



Characterization of waste from nanoenabled products

Occurrence, distribution, fate and nanoparticle release

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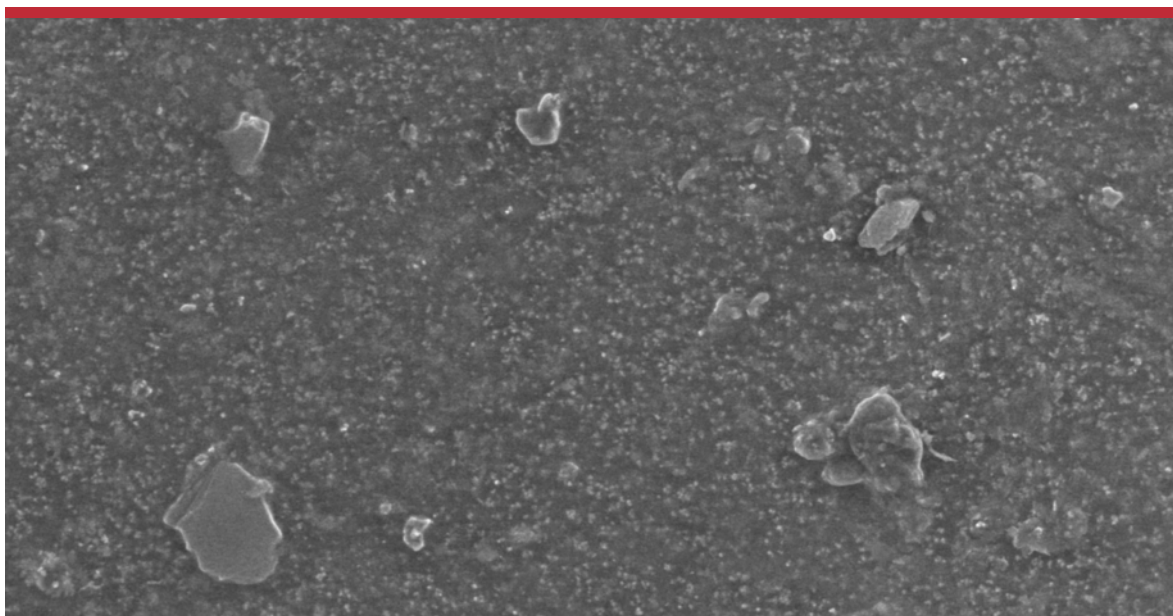
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Characterization of waste from nano-enabled products

Occurrence, distribution, fate and nanoparticle release



Laura Roverskov Heggelund

PhD Thesis
July 2017

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DTU Environment

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Characterisation of waste from nano-enabled products - occurrence, distribution, fate and nanoparticle release

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The synopsis part of this thesis is available as a PDF-file for download from the DTU research database ORBIT: <http://www.orbit.dtu.dk>.

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Preface

This PhD thesis presents research in the field of nanotechnology, with a specific focus on the characterisation of waste from nano-enabled consumer products. The PhD study was conducted from January 2014 to July 2017 at the Department of Environmental Engineering, Technical University of Denmark (DTU) under the supervision of Senior Researcher Alessio Boldrin PhD and the co-supervision of Associate Professor Steffen Foss Hansen PhD and Professor Thomas Fruergaard Astrup PhD.

The thesis is organised in two parts: the first part puts into context the findings of the PhD in an introductory review, while the second part consists of the papers listed below. These will be referred to in the thesis by their paper number, written in Roman numerals **I-III**.

- I.** Hansen, S.F., **Heggelund, L.R.**, Besora, P.R., Mackevica, A., Boldrin, A., Baun, A. Nanoproducts – What is Actually Available to European Consumers? *Environ Sci: Nano*, 2016, 3, 169.
- II.** **Heggelund, L.**, Hansen, S.F., Astrup, T.F., Boldrin, A. Semi-quantitative analysis of solid waste flows from nano-enabled consumer products in Europe, Denmark and the UK – abundance, distribution and management. *Waste Management* 56 (2016) 584-592.
- III.** **Heggelund, L.**, Mackevica, A., Olsson, M.E., Hansen, S.F., Astrup, T.F., Jurkschat, K., Crossley A., Boldrin, A. Methodological challenges regarding the characterisation of leaching from nanowaste products. *Submitted to Environ. Sci.: Nano*, 2017.

In this online version of the thesis, papers **I-III** are not included but can be obtained from electronic article databases, e.g. via www.orbit.dtu.dk or on request from DTU Environment, Technical University of Denmark, Miljøvej, Building 113, 2800 Kgs. Lyngby, Denmark, info@env.dtu.dk.

In addition, the following publications, not included in this thesis, were also concluded during this PhD study:

Nowack, B., Boldrin, A., Caballero, A., Hansen, S.F., Gottschalk, F., **Heggelund, L.**, Hennig, M., Mackevica, A., Maes, H., Navratilova, J., Neubauer, N., Peters, R., Rose, J., Schäffer, A., Scifo, L., von Leeuwen, S., von der Kammer, F., Wohlleben, W., Wyrwoll, A., Hristozov, D. 2016. Meeting the needs for Released nanomaterials required for further testing – the SUN approach. *Environ. Sci. Technol.*, 2016, 50 (6), pp 2747–2753.

Mackevica, A., Olsson, M.E., Mines, P.D., **Heggelund, L.R.**, Hansen, S.F. 2016. Estimation of dermal transfer of nanoparticles from consumer articles by wipe sampling. *Manuscript*.

Boldrin, A., **Heggelund, L.**, Hundebøll, N., Hansen, S.F. 2016. Guidelines for safe handling of waste flows containing NOAA. Deliverable report 7.6 for SUN – Sustainable Nanotechnologies, Grant Agreement Number 604305, October 2016. Available online: http://www.sun-fp7.eu/wp-content/uploads/2017/01/SUN_Deliverable_7_6.pdf

Boldrin, A., **Heggelund, L.**, Hansen, S.F. 2015. Report on methods for characterizing the composition and physical properties of NOAA-containing waste. Deliverable report 3.5 for SUN – Sustainable Nanotechnologies, Grant Agreement Number 604305. September 2015. Available online: http://www.sun-fp7.eu/wp-content/uploads/2017/01/SUN_Deliverable_3_5.pdf

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Summary

In the last decades, benefits provided by nanotechnology have been utilised for example to increase the sustainability and functionality of consumer products. Engineered nanomaterials (ENMs) are widely used in consumer products across different applications, but their use in nanoproducts has not been regulated specifically - as is the case for other chemicals and substances. This has caused concern regarding the possible release and effects of ENMs during the life cycle of nanoproducts. Specifically knowledge regarding the end-of-life phase is limited. In order to assess the potential environmental exposure or risks associated with ENMs in waste from nanoproducts, it is necessary to investigate what ENMs are being used and to which extent, how they are treated at the end-of-life of the nanoproduct and, finally, what is the likelihood of them being released during waste treatment. This PhD project addressed these knowledge gaps by mapping and analysing available nano-enabled products, developing a method for categorising waste material fractions of nanoproducts and estimating their likely waste treatment. Furthermore, new experimental data regarding ENM release from nano-enabled products was provided, applying a standardised waste characterisation test.

To investigate the abundance and distribution of nanoproducts, different product inventories exist, such as BUND, PEN CPI and The Nanodatabase. However, they are all limited by the lack of available quantitative information about ENM mass or particle number in the products. Overall, the most common product applications for ENMs are the “Health & Fitness” or “Home & Garden” sector, which was still the case, despite the increasing number of nanoproducts. The product inventories PEN CPI and The Nanodatabase are based on manufacturers’ claims regarding nanotechnology, which are often unsubstantial leading to many products being registered with an unknown ENM, such as 64% of all products registered on The Nanodatabase. It was discovered that out of all ENMs registered on The Nanodatabase nano-Ag was used in the greatest number of products and in a range of product applications (e.g. in cosmetics, textiles and food containers).

By utilising The Nanodatabase product inventory, a method was developed for analysing the distribution of ENMs in waste, which involved the estimation of ENM fate in selected waste treatments based on their main matrix ma-

terial. This information was included on The Nanodatabase to enable the online analysis of different waste treatment scenarios. The waste treatment analysis revealed that the most significant waste material fraction was “Plastic packaging” followed by “Electronic”, “Textile” and “Multi material” waste. “Plastic packaging” waste involved mainly the large number of products sold in plastic containers, meaning that the remaining ENM mass at the time of disposal is expected to be minor. Nano-Ag was widespread across the identified waste fractions, thereby corresponding with the wide use of the material in different product categories. Furthermore, titanium-, silicon- and carbon-based ENMs were also present in several different waste material fractions (i.e. “Electronic”, “Multi material”, “Unknown”, “Plastic, other” and “Plastic, packaging”), whereas nano-phosphate and bamboo charcoal were only found in “Batteries” and “Textile” waste, respectively. In terms of waste treatment, it was estimated that on average in the EU around 50% of nano-enabled products are recycled, 19% are incinerated and 26% landfilled. However, these percentages depend on the specific waste treatments available in the investigated region. It is also expected that more ENMs will eventually enter a landfill, since they may accumulate in sewage sludge or waste incineration ashes, both of which are often landfilled.

Another prerequisite for ENM characterisation in a waste scenario is the ability to quantify the potential ENM release from a nanowaste matrix. Experimental characterisation of ENM release from nano-enabled products or waste matrices is scarce, and most studies are limited by analytical constraints to detect the ENMs, or have investigated an artificial or “spiked” waste matrix. These studies cannot identify the behaviour of ENMs released from a real nano-enabled product nor how realistic environmental conditions will influence this release. The main challenges facing experimental nanowaste characterisation relate to the complexity of the matrices (both the waste matrix itself and the variety of ENM and product matrix combinations), the low concentration of ENMs present in the waste and, for some ENMs, the background quantities of natural particles being high making it near impossible to distinguish between engineered and natural entities.

In this thesis, selected nanoproducts were investigated using a standardised waste characterisation test and the potential ENM release was characterised using nano-specific methods, namely single particle-ICP-MS, TEM/EDX and zeta potential. Since more than 50% of ENMs are expected to be landfilled on

a global scale, a standardised batch leaching test was applied to characterise the nanoproducts. The case studies represented two different types of ENMs and product matrices: self-cleaning ceramic tiles with a nano-TiO₂ coating and wood painted with nano-CuO wood protection paint. Different environmental conditions were mimicked i.e. high ionic strength (added CaCl₂) and addition of organic matter. For both materials, the potential ENM release under these conditions was considered to be low, but they indicated that, there was an effect of media conditions on the particles released from a nano-enabled product. For nano-TiO₂-coated tiles, total titanium release was approximately 0.01 µg/g material or below detection limit, slightly higher concentrations were found in leachates from nano-enabled tiles. Particle sizes and number concentrations were below calculated limits of detection (with the exception of one sample, “Ti CAL”) and the sp-ICP-MS analysis generally suffered interference from calcium. For wood painted with nano-CuO paint, presence of nano-Cu particles, of approximately 60-80nm in size, was confirmed using sp-ICP-MS. However, these findings are associated with uncertainty, and so additional tests are needed to assess quantitatively the nano-CuO release in terms of particle size and number concentration. While these two case studies showed limited release, it cannot be excluded that other matrix and ENM combinations may cause more significant releases.

New approaches concerning nanowaste characterisation, both indirect and direct methods, were presented in this thesis, but further research is needed to develop and validate these methods. Future studies, assessing the potential release of ENMs from waste, should apply nano-enabled products and different product matrix combinations to take into account the transformations of the ENMs which may occur during the product life cycle. The development of analytical methods is promising e.g. the use of fingerprinting or other tracer techniques for ENMs, and sp-ICP-MS is becoming a routine analysis, though large challenges regarding matrix complexity and interferences still persist. Considering the large number of nanoproducts available, the potential release of ENMs from these products would have to be understood to perform a risk assessment of these products. Since ENMs are considered possible contaminants of the solid waste, it is important to include nano-specific characterisation tests in waste characterisation to ensure a safe disposal of the nanowaste.

Dansk sammenfatning

Nanoteknologi tilbyder mange fordele som kan udnyttes til at forbedre f.eks. bæredygtigheden eller funktionaliteten af forskellige forbrugerprodukter. Syntetiske nanomaterialer (SNM) bliver i dag brugt i mange forbrugerprodukter, men brugen af disse specifikt fremstillede materialer er ikke specifikt reguleret, som det er tilfældet for såkaldt konventionelle kemikalier. Dette skaber bekymring på grund af uvisheden omkring hvorvidt SNM frigives igennem produkternes livscyklus og de miljøeffekter dette kunne medføre. Særligt når det kommer til bortskaffelsesfasen, er der begrænset viden om tilgængeligheden af SNM fra forbrugerprodukter. For at kunne vurdere den potentielle miljørisiko associeret med SNM i affald er det nødvendigt at undersøge både hvilke SNM der bruges – og i hvilket omfang, hvordan SNM behandles i affaldsfasen afhængig af den produktmatrix de er til stede i, samt sandsynligheden for at SNM kan frigives under affaldsbehandlingen. Derfor havde denne PhD afhandling til formål at i. kortlægge tilgængelige forbrugerprodukter indeholdende SNM (nanoprodukter) samt analysere fordelingen og brugen af SNM i forskellige produktkategorier, ii. udvikle en metode til kategorisering af affaldsfraktioner for nanoprodukter og estimere hvilken affaldsbehandling disse produkter sandsynligvis vil underlægges, iii. analysere genereret nanoaffald fra forbrugerprodukter i forhold til udbredelsen, fordelingen og affaldsbehandlingen af SNM, iv. undersøge frigivelsen af udvalgte SNM fra nanoprodukter eksperimentelt ved hjælp af en standardiseret procedure for affaldskarakterisering og, v. at komme med anbefalinger til fremtidige studier, som kombinerer nano-karakterisering og standardiseret affaldskarakterisering.

Til at undersøge udbredelsen og fordelingen af nanoprodukter kan bruges forskellige produktregistre f.eks. BUND, PEN CPI og The Nanodatabase. Dog er alle disse registre begrænset af manglende informationer om SNM mængde, type og/eller antallet af nanopartikler i et produkt. Overordnet set bruges SNM mest i produkter til ”Sundhed og Fitness” eller ”Hjem og Have”, og dette har ikke ændret sig indenfor de seneste år på trods af den store tilgang af nye nanoprodukter. Registerne ”PEN CPI” og ”The Nanodatabase” er baseret på producentens påstand om, at produktet er baseret på nanoteknologi, men denne påstand er ofte ubegrundet hvilket medfører at mange nanoprodukter registreres med et ukendt SNM. Dette gælder f.eks. for

64% af alle produkter registreret i The Nanodatabase. Denne analyse viste også at nanosølv benyttes hyppigst i forbrugerprodukter og at det bliver brugt i meget forskelligartede produkter såsom kosmetik, tekstiler og fødevarebeholdere.

På baggrund af informationer om registrerede produkter i The Nanodatabase, blev udviklet en metode til at analysere fordelingen af SNM i affald, hvorved skæbnen for alle SNM i udvalgte affaldssystemer estimeres ud fra nanoproduktets primære matrix materiale, f.eks. metal eller plastik. Denne information blev inkluderet i The Nanodatabase for at muliggøre en online analyse af forskellige affaldsscenarier for de registrerede nanoprodukter. Affaldsbehandlings-analysen viste at den største affaldsfraktion for nanoprodukterne var ”Plastik indpakning”, efterfulgt af ”Elektronik” og ”Tekstil” affald. ”Plastik indpakning” omfattede her primært et stort antal produkter, som sælges i plastikbeholdere, hvilket betyder, at kun en lille andel af SNM forventes at være tilbage i produktet ved endt brug. Nanosølv var til stede i næsten alle affaldsfraktioner, hvilket stemmer overens med at det benyttes i mange forskellige produkttyper. I forhold til affaldsbehandling i EU blev det estimeret, at gennemsnitligt 50% af nanoprodukterne vil gennemgå en genbrugsproces, 26% vil deponeres og 19% vil afbrændes. Dog afhænger denne fordeling af det specifikke affaldssystem i den region, der undersøges. Det forventes også at en større andel af SNM vil ende i deponi, eftersom de kan akkumulere i slam fra vandrensningsanlæg eller aske og slagge efter affaldsafbrænding, hvilke ofte deponeres.

En yderligere forudsætning for karakterisering af SNM i et affaldsscenarie er at deres potentielle frigivelse fra nano-affaldsmatricen kan kvantificeres. Ydermere, er det vigtigt at opnå en forståelse for hvordan SNM transformeres igennem nanoproduktets livscyklus. Data for eksperimentel karakterisering af SNM frigivet fra nanoprodukter eller affaldsmatricer er knap. De fleste studier er præget af analytiske begrænsninger og undersøger kun kunstige affaldsmatricer med tilsat SNM. De primære udfordringer for eksperimentel karakterisering af nanoaffald, skyldes kompleksiteten af selve affaldsmaterialet, den store variation af SNM og produktmatrix kombinationer, den lave koncentration af SNM i affaldet, samt for nogle SNM den høje naturlige baggrund af partikler. For at kunne undersøge effekten af produktets matrix på frigivelsen af SNM, er det derfor vigtigt at studere nanoprodukterne i den form de er tilgængelige for forbrugere.

