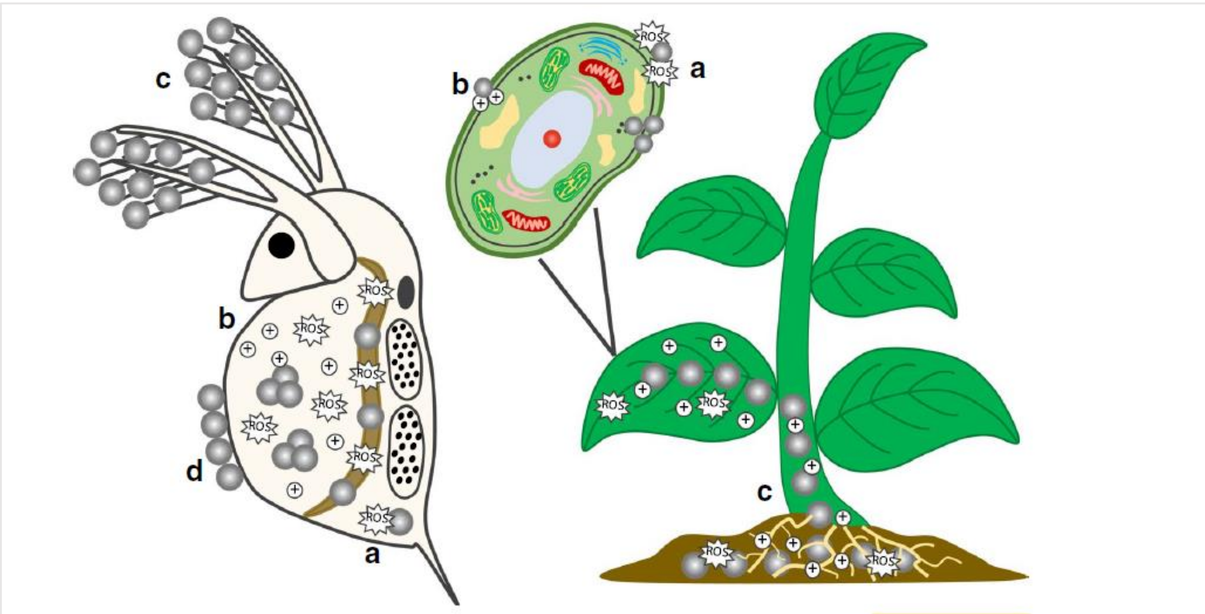

Figure 7. Description of four pathways for ecotoxicity that nanomaterials can give rise to in aquatic and terrestrial systems. The mechanisms of toxicity shown in the figure are: a. formation of reactive oxygen species that give rise to oxidative stress, b. ion release, c. internalization and d. biological surface coating. The image is reproduced with permission of Bundschuh et al., 2018.

Oxidative stress

In redox reactions, reactive oxygen species (ROS) are formed. These species are toxic to many organisms and can induce oxidative stress (Bundschuh et al., 2018). Some types of nanomaterials have the potential to harm plants and animals by forming reactive oxygen species that can damage biological structures and tissues.

Ion release

Some nanomaterials are known to emit ions when dissolved. In aquatic systems, this can happen throughout the life cycle of the nanomaterial. The ions emitted may harm aquatic plants and animals (Bundschuh et al., 2018). Silver nanomaterials are known to emit ions. Many studies show that nanosilver is toxic for most organisms and terrestrial microorganisms. Studies suggest that nanosilver and silver ions have the same toxic mechanism. Since nanosilver has a large particle surface and can dissolve and emit silver ions, silver in nanoform is believed to be more toxic than elemental silver in other forms. Nanosilver that ends up in the wastewater often undergoes sulfidation and becomes trapped in sewage sludge. Once the nanomaterial is sulfidized, it becomes less toxic (Bundschuh et al., 2018).

Biological surface coating

For nanomaterials that do not release toxic ions during the aquatic life cycle, a possible pathway of toxicity is the adsorption to the surface of an organism (Bundschuh et al., 2018). This is also referred to as the nanomaterial forming a biological surface coating. When a nanomaterial adsorbs to the surface of an organism, it can affect the ability of the nanomaterial to cause effects on the organism. The biological surface coating can affect photosynthesis, nutrient uptake, and nutrient movement in the organism.

Internalization

Internalization or endocytosis can be described as molecules such as nanomaterials or proteins being engulfed by the cell membrane, allowing them to enter the cell (Bannunah et al., 2014). This can affect the vital functions of an organism. The rate of uptake, which also affects toxicity, depends on the properties of the nanomaterial such as size and surface charge, and on the environmental conditions.

Long-term effects

Bioaccumulation and biomagnification

Many nanomaterials are persistent and therefore will accumulate in the environment and persist for a long time. Therefore, studies that investigate the long-term effects of nanomaterials are needed (Schwirn and Völker, 2016).

Some nanomaterials can be bioaccumulated and biomagnified in organisms (Mortimer and Holden, 2019). Bioaccumulation can occur when an organism is subjected to long-term exposure to nanomaterials. Uptake and accumulation of a nanomaterial can occur both from solid nanoparticles and from nanomaterials in solution.

