Nanomaterials in Waste Streams
Current Knowledge on Risks and Impacts

Chapter 1

Assessment and recommendations

This overview chapter highlights the findings from subsequent chapters that focus on four specific waste treatment processes: recycling, incineration, landfilling, and wastewater treatment. The chapter clarifies the current state of knowledge on the fate and possible impacts of nanomaterials in these processes, provides possible ways forward and identifies future research areas and possible approaches to further address the emerging issue of waste containing nanomaterials.

Nanotechnologies are increasingly utilised in advanced applications of industrial, commercial and medical sectors bringing many benefits to society (Brar et al., 2010). However, their potential risks and impacts to human beings and the environment are currently insufficiently understood and under investigation. Nanomaterials, defined as materials of which a single unit are sized between 1 to 100nm, have distinctive features which can benefit various applications from health and medical care, clothing, electronic equipment, construction material and sporting equipment (PEN, 2013). For example, some nanomaterials can be utilised in sunscreen for its properties of shielding Ultra Violet (UV) light, while other nanomaterials have anti-bacterial features useful for deodorant and textiles. Certain nanomaterials can be used in lithium ion batteries to extend their product life while other types of nanomaterials can be applied to building material and glass coating to retain self-cleaning features. Nanomaterials are also used in tennis rackets to achieve lightweight performance and durability.

The number of products containing nanomaterials has increased by 521% from 2006 to 2011 reaching over 1 317 products according to the Woodrow Wilson International Centre for Scholars (WWICS) Nanotechnology Consumer Products Inventory (WWICS, 2011). In 2012, the global market for nanomaterials was evaluated at 11 million tonnes with a market value of EUR 20 billion. Accordingly, products underpinned by nanotechnology are expected to grow from EUR 200 billion in 2009 to EUR 2 trillion by 2015. (EU, 2015, 2012).

However, due to their size, shape, structure and distinctive properties, recent research indicates that some nanomaterials may represent a risk to human health, living organisms and the environment. For example, some nanomaterials may potentially show cancer-causing properties in lungs while other nanomaterials with antibacterial properties may potentially harm ecosystems when they reach the environment (Struwe et al., 2012). Moreover, some nanomaterials are able to bypass important protective biological mechanisms such as the blood-brain barrier, which may produce adverse effects related to neurotoxicity (Australia, Department of Health, 2013). Nanomaterials, in some instances, can also increase the bioavailability of pollutants as a result of absorption and adsorption of toxic particles (Farré et al., 2009; He et al., 2012; Gao et al., 2008; Cheng et al., 2004; Yang et al., 2006).

The assessment of exposure to nanomaterials in the environment is identified as a significant issue (Gottschalk and Nowack, 2011), even though it is sometimes challenging to distinguish engineered nanomaterials (ENMs), which are designed and manufactured for specific purposes, from naturally occurring nanomaterials such as metallic silver nanomaterials naturally produced by UV radiation or metallic mercury naturally formed under anoxic conditions (von der Kammer et al., 2014).

This publication focuses on engineered nanomaterials as defined by the International Organization for Standardization (ISO) (see Box 1.1) and it focuses on these materials to the extent that they are contained in different waste streams, which in the following will be termed "waste containing nanomaterials" (WCNM). The term "nanowaste", which is also sometimes encountered in the literature, should only be used for specific waste containing high levels of nanomaterials generated by nanomaterial production, i.e. in an industrial context.

Box 1.1. **Definitions of nanomaterials**

Nanoscale:	Size range from approximately 1 to 100 nm.
Nanomaterial:	Material with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale. This generic term is inclusive of nano-object and nanostructured material.
Nano-object:	Material with one, two or three external dimensions in the nanoscale.
Nanostructured material:	Material having internal nanostructure or surface nanostructure.
Nanostructure:	Composition of inter-related constituent parts, in which one or more of those parts is a nanoscale region.
Engineered nanomaterial:	Nanomaterial designed for a specific purpose or function

Note: Engineered nanomaterials (ENMs) and manufactured nanomaterials (MNMs) are used synonymously in various research documents however we will align to ENMs in this documentation for the purpose to align with ISO standards.
Source: ISO/TS 80004-1:2015 and ISO/TS 12901-1:2012

What is the link to waste management?