I denne afhandling blev udvalgte nanoprodukter undersøgt ved hjælp af en standardiseret test til affaldskarakterisering og den potentielle frigivelse af SNM blev karakteriseret ved brug af nano-specifikke analysemetoder, her specifikt single particle-ICP-MS (sp-ICP-MS), TEM/EDX og målinger af zeta-potentiale. Eftersom mere end 50% af SNM globalt set forventes at blive deponeret blev der anvendt en standardiseret udvaskningstest til vurdering af mulig SNM frigivelse fra de udvalgte nanoprodukter. De to casestudier repræsenterede to typer af SNM og produktmaterialer: selvrensende keramiske fliser med nano-TiO₂ på overfladen og træ malet med træbeskyttelse indeholdende nano-CuO. Ydermere, blev forskellige miljøforhold efterlignet, her specifikt høj ionstyrke og tilstedeværelse af organisk materiale. For begge produkter blev det konkluderet, at den potentielle frigivelse af SNM var lav. Men især for nano-CuO viste sp-ICP-MS analysen en klar størrelsesfordeling af Cu-nanopartikler, hvor median størrelsen i udvaskningsprøver var væsentligt forskellig fra det rene udvaskningsmedie

Nye indgangsvikler og metoder til karakterisering af nanoaffald blev fremlagt i denne afhandling, men yderligere forskning er nødvendig for at videreudvikle og validere disse metoder. Fremtidige studier af SNM frigivelse fra affald bør anvende egentlige nanoprodukter i den form de produceres, samt undersøge forskellige matrixkombinationer for at tage højde for transformationer af SNM, som kan ske i produktets levetid. Udviklingen af analytiske metoder er lovende, f.eks. udvikles nye fingerprinting eller sporingsmetoder for SNM, og sp-ICP-MS bliver i højere grad end tidligere en rutineanalyse, dog med store udfordringer i forhold til matrixinterferenser. I forhold til at risikovurdere det store antal nanoprodukter, som er tilgængelige, er det nødvendigt at opnå en større forståelse af frigivelsen af SNM fra affaldsfasen. Eftersom SNM regnes som potentielle forurenende stoffer i fast affald er det vigtigt at inkludere nano-specifik karakterisering for at sikre en sikker bortskaffelse af nanoaffald.

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1 Background and aims

When materials are constructed or engineered on a very small scale, their properties differ from the natural counterpart, and their functionality can increase greatly. When considering materials on the nano-scale (10^{-9} m), some are known to change their optical properties (nano-Au) or become photo-reactive (nano-TiO₂), and it is this increased reactivity per mass that opens up many new opportunities for developing products that exploit these properties. Currently, engineered nanomaterials (ENMs) are used in a wide range of consumer products, such as personal care goods, textiles, paints or other surface coatings (The Nanodatabase, 2017). Though the great potentials and specific properties of these ENMs are recognised, their use in products aimed at consumers is not specifically regulated, which has caused concern due to their potential toxic effects and persistency (CIEL et al., 2012; Schwirn et al., 2014). The manufacture and availability of these nano-enabled products is increasing (Hansen et al., 2016 – Paper I; The Nanodatabase, 2017; PEN CPI, 2017), thereby also increasing the generation of waste containing ENMs, which has led to a growing focus on the need to understand the fate and transformations of ENMs throughout the many products' life cycle (Heggelund et al., 2016 – Paper II; OECD, 2016; Andersen et al., 2014).

However, knowledge and quantitative information about products enabled by nanotechnology are lacking, partly due to discussions regarding the definition of nanomaterials or nanoparticles. Boholm and Arvidson (2016) found 36 different definitions regarding nanomaterials, which highlights the disconsensus in this field. The definition applied in the European Union (EU) refers only to the size or particle number size distribution of the material, stating that a *”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*’ (EU Commission, 2011). It has been criticised that the definition by the EU does not consider any specific properties of purposely engineered NMs, since these are what set them apart from other materials or chemicals. In terms of the waste generated from products enabled by nanomaterials, herein referred to as “nanoproducts”, no consensus regarding its definition exists either. It was proposed by Boldrin et al., (2014) that nanowaste should be *collectable or collected waste materials being, containing or carrying en-*

gineered nanomaterials. Through this definition, it is implied that ENMs are a contaminant and not a property of the waste, and the level of contaminant (ENM) determines whether or not the waste requires special treatment. Sources of nanowaste, according to Boldrin et al. (2014), are (i) manufacturing by-products (ENMs as a single fraction) (ii) end-of-life nanoproducts and (iii) individual waste materials contaminated with ENMs (Boldrin et al., 2014).

Concerns regarding nanowaste, i.e. waste contaminated with ENMs, relates to the uncertainty about the release or accumulation of ENMs in waste treatment systems, and their associated transformations, which possibly affect their distribution. For example, if nanoproducts are incinerated, how much ENM will distribute for instance to bottom ashes, fly ashes or be caught in the filtering system? And if these ashes or filters are landfilled, how available are the ENMs for release? In order to gain more knowledge about these potential nanowaste impacts, information regarding yearly generation rates and knowledge about the fate and transformations of ENMs in waste is necessary. For the moment, it is not clear what comprises the annual loads of nanowaste going into waste treatment systems. Keller and Lazareva (2014) attempted to predict the release of ENMs on a global scale and found that the largest recipient of ENMs was landfills. However, the results from this study will depend greatly on estimated ENM production volumes and the waste treatment systems available, both of which vary greatly. Other studies have also identified waste compartments such as landfills (Reinhart et al., 2010), sewage sludge and waste incineration ashes (Sun et al., 2014) as constituting likely recipients and possible sinks for ENMs present in waste. Concerning knowledge on the fate and transformations of ENMs in waste, very few studies to date have experimentally investigated these processes (Mitrano and Nowack, 2017). ENMs can be released during any waste handling and treatment process, such as collection, recycling, incineration and landfilling (Boldrin et al., 2014), but the study of these releases is challenged by analytical constraints on detecting low concentrations of ENMs in complex matrices. Furthermore, the availability of ENMs depends on their location in the product matrix, the properties of this matrix and how the nanoproduct is treated at the end of its life (Hansen et al., 2007). The release of ENMs during use and disposal has been identified as a main concern for quantitative risk assessment (Gottschalk and Nowack, 2011), which emphasises the need for analytical tools to characterise and quantify this release. For these reasons, it is therefore important to assess the

whole life cycle of nanoproducts, and in order to do so clarify the potential for nanowaste generation, ENM types and distribution in nanowaste and the potential treatment of nanowaste, and understand the specific transformations, releases and interactions that occur during the product life cycle.

The overall aim of this PhD thesis is therefore to **investigate the occurrence and distribution of ENMs in waste from nano-enabled consumer products and to evaluate the applicability of current waste characterisation procedures to nanowaste**, focusing specifically on the following tasks:

- Mapping of available nano-enabled products and analysis of the distribution and use of ENMs (Hansen et al., 2016 - Paper I)
- Developing a method for categorising waste material fractions of nanoproducts and estimating the likely waste treatment of these fractions (Heggelund et al., 2016 - Paper II)
- Analysing nanowaste generated from nano-enabled consumer products in terms of the abundance, distribution and waste treatment of ENMs (Heggelund et al., 2016 - Paper II)
- Experimentally investigating the release of selected ENMs from real nano-enabled products using a standardised waste characterisation test (Heggelund et al., 2017 - Paper III)
- Provide recommendations for future studies regarding the combination of nano-characterisation and standardised waste characterisation tests (Heggelund et al., 2017 - Paper III)

These tasks were completed by performing a literature review and by using available online nanoprodut inventories and other online resources to clarify how ENMs are used in consumer products and how the waste materials from these products are treated at the products' end-of-life. Specifically, a method for categorising and analysing the waste material fraction and likely waste treatment of nano-enabled products in The Nanodatabase was developed in the form of an analysis tool, available at www.nanodb.dk (<http://nanodb.dk/en/analysis/waste-treatment/#chartHashsection>). Furthermore, the fate of ENMs was experimentally investigated using a standardised waste characterisation test and nano-specific characterisation methods (zeta potential, electron microscopy and single-particle inductively coupled plasma mass spectrometry) applied to selected nanoproducts (self-cleaning ceramic tiles and wood protection paint). The obtained results are discussed

in terms of their implications and the challenges that still to be overcome for nanowaste characterisation. Papers I (Hansen et al., 2016) and II (Heggelund et al., 2016) are based on the analysis of available online information about ENMs in consumer products and a subsequent categorisation of each nanoproduct according to their main matrix material. The identified matrix materials were used in Paper II (Heggelund et al., 2016) to predict a plausible waste treatment regime for each nanoproduct and to analyse the implications of different waste treatment options on the distribution of ENM. Paper III (Heggelund et al., 2017) included the experimental study of a nano-enabled consumer product within terms of estimating and characterising ENM release in the frame work of a waste characterisation test.

2 Nanoproducts available to European consumers

2.1 Abundance and distribution of nanoproducts

Knowledge about the quantity and identity of engineered nanomaterials (ENMs) used in consumer products is a prerequisite for assessing environmental and consumer exposure to ENMs. As long as this information is not readily available, risk assessment of these materials will not be accurate and cannot provide proper information to consumers and society or protect them appropriately.

Currently, several nanoproduct inventories exist, such as Consumer Product Inventory from the Project on Emerging Nanotechnologies (PEN CPI), Nanoprodukt Datenbank (BUND) and the ANEC/BEUC inventory of products containing nano-Ag. Nevertheless, none of these registries is sufficient for informing regulators or consumers, and they all have their limitations. National registers of nanomaterials or nanoproducts have also been established in Belgium, France and Denmark, due to the lack of interest in an EU-wide catalogue.

The main limitations of existing nanoproduct inventories are that they are not continuously updated, and consequently they do not follow the development of nanoproducts in the market in terms of both new products being introduced and products being taken off the market or losing their nano-claim. Moreover, some inventories are not available to the public, which means that consumers cannot access information regarding the products they buy. Additionally, none of the inventories allows for independent analysis of the included data, and they do not provide health and safety information about their products or materials.

The Nanodatabase was established in 2012 to address some of these limitations. It was founded as a collaborative effort between the Danish ecological council and DTU Environment. The Nanodatabase is updated on a daily basis, and all of its content is readily available online. Furthermore, the user has access to different analysis tools, to sort products and extract different information, and a health and safety profile is provided for each product.

Limitations of The Nanodatabase include the fact that, similarly to the PEN inventory, it is based on manufactures' claims regarding their products. This means that the inventory potentially also includes products which are in fact not based on nanotechnology, or it might fail to include products where nano-enabling is not advertised. Furthermore, The Nanodatabase focuses on nano-products available on the European market and does not have a global focus. However, this inventory does include products available for online purchase in the EU, which also accounts for products stemming from outside the European Union.

Hansen et al. (2016 – Paper I) found that by the end of 2015, The Nanodatabase already included 400 nanoproducts more than the CPI despite only being online for four years versus ten years for the latter. This is mainly due to the update frequency of The Nanodatabase (i.e. daily) which is much higher than for the CPI. The difference in update frequency still exists and only 13 products have been added to the CPI since the end of 2015 (PEN CPI, 2017), giving a total of 1,827 products. In the same time period, 726 products were added to The Nanodatabase, giving a total of 3,000 products (The Nanodatabase, 2017 (3/4)). The additional products contained in The Nanodatabase are spread evenly across the product categories, e.g. the categories “Home and Garden”, “Automotive”, “Health and Fitness”, “Appliances” and “Goods for Children” contain between 20 and 53% more products compared to the CPI (Hansen et al., 2016 – Paper I). However, in both inventories, “Health and Fitness” constitutes the largest number of products. Based on the distribution of nanoproducts in The Nanodatabase, Hansen et al. (2016 – Paper I) showed that in some fields, such as the “Health and Fitness” sector, there is a broad application of ENMs, meaning that the products fall into several different subcategories, e.g. “Personal care”, “Clothing” and “Sporting goods”. In other product categories, such as “Home and Garden”, the analysis revealed potential for the further development and utilisation of nanotechnologies, since the nanoproducts seem to be limited to one main subcategory (“Cleaning”). Hence, there might be a potential development in the use of ENMs in subcategories such as “Paint” and “Construction materials”. Alternatively, it might be that currently the nano-claim is not extensively used in the advertisement of these product types, and therefore they are not registered in The Nanodatabase.

Across all product categories, nano-Ag is the most frequently used ENM in consumer products (Hansen et al., 2016 – Paper I; PEN CPI, 2017; The Nanodatabase, 2017). Other nanomaterials are represented only in one product category, e.g. nano-phosphate in “Appliances”. However, for a large number of products, the identity of the used ENM is unknown accounting for approximately 80% or more of the total number of products in some categories (i.e. “Automotive”, “Electronics and Computers” and “Home and Garden”). For the product categories “Appliances” and “Goods for Children”, the percentages of products with an unknown ENM were only 15% and 17%, respectively. This could indicate that perhaps goods for children are regulated more in terms of their chemical or material content. The study by Hansen et al. (2016 – Paper I) also showed that there is a transatlantic difference in the usage of different ENMs (see Figure 2.1). For example, the ENMs titanium/titanium dioxide, carbon, carbon nanotubes and gold are found more frequently in The Nanodatabase products (between 26% and 62% more frequent), which has a European perspective compared to the global/North American perspective of the PEN CPI.

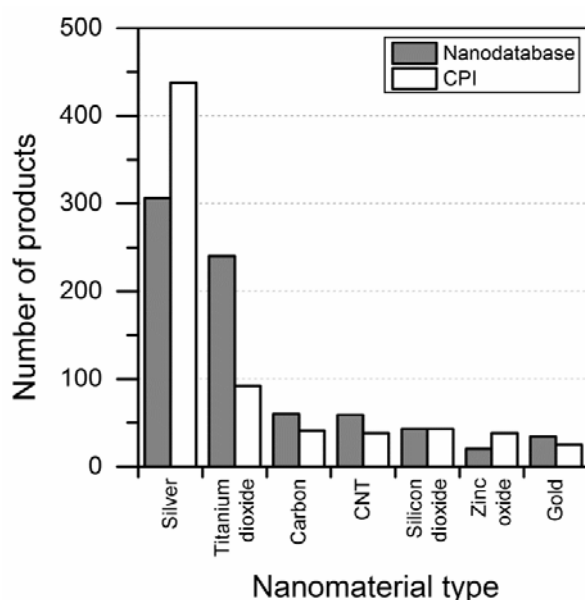


Figure 2.1. Number of nanoproducts registered on CPI and The Nanodatabase containing a certain nanomaterial type (from Hansen et al., 2016 – Paper I). The analysis is based on selected products from a total of 1,827 nanoproducts.

On the other hand, the CPI contains 43% more products with nano-Ag which might be due the products' country of origin or the historical emphasis on nano-Ag products by this inventory (Hansen et al., 2016 – Paper I). It might also be related to differences in the regulation of nano-Ag between the EU and the US, or differences in consumer behaviour and demands.

Generally, there seems to be a discrepancy between the ENMs reported to be used in various products (on The Nanodatabase, PEN CPI and BUND) and those actually being used in industry (Hansen et al., 2016 – Paper I). The problem stems from the fact that many ENMs are used in consumer products without being disclosed by the manufacturers. The European Commission has documented this contradiction in their Staff Working Paper (from the Second Regulatory Review on Nanomaterials), in which they mention the widespread use of, for instance nano-silica, carbon black and CNTs in products used on a regular basis by consumers (EU Commission, 2012). This lack of mandatory reporting of ENMs in consumer products continues to be a limiting factor for risk assessment. According to Hansen et al. (2016 – Paper I), only the European Cosmetics Directive demands the declaration of nano-sized ingredients; yet still almost 50% of the products in the “Cosmetics” category on The Nanodatabase contain an unknown ENM.

2.2 Recent developments in the distribution of nanoproducts and nanomaterials

Figure 2.2 depicts the overall development in the number of nanoproducts available on The Nanodatabase, while the individual differences based on each ENM are summarised in Table 2.1. Compared to the analysis from 2015 (Hansen et al., 2016 – Paper I), “Health and Fitness” is still the largest product category (see Figure 2.2), and nano-Ag, which is still the most predominant ENM, has seen its use increase by 15% in the last two years (see Table 2.1). However, while reviewing the inventory, it was found that some development has taken place in the “Home and Garden” product category. Currently, ten subcategories are represented in it, compared to only eight in 2015 (The Nanodatabase, 2017). Although, the overall distribution of products is similar to 2015, the total number of products has also risen, from 298 products in 2015 to 555 products in 2017, which corresponds to an increase of 86% (see Table 2.1).

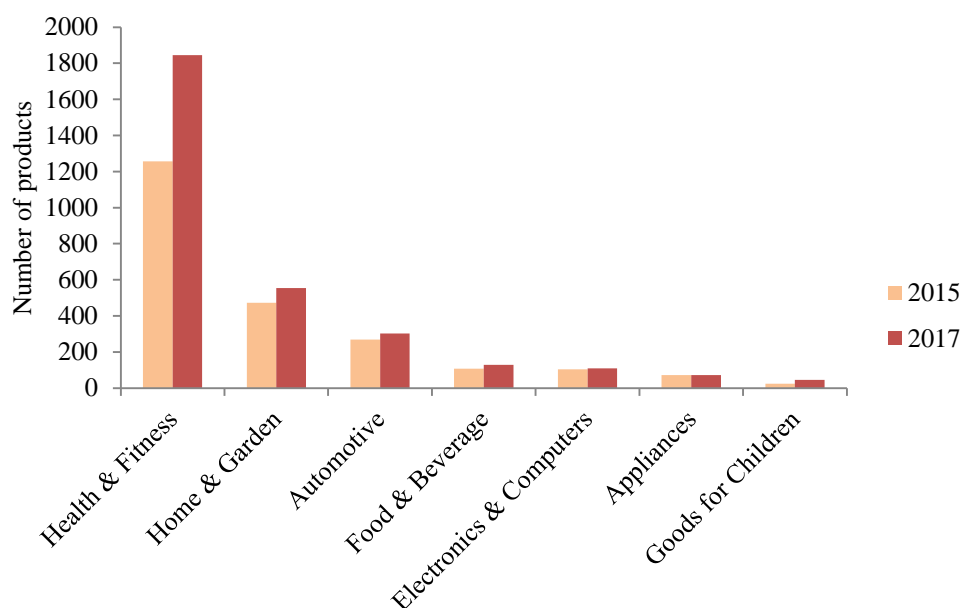


Figure 2.2. The graph compares the number of nanoproducts in each main category of The Nanodatabase in 2015 (orange) and 2017 (red). The analysis is based on the 3000 nanoproducts registered on The Nanodatabase in 2017 (April).