Crops can absorb nanomaterials from the soil and transport both the material itself and its transformation products to other parts of the plant, including the fruit. Few studies have investigated how nanomaterials are transferred in the food chain. However, there are studies showing how nanomaterials can be transferred to a secondary consumer that feed on a primary consumer exposed to nanomaterials. One example is the uptake of CeO_2 in nanoform from soil into zucchini leaves, which subsequently accumulated in crickets who fed on the leaves. In turn, the crickets were consumed a wolf spider *(Lycosidae)* after which Ce was detected in the wolf spider.

Similar studies are available on La_2O_2 nanoparticles (Mortimer and Holden 2019*)* and polystyrene nanoparticles in aquatic systems (Cedervall et al., 2012). These studies demonstrate that nanomaterials can be transported and accumulated in terrestrial and aquatic food chains. Little is known about which nanomaterials are biomagnified in the food chain and it is not possible to draw any general conclusions about this based on the current state of knowledge (Swedish Chemicals Agency, 2007).

Ecotoxicological effects on ecosystems

Most of the available studies on ecotoxicological effects on organisms exposed to nanomaterials cover aquatic organisms (Xu et al., 2020). A few studies are available on the toxicity of nanomaterials for terrestrial organisms (Schwirn and Völker, 2016). Studies conducted on photocatalytically active forms of titanium dioxide nanoparticles show increased toxicity when the material is exposed to sunlight (Schwirn and Völker, 2016). Thus, some nanomaterials can exhibit a higher toxicity when present in the atmosphere. To date, the toxicity of mainly first-generation nanomaterials has been addressed. There is a lack of studies evaluating complex nanomaterials from an ecotoxicity perspective. However, we know that organisms often are sensitive to exposure of chemicals at different stages of their life cycle (Besha et al., 2020). Nevertheless, many of the studied nanomaterials show moderate, low or no toxicity for organisms after short-term exposure. The exception is nanomaterials that can release ions, such as silver or zinc. These have shown to have a high acute toxicity for aquatic organisms (Schwirn and Völker, 2016).

It is difficult to predict how an ecosystem will react when exposed to nanomaterials. Nanomaterial exposure to aquatic systems can lead to structural and functional changes. However, relatively high concentrations of nanomaterials are required for these effects detectable. The effects of nanomaterial exposure can affect photosynthesis efficiency or how biological material decomposed. Nanomaterials can affect species as well as the interaction between species at various trophic levels. To date, no studies have addressed how mechanisms driving functional and structural changes affect the food web and the whole ecosystem (Bundschuh et al. 2018). One example of changes in an ecosystem can be found in algae that have adsorbed nanomaterials via a biological surface coating. This has shown to accelerate the sedimentation of the algae. As a result, pelagic animals must invest more energy in collecting algae closer to the bottom and in the bottom sediment (Bundschuh et al., 2018. There are also studies showing that aquatic organisms show changes in feeding habits after short-term exposure to certain types of nanomaterials. Exposure may also increase their flight behavior (Schwirn and Völker, 2016).

Studies show that there is a correlation between titanium dioxide nanomaterials and negative effects on the biodiversity of terrestrial organisms (Schwirn and Völker, 2016). Exposure to nanomaterials could lead to effects on reproduction, likely due to the altering of hormones by nanomaterials. Furthermore, there are studies indicating that microbial organisms avoid soil that is contaminated by nanomaterials (Bundschuh et al 2018).

Silver can occur in various forms after being transformed in the environment. Sulfidized nanosilver, pristine nanosilver and silver ions can be present in sewage sludge from treatment plants that is applied to agricultural fields. This can lead to direct exposure of nanomaterials to terrestrial microorganisms (Bundschuh et al., 2018). The microorganisms in the soil exhibit a difference in sensitivity. Nitrogen-fixing organisms are one of the most sensitive groups to nanomaterials. These organisms can be adversely affected by sulfidized silver nanomaterials, which are generally considered to have low toxicity (Kraas et al., 2017).

Nanomaterials can be absorbed by plants. Research on plants such as wheat and cucumber have shown that sulfidized silver is translocated from the roots to the leaves, affecting the growth and activating the plant's defense system (Bundschuh et al., 2018). It has also been shown that copper oxide in nanoform has different effects on plants than copper ions do. Copper oxide nanomaterials reduces root length and stimulates root hair growth but does not affect the shoot growth. On the other hand, copper ions have been shown to reduce both root and shoot growth. Similar effects have been observed for zinc oxide in nanoform. For soil organisms such as nematodes, zinc oxide nanoparticles appear to have higher toxicity than zinc ions. Thus, no general conclusions can be drawn on the toxicity of metal ions released from nanomaterials relative to the toxic effects induced by the nanomaterial itself (Bundschuh et al., 2018). The toxicity of ions and nanomaterials depends on several factors such as the biological system, coating, properties of the nanomaterial and environmental conditions such as the content of natural organic matter.

There are studies on the uptake of zinc oxide in nanoform from agricultural fields in plants carried out over a long period of time. These show a correlation between uptake and pH of the soil. If the soil has a lower pH, more zinc accumulates in the plants. Furthermore, acidic soil promotes production of reactive oxygen species which can cause oxidative stress (Bundschuh et al., 2018).