With increasing industrial and commercial applications of nanomaterials, it can be asserted that more nanomaterials are entering waste streams and could subsequently affect end-of-life disposal processes (NEEPH, 2011).

The purpose of waste management is either to recycle waste materials to produce secondary raw materials or to dispose of waste materials, by landfilling, incinerating or storing them in an adequate manner. End-of-life products containing nanomaterials are part of the main solid municipal waste stream and thus subject to four different treatment pathways:

1. *Recycling facilities*

   There are generally several stages in the recycling process. For example, synthetic materials and metals are shredded in order to homogenise the size of waste particles or separate out unwanted materials. Particles can be released and dust containing nanoparticles can be created. For work safety reasons these processes already take place under specific conditions that prevent such dust from coming into contact with human beings or the environment.

2. *Incineration facilities*

   Waste is mixed and thermally treated in incineration plants. Combustible parts are destroyed and residues leave the combustion chamber either as slag or as dust in the flue gas. Modern flue gas filter and cleaning facilities reduce the amount of hazardous substances to the detectable minimum. However, very little information exists about the efficiency of cleaning in respect to nanomaterials. In the worst case the particles are not collected or destroyed and leave the chimney unfiltered into the environment.

3. *Landfilling facilities*

   Landfilling of untreated (biodegradable, combustible) waste is still the major waste management technique in many countries. Depending on how and where landfilling is organised and practised, nanomaterials may leave the landfill by emission into air, water, and possibly soil.

4. *Wastewater treatment facilities*

   Products containing nanomaterials can release nanomaterials during their use-phase and in contact with water. This is the case for example when textiles are washed in a washing machine or from surface coatings. As a result, nanomaterials can be found in waste waters and thus in the sewage sludge of waste water treatment plants which may be incinerated or used as a fertiliser in agriculture. A lack of knowledge exists on environmental impacts resulting from the use of sewage sludge in agriculture.

To what extent are increasing amounts of ENMs in waste streams retained or eliminated by different waste treatment processes and what is their impact on the effectiveness of these processes? This is the main question that is posed to this research. To this end, this publication provides a literature review of the four specific waste treatment processes of recycling, incineration, landfilling, and wastewater treatment. It aims to clarify the current state of knowledge on the fate and possible impacts of ENMs in these processes.

This section will first summarise the current state of knowledge on the fate of WCNMs in waste treatment processes based on the insights provided in the four subsequent chapters and then identify some possible ways forward. Following this overview, a study on the fate and possible impact of nanomaterials in recycling facilities is provided in Chapter 2, a study on the current information of WCNMs in incineration processes in Chapter 3, an investigation on the possible impacts of WCNMs in landfills in Chapter 4, and an examination on WCNMs in wastewater treatment processes in Chapter 5.

What is the current state of knowledge on the fate of WCNMs in waste treatment facilities?

Although state of the art waste treatment facilities are likely to collect, divert or eliminate a large share of nanomaterials from these waste streams, there is still a fair amount of uncertainty associated with their final disposal, requiring more research in this area. This is the main conclusion that is drawn from the four literature surveys illustrated in the following chapters. The possible sources of WCNMs and the interconnections between these waste treatment processes are fairly well identified. However, the types and quantities of ENMs entering these waste streams are still largely unknown. Moreover, the available studies on the fate and possible impact of ENMs in waste treatment processes provides a mixed picture, with certain types of ENMs relatively more researched, for example nano-silver (nAg), nano-titanuim oxide ($nTiO_2$), nano-zinc oxide (ZnO), nano-cerium oxide ($nCeO_2$) and carbon nanotubes (CNTs). On the other hand, others lack information, for example metals such as nano-iron (nFe), nano-aluminium (nAl), nano-platinum (nPt), or nano-zirconium (nZr), metal oxides such as nano-silica ($nSiO_2$), or nanoclay. In general, research is not sufficiently developed to draw concrete conclusions at this point.

What are the types and quantities of ENMs in waste streams?