This increase in the number of products shows that the market for nanoproducts in this area (“Home and Garden”) has increased markedly in the last two years, although the range of applications has not significantly expanded. Other explanations might be that the nano-claim is now used more often as a market strategy, or that the products are now available to a greater extent for purchase online. In some cases, the use of ENMs have changed; for example, as seen in Table 2.1, nano-Au is no longer significantly used in the “Appliances” category but is now being used in the “Food and Beverage” and “Automotive” categories. There has also been an overall increase of 11% in the number of products containing gold ENMs, which suggests that this ENM is used more widely now (2017) compared to 2015 (see Table 2.1). This seems surprising considering the high price of raw gold, and it might be that some nano-Au products are based on “empty nano claims”. A similar development is observed for nano-SiO₂, the use of which in consumer products on The Nanodatabase has increased by 22% from 2015 to 2017. This ENM is now used in four product categories (“Food and Beverage”, “Home and Garden”, “Automotive” and “Health and Fitness”) compared to only one (“Health and Fitness”) in 2015 (see Table 2.1).

Table 2.1. Summary of the development in the use of selected ENMs (i.e. the ones analysed by Hansen et al., 2016 – Paper I) in consumer products from 2015 to 2017. The total numbers refer to the number of products containing the specific ENM. (Analysis performed on 3000 products on The Nanodatabase (April, 2017))

Nanomaterial	Notes	Total number 2015	Total number 2017
ZnO	No change.	20	21
Graphite	No change.	20	20
Au	No longer significantly present in Appliances, instead in Food & Beverage and Automotive. More widely used, 11% increase in total number of products.	35	39
SiO ₂	Used in four categories compared to only one in 2015 (Health & Fitness). 22% increase in total number of products.	45	55
Bamboo charcoal	No change.	43	43
Phosphate	No change.	42	43
CNTs	Apart from Health & Fitness, also used in Home & Garden and Electronics. More widely used, 8% increase in total number of products.	59	64
Carbon	Predominantly used in Health & Fitness, 5% increase in total number of products.	60	63
TiO ₂	Along with Health & Fitness and Home & Garden, now also used in Food & Beverage. 21% increase in total number of products.	102	123
Ti	No change in distribution, slight increase in total number of products (4%).	139	145
Ag	No change in distribution, but large increase in total number of products (15%).	331	379

Interestingly, the use of nano-TiO₂ has also increased significantly from a total of 102 to 123 products, corresponding to a 22% rise, and it seems the expansion has taken place in the market for “Food and Beverage” products (The Nanodatabase, 2017). CNTs are also more widely used across the different product categories in 2017 compared to 2015, although the increase in the use of the material only corresponds to an 8% increase overall (see Table 2.1). Some ENMs were not mentioned specifically by Hansen et al. (2016 – Paper I) (grouped as “others”), but due to the increase in the number of products, they are now contained in 20 products or more. Specifically, this applies to nano diamond (26 products, “Health and Fitness” and “Automotive”), silicon (25 products, “Health and Fitness”, “Electronics and Computers” and “Automotive”) and Bisoctrizole (20 products, only “Health and Fitness”).

Compared to 2015, the percentage of products with an unknown nanomaterial type continues to be high (see Table 2.2). Only in the “Automotive” and “Food & Beverage” categories we do see a slight decrease (1-3%) in the number of products with unknown ENMs. The categories “Goods for Children” and “Health & Fitness” represent most of the increase in the number of products with unknown ENMs, and here the percentages have increased by 38 and 10%, respectively (Table 2.2). Concerning “Goods for Children”, this forms a very different picture compared to the analysis by Hansen et al. (2016 – Paper I).

Table 2.2. Percentage of products in each main category with an unknown ENM and the development in percentage terms from 2015 to 2017. Total numbers refer to the number of products containing the specific ENM. (Analysis performed on 3,000 products on The Nanodatabase (April, 2017)).

Category	% of ENMs unknown in 2017	Δ% (2015 to 2017)
Automotive	86	-3
Electronics	80	1
Home & Garden	83	3
Appliances	15	0
Goods for Children	55	38
Food and Beverage	34	-1
Health & Fitness	57	10
Total (% of all products)	64	6

The large number of products with unknown ENMs indicates the need for regulation or transparency in the market for nano-enabled consumer products. In some areas, such as European regulations on cosmetics, a declaration of nanomaterials in a product is required. However, information on The Nanodatabase for cosmetic products (“Health and Fitness” category) indicates that the implementation or enforcement of this regulation is still not sufficient, since 57% of these products contain an unknown ENM type (Table 2.2).

3 Nanowaste from consumer products: distribution and treatment

3.1 Introduction to the assessment of nanowaste distribution and treatment

The increasing number of nanoproducts entering the market is causing concern due to a lack of knowledge about the fate of ENMs inside these products throughout the life cycle. In particular, empirical data investigating the end-of-life phase of ENMs in nanoproducts is scarce, due mainly to analytical challenges, since it is difficult to investigate ENMs in complex matrices such as solid waste. Therefore, the quantities of generated nanowaste are largely unknown (Reinhart et al., 2010). In light of these challenges, studies have tried to model the likely distribution and fate of ENMs in different waste treatment scenarios (Gottschalk et al., 2009; Caballero-Guzman et al., 2015; Sun et al., 2014; Keller et al., 2014; Asmatulu et al., 2012; Heggelund et al., 2016 – Paper II; Boldrin et al., 2014). Different modelling approaches have been applied, such as probabilistic material flow modelling, market analysis and life cycle assessment, but the major limitation of these approaches is the poor availability of input data for the models. In some cases, this is compensated for by using probability distributions as inputs rather than definite numbers (probabilistic material flow analysis). For example, Sun et al. (2014) conducted such an analysis of selected ENMs (nano-TiO₂, nano-Ag, nano-ZnO, fullerenes and CNTs) and looked at the likely distribution of each ENM in: different environmental compartments, possible end-of-life treatments (sewage treatment plant, waste incineration plant and landfill) and the emissions/residues from these treatments. The authors predicted the highest concentrations would occur in residue from waste treatment such as sewage sludge, and bottom ash and fly ash from waste incineration. This means that waste treatment compartments are likely to be a sink for ENMs in nanoproducts, which lends support to the prioritisation of experimental studies on their characterisation in solid waste. Boldrin et al. (2014) employed a market product analysis to three nanoproduct case studies (nano-Ag in textiles, nano-TiO₂ in sunscreen and CNTs in tennis racquets) and were able to estimate the yearly amounts of ENMs present in waste from these selected products. The quantification of ENM amounts in this waste was based on the best available data on yearly production of the product and its expected life time, the market

penetration of the nanoproduct and estimates of ENM lost while using the product. Overall, Boldrin et al. (2014) estimated global environmental ENM exposures from the three case studies of 0.78-5.3, 14.3-143, 0.47-1.23 Mg/year for nano-Ag, nano-TiO₂ and CNTs, respectively. Another approach was adopted by Heggelund et al. (2016 – Paper II), whose modelling was based on the categorisation of nanoproducts available on the market and a subsequent analysis of the numbers of products. The advantage of this approach is that it was based on nanoproducts actually known to be currently on the market, by utilising the analysis tools in The Nanodatabase (www.nanodb.dk).

3.2 Distribution and treatment of nanowaste based on number of products

Heggelund et al. (2016 – Paper II) describe how knowledge about each nanoproduct on The Nanodatabase is combined with an assigned solid waste material type and a likely waste treatment scenario based on waste management statistics for any chosen country or region. The method involves four steps: first, the categorisation of available nano-enabled products into waste material fractions; second, an estimation of the types of ENMs present in waste material fractions; third, an estimation of the region-specific waste treatment of individual waste material fractions and fourth, a combination of steps two and three, to determine the distribution of ENMs routed to specific waste treatment options. In order to complete step one, nine solid waste material fractions were identified based on the main matrix material of each product. Table 3.1 presents the fractions identified by Heggelund et al. (2016 – Paper II).

Table 3.1. Descriptions of waste material fractions on The Nanodatabase (From Heggelund et al., 2016 – Paper II).

Waste material fraction	Description and examples
Batteries	Typically these products are batteries for an electrical item, with the nanocomponent only present in the battery.
Electronics	Generally products with electrical connections, e.g. refrigerators, hairdryers, electric toys, etc.
Glass	Cosmetic products, supplements or other products sold in glass containers.
Metal	Generally consists of containers such as cans or metal sports equipment.
Multi-material waste	These products contain more than one material that cannot readily be separated, e.g. camera lenses, a baby carriage and a water filtering unit.
Plastic, packaging	Typically waste from used plastic containers for cleaning/cosmetic products, which contain nanoproduct residue.
Plastic, other	Generally plastic products whereby the nano component is embedded in/surface-coats the plastic, such as sports equipment, baby bottles, food containers and toothbrushes.
Textile	Fibrous material, typically clothing or bandages, with a nano coating or nanomaterial embedded in the fibres.
Unknown	If no image is available showing the specific product and the container it is sold in, or it cannot be derived from the product description, this category is used.

Steps two and three were based on information available on The Nanodatabase, which meant that certain limitations applied. In some cases, no image or description of a product was available, and therefore the appropriate waste material fraction could not be identified. These products were placed in the “Unknown” waste category. Similarly, for approximately 40% of the products analysed in the study, the ENM was unknown which meant that they could not be included in the final waste treatment analysis (Heggelund et al., 2016 – Paper II). After modifying the data the analysis was based on a total of 963 nanoproducts.

Nanoproducts registered on The Nanodatabase, the number of products in each solid waste fraction and the distribution of ENMs in each fraction as analysed by Heggelund et al. (2016 – Paper II) are depicted in Figure 3.1. The largest solid waste fractions identified by Heggelund et al. (2016 – Paper II) were “Plastic, Packaging”, “Textile” and “Electronics”, and the most predominant ENM was nano-Ag.

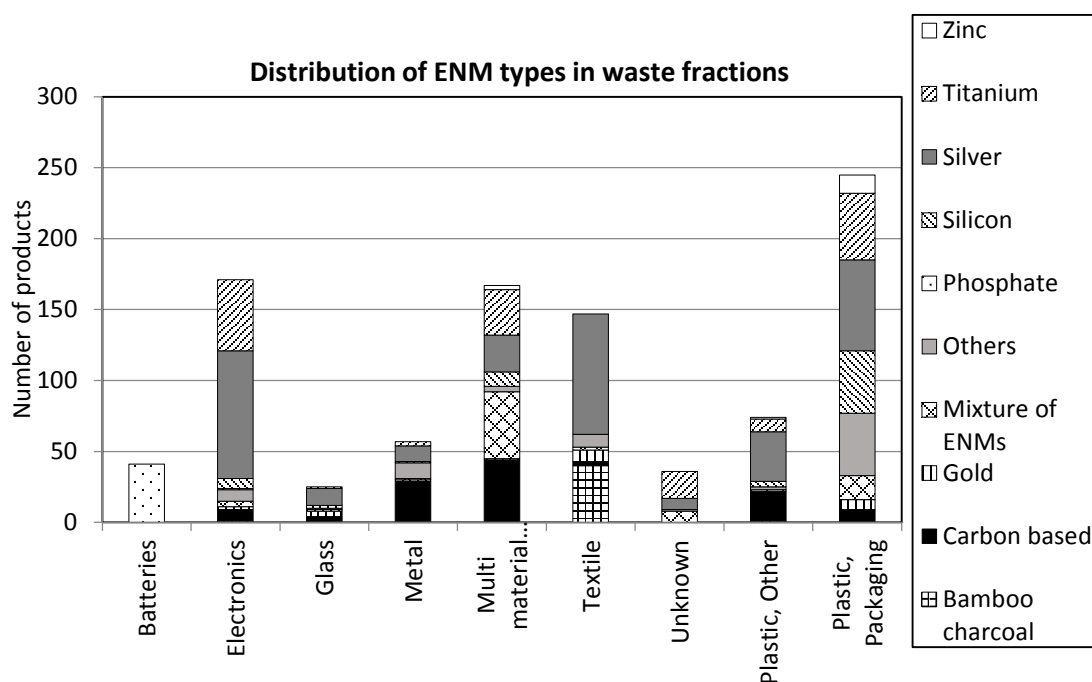


Figure 3.1. Distribution of ENMs in solid waste fractions according to ENM types. The analysis is based on 963 nanoproducts on The Nanodatabase in 2015 (products with unknown ENMs are not included) (Heggelund et al., 2016 – Paper II).

Nano-Ag is present across almost all the identified waste material fractions (Plastic, Packaging; Plastic, Other; Textile; Multi material waste; Metal; Glass and Electronics), confirming that it is used in many different product applications (e.g. electronics and personal care products). In terms of number of the number of products, the most widespread ENMs, apart from nano-Ag, are titanium-, silicon- and carbon-based ENMs. Other ENMs, such as nano-phosphate and bamboo charcoal, are only present in one waste material fraction, namely “Batteries” and “Textile” waste, which is consistent with the use of these materials.

To obtain statistical data on the treatment of solid waste fractions, Heggelund et al. (2016 – Paper II) used the most recent figures available from Eurostat (<http://ec.europa.eu/eurostat/web/waste>). Information about the treatment of selected waste fractions yielded four different treatment options namely incineration, recycling, landfilling and anaerobic digestion/composting. Figure 3.2 shows the relative distribution of nanoproducts across the four different waste treatments in selected countries/regions (Denmark, United Kingdom and the EU). It is clear that “Compost/Anaerobic digestion” is not a likely

waste treatment for nanoproducts, since all selected regions route less than 10% of their waste through this process. Meanwhile, “Recycling” is identified as the most likely waste treatment for nanoproducts in all three regions. However, this method can involve many types of activities, e.g. extrusion and remoulding of plastic or re-melting of glass and metal waste, and in some cases, it is not the final end-of-life for the nanoproducts (Caballero-Guzman et al., 2015). Furthermore, ENMs are not always expected to be associated with the recyclable material fraction of a product, meaning that they will be discarded from the recycling stream and instead may be incinerated or landfilled (Hincapie et al., 2015). The differences between regions lie mainly in the incineration and landfilling treatment scenarios. According to Heggelund et al. (2016 – Paper II) the UK routes 13% of nanoproducts to incineration and 29% to landfilling, whereas the estimated numbers for Denmark are 38% and 8%, respectively. However, it might be that residues from incineration (bottom ash, fly ash, APC residues) are landfilled as hazardous waste, and in this sense incineration may not be the final destination for nanoproducts (Part et al., 2016; Mitrano et al., 2017).

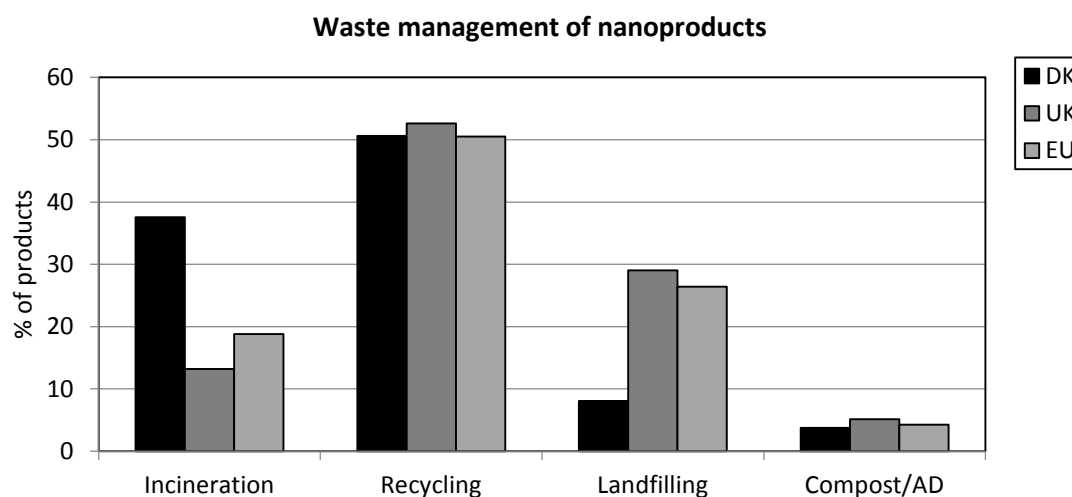


Figure 3.2. Relative distribution (%) of end-of-life nanoproducts into waste treatment options in the three analysed scenarios: Europe (EU), Denmark (DK) and the United Kingdom (UK) (total number of products: 963 products; products with unknown ENMs are not included) (From Heggelund et al., 2016 – Paper II).

Country-specific waste statistics for Denmark and the UK were applied to the nanoproduct analysis and the identified waste material fractions to illustrate possible ENM distributions, depending on the country's waste treatment options (Figure 3.3, Heggelund et al., 2016 – Paper II). The relative importance of each waste treatment (i.e. incineration, recycling, landfilling and anaerobic digestion) is reflected in the size of each pie-chart in Figure 3.3, from which Heggelund et al. (2016 – Paper II) concluded that for all country profiles, recycling was the most important way of treating nanoproducts. Denmark utilises waste incineration with energy recovery to a high extent, whereas the EU and the UK depend more on landfilling. The main difference in the distribution of ENMs between the scenarios analysed by Heggelund et al. (2016 – Paper II) stems from differences in the management of plastic and textile waste. Plastic waste, from both used product containers (“Plastic, packaging”) and other sources (“Plastic, other”), seems to be landfilled to a greater extent in the UK compared to Denmark. Consequently, titanium- and carbon-based ENMs will be more prevalent in the UK landfill scenario (Figure 3.3). According to Heggelund et al. (2016 – Paper II), textile waste is landfilled to a higher extent in Denmark, and therefore nano-Au and bamboo charcoal ENMs will be present in the Danish landfill scenario. However, it has to be noted that in both cases, i.e. “Plastic packaging” waste in the UK and “Textile” waste in Denmark, it seems that the Eurostat statistical data, are not representative of the actual waste management setting in the UK and Denmark. For example, landfilling of “Textile” waste is not permissible in Denmark and “Plastic packaging” waste in the UK is recycled or exported to a high extent (WRAP, 2016).