An article by Zuverza-Mena et al. from 2017 compiles several studies on how different nanomaterials affect plants, as shown in Figure 8. The overview illustrates the challenge in predicting how nanomaterials affect plants. The effect depends on the concentration of the nanomaterial and the plant species. As figure 8 shows, nanomaterials have an effect on the plants' ability to germinate, the water balance, photosynthesis, nutrient uptake, and growth, among others. The figure clearly shows that different nanomaterials affect plants in different ways. In many cases, we do not know if the nanomaterial has an inhibitory or stimulating effect on the plant, or whether it affects the plant at all. More research is needed in this area.

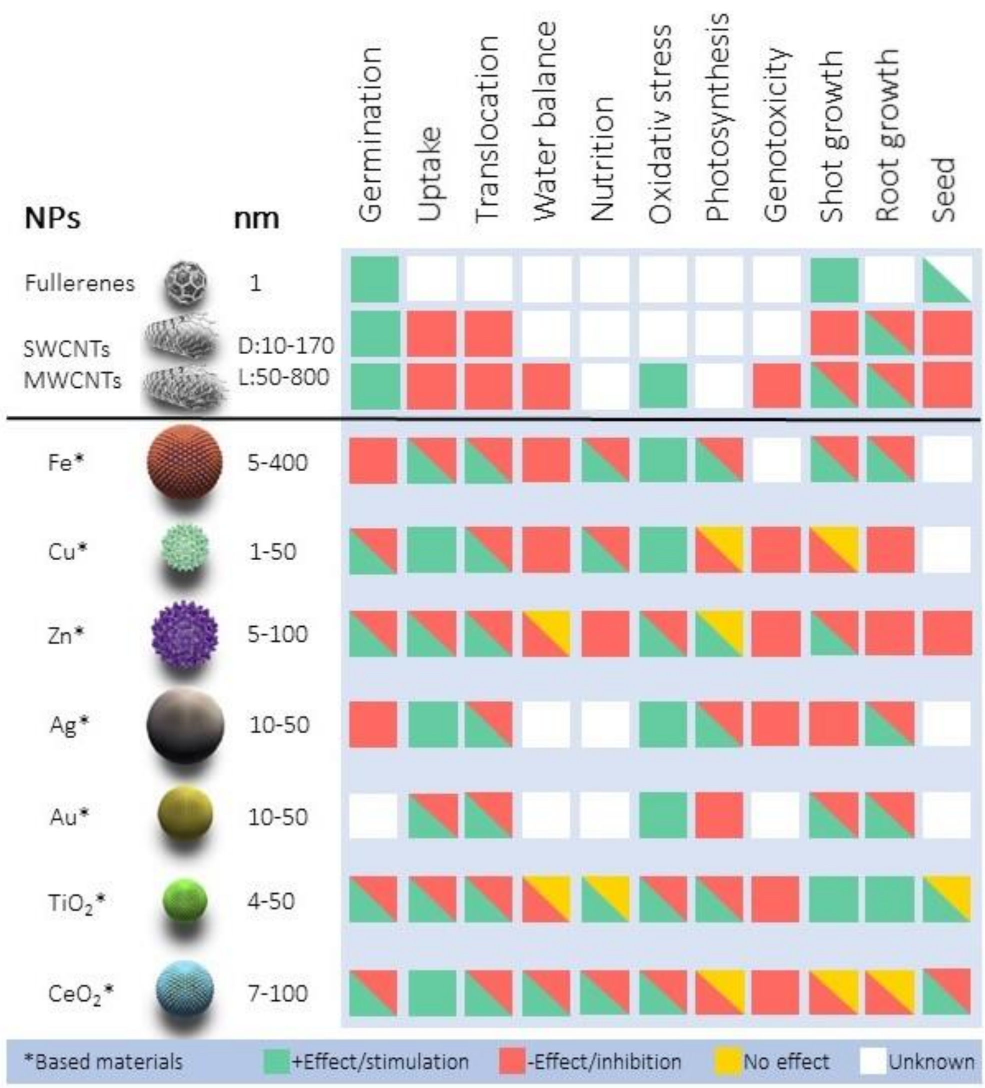

Figure 8. Overview of how different types of nanomaterials can affect different functions in cultivated plants. Image adapted from Zuverza-Mena et al., 2017.

Studies on algae suggest that we do not yet know how they react as a result of being exposed to nanomaterials. However, there are studies suggesting that algae exposed to nanomaterials may also be exposed to oxidative stress. This retarded algae growth by reducing the cell density. The toxic effect is strongly dependent on dose and concentration (Chen et al., 2019). Other studies indicate that nanomaterials affect the photosynthetic pigment composition of algae and aquatic plants. The change is believed to be transgenerational and affects the ability of plants and algae to photosynthesize (Bundschuh et al., 2018). Studies also suggest that algae to some extent have developed a defense mechanism. Through a biobarrier, they can prevent nanomaterials from entering the cells (Chen et al., 2019).