The possible sources of ENMs entering waste treatment facilities are fairly well identified among the four typical treatment processes of recycling, incineration, landfilling and wastewater treatment even if little is known about which products contain ENMs and which ENMs these are. ENMs can be in forms of pure nanomaterials, items contaminated with nanomaterials, liquid suspensions containing nanomaterials or solids which have friable nanomaterials (BSI, 2007), and they could be potentially released through mass production of ENMs, distribution, consumption and final disposal of products containing ENMs (NEEPH, 2011). They can be collected to recycling facilities as a part of municipal solid waste and end-of-life products. They can also enter incineration plants as municipal solid waste or wastewater sewage sludge (Asmatulu et al., 2012; Boldrin et al., 2014; Ganzleben et al., 2011; Keller A.A. et al., 2013; Reinhart et al., 2010; Nowack et al., 2013), or appear in waste water treatment facilities through household drainage, commercial and industrial sewage or landfill leachate (Auffan et al., 2010a, 2010b; Musee, 2011; Kiser et al., 2009; Westerhoff et al., 2011). Ultimately, they can end up in landfills as contaminants in industrial and household waste along with ash and slag generated from incinerators or bio solids from wastewater treatment plants (DiSalvo et al., 2008; Mueller et al., 2012).

These possible sources are compiled in Table 1.1.

Table 1.1. **Possible sources of WCNMs**

Waste treatment processes	Possible sources of ENMs
Recycling facilities	• Municipal solid waste • End-of-life products
Incineration plants	• Municipal solid waste • Sludge and bio solids from wastewater treatment plants
Landfills	• Municipal solid waste • Fly ash and bottom ash from incinerators • Sludge and bio solids from wastewater treatment plants
Wastewater treatment facilities	• Household drainage • Commercial and industrial sewage • Landfill leachate

However, the types and quantities of ENMs entering these waste streams are still unidentified to date (Health Council of the Netherlands, 2011). Given that there is a significant increase in products containing ENMs and that eventually need to be disposed of, it is anticipated that more and more ENMs are entering these waste streams. The waste treatment processes can be potentially affected according to the types and/or volumes of ENMs and therefore the identification and quantification of flows of ENMs has been recognised as one of the priority issues from all four chapters of recycling, incineration, landfilling, and wastewater treatment.

Are ENMs being captured in waste treatment processes?

Initial findings suggest that a large share of ENMs could be captured, diverted or eliminated by state of the art waste treatment processes, however with different levels of uncertainty. While a large amount of ENMs may be retained or eliminated by state of the art waste treatment processes, a significant share of ENMs may still be released as emissions, which is a cause for concern.

Municipal wastewater treatment has been investigated for some types of nanomaterials such as nano-titanuim oxide ($nTiO_2$), nano-silver (nAg), nano-cerium oxide ($nCeO_2$) or nano-copper (nCu). Pilot wastewater treatment plants were able to capture and divert over 80% of ENMs by mass into solid sludge in its aerobic processes through transformation, bacterial aggregation, biological polymer adsorption and sedimentation (Kiser et al., 2009 and 2010; Kaegi et al., 2011; Ganesh et al., 2010; Wang et al., 2012; Gomez-Rivera et al., 2012). As a result, the residuals would remain in the form of ENMs and appear in surface water (Tiede et al., 2010; Kim et al., 2010).

Other studies focused on waste incinerators and found that state-of-the-art flue gas treatment systems could capture a significant share of ENMs diverting them into fly ash and bottom ash. However, the removal efficiency of ENMs was reported differently across several studies. Some studies suggest that electrostatic precipitators and wet flue gas purification systems effectively remove most ENMs from emissions in the case of nano-cerium dioxide ($nCeO_2$) (Walser et al., 2012), whereas other studies conclude that up to 20% could pass through these systems requiring additional preventive mechanisms to retain these (Roes et al., 2012).

There is significantly less information available for landfilling operations. Based on the results of municipal wastewater treatment studies, it is suspected that the treatment processes for landfill leachate may display similar levels of effectiveness in capturing ENMs through aggregation and agglomeration with organic matter and bacteria (Bottero et al., 2015; Kaegi et al., 2011; Westerhoff et al., 2013). However, leachate is an aqueous effluent that is quite different from municipal wastewater and more specific studies would be required to confirm this expectation. Only very few studies investigate the effectiveness of landfill liners in retaining ENMs from leaching to the environment and initial findings are contradictory where they are available (Boylard et al., 2013; Lozano and Berge, 2012; Siddique, 2013). Moreover, the extent to which the landfill surface or landfill gas can release ENMs to the environment has never been studied in depth.