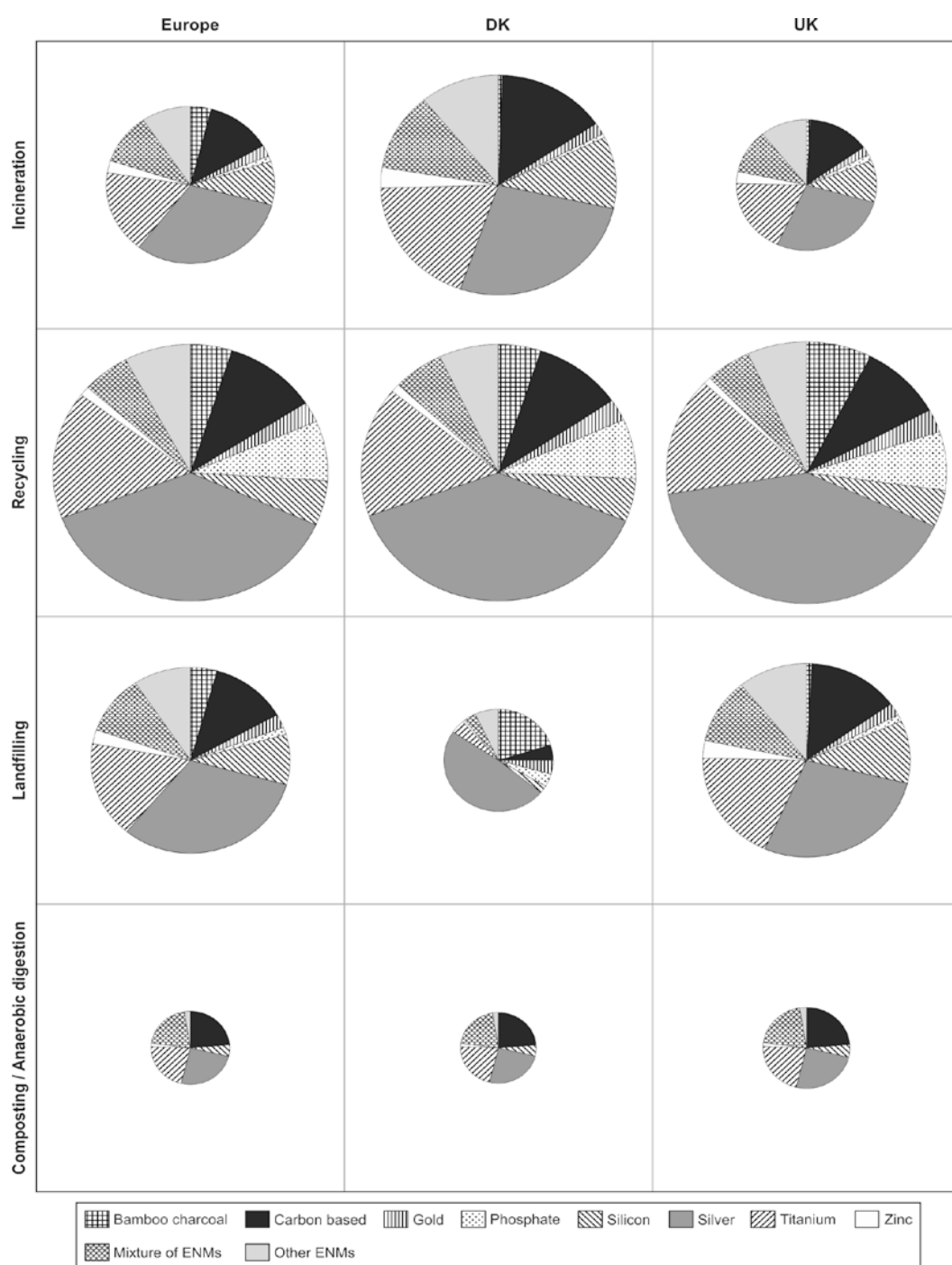


Figure 3.3. Distribution of ENMs in waste treatments (incineration, recycling, landfilling and anaerobic digestion) based on the number of nanoproducts (total number of products: 963 products, products with unknown ENMs are not included) containing a certain ENM (From Heggelund et al., 2016 – Paper II).

3.3 Recent development in the distribution of ENMs in waste

The generation of certain nanowaste material fractions has increased markedly in the past two years. The current development, from 2015 to 2017, is summarised in Table 3.2. Using the The Nanodatabase's nanoproduct inventory, it was found that "Glass", "Metal" and "Textile" waste fractions have grown by more than 50% from 2015 to 2017, whereas "Battery" waste or "Unknown" waste (as defined in Heggelund et al., 2016 – Paper II) fractions have stagnated (Table 3.2). The "Plastic, packaging", "Plastic, other" and "Multi material" waste fractions have increased by 13, 20 and 42% respectively, and a slight increase of 6% is observed in the "Electronic" waste fraction. Moreover, two new waste material fractions have been added to the inventory, namely "Ceramics" and "Large Appliances" (Table 3.2). The latter is a sub-fraction of "Electronic" waste, but since it is considered very different from the rest of the electronic waste, it was decided to keep these products in a separate fraction. When Heggelund et al. (2016 – Paper II) performed their product inventory analysis in 2015/6, the fractions "Wood", "Paper" and "Hazardous waste" were not relevant for nanoproducts included on The Nanodatabase. This is largely still the case, but a few products are now categorised as "waste wood". Currently, nanomaterials are neither specifically regulated in nor excluded from European waste legislation, and no nano-specific entries exist for classifying waste as hazardous (Reihlen and Jepsen, 2015), and so hazardous waste was excluded from this updated analysis. Another relevant update to The Nanodatabase is that some products are no longer assigned to a solid waste fraction but instead to wastewater (Table 3.2). These are products such as solid soaps and solid food items such as candy, where the ENM is assumed to be located inside the product and leaves no residue in packaging, if used as intended. Currently, The Nanodatabase includes 33 products without a solid waste fraction, which accounts for approximately 1% of the product inventory. ENMs present in these nanoproducts might accumulate in sewage sludge (e.g. nano-Ag), but this will depend on the specific ENM and its dissolution/aggregation kinetics and affinity towards the organic sludge material. For most of these products the ENM is unknown (approximately 50%); otherwise, they contain nano-TiO₂, nano-Ag, calcium or silicon dioxide ENMs.

Table 3.2. Development of ENMs in consumer product waste from 2015 to 2017. Total numbers refer to number of products assigned to the given waste material fraction. Analysis was performed on 3,005 products registered on The Nanodatabase (2017).

Waste material type	Notes for ENMs	Total number 2015	Total number 2017	% Increase
Batteries	Only phosphate (1 unknown)	42	42	0
Electronics	Ag, Ti, silicon, CNTs, nano-diamond, TiO ₂ , carbon (168 Unknown)	302	321	6
Glass	TiO ₂ , Ag, ZnO, carbon black, Au, fullerenes, silicon (57 unknown)	64	115	80
Metal	CNTs, nano diamond, Ag, steel, carbon, Ti (256 unknown)	138	327	137
Multi material waste	Ti, Carbon, Ag, graphite, CNTs, fullerenes, silicon, Cu, Zn (103 unknown)	187	266	42
Textile	Ag, bamboo charcoal, Au, silicon, polytetrafluoroethylene, CNTs, Ti (465 unknown)	396	628	59
Unknown	TiO ₂ , Ti, Au, Ag (51 unknown)	85	86	1
Plastic, Other	Ag, CNTs, carbon, bamboo charcoal, silicon/silicone, Ti (61 unknown)	107	128	20
Plastic, Packaging	Ag, TiO ₂ , SiO ₂ , bisoxtrazole, ZnO, Au, carbon black, Ti, silicon, Zn, Cu, Ca, Pt, nano diamond, polytetrafluoroethylene, Al, CaO ₂ , Ir, Pl (736 unknown)	908	1034	13
Wood	CNTs (2 unknown)	3	3	Excluded from analysis
Ceramics	All with unknown ENM	3	3	Excluded from analysis
Large appliances	Ag, carbon, Au, Fe (21 unknown)	Some products (38) present in 2015, but not separated from WEEE	45	N.A.
Wastewater* (Category is not yet online on nanodb.dk)	ENMs expected to end up in waste water are primarily Ti based, Ag or silicon (15 unknown).	Excluded from analysis in 2015 (non-known no. products)	(33)	N.A.
TOTAL		2273	2998	

It has to be noted that the total number of products along with the total numbers for each waste fraction, refer to the numbers currently available on The Nanodatabase. They therefore reflect the continuous updating, addition and re-categorisation of products. Currently, a new category, “Wastewater”, is being implemented, and so seven products are not placed in a solid waste fraction at the moment, and the total number for 2017 is 2,998 (Table 3.2) instead of 3,005. Another factor is the re-categorisation of products. For example, the same product placed in the multi material waste fraction in 2015 might have been re-categorised as metal waste in 2017, due to the increasing understanding or development of waste categories. This factor partly explains the large percentage increase in the metal waste category. Similarly, it is difficult to compare the number of products used for the analysis in Heggelund et al. (2016 – Paper II) to those in Table 3.2, since data were modified according to the purpose of the analysis, and sometimes only concerned selected ENMs or grouped ENMs in certain ways. Furthermore, the number of products with unknown ENMs would be excluded from the final analysis.

The updated analysis of ENMs in waste (Figure 3.3) was performed in the same way as in Heggelund et al. (2016 – Paper II), to allow for direct comparison, but it was based on the waste fractions and ENMs currently represented on The Nanodatabase (April, 2017). furthermore, new ENMs present in more than 10 products (Nano diamond and bisoctrizole) were included along with products to be placed in the “Wastewater” category. The distribution and abundance of ENMs in solid waste fractions has not changed markedly from 2015 to 2017 (c.fr. Figure 3.1 and Figure 3.3).

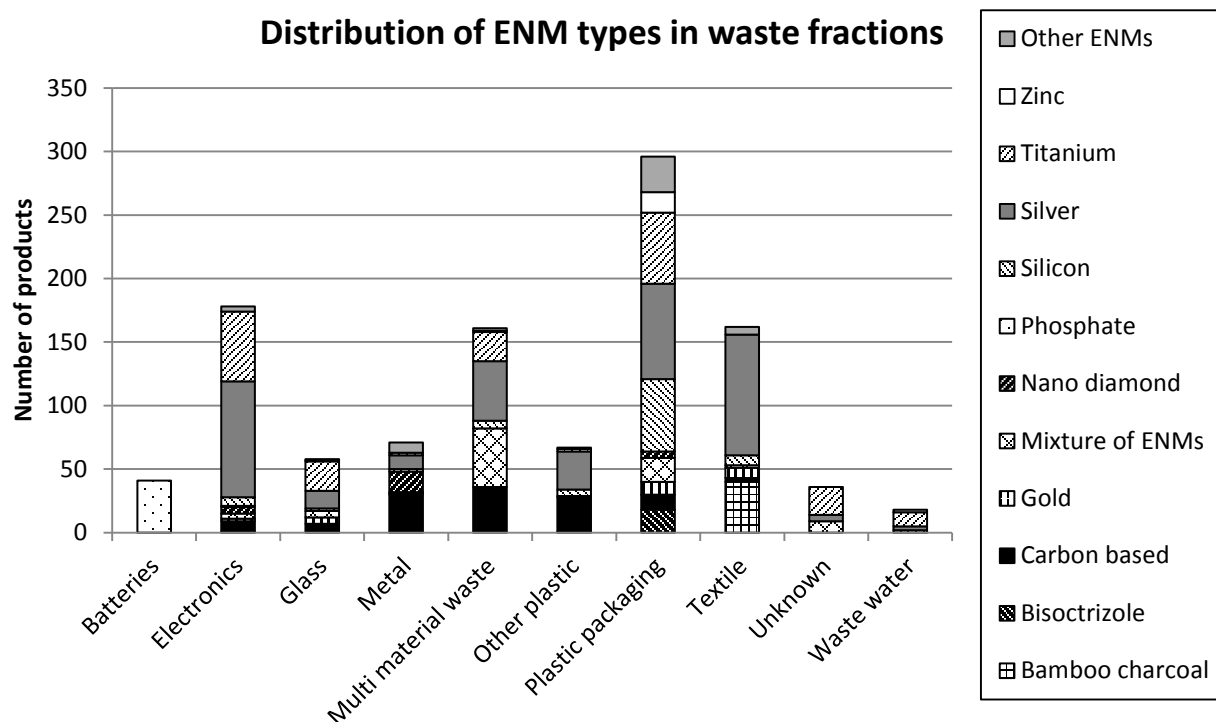


Figure 3.3. Distribution of ENMs in waste fractions (edited data from The Nanodatabase, 2017). Products with an unknown ENM are not included in this graph, and ENMs are grouped according to their main component (Ti, Zn, Silicon, Carbon-based). ENMs used in 10 products or fewer are grouped (Other ENMs) as well as products containing more than one ENM (Mixture of ENMs). The graph is based on 1,088 nanoproducts, and products with unknown ENMs are excluded.

3.4 Recent development in the treatment of ENMs in waste

The most dominant change in nanowaste generated from 2015 to 2017 was seen for the metal and glass waste fractions (137 and 80% increases, respectively). These waste material fractions are recycled to a high extent, i.e. 73% on average in the EU (Eurostat, 2017), and therefore the changes are expected to affect primarily the distribution of ENMs in the recycling treatment scenario. However, from Figure 3.4, it is clear that the ENM distribution is not significantly affected by the increase in metal and glass waste, possibly because these waste fractions only represent approximately 15% of the total number of products on The Nanodatabase. However, politically there is an increasing focus on recycling in the EU (EU Commission, 2010), which may have an impact on the distribution of ENMs in the longer term.

One limitation of the study by Heggelund et al. (2016 – Paper II) was the lack of region-specific waste treatment statistics. Specifically in terms of textile waste in Denmark and plastic packaging waste in the UK, there were some discrepancies between local legislation and the statistical data obtained from Eurostat (Heggelund et al., 2016 – Paper II).

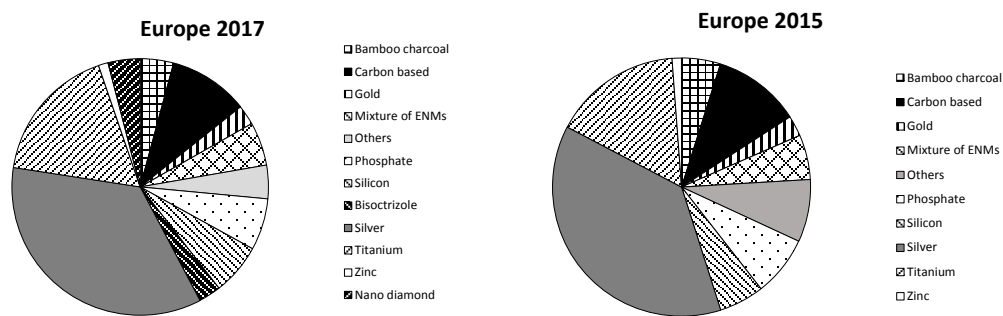


Figure 3.4. Comparison between ENM distribution in recycling treatments based on Heggelund et al. (2016 – Paper II) and modified according to product numbers in 2017 on The Nanodatabase (2017). Graphs from 2017 and 2015 are based on 1,088 and 963 nano-products, respectively. Products with unknown ENMs are excluded.

Concerning the treatment of plastic packaging waste in country, a recent report from the Waste and Recourses Action Programme (WRAP) in the UK (WRAP, 2016) showed that significant progress has been made in terms of annual recoveries of plastic packaging waste in the UK. However, still only 14% of the plastic packing waste generated is being recycled, and an estimated 23% is being exported for recycling abroad, mainly to Asia (Figure 3.4). This gives a total recycling rate for plastic packaging of 37%, compared to a recycling rate of 25% (Eurostat, 2017) used in the analysis by Heggelund et al. (2016 – Paper II). The report also estimates that almost 64% of consumer and non-consumer plastic packaging waste goes to disposable routes such as waste-to-energy or landfills (WRAP, 2016). By using data from Eurostat, Heggelund et al. (2016 – Paper II) estimated that 74% of plastic packaging waste would be either landfilled or incinerated. Developments in the treatment of plastic packaging waste, or other types of waste, can be highly influenced, for example by current politics, the demand for recycled products/materials and the price of raw materials (WRAP, 2016). These types of changes are not reflected in the analysis in Heggelund et al. (2016 – Paper II), since the statistical data used in this study do not originate from local/region-specific waste collectors, but from the Eurostat database. This underlines the importance of obtaining as detailed as possible local information regarding the waste management system in a specific region, in order to maximise the relevance and accuracy of the estimated ENM distribution.

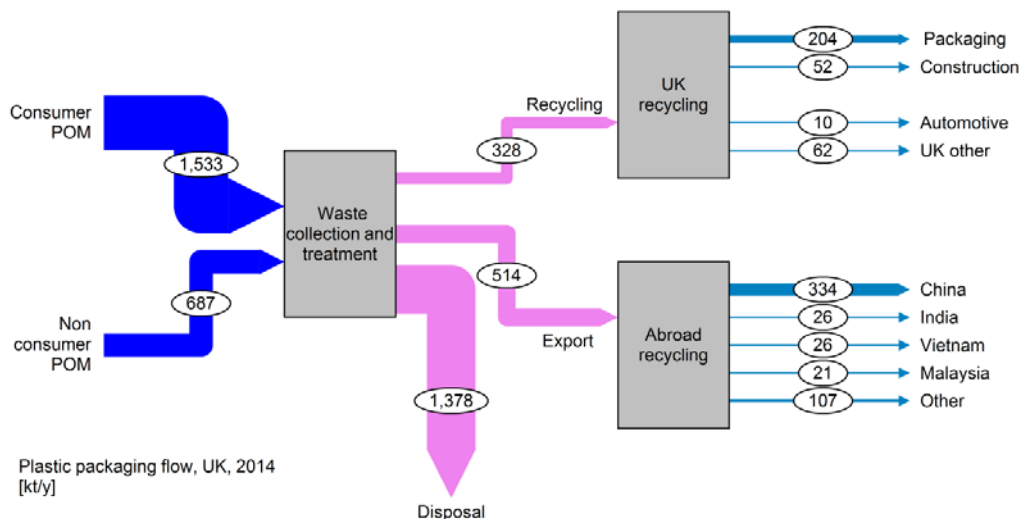


Figure 3.4. Yearly flow of plastic packaging waste in the UK (kt/y). Redrawn from WRAP (2016), based on data from 2014.