Studies on small aquatic daphnids show that their swimming behavior is affected when they have a biological surface coating of nanomaterials. This and other effects may be chronic. Other studies have shown that daphnids with biological surface coatings of TiO_2 and Fe_3O_4 are acutely affected. The coating seems to inhibit molting, which subsequently leads to death (Bundschuh et al., 2018). Long-term effects of nanomaterials on invertebrates have only been studied for a few nanomaterials, such as titanium dioxide, zinc oxide and silver. Studies have shown that nematodes and daphnids exposed to nanosized titanium dioxide, silver or gold can lead to losses in the progeny. Over several generations, this leads to increased mortality and limitations in reproduction (Schwirn and Völker, 2016).

Knowledge Gaps

- The application of nanomaterials is increasingly moving from simple to complex. At the same time, there are no studies on the toxic effects of complex nanomaterials. The ecotoxicological studies available have mainly been carried out on simple nanomaterials. New ecotoxicological studies focusing on the effects of complex nanomaterials are needed.
- Some nanomaterials are persistent and will accumulate in the environmental matrix. Therefore, studies examining the long-term effects of exposure, even with low doses, are needed.
- In recent years, several studies of bioaccumulation and biomagnification of nanomaterials have been published. However, applying different analytical methods, these studies are difficult to compare to each other. There is a need for a uniform way of evaluating bioaccumulation and biomagnification that allows for comparison.
- In an ecosystem, organisms affect each other. Since organisms have different functional and structural properties, their function can change when exposed to nanomaterials. To date, no studies have addressed how mechanisms contributing to functional and structural changes affect the food web and the ecosystem. More studies in this area are needed.
- Both the bioavailability and toxicity of nanomaterials are affected by the properties and by the predominant environmental conditions. It is important to understand what conditions lead to high bioavailability. This is necessary for purposes of predicting the ecotoxicological effects in an organism or ecosystem. Therefore, studies are needed that identify the relationship between bioavailability, the properties of nanomaterials and external environmental factors.

Management of environmental risks linked to nanomaterials

It is difficult to propose general statements on health and environmental effects of nanomaterials. This is because nanomaterials is a versatile group of chemical substances. The potential environmental risks must be assessed on a case-by-case basis (Fadeel et al., 2018). In this chapter, we describe the challenges of making environmental risk assessments of nanomaterials. We also show how we can ensure that newly developed products containing nanomaterials are safe throughout the life cycle.

Environmental risk assessments

To carry out reliable risk assessments of nanomaterials, estimates for concentrations that have ecotoxicological effects on the environment is needed. In addition, the concentrations must be assessed in different environmental matrices, i.e., the environmental exposure (Schwirn and Völker, 2016). In terms of risk assessments, more research is needed on the long-term effects of nanomaterials. Furthermore, the effects on soil and sediment living organisms need to be evaluated and the risks that nanomaterials pose need to be assessed. In terms of environmental exposure, more information is needed about nanomaterial transformation processes. For example, agglomeration or rate of dissolution in relation to environmental factors need to be studied. Also, the effects when the factors change are of interest. In turn, these parameters must be incorporated into the environmental exposure models.

New applications of nanotechnology are likely to present new risks and hazards. By introducing the principle of so-called Safe-by-Design as early as at the design stage or even in the research and development phase of a product, it is possible to proactively counteract against such risks. Safe-by-Design aims to ensure that products are designed to be sustainable and safe already at the design phase (van de Poel, I., and Robaey, Z., 2017).

One of the biggest challenges for regulators is how regulatory processes that are robust enough to handle the changing landscape of new nanomaterials should be designed and implemented (Soeteman-Hernandez et al., 2019). The credibility of such a regulatory system that is supported by implementing Safe-by-Design is crucial for the industry. However, such system needs to be introduced in an agile and cost-effective manner for the industry to accept it. To properly assess the risks and hazards of nanomaterials, it is important to look at the whole life cycle of products (Fadeel et al., 2018).

To assess the hazards and risks in the environment linked to the release of nanomaterials, models are required for the estimation of material flows, the fate and transport as well as uptake/bioavailability (Sørensen et al., 2019; Schwirn and Völker, 2016). Today, there are more than 500 tools to assess the safety of nanomaterials. They can be categorized into five models for environmental risk assessment (Sørensen et al., 2019):

i. Flow models that simulate nanomaterial flows to the environment from different sources, as well as the transport between different environmental matrices.
ii. Fate and transport models that simulate nanomaterials movement within and between different environmental matrices, and nanomaterial transformations that can affect their state and form in the environment.
iii. Hazard assessment models that estimate the effects of nanomaterials on different species.

iv. Uptake/bioavailability models that assess the uptake and accumulation of nanomaterials in organisms.
v. Risk assessment models that estimate the potential environmental risk of nanomaterials.

The models can be linked to the innovation steps when creating new nanomaterials.

Three criteria have been identified in the study by Sørensen et al., 2019, as critical in risk assessment of a nanomaterial:

i. Time/cost
ii. Level of expertise needed to use the model
iii. Possibility to compare risk assessment models with PEC and PNEC.