Finally, the fate of nanomaterials in recycling processes, including dismantling, shredding and thermal processes is unclear because of challenges in ENM exposure measurement in actual working environments (Gottschalk and Nowack, 2011). Therefore, these studies have largely relied on modelling results.

In general, initial research has only been able to draw findings for a few types of ENMs and many studies have relied on laboratory experiments or modelling results, rather than investigating existing facilities. The fate of ENMs in different waste treatment plants, therefore, still comprises of a level of uncertainty and requires further investigation.

Can ENMs negatively affect leachate and wastewater treatment processes?

Beyond concerns relating to the capacity of waste treatment operations in retaining ENMs, there are also questions as to whether ENMs could have negative effects on the waste treatment processes itself. For instance, surface functionalised nanomaterials, which are relatively stable with limited aggregation and sedimentation levels in the aerobic processes, may slow down the transformation kinetics of nanomaterials in wastewater treatment plants and negatively affect the entire process (Auffan et al., 2010a; Barton et al., 2013; Kiser et al., 2010).

Furthermore, research suggests that certain ENMs may also inhibit anaerobic or denitrification processes in municipal wastewater treatment facilities. It is reported that

ENMs with metallic properties at high concentrations may inhibit the anaerobic or denitrification process with impact on bacterial communities and ultimately deteriorate the plant's capacity to reduce toxicity in sludge (Arnaout and Gunsch, 2012; Holden et al., 2014; Kiser et al., 2010; Klaine et al., 2008; Nguyen, 2013; Yang et al. 2013). Better information on the types and quantities of ENMs entering these processes could help to anticipate the potential risks.

Similarly, organics such as humic and fluvic acid in leachate could also stabilise ENMs minimising aggregation and reducing precipitation potentially leading to poor performance of leachate treatment facilities (Hyung and Kim, 2008; Saleh et al., 2010; Lin and Xing, 2008).

What are the issues raised by the linkages of waste treatment processes and residual waste?

Even though there is some evidence that state of the art waste treatment processes may successfully capture, divert or eliminate ENMs from waste streams into solid sludge in wastewater treatment processes or fly ash and bottom ash in incineration processes, there are concerns that subsequent steps of treating the residual wastes and/or material recovery may lead to potential releases into the environment.

The most alarming case is perhaps the agricultural application of wastewater sludge. According to a study from France, more than half of the country's wastewater sludge is currently used for soil fertilisation in agriculture (ADEME, 2004). Given that increasing amounts of ENMs are entering wastewater treatment processes, there is a risk that more and more ENMs are contained in wastewater sludge. The potential transformation of ENMs in soil, their interactions with plants and bacteria in the rhizosphere, and their transfer to surface water has never been studied in depth, and the ultimate fate of ENMs disposed of in this way therefore remains a major area of uncertainty.

Similarly, the relatively limited knowledge of the fate of ENMs in landfills is another cause of concern as these are typically the final sinks where residual waste from incineration and wastewater treatment will be disposed of. Incinerators collect ENMs through their filters, accumulate them as fly ash and bottom ash, which is then sent to landfills for final disposal (Mueller et al., 2013). Similarly, solid sludge from wastewater treatment may be sent to landfills in some occasions (DiSalvo et al., 2008; Lui et al., 2014; Westerhoff et al., 2013).

Further issues may arise when material is recovered from the waste stream for the use in different applications, as secondary materials may be contaminated with ENMs and their potential risks are largely unknown (Chaudhry et al., 2009). This includes cases of industrial application of incinerator fly and bottom ash, for instance in road construction. The possible leakage routes from waste treatment operations are summarised in Table 1.2.

Table 1.2. **Possible leakage routes of ENMs from waste treatment operations**

Waste treatment processes	Possible leakage routes
Recycling	• Imbedded in secondary materials
Incineration	• Flue gas emissions to the environment • Fly ash and bottom ash to landfills • Fly ash and bottom ash to storage facilities • Bottom ash to industrial applications (e.g. roads)
Landfilling	• Landfill gas emissions to the environment • Landfill surface emissions to the environment • Leachate to leachate treatment facilities • Leachate to wastewater treatment facilities
Wastewater treatment	• Emissions to surface water • Wastewater sludge to incinerators • Wastewater sludge to landfills • Wastewater sludge to agriculture applications

How much do we know about the best ways to manage the risks identified so far?