3.5 Recycling of waste nanoproducts, and factors affecting their release

Studies have identified recycling as a significant waste treatment approach for ENMs at their end-of-life (Hincapie et al., 2015; Sun et al., 2014; Heggelund et al., 2016 – Paper II; Caballero-Guzman et al., 2015). For example, Sun et al. (2014) estimated that 18% of nano-TiO₂ waste and 37% of nano-Ag waste will end up in recycling systems, although as a whole, the primary waste fraction for all the metal-based ENMs investigated by Sun et al. (2014) was estimated to be sewage sludge. The waste material fractions “Plastic, other”, “Metal” and “Glass” are expected to have great potential for recycling (Eurostat, 2017). According to The Nanodatabase (2017), currently 128, 327 and 115 nanoproducts, respectively, fall into these material fractions, and the ENMs present in these fractions are primarily nano-Ag, carbon-based ENMs or nano-TiO₂ respectively (see example for “Plastic, other”, Figure 3.6). In a report by Boldrin et al. (2016), the possible factors affecting the release of nanomaterials during different recycling processes were investigated. In terms of plastic recycling, it was identified that, first of all, the type of plastic used in the product can have an impact, since different variants have different properties and thereby different potentials for recycling.

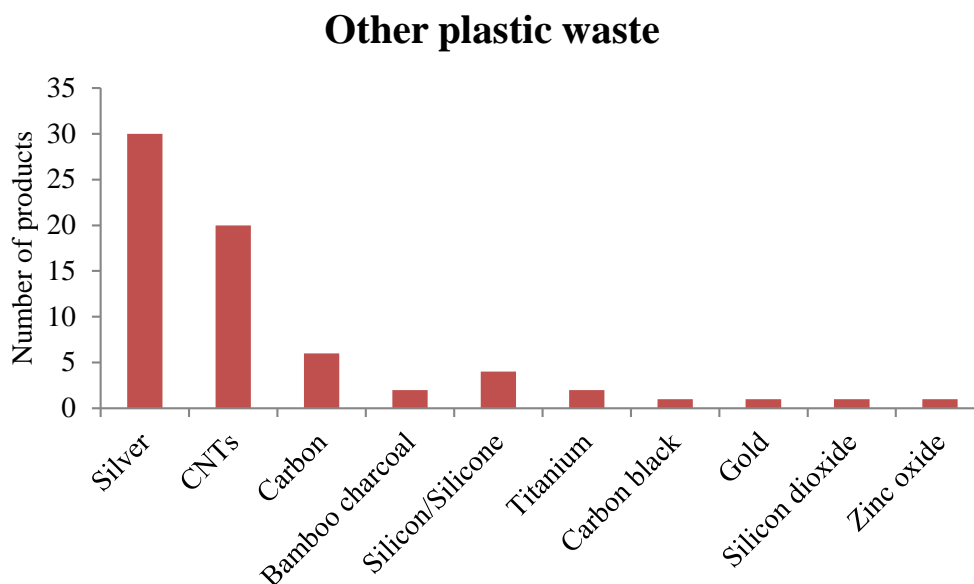


Figure 3.6. The distribution of ENMs in the waste fraction “Plastic, other” (exported from The Nanodatabase, April 2017, based on 3,000 available products; products with unknown ENMs are excluded).

The two main types of plastic are thermoplastics and thermosetting plastics. Thermoplastics do not undergo chemical change in their composition when heated and can be moulded again and again (Hansen et al., 2013), meaning they are to some extent suitable for mechanical recycling, which involves extrusion and remoulding of the plastic material. Examples of thermoplastics include polyethylene, polypropylene, and polystyrene (Hansen et al., 2013). Thermosetting plastics can melt and take shape only once (Hansen et al., 2013), so they are less suitable for traditional mechanical recycling and in most cases they are sent for incineration in Europe (Boldrin et al., 2016). Nanoproducts on The Nanodatabase belonging to the “Plastic, other” waste material fraction (Figure 3.6) include for example, hockey sticks, other types of sports equipment or food storage containers. In the case of sports equipment, the ENM used is primarily CNTs or another carbon-based technology (The Nanodatabase, 2017) used to reinforce the material. According to manufacturers’ information on The Nanodatabase, sports equipment is often made from a thermosetting plastic, which according to Boldrin et al. (2016) would most likely be sent for incineration.

Details on the potential for the release of different substances from plastics are often not available; however factors generally affecting the migration include the substances’ size, their concentration, their boiling point, vapour pressure and their solubility in both the plastic and the environment (Hansen et al., 2013) (see Figure 3.7).

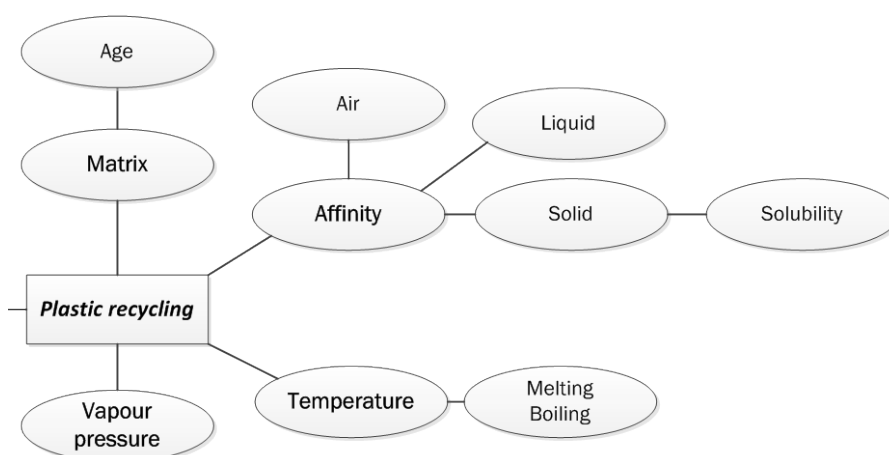


Figure 3.7. Factors possibly affecting the release of ENMs during plastic recycling (Modified from Boldrin et al., 2016).

These factors are also expected to be relevant for ENMs. Boldrin et al. (2016) point to a possible route of release occurring during extrusion and before re-palletisation of the plastic. If the temperature needed to melt the plastic polymers during this process exceeds the boiling point of the ENMs, the material might be released into the gas phase. However, for most inorganic ENMs this is not the case, and Boldrin et al. (2016) concluded that the release of ENMs into the gas phase was unlikely, at least for this type of plastic recycling process.

In terms of glass waste recycling, Boldrin et al. (2016) describe the most common processes as reuse, as an inert aggregate, or re-melting for the production of new glass products. When reused as an inert aggregate, the release of ENM could occur through surface abrasion and release into the water phase, i.e. similarly to during the use phase. Glass re-melting occurs at high temperatures (e.g. 1400-1600 °C), which could induce the evaporation of ENM and its subsequent release through exhaust gases. The magnitude of this phenomenon will again depend on the boiling/melting point of the individual ENM. The same notion applies to metal recycling which, depending on the type of metal, will occur in ovens at very high temperatures, in which case the evaporation and airborne release of ENMs might occur. However, as far as glass recycling is concerned, the scale of this phenomenon will depend on the boiling/melting point of individual ENMs, which can be rather different (Boldrin et al., 2016).

It should also be mentioned that most modern metal smelting facilities are equipped with advanced flue gas cleaning systems, which may retain heavy metals and ENMs (Boldrin et al., 2016). In this case, residues from the gas cleaning process (e.g. filters), would be a possible sink for ENMs, which then might have to be disposed of via incineration or landfilling.

Another type of waste, not dealt with by Heggelund et al. (2016 – Paper II) but which might be relevant in terms of ENM recycling is “construction and demolition” waste. Examples in this regard are recycled and used in many applications, such as down-cycling into aggregates as sub-base for roads, backfilling of excavations and as a filler in asphalt concrete, and they involve different waste materials, such as hard resources (i.e. concrete, tiles, mortar), wood and metals (Boldrin et al., 2016). Hard materials represent the majority of building waste, and some of these are to some extent enabled by nano-materials. According to Synnott et al. (2013), self-cleaning building materials such as tiles and concrete, enabled by nano-TiO₂, are patented and used globally, which means that “Construction and demolition” waste will hold a certain share of these nano-enabled products. Boldrin et al. (2016) identify two main routes of ENM release during “Construction and demolition” waste recycling. Firstly, the authors have previously shown experimentally (Boldrin et al., 2015) that non-negligible amounts of ENM may become airborne during the crushing activities of hard materials. This may suggest that when ENMs are present in “Construction and demolition” waste, recycling operations may be conducted in enclosed environments, thereby making use of filtering systems for exhaust air (Boldrin et al., 2016). Secondly, these ENMs may be released from aggregates used in road construction, if they come in contact with water and leachate is formed. Factors affecting the release of ENMs into liquid media are dealt with in more detail in Chapter 4 of this thesis.

Assessing potential ENM release during recycling operations is related to both the properties of the matrix e.g. its hardness, due to possible dust formation and airborne release of ENMs in connection to size reduction steps, and those of specific ENMs such as the melting/boiling point and their affinity to liquid, gas and solid phases (Boldrin et al., 2016).

4 Experimental characterisation of nanowaste and released ENMs

Generally, solid wastes are characterised, for instance, to provide data for policy-making, in order to classify the waste or to control that it meets certain quality criteria. This characterisation takes place at different levels. At an overall level, waste is categorised according to its source, for instance residential waste, industrial waste or construction and demolition waste, albeit the mixtures of materials within these main types are usually complex. The next step involves a compositional analysis of the waste in relation to, for example, the relative amounts of concrete, tiles and mortar and asphalt in construction and demolition waste, or if the waste is going to be landfilled, it may be important to assess the leaching potential of toxic elements and establish compliance with the landfill acceptance criteria of the Landfill Directive (EU Commission, 2002). Currently, in the EU no nano-specific quality criteria exist for waste assessment (EU commission, 2012; Reihlen and Jepsen, 2015).

4.1 Types of waste characterisation

Different approaches for waste characterisation exist, with the overall distinction being direct and indirect methods (Figure 4.1). Up until now, the methods dealt with in this thesis for solid waste characterisation have been indirect and based mainly on market product analysis or material flow analysis (Chapter 3). This type of study can provide estimations on the amount of waste generated and its composition based on the goods/products entering a specific region, taking into account the expected life time of the products (Boldrin et al., 2015). However, as mentioned in Chapter 3, a serious drawback to this approach is the lack of data and information about nanoproducts in general, which hampers the quantitative assessment of ENMs in waste flows.

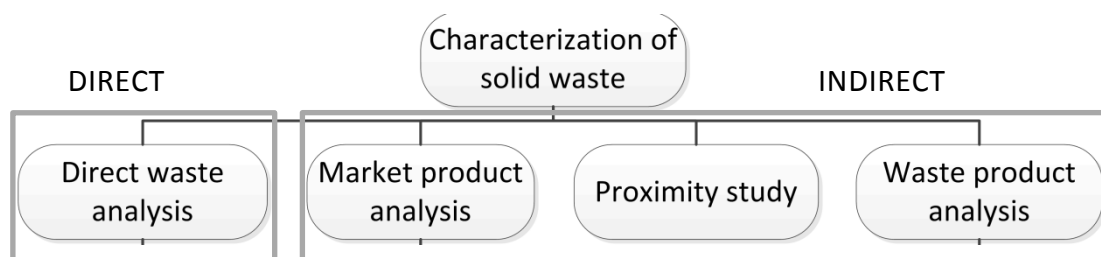


Figure 4.1. Overview of solid waste characterisation approaches. Modified from Boldrin et al. (2015).

Boldrin et al. (2014) proposed a quantitative exposure assessment framework for ENMs in waste, based on the market product analysis approach, which includes five steps (Figure 4.2). In the first step, the amount of nanowaste generated from manufacture-by-products and from nano-enabled products is estimated. Concerning waste from nano-enabled products, the quantification relies on estimations of annual production, market penetration and amount of ENM left in the product by the time of disposal (Boldrin et al., 2014). Step two deals with the treatment of the product at its time of disposal, and the waste matrix material and possible waste treatment for the product are identified. These two factors (i.e. waste matrix materials and their possible waste treatment) have already been estimated for all nanoproducts available on The Nanodatabase and a waste treatment analysis, based on numbers of products, for different country profiles can be carried out using the online waste treatment tool (The Nanodatabase, 2017). Step three involves information about the nanomaterial structure and how the material is embedded in the product matrix, e.g. suspended in a solid or bound to a surface. This information is also logged with each nanoproduct on The Nanodatabase. Step four describes the relevant ENM transformation and release processes that could occur during nanoproduct waste treatment, e.g. for landfilling; for instance dissolution/precipitation and adsorption/desorption have been identified. This step is limited by the lack of studies investigating the transformation and release of ENMs in waste treatment regimes, especially studies using relevant experimental set-ups and conditions (see section 5.3). The fifth and final step is the assessment of the magnitude, duration and frequency of the ENM exposure from nanowaste, which is described qualitatively as “low”, “medium” or “high” for the affected environmental compartments (Boldrin et al., 2014).

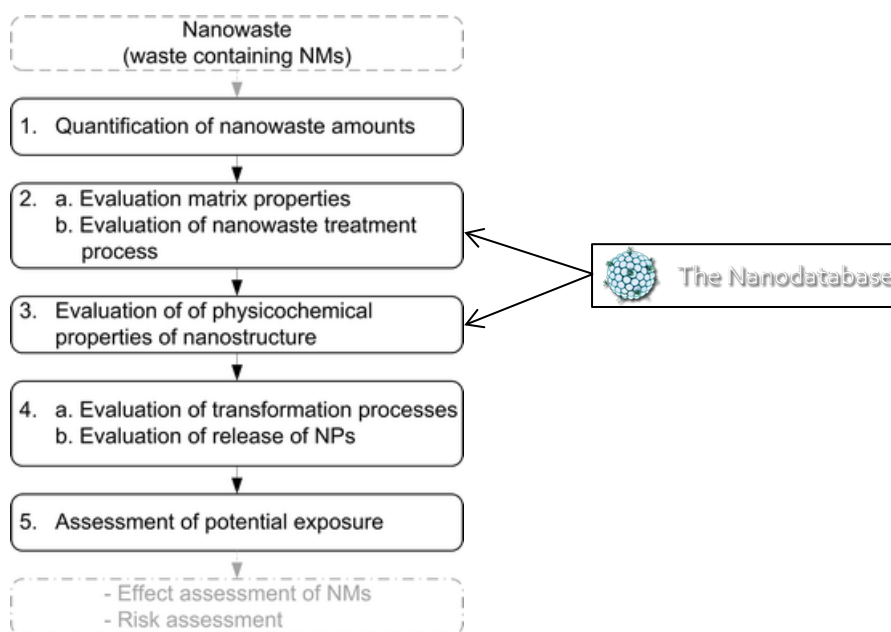


Figure 4.2 The 5-step exposure assessment framework for nanowaste proposed by Boldrin et al. (2014). Information for steps 2 and 3 can partially be found via The Nanodatabase.

Proximity studies refer to an approach where social, economic and commercial data are combined with proximity data to extrapolate waste compositions in a region with similar characteristics and where data on waste composition are available (Boldrin et al., 2015). This method relies on many assumptions and estimations, and as for market product analysis, the required information is often not available for nanoproducts. Waste product analysis is based on measuring outputs/products/by-products of waste treatment and estimating waste characteristics by back-calculating from these points (Boldrin et al., 2015). To some extent this approach has been applied to nanowaste, e.g. by Walser et al. (2012), but it is not clear if this method could be used to calculate initial ENM concentrations in the waste, since much is still unknown about the potential transformations of ENMs during waste treatment processes (Mitrano et al., 2015). Also, it might be complicated to close the mass balance in some cases, considering the low concentration of ENM.

In the rest of the current chapter (Sections 4.2 to 4.5), the focus falls on the direct waste analysis approach, which generally involves the sorting, sampling, weighing and direct analysis of waste (Boldrin et al., 2015). However, in the case of nanowaste sorting, sampling and weighing are not possible, since the features that define the waste in most cases cannot be identified, i.e. no ENM labelling for consumer products (besides cosmetics). Alternatively,

waste characterisation tests, such as batch leaching tests, can be carried out to characterise and quantify the potential ENM release from nano-enabled products, or residues from waste treatment, which will aid the understanding of ENM transformation and environmental exposure.

4.2 Analytical methods for ENM characterisation in nanowaste

Many methods for characterising ENMs exist, and these have been reviewed with regards to their pros and cons by, amongst others, Part et al. (2015), von der Kammer et al. (2012, 2014), Mitrano et al. (2015) and Mitrano and Nowack (2017). In the recent review by Mitrano and Nowack (2017), it was discussed how current analytical techniques can obtain measurements of aged or transformed ENMs and which techniques are relevant for real-world scenarios. The authors pointed to the following techniques as relevant in terms of characterising ENMs in real-world studies: (i) single particle-ICP-MS, (ii) chromatographic methods coupled with elemental-specific detection (e.g. AF4– ICP-MS), (iii) nanoparticle tracking analysis, (iv) electron microscopy, (v) energy-dispersive X-ray spectroscopy and (vi) small-angle x-ray scattering. The basic principles, pros and cons of each method are presented in Table 4.1.