In the risk assessment of nanomaterials, it is important to know how fast a material is transformed under the environmental conditions and in the matrix, as well as how ecotoxic mechanisms and bioavailability are affected by the predominant conditions. Thus, both current environmental conditions and the environmental matrix affect the outcome of a risk assessment for a nanomaterial (Mortimer and Holden 2019). Predicted No-Effect Concentration (PNEC) is the concentration that is the limit at which below no adverse effects of exposure in an ecosystem are expected. Thus, PNEC values are the concentration at which below a substance is unlikely to have a toxic effect. PNEC values are often used to calculate a substance's risk quotient. The value is calculated by dividing the Predicted Environmental Concentration (PEC) of a substance by the PNEC, as the equation below shows.

$$Risk\ Quotient = PEC/PNEC$$

If the risk quotient is below 1, a low risk of harmful effects on organisms or low environmental impact can be expected of the substance. If the risk ratio is above 1, there is a risk that organisms in the environment will be affected by the substance, or that it will have an environmental impact (Walker et al., 2012).

For nanomaterials, robust PNEC values are scarce (Schwirn et al., 2020). One reason for this is that the available data is mainly based on acute ecotoxicity. However, data is often lacking for long-term effects. In addition, information on actual exposure to nanomaterials is often lacking.

PNEC values are, among other information, required for the registration of a material on the European market in accordance with REACH. REACH is the European Union regulation that addresses the legislation of chemicals. It stands for registration, evaluation, authorization and restriction of chemicals. As PNEC values for nanomaterials are scarce, it is difficult to carry out accurate risk assessments of nanomaterials. Since the REACH regulation today also requires that substances in nanoform are evaluated when substances are registered, this knowledge gap is expected to decrease over time.

Simple models are needed to identify potential risks and to develop risk management measures in early stages of product development. These will facilitate accurate identification of risks associated with nanomaterials. They should be used without increased costs or higher resource requirements that would hinder innovation. Figure 9 presents a model that facilitates the identification of risks at different stages of product development.

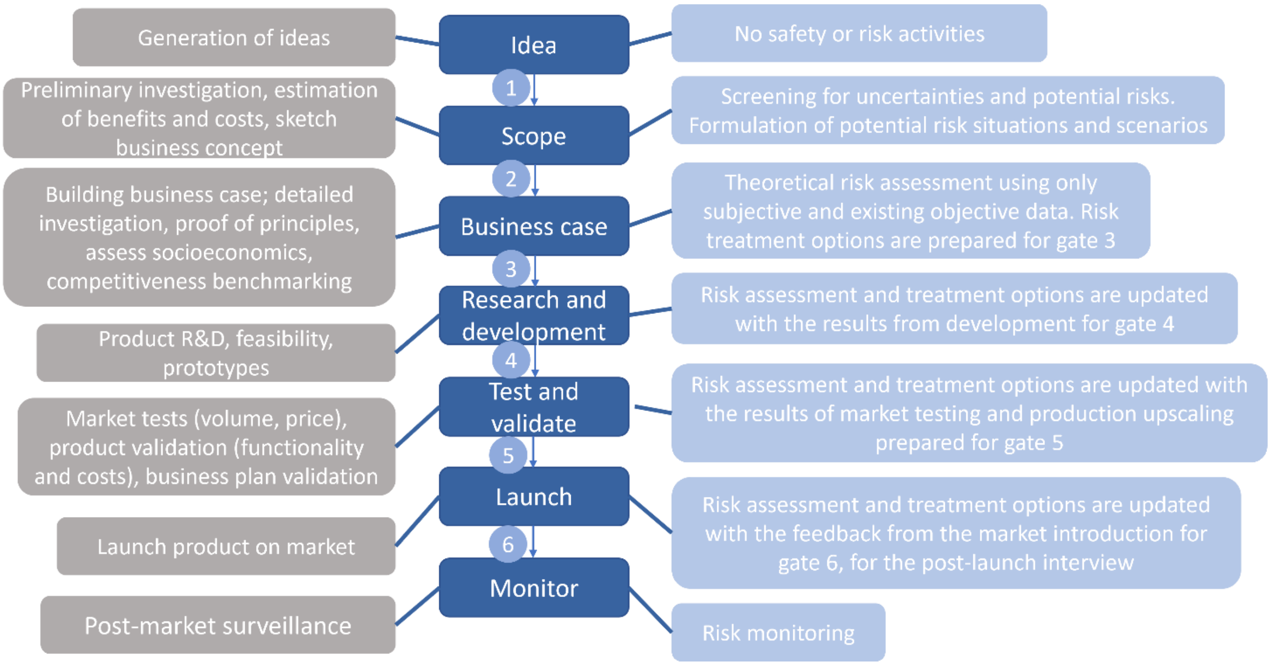

Figure 9. Overview of product innovation (grey) and safety-related activities (light blue) reported by EU's Seventh Framework Program "Nanoreg II" at the different stages of the product innovation process (centered in blue). This process only considers parts of the life cycle of the nanomaterial and does not cover the utilization and end-of-life phases. Image modified from Sørensen et al., 2019.

An article by Fadeel et al. from 2018 addresses the type of organization needed to assess environmental and health risks presented by nanomaterials. The researchers point out a need for harmonized methods for producing data, such as exposure levels and PNEC. This data should be searchable and reliable, and collected in an accessible place. Then, it can be used to develop models, assess risks and other important applications. According to the researchers, the data should be available to both companies and authorities. Once this internal organization is in place, collaboration is needed to establish financial resources, software and tools with companies and authorities. When these components are in place, it will be possible to make a reliable risk assessment of nanomaterials.