In a context where the fate, impacts and risks of ENMs are still relatively uncertain, a number of studies suggest that the application of best available technologies may constitute a pragmatic approach in dealing with these potential risks and the related uncertainty (Boeni, 2013; Japan Ministry of Environment, 2009; NEEPH, 2011; SRU, 2011; Struwe et al., 2012). Although best available technologies (BAT) are not typically designed to deal with ENMs (OECD, 2004/2007; EU, 2008), their use may be an effective way of minimising exposure. For example, in the case of Europe, the application of BAT for incineration flue gas treatment is seen to be more effective than conventional technologies in scrubbing ENMs from flue gas. Similarly, it is perceived that modern engineered landfills are better able to prevent releases of ENMs than un-engineered landfills.

In recycling facilities, where workers may be exposed to ENMs through shredding, thermal and dismantling processes, workers could be protected through a range of safety measures such as:

1. technical measures (minimising dust through sealing, extracting, filtering, isolation and ventilation, use of wiping by damp cloth altering blowing etc.),
2. organisational measures (minimise exposure time, minimisation on persons exposed, restriction of access and instructions of personnel on hazards and protection measures), and
3. personal measures (respiratory protection with particle filters, protection gloves, closed goggles, protection suit etc.) (Struwe et al., 2012).

As a consequence, the potential risks emanating from ENMs in different waste treatment facilities are probably significantly larger in sub-standard operations, of which many are still in operation around the globe and which are predominant in less developed parts of the world. This is an area where further research is urgently needed.

The current state of knowledge and knowledge gaps of the fate of ENMs in waste treatment processes are compiled in Table 1.3.

What is the possible way forward?

The four chapters of this book show that while there has been some research into different aspects of wastes containing nanomaterials, this is insufficient to be conclusive

Table 1.3. **Current state of knowledge and knowledge gaps of the fate of ENMs in waste treatment processes**

Key Issues	Recycling	Incineration	Landfilling	Wastewater treatment
Identifying possible sources	• The possible sources of ENMs entering waste treatment facilities are fairly identified • Information on types and quantities of ENMs entering these waste streams need to be clarified			
Capturing ENMs in waste treatment processes	• Fate of nanomaterials in recycling processes is unknown • Challenge in measuring the exposure of ENMs in actual working environments. • Available studies largely relied on modelling results.	• Incinerators with effective flue gas treatment systems are likely to capture a majority of ENMs and divert them to fly ash or bottom ash. The effectiveness however differs according to different studies.	• Landfill design, site conditions, and sophistication of control measures including landfill gas recovery, leachate collection and treatment systems heavily influence the release of contaminants through landfill gas and leachate. • It is anticipated from wastewater treatment studies that leachate treatment would be effective in capturing ENMs. • There is a lack of conclusive findings to determine whether ENMs penetrate or migrate through landfill liners. • Further research on the release of ENMs from landfill surface or landfill gas to the environment is needed.	• For few nanomaterials (TiO2, Ag, CeO2, Cu) pilot wastewater treatment plants were able to capture and divert over 80% of injected ENMs by mass into solid sludge in aerobic process. • Relatively small amount of residuals would appear in surface water.
Potential negative effects of ENMs on waste treatment processes	• Exposure in working conditions and to the environment is of concern.	• Unidentified	• Organics (e.g. humic and fluvic acid) in leachate could stabilise ENMs, which reduces particle aggregation (generally associated with greater material mobility) and potentially affect the performance of leachate treatment. • ENMs may have the potential to inhibit microbial processes of landfill leachate treatment at high concentrations.	• Surface functionalised nanomaterials may slow down sedimentation and precipitation processes of ENMs in wastewater treatment plants. • ENMs at high concentrations may inhibit the anaerobic or denitrification process and deteriorate the plants ability to reduce toxicity in sludge.
Linkages between waste treatment processes and residual waste	• Possibly imbedded in secondary materials. • Growing interest in the recycling industry to recover material from bottom ash.	• Incinerators can collect ENMs through filters and accumulate them as fly ash or bottom ash, however, they may lead to landfills where more investigation is necessary. • Fate of ENMs in solid residuals need further research (e.g. case of road application in Germany).	• Potential pathway to the environment if ENMs pass through landfill liners and leachate treatment. Secondary pathways could include landfill surface and landfill gas.	• Wastewater sludge can be transferred to agricultural applications. Potential transformation of ENMs in soil, their interactions with plants and bacteria in the rhizosphere, and their transfer to surface water has never been studied in depth.
Available measures for risk minimisation	• Best available techniques (BAT) do not typically address specific measures for ENMs, however may be a good approach to minimise exposure.			