These methods are selected due to their ability to measure elements at trace levels in complex systems and because they are capable of identifying nano-specific information (Mitrano and Nowack, 2017). Single particle inductively coupled plasma mass spectrometry (sp-ICP-MS) is unique in the way that the method can provide both particle size, size distribution and particle number concentration in a suspension, along with elemental information about the particles and the dissolved concentration of the selected element (Pace et al., 2011). The draw backs of sp-ICP-MS are that size estimations are based on many assumptions which are unlikely to be fulfilled in the case of nanowaste characterisation and the fact that only one element can be measured at the time. Furthermore, method development can be challenging and depends on the ENM and media combination in question.

Chromatographic methods, such as asymmetrical flow field flow fractionation, have the advantage that they can quickly separate poly-disperse samples and measure each fraction separately (Mitrano and Nowack, 2017). If coupled to an ICP-MS, they can detect multiple elements at the same time, along with changes in particle size over time (e.g. by dissolution) or surface complexation and core-shell structures (A4F-ICP-MS) (von der Kammer et al., 2012). A different approach is provided by nanoparticle tracking analysis, which is based on the combination of laser light scattering microscopy and a charge-coupled device (CCD) camera (Filipe et al., 2010). The camera records the movements of individual nanoparticles under Brownian motion, following which the hydrodynamic size of an equivalent spherical particle is calculated. Electron microscopy methods (SEM and TEM) are essential in characterising nanomaterials in complex media since they visualise the particles and their agglomeration state along with characteristics such as shape, morphology and coatings. Often, SEM and TEM imaging are performed together with EDX analysis, which provides elemental information regarding the observed particles in a non-invasive way and based on the x-ray spectra of sample.

Experimental characterisation of ENMs in a waste matrix, or ENMs released from nanowaste using the methods presented in Table 4.1, has been performed in a limited number of studies (see Table 4.1), for example on incineration residues (Walser et al., 2012, Vejerano et al., 2014, Buha et al., 2014, Massari et al., 2014), in landfill leachate (Bolyard et al., 2013, Hennenbert et al., 2013, Mitrano et al., 2017) and ENMs released from a spiked waste matrix (e.g. Dulger et al., 2016). Leaching from nano-enabled products, using a waste characterisation-based test, was performed by Heggelund et al. (2017 – Paper III) and Bossa et al. (2017). The methods used in these studies were a combination of high-resolution electron microscopy imaging (SEM or TEM) with energy-dispersive x-ray spectroscopy (EDS) and elemental analysis (ICP-MS). Other studies (e.g. Sakallioğlu et al., 2016) did not apply any of the methods recommended for ENM characterisation in complex media but investigated leachate from a spiked solid waste matrix. In addition, Part et al. (2016) investigated the fate of quantum dot nanoparticles in mature landfill leachate, using fluorescent spectroscopy, and observed interactions with humic and fulvic acids.

Experimental data with particle specific-analysis of ENMs in waste are still scarce (Table 4.1, Columns 5 and 6), especially when it comes to characterising solid waste. Most studies to date have applied electron microscopy methods and EDS for nano-specific characterisation. In terms of experimental set-up, a few studies have been conducted using real nano-enabled products or waste matrices, but these studies have investigated ostensibly spiked/artificial nanowaste systems. Therefore, there is need for experimental studies on real nano-enabled products, and for applying methods that enable the quantification of ENM release and possible transformations. These aspects will be dealt with later in this chapter (Section 4.4).

Table 4.1. Overview of analytical methods for characterising released ENMs in complex media (modified from Mitrano and Nowack, 2017 and Part et al., 2015). Studies mentioned in Column 5 use a waste characterisation test or a real/artificial waste matrix.

1 - Method	2 – Principle	3 – Pros	4 - Cons	5 - Applied to solid nanowaste characterisation?	6 - Applied to real nano-product / waste matrix?
Single particle-Inductively coupled Plasma-Mass Spectrometry (sp-ICP-MS)	Sequential analysis whereby NPs are atomised and ionised in the plasma and are detected as a pulse above the background elemental signal. Intensity signal is related to particle size.	-Possible to identify particle concentration, size, size distribution and chemical element of ENMs along with dissolved concentration of element -Very low particle detection limit -Can detect changes in particle size over time	-In most cases, only one element can be measured at a time -Assumes spherical, monodisperse particles -Only suitable for metallic ENMs -Difficult for ENMs with high natural abundance (e.g. TiO ₂)	To some extent: Leachate from nanoproduct (Heggelund et al., 2017 – Paper III), Landfill leachate (Mitrano et al., 2017). Other studies have investigated ENMs in wastewater (e.g. Kaegi et al., 2011; Tuoriniemi et al., 2017; Bitragunta et al., 2017)	To some extent, though primarily applied to wastewater, not solid waste.
Asymmetrical flow field flow fractionation coupled to ICP-MS (AF4-ICP-MS)	Separation based on a force field applied to particles in liquid suspension of particles travelling through a capillary, and the difference in particle mobility within the field (Part et al., 2015)	-Provides information about hydrodynamic particle size, size distribution and concentration -Better size resolution compared to sp-ICP-MS -Detects multiple elements, complexation and core/shell structures	-Higher particle number detection limit compared to sp-ICP-MS -Assumes spherical particles -Difficult for ENMs with high natural abundance (e.g. TiO ₂) -Complex method development	No: but has been used e.g. on wastewater (Lee et al., 2016) and a food matrix (Wagner et al., 2015)	No
Nanoparticle Tracking Analysis (NTA)	A suspension of particles is injected onto a metallised optical element and illuminated by a laser beam. The particles are visualised individually in real time using a conventional optical microscope and a video camera (Filipe et al., 2010).	-Provides information about particle hydrodynamic size, size distribution and concentration -Little sample preparation -Information about ageing over time	-Particles are visualised, not imaged -Requires several optimisation steps (video capture and analysis) -Assumes spherical particles	To a small extent: Landfill leachate (Mitrano et al., 2017; Mehrabi et al., 2017)	To a small extent
Electron microscopy (SEM and TEM)	Electrons emitted from an electron source and are focused onto a thin specimen. TEM images are based on the electrons passing through the sample (transmitted) and SEM images on the electrons re-emitted from scanning the specimen surface.	-Direct visualisation of particles -Information about shape, size, morphology, agglomeration state and surface characteristics	-Costly and time consuming when dealing with low concentrations in environmental samples -Artefacts from sample preparation (e.g. drying or embedding)	Yes: incineration residues (Walser et al., 2012; Vejerano et al., 2014; Massari et al., 2014; Buha et al., 2014), leachate from nanoproduct (Heggelund et al., 2017 – Paper III; Bossa et al., 2017), landfill leachate (Bolyard et al., 2013; Hennenbert et al., 2013; Mitrano et al., 2017), leachate from waste matrix (Dulger et al., 2016)	Yes
Energy dispersive X-ray spectroscopy (EDS)	A sample is radiated by an electron beam and specific x-rays are emitted from the atoms in the sample. Elements are identified based on their specific absorption spectrum.	-Provides elemental information, identifies changes in speciation and core /shell of individual particles -Less invasive compared to EM techniques	-Small sample number, since each particle is analysed individually	Yes: incineration residues (Walser et al., 2012; Buha et al., 2014), leachate from nanoproduct (Heggelund et al., 2017 – Paper III; Bossa et al., 2017), landfill leachate (Hennenbert et al., 2013; Mitrano et al., 2017)	Yes

4.3 Factors affecting ENM release – with focus on release from landfilled nanowaste

Current standard methods for waste characterisation do not include any nano-specific analysis (Part et al., 2015), and very little knowledge or experimental studies of the occurrence of ENMs compared with natural/incidental nanomaterials in waste treatment systems exist. This is of concern, since many ENMs, mainly metal/metal oxide-based, are expected to accumulate in secondary waste streams such as incineration residues or sewage sludge, both of which are often landfilled (Part et al., 2016; Mitrano et al., 2017) and can potentially cause exposure to the environment. Therefore, it is highly relevant to assess the leaching potential of waste from nano-enabled products. Leaching tests, such as batch tests, are simple and very used, for instance, for compliance testing waste, before it enters a landfill (EU Commission, 2002). These batch tests can provide some initial information about the likelihood of ENMs leaching from the waste matrix into liquid media. However, ENM distribution in a landfill is also dependent on the location and form of the ENM in the original product (Reinhart et al., 2010), along with the product matrix material and how it is degraded. Some factors potentially influencing ENM release in a landfill are summarised in Figure 4.3.

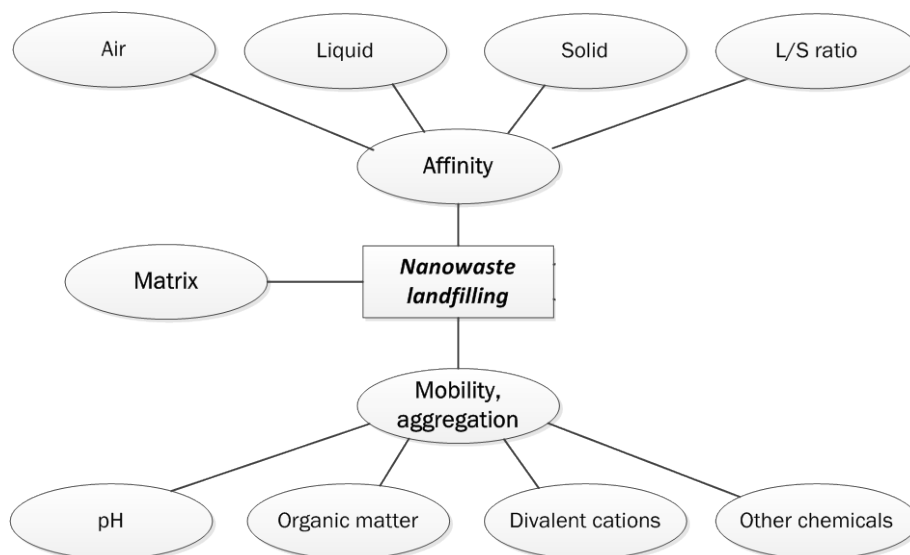


Figure 4.3. Overview of factors potentially affecting the release of nanomaterials from landfilled nanowaste. Modified from Boldrin et al., (2016).

The environmental conditions in a landfill, namely pH, the presence of organic matter or divalent cations, are important for potential ENM release from nanowaste, since they are expected to influence the aggregation or mobility of the released particles (Boldrin et al., 2016). Organic material has been shown to bind to the surface of ENMs or stabilise them via steric forces. However, elevated concentrations of organic matter can also lead to flocculation and cause the ENMs to sediment. Furthermore, the age of the landfill might influence these parameters, since it goes through certain stages, for example the aerobic, acid and methanogenic phases (Kjeldsen et al., 2002). In the acid phase, for instance, the leachate of the landfill becomes very acidic, which can increase the solubility of many compounds (Kjeldsen et al., 2002), most likely including ENMs. Another aspect that affects the release of ENMs in landfills is the affinity of the specific ENM to different compartments, e.g. liquid or solids (Figure 4.3). If released ENMs have a very high affinity for soil, the potential exposure to aquatic environments, for example, would be lower than if the affinity for liquid was high.

Regarding the significance of the product matrix and ENM location, Figure 4.4 presents the locations of each ENM in consumer products included on The Nanodatabase, along with the waste fractions with which the products are placed (The Nanodatabase, 2017). This analysis revealed that approximately 21% of the products in “Plastic packaging” waste will include ENMs suspended in liquid (983 products) (Figure 5.1), with 359 (37%) of these products belonging to the “Cosmetics”, “Personal Care” and “Sunscreen” subcategories. In these products, the ENM will most likely be suspended in a crème at a low concentration, and the crème might contain fragments of plastic from the product container. The potential release from this type of waste is expected to be determined by the degradation of the matrix, which will expose ENMs to their surroundings, or the ENMs will be released together with fragments of the product matrix, which has been seen in some studies (Mackevica et al., 2017, Bossa et al., 2017), depending on their affinity to the matrix or the environmental compartments. This goes to show that the characterisation of ENM release from waste nanoproducts requires a high sensitivity in a complex matrix, even under laboratory conditions dealing with artificial samples, and it also illustrates one of the main challenges concerning nanowaste characterisation.

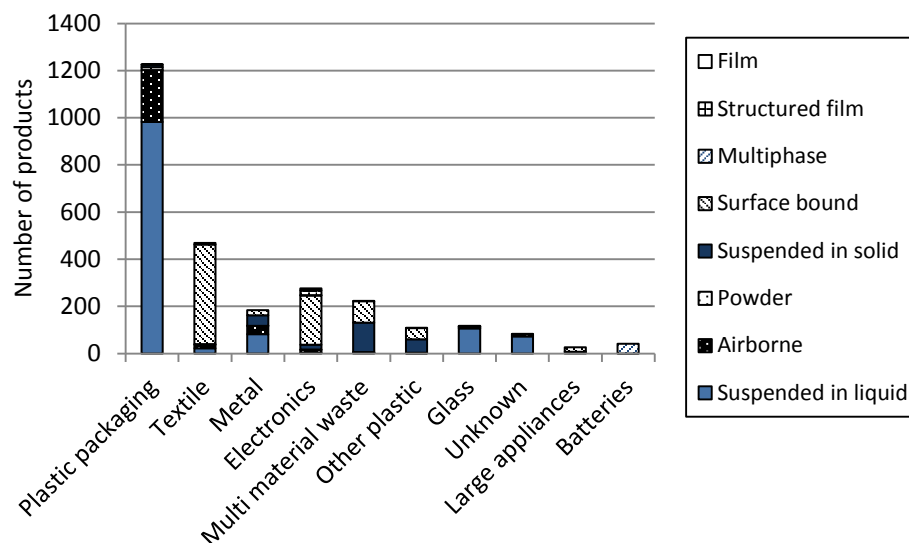


Figure 4.4. Waste fractions represented on The Nanodatabase and the locations of ENMs in the products placed in each fraction (The Nanodatabase, 2017).

Another example is the use of surface-bound ENMs especially in “Textile” and “Electronic” waste products (Figure 4.4). Depending on the available waste treatments, these types of products may have a high release potential, since ENMs are present on the surface of the product and therefore directly in contact with their surroundings.

4.4 Use of batch leaching tests for the quantification of ENM release in liquid media

Despite the increased use of nanoproducts (c.fr. Figure 2.2, Chapter 2), experimental data on the release of ENMs from end-of-life nanoproducts is lacking. The literature on release of ENMs from solid composites, in the framework of consumer exposure assessment, was recently reviewed by Mackevica & Hansen (2016), whose main conclusions were that the release of nano-Ag and nano-TiO₂ from paints or textiles was most commonly studied, and that most of the identified studies did not provide nanoparticle characterisation data. The paucity of nano-specific characterisation data continues to hamper the exposure assessment of nanomaterials since the nanoproperties of the materials cannot be taken into account.

A few studies have investigated and characterised the release of ENMs from waste matrices/emissions, such as incineration residues (Walser & Gottschalk, 2014) and landfill leachate (Mitrano et al., 2017). However, most studies to date have investigated an artificial sample where the waste matrix was spiked with a certain ENM concentration (e.g. Walser et al., 2012; Bolyard et al., 2013; Dulger et al., 2016; Part et al., 2016) and the distribution and fate of the ENMs in a particular waste treatment scenario was investigated. In these studies, the influence of ENM location and the product matrix cannot be taken into account when investigating release, and so the quantified release is likely to be overestimated. Therefore, these experiments have limited relevance when it comes to understanding ENM discharge from consumer products.

Heggelund et al., investigated the release of nano-TiO₂ (Heggelund et al., 2017 – Paper III) and nano-CuO (data not published) particles from ceramic tiles and painted wood, respectively. The two case studies represented one hard (tiles) and soft (wood) material and two different types of ENMs: self-cleaning ceramic tiles with a nano-TiO₂ coating and wood painted with nano-CuO wood protection paint. The aim of both studies was to establish a procedure for quantifying ENM discharge from waste nano-enabled consumer products. For both studies, a combination of a standardised waste characterisation test and nano-specific characterisation methods was used. In order to assess the potential release under environmentally relevant conditions, only nano-enabled and identical reference products were used, instead of a spiked matrix, and three different media conditions were tested.

4.4.1 Release of nano-TiO₂

Nano-TiO₂ is used in many different nanoproducts (c.fr. Table 2.1 Chapter 2), one example being the utilisation of nano-TiO₂ in different building materials, such as glass and ceramics, to make so-called self-cleaning materials (Synnott et al., 2013). Self-cleaning properties originate from the photocatalytic activity of nano-TiO₂, which generates reactive oxygen species that decompose organic compounds attached to the material (Synnott et al., 2013). This technology is widespread and patented worldwide, and so these nano-enabled building materials will eventually end up in waste streams, where plausible end-of-life scenarios include disposal in landfills or reuse as aggregate materials in the construction of roads or parking areas. Heggelund et al. (2017 – Paper III) investigated the release of nano-TiO₂ from commercially

available ceramic tiles, made with a coating of nano-TiO₂ particles to make them self-cleaning. The tiles consisted of two/three layers of different materials: a ceramic support, glaze and a coating, all containing different levels of titanium and from different sources. The total concentrations of titanium were measured in the reference and nano-enabled tiles before commencing the leaching tests, and the values were reported as 2.28 ± 0.02 mg/g and 3.39 ± 0.10 mg/g, respectively. The experimental set-up for investigating nano-TiO₂ release is shown in Figure 4.5, where DW, CAL and NOM represent the different media conditions tested, namely deionised water, deionised water with additional calcium and deionised water with added natural organic matter (Heggelund et al., 2017 - paper III). The set-up is a combination of a standardised batch leaching test (EN 12457-1 (CEN, 2002)) and nano-specific characterisation methods: zeta-potential, sp-ICP-MS and TEM/EDS analysis (Heggelund et al., 2016 – Paper III). Furthermore, total titanium concentrations in solid material and leachates were quantified using ICP-MS.

The results for pH and conductivity measurements are depicted in Table 4.2, whereby all leachates from nano-enabled tiles have significantly higher pH and conductivity values. The zeta-potential measurements are not shown, since they did not differ between samples or media type, and all measurements were in the range between -30 to 30 mV, which indicates an unstable suspension. It was concluded by Heggelund et al. (2017 – Paper III) that the zeta-potential, as measured by dynamic light scattering, was not an appropriate tool for a surface charge or the size characterisation of these samples.