Knowledge Gaps

- Risk assessment of nanomaterials is crucial for assessing the impact on organisms and the environment. To carry out risk assessments of nanomaterials, hazard and exposure assessments are required. More studies are needed on the long-term effects of nanomaterials on organisms and the environment. Additionally, studies examining effects on living organisms in sediment and soil are required.
- Current environmental risk assessments and regulations are primarily based on research results for pristine nanomaterials and relatively simple environmental systems. However, these are not applicable to real-life conditions since they are much more complex and dynamic. More research is needed on methods for risk assessment of nanomaterials in complex and dynamic systems.
- In general, there is little knowledge on how the properties of soil affect the fate of nanomaterials. This is of particular importance as sludge dispersion is a common fertilization method in Sweden. The sludge may contain nanomaterials. To assess the risk of dispersion of sludge containing nanomaterials, it is important to understand the impact of soil properties on the fate of the nanomaterial. More research is needed in this area.
- PNEC values are crucial for calculating risk ratios and assessing the risk of different nanomaterials in the environment. Few PNEC values have been reported for nanomaterials. More studies are needed to develop and establish PNEC values for different nanomaterials.
- Safe-by-Design aims to ensure that products are designed to be sustainable and safe already at the design phase. To produce safe technical equipment, it is important to keep Safe-by-Design in mind and to focus on known risks and expected scenarios. In order not to miss out on important technological innovations, we need models that weigh risks against opportunities.

Discussion

Nanomaterials can be emitted throughout a product's life cycle (Arvidsson, 2015; Bundschuh et al., 2018). Since the use of nanomaterials in our society will likely increase (Gottschalk et al., 2015; Schwirn, and Völker, 2020), it is important to understand when in the life cycle of a nanomaterial emissions to the environment occur. Only then is it possible to make priorities to prevent major emissions.

Today, information on the amount of nanomaterials accumulated in environmental matrices is often based on calculations and assumptions (Gottschalk et al., 2015). To determine the reliability of these models, the volume of nanomaterials released to the environment need to be quantified. Knowledge on volume of nanomaterials that circulate in society is important to produce reliable models, risk assessments, and to predict the consequences of a nanomaterial emissions into the environment. A dynamic material flow model is required to make a realistic estimates and assessments of flows to the environment. Models should be designed to show a simplified picture of reality while remaining reliable. To determine the quantities of nanomaterials emitted and present in environmental matrices such as soil, water and air, estimates must always be supplemented by analyses. It is also important to understand in what form the nanomaterials are released. The form affects the behavior of the nanomaterial and its fate in the environment. When nanomaterials have ended up in the environment, it is important to understand how they are transported and in which environmental matrices they can be expected to accumulate or end up. Nanomaterials can be transported as primary particles, aggregates, suspensions and more. To predict the environmental effects of nanomaterials, it is important to know how long they remain in different matrices, how persistent they are and how they are transformed.

Since 2019, anyone who manufactures or imports notifiable chemical products containing nanomaterials must report it to the Products Register of the Swedish Chemicals Agency. The properties of the nanomaterial such as size, function, surface charge must also be reported to the register (Swedish Chemicals Agency, 2020b). The European Chemicals Agency (ECHA) has introduced a similar register within REACH, where anyone who manufactures or imports nanoforms must inform ECHA accordingly (ECHA n.d). These two registers will increase knowledge both on which nanomaterials are present, and on the volume in which they occur in our society. Additionally, the registers will also be valuable in justifying why producers/suppliers choose to add nanomaterials to products. Thus, the knowledge on the function of nanomaterials in products will increase.

To be able to register a substance in nanoform under REACH, PNEC values are required. A major boost in knowledge is expected when the values become available for different nanomaterials. This means that information on the potential environmental impact of a nanomaterial will become available. Other toxicological values will also be available, which will further increase knowledge and understanding of nanomaterials. Registration will provide information on individual nanomaterials, and it is possibly also an opportunity to detect whether any nanomaterials are more hazardous to health and the environment than others. This will promote replacing the hazardous material with an equivalent, but less harmful, alternative.

The knowledge on products with added nanomaterials is scarce. Partly, there is a lack of information on which products contain nanomaterials. Additionally, it is difficult to know which nanomaterials are present in products and what function they have. This is particularly true for imported goods from outside the EU. By knowing in which applications nanomaterials occur, we can predict where in the life cycle of the product nanomaterials could be released to the environment. Furthermore, it would assist in determining how these products should be handled throughout their life cycle, including waste management.

Being able to analyze nanomaterials in different environmental matrices is a prerequisite for making reasonable and accurate estimates of the fate and behavior of the nanomaterial, as well as for assessing its toxicity, environmental impact, contamination, and remediation. The analyses are also important for monitoring and reviewing the development of nanomaterials in the environment. In view of this, the existence of validated and relevant analytical methods for nanomaterials is a requirement. Analytical methods are needed for different types of nanomaterials and for different environmental matrices. Methods are also needed to distinguish manufactured nanomaterials from natural nanomaterials. In general, it seems that air-borne nanomaterials are most straight-forward to analyze. Nanomaterials in water are also relatively simplistic in their analysis. However, nanomaterials in soil have shown to be challenging to analyze. This is due to that soil is a complex matrix containing various substances and components.