and significant additional research is going to be needed, building-up to an almost overwhelming research agenda. The lack of knowledge and data is due to the fact that this is an emerging and active area of research in which new publications are constantly being released. However, the material also provides some indication on how work could be prioritised. Some of these suggestions are relatively straightforward and typically apply to the assessment of chemicals, such as to focus attention on high volume and high risk ENMs. The OECD's Working Party on Manufactured Nanomaterials is currently looking into assessing the hazard and exposure of different types of ENMs and should be able to provide important guidance in this respect. Similarly, it is suggested that research should focus on those ENMs that are contained in gases and liquids first, since the exposure to these is potentially greater than to solids, due to the fact that they spread more quickly and more easily enter the human body through inhaling or ingestion.

Research is also too often carried-out in the laboratory rather than using real products containing ENMs in actual waste treatment facilities. More needs to be done to assess the effectiveness of existing facilities, including those that do not operate according to best available technology standards, which are widespread in some parts of the world where most waste is treated in such operations.

The survey also suggests that, due to the linkages that exist between different waste treatment operations, there should be particular attention brought to those treatment technologies that are used to deal with residual wastes. Landfills are potentially going to receive the largest concentrations of ENMs as is suggested by the accumulation of ENMs in fly and bottom ash from incinerators as well as sewage sludge, all of which are frequently disposed of in landfills. Similarly, little attention has been brought to the use of sewage sludge that contains ENMs in agriculture or the risks that may be linked to ENMs that are contained in recycled materials.

Finally, there are a number of areas where the scientific evidence is currently contradictory, such as for anaerobic and denitrification processes in wastewater treatment, or where an insufficient body of research is available, such as for landfills and where more research is urgently needed.

Recommended areas for further research on waste containing nanomaterials

Recommended areas that require further research identified by the literature review are provided below.

Identification and quantification of ENMs in waste flows

- Identify the types and quantities of ENMs entering waste treatment processes.

Behaviour and fate of nanomaterials in waste treatment processes

- Assess the effectiveness of real scale operations such as actual plants or pilot plants incorporating all stages of waste treatment processes and using actual waste products.
- Deepen the understanding of the fate of ENMs in waste treatment processes in the following areas in particular:
  - Where scientific findings are currently contradictory (anaerobic and denitrification processes of wastewater treatment, flue gas treatment of incinerators).
  - Where there is an insufficient number of studies available (recycling facilities, landfills).

Potential emissions of ENMs from residual waste and/or material recovery

- Investigate the impact of agricultural application of sludge containing ENMs.
- Investigate the effectiveness of landfills in serving as a final sink for ENMs.
- Investigate potential risks of secondary materials that contain ENMs.

Emission control and Best Available Technologies

- Determine the effectiveness of best available waste treatment technologies in retaining or eliminating ENMs and protecting workers from exposure to ENMs.
- Assess effectiveness or impacts of sub-standard waste treatment technologies (e.g. incinerators with inadequate flue gas treatment, clay liners in older landfills or uncontrolled landfills).
- Research effective measures to capture, divert or eliminate ENMs from waste streams and residual waste.

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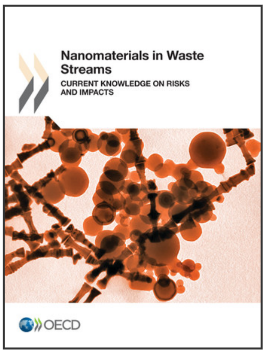

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