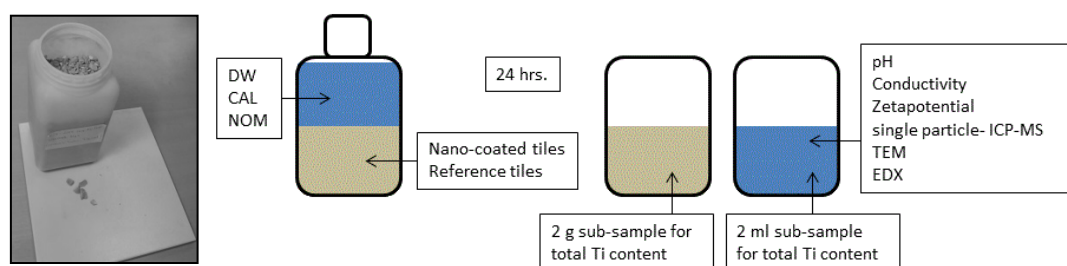


Figure 4.5. To the left, an image of the tiles and the size of tile aggregates used in the test. To the right, the experimental set-up and analytical techniques used for characterisation (modified from Heggelund et al., 2017 – Paper III).

Table 4.2. pH and conductivity in the leachates from reference and nano-TiO₂-coated tiles (mean \pm std, n=3). All samples were measured on the same day (from Heggelund et al., 2017 – Paper III).

Leachant media	Nano-TiO ₂ -coated tiles		Reference tiles	
	pH	Conductivity [mS/cm]	pH	Conductivity [mS/cm]
Deionised water (DW)	10.7 \pm 0.01	1.6 \pm 0.02	10.2 \pm 0.07	0.5 \pm 0.01
Additional calcium (CAL)	10.6 \pm 0.02	2.1 \pm 0.03	10.1 \pm 0.02	1.2 \pm 0.01
Natural organic matter (NOM)	10.7 \pm 0.01	1.5 \pm 0.02	10.3 \pm 0.01	0.5 \pm 0.01

Overall, Heggelund et al. (2017 – Paper III) found that the release of titanium under these conditions was minor (Figure 4.6). Generally, absolute titanium release was higher from the nano-enabled tiles, which may be related to the nano-TiO₂ coating of the tiles. However, due to large inter-sample variation, the difference between the two tile types was not always statistically significant (Figure 4.6). The total concentrations of released titanium found by Heggelund et al. (2017 – Paper III) were affected slightly by adding organic matter, thereby yielding lower titanium concentration in leachates from both the reference tiles and the nano-enabled tiles – a trend was also observed to some extent for the leachates with added calcium (Figure 4.6). These findings substantiate the statements made in Figure 4.3, and although only nano-TiO₂ was investigated, this mechanism could be expected to apply to other metal/metal oxide-based ENMs (Mitrano et al., 2017).

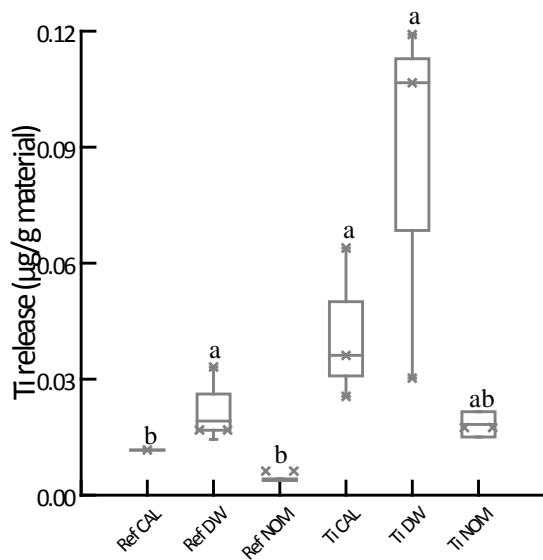


Figure 4.6. Boxplots showing total titanium concentrations released from the reference (Ref DW, Ref CAL and Ref NOM) and nano-TiO₂ coated (Ti DW, Ti CAL and Ti NOM) tiles, n=3 (for Ti NOM, n=2). Boxes = min and max values, line = median and whiskers = 1. and 3. quartiles. Letters “a” and “b” indicates significant differences by pairwise comparison of all samples ($p \leq 0.05$) (modified from Heggelund et al., 2017 – Paper III).

Bossa et al., (2017) investigated nano-TiO₂ release from an anhydrous cement material and found only minor particulate release over a seven-day period, corresponding to less than 1% of the total titanium content in the material. Bossa and co-workers found that the release was solely particulate and no dissolved titanium was found. The authors refer to this particulate release as “nano-product degradation residues”, which are different from the pristine particles originally incorporated into the product. The observed released particles were agglomerated/aggregated with silica aluminium particles and had an average individual size of 148 ± 41 nm, as measured by scanning electron microscopy analysis. Heggelund et al. (2017 – Paper III) also investigated the particle size and particle number concentration of titanium particles released in the leachates from ceramic tiles, using sp-ICP-MS and TEM coupled with EDS analysis. Unfortunately, Heggelund et al. (2017 – Paper III) were not able to quantify the number of particles by sp-ICP-MS analysis under these conditions, due to major interference from dissolved calcium, and all samples were below the particle number detection limit (Heggelund et al., 2017 – Paper III) (see Figure 4.8). Nevertheless, the measured particle size distribution for each leachate is depicted in Figure 4.7. In the case of the size detection limit, all samples but one (Ti CAL) were below this limit as well (Figure 4.7).

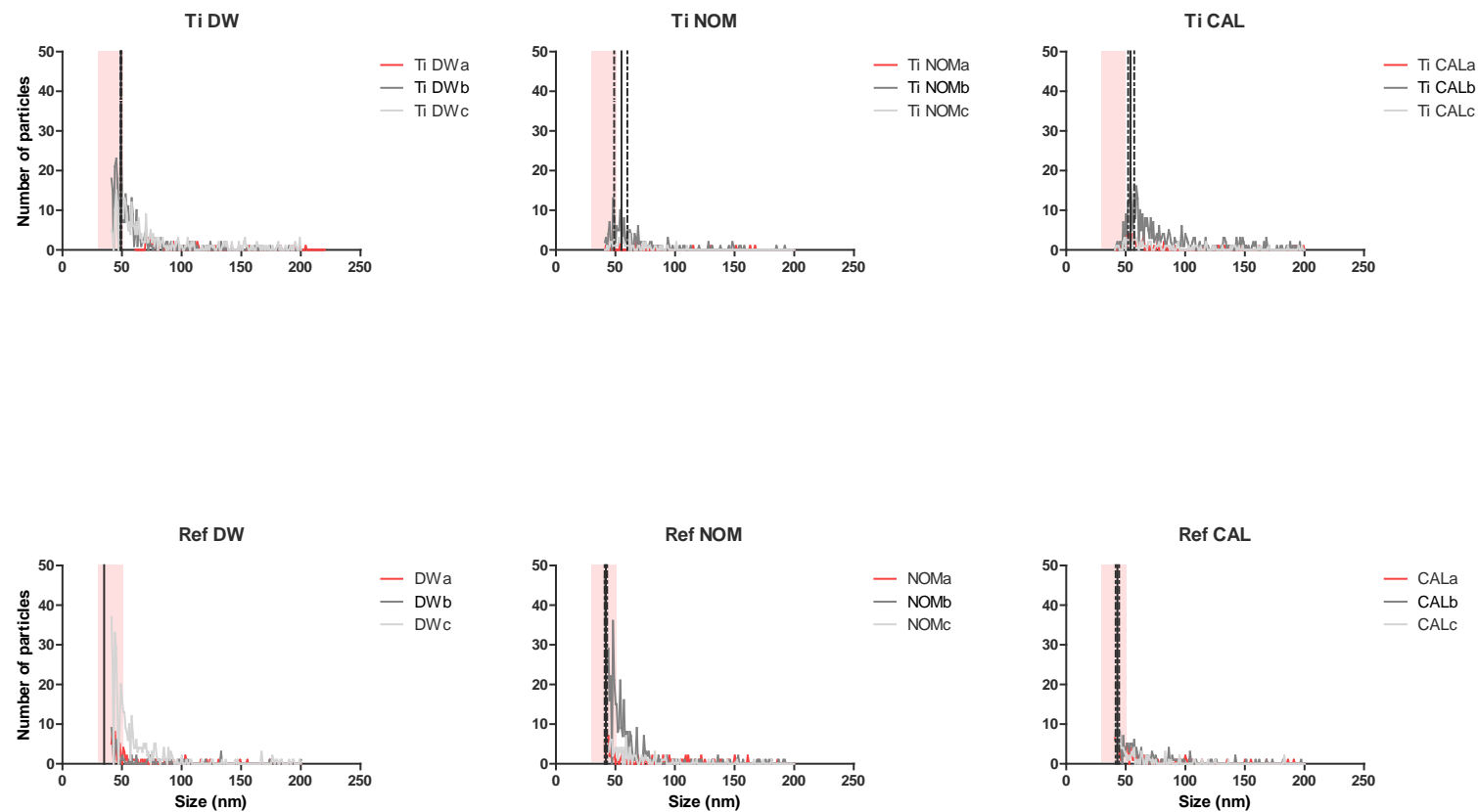


Figure 4.7. Size distributions (nm) of released particles from the nano-TiO₂ coated tiles (top; Ti DW, Ti NOM, Ti CAL) and reference tiles (bottom; Ref DW, Ref NOM, Ref CAL) into the three different media (DW, NOM and CAL), as measured by sp-ICP-MS. The x-axis represents the particle size [nm] and the y-axis the number of particles. Light-red boxes indicate interval of LOD size. Full lines: most frequent size (mean), Dotted lines: standard deviation around mean. Measuring range: 41-200 nm and bin size: 1 (modified from Heggelund et al., 2017 – Paper III).

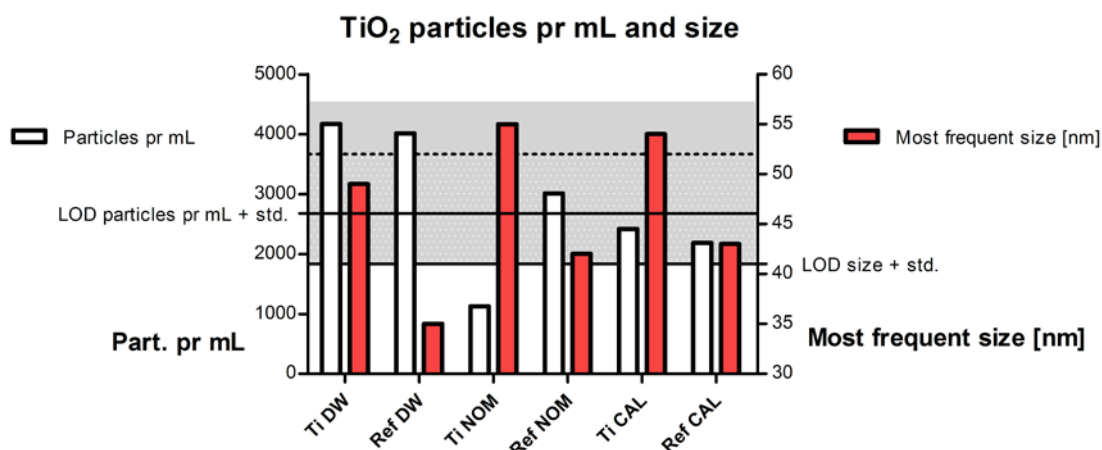


Figure 4.8. Calculated particle number concentrations and most frequent sizes measured in leachates from ceramic tiles. The solid black lines indicate the LOD values + std. for size (41 + 11 nm) and particle number concentration (2678 + 1847 part./mL). Dotted and solid grey areas represent the std. for LOD size and LOD particle number concentration respectively (modified from data in Heggelund et al., 2017 – paper III).

Figure 4.8 depicts the calculated particle number concentrations and most frequent particle sizes in the leachate samples from the ceramic tiles. The graph supports the conclusion made by Heggelund et al. (2017 – paper III) that no particle numbers were above the detection limit, due mainly to the large standard deviation around the mean. Two samples, Ti NOM and Ti CAL, have their most frequent sizes above the LOD size; however, the size estimates are based on a very small number of particles, which makes them unreliable for further interpretation. The graph makes it easier to distinguish between false positives and actual particles measured in the samples, and it could be used as an initial data visualisation/evaluation tool for sp-ICP-MS data.

The TEM/EDS analysis performed by Heggelund et al. (2017 – Paper III) showed similar observations compared to Bossa et al. (2017) and confirmed the very low release of titanium. In fact, Heggelund et al. (2017 – Paper III) only found one particle in their leachates, which had a notable titanium content (Figure 4.9). However, the authors were not able to identify aggregates/agglomerates of engineered TiO₂ nanoparticles based on their morphology.

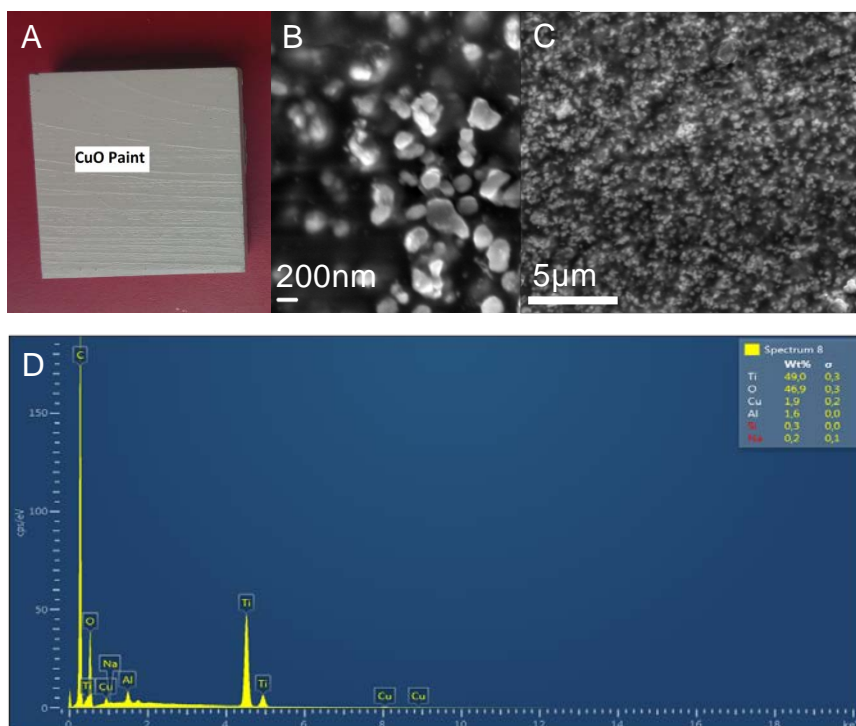


Figure 4.10. A) Image of a painted wood block, B + C) Low vacuum SEM images of the wood surface at different magnifications, using a large field detector and D) EDS spectrum of the painted surface confirming the presence of Cu. The higher magnification SEM image (B) indicates the presence of large aggregated particles with higher z-number (white particles), most likely consisting of TiO_2 .

The experimental set-up was similar to the one described in section 4.4.1 (Figure 4.5) and combined a standardised waste characterisation test (EN-124571, (CEN, 2002)) with nano-specific characterisation methods (i.e. zeta potential and sp-ICP-MS) to assess potential ENM leaching after 24 hrs. Since this was a preliminary study, only a small set-up without replication was used, meaning that the results are only interpreted qualitatively. It was not possible to conduct a larger replication study due to the limited production and supply of material (nano-CuO paint) from project partners and as currently, CuO is banned in the European market. Similar to section 4.4.1, three different media were used, i.e. deionised water (DW), deionised water with added natural organic matter (NOM) and, finally, deionised water with added calcium (CAL).

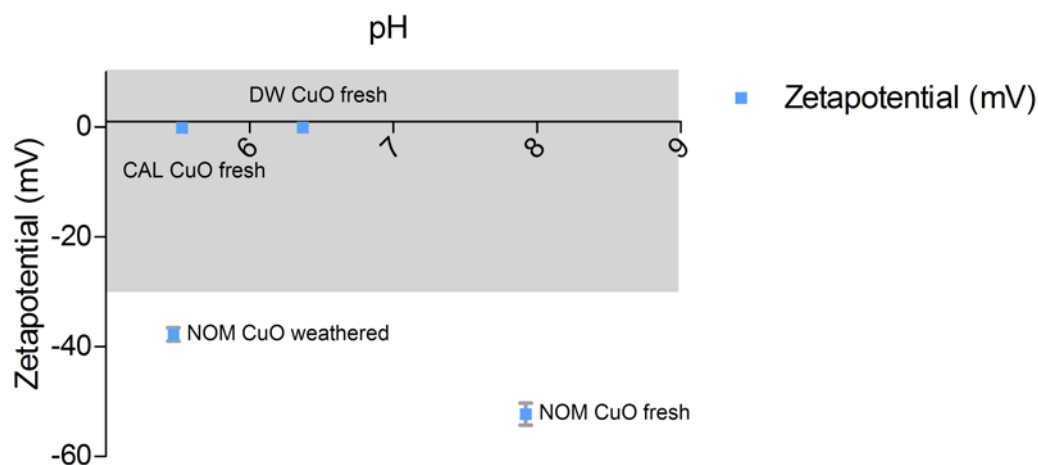


Figure 4.11. Measurements of pH and zetapotential in the three different leachant media. Only selected samples expected to contain nano-CuO particles are included (leachates from nano-CuO painted wood blocks). Grey area indicates the unstable range for the zeta potential of a suspension.