Current methods for detecting and quantifying nanomaterials have proven to be best applicable in a laboratory setting (Zhang et al., 2019). It is important to improve and develop analytical methods for analyzing nanomaterials in different environmental matrices. In order to obtain comparable results, the methods of analysis must be standardized. Reliable and adapted analytical methods are necessary to understand how and to what extent nanomaterials are dispersed in environmental matrices. Following this, assessment of whether and to what extent a manufactured nanomaterial poses an environmental threat can be made.

Adequate analytical methods are also a prerequisite for validating models of flows and accumulations of nanomaterials in the environment. If it is impossible to quantify nanomaterials at natural concentrations and to distinguish them from the natural (background) particles, the modelled concentrations constitute the only available source of information (Sun et al., 2016). There is a need for methods that measure actual levels in different locations and in different environmental matrices. For this to be possible, sampling and analysis methods need to be developed. Knowing concentrations in the environment is important for environmental risk assessments and for determining thresholds for when organisms are adversely affected.

Standardized methods for measuring nanomaterials in different environmental matrices would also facilitate developing a monitoring program for nanomaterials in the environment. Environmental monitoring programs are designed to provide early warnings when environmental threats appear in new places or in previously unknown contexts (Granqvist, 2020). It would be valuable to be able to track how different types of nanomaterials are transported and transformed in various environmental matrices, as well as how they accumulate over time. Monitoring registers already exist for a large number of substances in matrices. The Swedish Environmental Protection Agency currently manages these registers. A similar register for nanomaterials is desirable.

The environmental fate of nanomaterials is governed by their properties and by the current environmental conditions. It is rare for nanomaterials to occur in pristine form in the environment. Often, they are transformed after emissions. The transformation processes can be chemical, physical or biological. Once in the environment, nanomaterials will either be transformed in the environment itself or transformed in organisms. A nanomaterial often has several transformation processes. The process it undergoes is determined by the surrounding environmental conditions and how these conditions interact with the properties of the nanomaterial. An illustrative example is silver, which when in nanoform can be oxidized, sulfidized or dissolved and emit ions. Depending on the transformation process, bioavailability and toxicity can increase or decrease. Silver that dissolves, i.e., emits ions, has an increased toxicity. On the other hand, if the silver sulfidizes, the nanomaterial becomes stable and sterically hindered and the toxicity decreases. However, it is difficult to predict what transformation process a nanomaterial will go through.

The more complex a nanomaterial becomes or the more complex the surrounding environment is, the more difficult it is to predict how the nanomaterial will behave when it enters an organism or the environment (Teunenbroek et al., 2017). Information is still limited, and more research is needed to predict the environmental effects of how complex nanomaterials interact with biological and geochemical systems. Knowledge on this will assist in avoiding causing harmful effects on the environment.

A nanomaterial can be transformed several times. There is limited knowledge on how previously transformed and stable nanomaterials react when environmental conditions change. It is likely that transformation is a reversible process and in the event of a change in environmental conditions, nanomaterials could be released and the bioavailability and toxicity of a previously stable and non-reactive nanomaterial could increase.

The environmental corona is believed to be of highly relevant for the bioavailability and toxicity of nanomaterials. The formation of an environmental corona is a common transformation process. The process is dynamic and is affected by the surrounding environment. A nanomaterial often becomes less toxic when encapsulated. For the environmental corona, the toxicity is determined by the substances that the corona comprises of.

The number of ecotoxicological mechanisms of nanomaterials are likely larger than described in the chapter about acute effects (Bundschuh et al., 2018). Since nanomaterials are a versatile group of chemical substances, different nanomaterials are likely to have different toxic effects. Therefore, it is not possible to draw any general conclusions regarding ecotoxicological mechanisms for nanomaterials. The toxicity of a nanomaterial is determined by its bioavailability and how readily an organism absorbs the substance. Toxicity is also determined by the intrinsic properties of the nanomaterial, such as size, shape, and coating, as well as the environmental conditions. The life cycle stage of the organism matters since sensitivity to toxins varies at different stages of life. Organisms in early stages of the life cycle are generally more easily affected. The route of exposure also plays a role in how a nanomaterial is absorbed by an organism and how this affects its toxic effect.

It is important to study the most widely used nanomaterials, as these are likely to occur in the highest concentrations in the environment. As the development is moving towards using complex nanomaterials, reliable ecotoxicological studies on these are needed.

Today, it is difficult to quantify the nanomaterials in our environment and whether the concentration can pose a danger. Therefore, threshold values for harmful effects of nanomaterials should be determined.

To date, analytical technologies for the measurement of nanomaterials in their pristine form are available. However, due to the rapid transformation of nanomaterials when released to the environment, the methods are insufficient. The product of transformation is therefore difficult to measure in the environment, as well as in and organisms (Abbas et al., 2020). Scientific studies rarely account for whether pristine or transformed nanomaterials are being investigated.

Nanomaterials can affect entire ecosystems and cause functional and structural changes. This happens since ecosystems are dynamic systems in which all organisms affect each other. One example is when nanomaterials are adsorbed on algae, resulting in sedimentation, and in forcing food-seeking animals to change their behavior and look for food closer to the seabed (Schwirn and Völker, 2016). Research has not yet addressed the long-term effects of this on ecosystems. Chronic effects of exposure to nanomaterials need to be studied at the individual, populational and ecological levels.

A prerequisite for transitioning from a linear economy to a circular one is clean and non-toxic material flows. If we do not stop adding substances that are harmful to health and to the environment to products, it will be impossible to achieve the environmental goal of a non-toxic environment and to transition to a circular economy. One of the requirements is the availability of robust toxicological values for nanomaterials. These are often lacking today. As early as in the development phase, it must be guaranteed that the product will be reusable and recyclable. The Swedish Chemicals Agency's report "Giftfritt från början" (English translation "Non-toxic from the beginning") presents milestones for the environmental goal of a non-toxic environment. The focus is on avoiding harm to humans and the environment. The report highlights the importance of increasing knowledge on substances such as nanomaterials. According to the report, it is important to see the product from a life cycle perspective. This allows for the product to retain its function while also being manufactured to be safe. Also, this encourages using the best possible materials from an environmental and health perspective. To know the components of a product requires transparency in manufacturing. Safe-by-Design is a concept for this, developed in several projects and EU initiatives. Safe-by-Design has two main objectives: firstly, to make product developers aware of the risk of certain materials and secondly, to develop rules for the design resulting in a safe production without losing the function of the product (Teunenbroek et al., 2017).

Today, environmental risk assessments of nanomaterials are scarce. There is a large gap between the time when a new product containing nanomaterials is marketed and when the product has received a risk assessment as required by the REACH registration (Teunenbroek et al., 2017). To carry out an environmental risk assessment that meets the requirements of REACH, a PNEC value is required, among other information. However, these are often lacking for nanomaterials. Complete and reliable environmental risk assessments require an in-depth understanding of the mechanisms of toxicity, pathways and toxic effects of nanomaterials in the relevant organism (Teunenbroek et al., 2017).

Many SMEs do not have the resources to carry out accurate and reliable risk assessments. Therefore, it is of great importance that simpler models and reliable data are available so that they can assess the environmental risk of their products. Measures to increase the knowledge are required to enable SMEs to carry out relevant risk assessments and trade-offs when designing, producing, using or purchasing products containing nanomaterials. Only through the implementation of this type of knowledge and risk assessments can we ensure a sustainable development of nanotechnologies that meet and support the sustainable development goals.

Authors' recommendations

The authors of this report had the task of identifying and proposing areas where there are gaps in knowledge and how these could be bridged. This resulted in the following summary.

Nanomaterials are a broad group of chemical substances. In the environment, they interact with other substances and the environmental conditions. There is research studying individual materials or areas of use, while research examining a broader perspective and complex environmental matrices is largely lacking. There is also a lack of consensus on the environmental effects of nanomaterials. Instead, most studies available today provide indications of how nanomaterials can affect the environment and what effect they can have on different organisms. Current research focuses on laboratory studies. Research is needed regarding nanomaterials in the environment and organisms, as well as the effects of nanomaterials on an individual, populational and ecological level.

To determine the environmental effects of nanomaterials, we need to develop robust analytical methods that are reliable and produce outcomes that can be compared. Standardized analytical methods are needed to measure concentrations of nanomaterials in different environmental matrices and to follow how nanomaterials change and accumulate over time. Analytical methods for distinguishing manufactured nanomaterials from natural nanomaterials and detecting the transformation products of a nanomaterial are also necessary.

Robust analytical methods can quantify to what extent nanomaterials are present in society. By measuring the quantity of nanomaterials in different environmental matrices, models that calculate how transport takes place between different environmental matrices and the order of magnitude of volume can be verified. When this information is available, the models can be used to identify the environmental matrices in which accumulation occurs, and therefore also where there is a risk of high concentrations and potential environmental effects are present.

Studies highlighting ecotoxic mechanisms in nanomaterials should consider that nanomaterials are a broad group of chemical substances, and no general mechanism of toxicity can be expected. Environmental conditions are dynamic and transformation processes of a nanomaterial may be reversible. The nanomaterials and environmental conditions for which this applies are currently uncertain. More research is needed to identify how dynamic relationships affect nanomaterials and their toxicity.

The knowledge and research on how the environmental corona of nanomaterials affects its environmental effects are scarce. For example, the environmental corona affects how the nanomaterial interacts with aquatic organisms and their biological effects. Since the environmental corona is believed to be highly relevant, it is important to identify its ecotoxic effects.

Environmental risk assessments of nanomaterials will need to be carried out on a case-by-case basis due to their differing composition and toxicity. Reliable environmental risk assessments require estimation of concentrations in environmental matrices, knowledge of exposure pathways and threshold values for when effects are detectable in organisms. Credible risk assessments also require long-term studies to predict effects over time. Analytical methods form the basis of accurate and reliable environmental risk assessments. Reliable environmental risk assessments are crucial for predicting and preventing negative environmental effects resulting from the use of nanomaterials.

Thank you

Thanks to Mirco Bundschuh, Juliane Filser, Simon Lüderwald, Moira S. McKee, George Metreveli, Gabriele E. Schaumann, Ralf Schulz & Stephan Wagner for Figure 7 published in this report in its original form from "Nanoparticles in the environment: where do we come from, where do we go to?" published in Environmental Sciences Europe 2018, Springer publisher.

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