Figure 4.11 shows the effect of media composition and pH on the zeta-potential of the leachates. For the NOM medium, an additional wood material previously subjected to sanding was also included (NOM CuO-weathered). The initial pH of all media was 6.9, but during the 24 hrs' leaching test the pH decreased in almost all leachates (Figure 4.11). However, in the sample "NOM CuO fresh", it increased by approximately 1.5 pH units, which was unexpected, and from this small set-up the reason could not be identified. Possibly, the negatively charged organic matter added to this sample might have affected the solution's pH. However, the same tendency was not observed regarding leachate from the weathered/sanded sample in the NOM medium ("NOM CuO-weathered").

Generally, nanoparticle suspensions are considered stable, if their zeta potential is above 30mV or below -30 mV. In this study, only the two samples with added organic matter were in the stable range, below -30 mV. On the contrary, the deionised water and calcium added samples are highly unstable with a zeta potential around 0 mV, indicating that pH 5.5 or 6.5 approximately corresponds to the isoelectric points of the suspensions (Shaw, 1966). These observed tendencies are somewhat in line with other studies, since the presence of organic matter is known to stabilise particle suspensions via steric forces, and divalent cations (here Ca^{2+}) are expected to suppress the electric double layer surrounding particles in suspension and cause agglomeration and instability (Baalousha et al., 2013; Cupi et al., 2015). These results, even if pre-

liminary, indicate that there is an effect of media conditions on the stability of particles released from a nano-enabled product.

The results from the sp-ICP-MS analysis regarding the most frequent particle sizes and particle number concentrations are depicted in Figure 4.12. For the analysis, Cu^{63} was measured for the highest response and He was used as a collision gas to eliminate interference (flow: 5mL/min). There is a clear difference between samples leached from nano-CuO paint, the control paint and the pure media samples. To indicate the background level of particles, an LOD for particle number concentration was calculated as the mean of the estimated particle number concentrations in the pure media samples (see Figure 4.12). To provide a visual representation of this LOD, Figure 4.12 displays both the most frequent particle size in each leachate (based on a Gaussian model fit) and the corresponding particle number concentration for each leachate, where the LOD is indicated by the black dotted line. The average of most frequent particle sizes found across the pure media is indicated by the horizontal blue line.

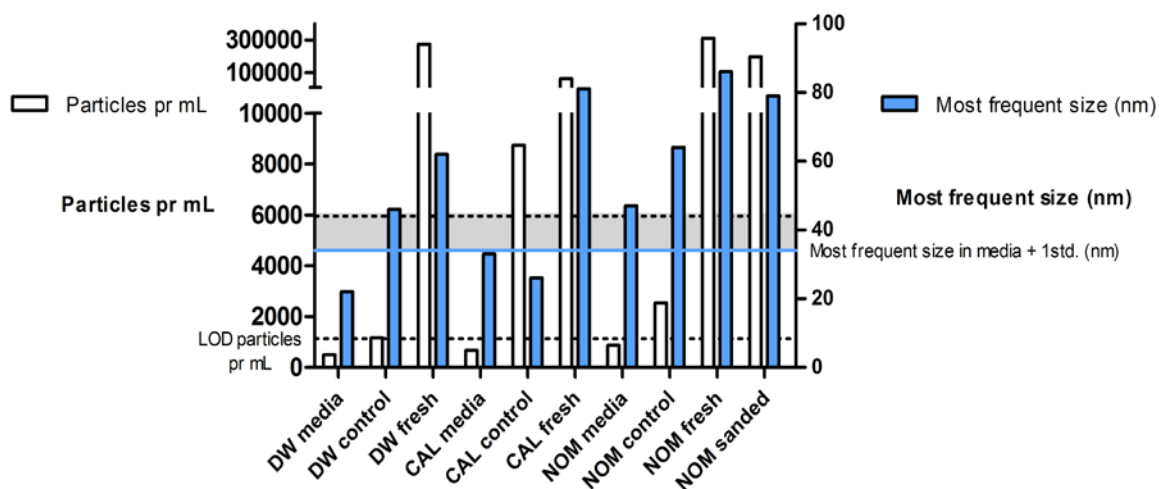


Figure 4.12. Calculated particle number concentrations and mean size of particles in each leachate, as analysed with sp-ICP-MS. Dotted black line represents LOD particle number concentration, based on pure media samples (LOD: 1130 part/ml), while the solid blue line represents size means across the pure media samples.

Figure 4.12 illustrates how particle size measurements from the sp-ICP-MS analysis might be excluded if they are based on a very small number of particles. For example, in “DW control,” the most frequent particle size was approximately 80 nm, comparable to the “DW fresh” sample; this size estimation is however based on very few particles, as the particle number concentration was in fact below the average in the pure media (dotted black line, Figure 4.12). Therefore, it is reasonable to assume that the particle size estimation is not valid in this case, and this goes for all the pure media samples and DW and CAL “Control” samples. In the case of “CAL Control”, particle number concentration is slightly higher than in “DW Control”, though the estimated particle size is very small and not different from the average size in pure media, which confirms that false positives are being measured, and most likely instrumental background/noise. As expected, in the samples which had been in contact with the nano-CuO paint (“Fresh” and “Sanded” samples), particle number concentration was several orders of magnitude higher compared to all other samples. Together with the particle size distributions displayed in Figure 4.13, these results indicate that there is a genuine release of engineered nano-CuO particles from the wood protection paint after 24 hrs.’ leaching.

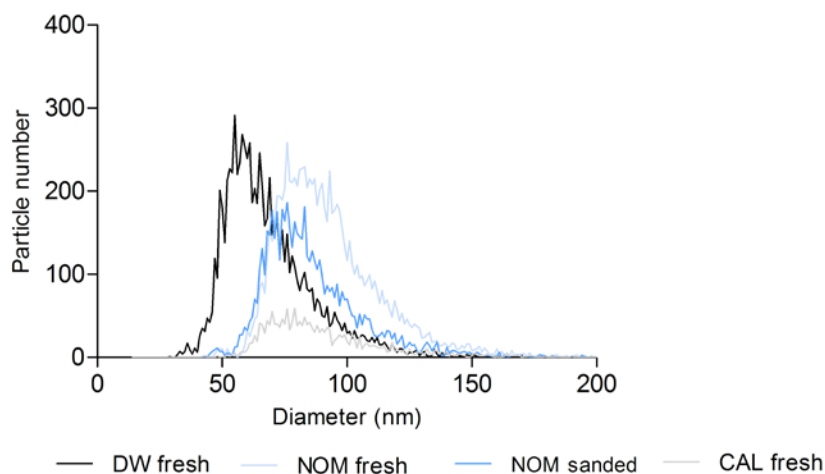


Figure 4.13. Sp-ICP-MS analysis of selected leachates from nano-CuO painted wood blocks. Instrumental settings: sample flow rate was 0.324 mL/min, scan time was 100 s and transport efficiency was 5.5%. Measuring range was 14 – 200 nm and bin size was 1.

However, since this was a preliminary study the results can only be used for a qualitative assessment of ENM release and further research is needed in order to draw conclusions about the possible environmental exposure from nano-Cu caused by this type of wood protection paint.

Particle size distributions obtained from the sp-ICP-MS analysis were separated from the dissolved background and thereby indicated that nano-CuO particles were present in the leachates (Figure 4.13). In this case, it was not considered necessary to determine a more robust LOD size for the dataset, since this is used mainly to separate the particles and dissolved signals. The size distributions of the four samples were similar, though the median size of particles in the DW medium was slightly lower compared to the other samples (55 nm compared to 80 nm). Fewer particles were detected in the CAL medium sample, possibly indicating increased particle dissolution or sedimentation. The zeta potential measured in the “CAL fresh” sample also indicated an unstable suspension, and the lower pH (around 5.5) might also have affected the particle dissolution rate (Figure 4.11). Again, it seems that media conditions have some effect on the size and number concentration of particles released from a nano-enabled product. As part of this preliminary study, concentrations of total Cu in acid digested leachate samples were also measured and compared with the dissolved concentrations, following which corresponding particle mass from the sp-ICP-MS analysis was calculated. All analysis confirmed the presence of Cu in the samples of leachate from nano-CuO painted wood. However, due to interference from the matrix (both leachate media and wood material), which potentially causes a higher dissolved signal in the sp-ICP-MS analysis, it was not possible to compare quantitatively the measured concentrations. It is known that Cu(I) and Cu(II) form complexes with organic matter (Maurer et al., 2013), which might have caused instability in the samples, meaning that they could not be compared with the acid-digested samples which are stabilised. More in-depth investigations and optimisations are necessary to establish the background and media effects in this set-up.

5 Discussion

In the previous four chapters, different aspects and levels of nanowaste characterisation have been reviewed: the occurrence of nano-enabled products and what this means in terms of possible ENM exposure to consumers, the fate of nano-enabled products in terms of their waste material fraction and their possible distribution in end-of-life waste treatments. Furthermore, the current state of knowledge has been expanded through experimental data on the release of ENMs from nano-enabled products. This section will discuss some key points of the thesis and provide recommendations for ways to address these challenges.

5.1 Addressing the lack of knowledge about ENMs in consumer products

The environmental assessments of ENMs and the products in which they are used in are still hampered by the lack of clarity and transparency in the way nanoproducts are marketed. This translates into more than half of the products in The Nanodatabase containing an unknown nanomaterial or nanotechnology (Hansen et al., 2016 – Paper I), and especially concerning “Goods for Children,” the number of products with an unknown ENM has increased significantly in the past two years (c.fr. Table 2.2). The Nanodatabase could include information regarding ENM mass or particle concentration in products, if this information were made publicly available. Based on the approach presented by Boldrin et al. (2014), information about the yearly production volume of a specific nanoproduct, the amount of ENM contained therein and the specifications of the product matrix could be logged together with existing information on The Nanodatabase. Specifically, this information could be processed as outlined in step one (“Quantification of nanowaste amounts”) of the exposure assessment framework presented in Boldrin et al. (2014) (see Figure 4.2), if it were publicly available. However, information on the fraction of the nanoproduct reaching the end-of-life stage and the ENM still present in the nanoproduct at this time would still be missing. These are referred to as the “EOL factors” and would be estimated from knowledge on the release/loss of product and ENM during use of the product (Boldrin et al., 2014). If this nanowaste quantification was incorporated into The Nanodatabase, some of the results from the analysis in Heggelund et al. (2016 – Paper II) might look different. For example, the dominant waste fraction in terms of

product numbers is “Plastic, packaging” (Heggelund et al., 2016 – Paper II), often including cosmetic products or sunscreens whereby the ENM is suspended in the liquid matrix. However, the solid waste material might only contain 10–20% of the original liquid containing the ENM by the time of disposal (Boldrin et al., 2014). Therefore the mass of ENMs present in this waste fraction might be negligible. Nevertheless, since information on production volumes, ENM masses and associated estimations are not yet available, the evaluation of nanowaste flows in Heggelund et al. (2016 - Paper II) is based on the number of products containing a certain ENM and belonging to a certain waste material fraction. The advantage of using The Nanodatabase product inventory is that it attempts to reflect the changing market for nano-products, by continuously updating with regards to products added to or taken off the market (Hansen et al., 2016 – Paper I). At the same time, products are added to the database based primarily on online available information and manufacturers’ claims to nanotechnology, and it is unknown whether or not the products are truly based on thereon (Hansen et al., 2016 - Paper I). Relying on manufacturers’ claims on the one hand might lead to an overestimation of the number of nano-enabled products available to European consumers. On the other hand for some product categories, it might lead to an underestimation (Hansen et al., 2016 – Paper I). In addition, the fact that The Nanodatabase is based on online information might lead to the exclusion of some products that are only sold in physical shops.

In light of the uncertainties still related to assessing potential exposure to ENMs from nano-enabled products, Hansen et al. (2016 – Paper I) recommended that it is made mandatory to disclose and report the use of any nanomaterials in a consumer product, not just cosmetics, and that this legislation is actively enforced. The demand for registration would hopefully also create coherence between ENMs registered on product inventories and those actually produced by industry. Furthermore, the authors advise that it should be illegal to advertise and market products using the word “nano” if they do not in fact contain ENMs, and manufacturers should preferably conduct a comprehensive consumer exposure assessment before the product goes on the market. Possibly, the reporting of production volumes and ENM masses could be prioritised. Boldrin et al. (2014) identified nanomaterial locations most prone to releasing ENMs as surface nanofilms, ENMs bound to a solid surface, ENMs suspended in liquids or solids and airborne ENMs.

These types of nanoproducts might serve as a starting point for implementing the mandatory disclosure of information on production volumes and ENM specifications.

5.2 Limitations of analytical methods for nanowaste characterisation

Experimental characterisation of nanowaste and released ENMs from nano-enabled products is challenging, especially in environmentally relevant conditions. The challenges stem from dealing with a complex mixture of materials, namely the unknown composition of the solid waste matrix, unknown type and low concentration of ENMs and the effect of different environmental conditions that may change the system (von der Kammer et al., 2012). These factors all complicate the choice of appropriate analytical methods and make it challenging to optimise the conditions for these analyses. In the case of nano-TiO₂-coated ceramic tiles, the high content of calcium in the ceramics, and its dissolution, caused a great deal of interference and hampered sp-ICP-MS analysis (Heggelund et al., 2017 – Paper III). However, if the target ENM had been different, calcium concentration might not have caused any concerns. In the case of nano-CuO release, some matrix interference was observed; however, it was not a significant issue in the sp-ICP-MS analysis. These two examples illustrate the need for the further development of very specific analytical methods, which requires time.

Nevertheless, in many cases, sp-ICP-MS is a very useful tool for ENM characterisation in a complex matrix (Mitrano and Nowack, 2017; Ruud et al., 2015). However, it can be difficult to run an optimised analysis of ENMs at low concentrations in unknown environmental samples, since three detection limits have to be taken into account: (i) the detection limit of the primary element of the particles (e.g. ⁴⁸Ti), (ii) the particle size detection limit, which determines the lower size cut off, and (iii) the detection limit for particle number concentration, which determines whether particles in the samples can be distinguished from the instrumental or blank background (Heggelund et al., 2017 – Paper III). Since particle size estimations and particle number concentrations are based on calculations with certain assumptions (Pace et al., 2011), it is important to obtain good measurement statistics in the analysis. Therefore, it is crucial to optimise the number of particles (data points) in the sample by making appropriate dilutions and setting the lower size detec-

tion limit for excluding false positives. These considerations make it harder to use the sp-ICP-MS method for screening purposes of different samples, although this approach has been recommended by other studies (e.g. Ruud et al., 2015). In Heggelund et al. (2017 – Paper III), it was observed that, changing the lower size detection limit by just 5 nm, could have a great impact on the LOD for particle number concentration and LOD particle size. In fact, Heggelund et al. (2017 – Paper III) were not able to obtain optimal conditions for the sp-ICP-MS analysis of leachate samples from nano-enabled tiles. On the other hand, in the case of nano-CuO release (see Section 4.4.2), particle size distributions were completely separated from the dissolved background, and it was not necessary to establish/calculate a lower size detection limit. However, it can still be beneficial to establish an understanding of the sp-ICP-MS results (particle size and number concentration) from a blank sample of the media corresponding to the sample media (e.g. water with added natural organic matter), since this can provide a more realistic picture of the background signal in the samples. One way to address the need for standardising detection limits and increasing understanding of the mechanisms governing ENM release from nanowaste could be to perform tracer experiments with purpose-made products in different settings. For example, this might be accomplished by manufacturing “standardised” materials with different matrix and ENM combinations, thereby imitating real nanoproducts but adding a certain tracer, e.g. a fluorescent material, which would only be associated with the purpose-made product (Part et al., 2016).

Another challenge concerning the characterisation of ENMs in waste is the fact that many, or their primary components, occur naturally in the environment, for example as particles/colloids or minerals (von der Kammer et al., 2014). Titanium is one of the most abundant elements in the earth’s crust at concentration ranges between 0.3-6% in soil (von der Kammer et al., 2012). Until recently, there were no methods available to separate natural particles directly from engineered ones, unless the ENMs were given certain tracers such as a specific isotopic composition, unique elemental ratios that distinguish them from their natural counterpart or an amendment of rare elements. In some cases, electron microscopy can be used to identify certain characteristics of ENM such as coatings, which are not expected in the bulk material (Kaegi et al., 2008). However, since little is still known about the transformations of ENMs during their life cycle and at their end-of-life in waste treatment systems, it is possible that their features will change and no longer

render them recognisable from the bulk material. Just recently, Praetorius et al. (2017) published a new, promising hyphenated finger-printing method for distinguishing ENMs from natural element backgrounds in soils. It is based on sp-ICP-MS but has an additional time of flight detector between the plasma and the mass spectrometer (sp-ICP-TOFMS). This analytical method is capable of measuring multiple elements at a time, and subsequently the data are fed into a model that deduces the patterns of the natural background and the engineered material.

5.3 Implications of the chosen experimental design

To ensure the relevance of nanowaste characterisation, and for quantifying potential environmental exposure, it is important to perform studies in realistic conditions, taking into account the full life cycle of the nano-enabled product (Mitrano and Nowack, 2017). In their review, Mitrano and Nowack (2017) found that when it comes to pristine ENMs, aged/transformed ENMs and released ENMs, most studies are performed in controlled laboratory experiments, sometimes mimicking different environmental conditions. Likewise, the toxicity of ENMs is assessed from tests in laboratory conditions that do not closely represent the life cycle of the ENMs or their potential hazards (Mitrano and Nowack, 2017). Studies testing pristine or aged ENMs mimicking certain life cycle processes, in terms of waste treatment, e.g. Bolyard et al. (2013), Dulger et al. (2016) and Walser et al. (2012), have the advantage of increased control over variables and observing effects. However, they are not able to take into account the different types of release, transformations and the influence of the product matrix (Mitrano et al., 2015). Furthermore, since ENMs are added artificially to the system, their release might be overestimated, because they are more available for release. Heggelund et al. (2017 – Paper III) also pointed out that, in order to perform a realistic evaluation of potential ENM exposure from consumer products, real nano-enabled products, and the ENMs released from these, should be tested.

The type and purpose of the study performed will also affect the choice of experimental regime or setup. For example, in ecotoxicology studies, it is essential to reach a concentration where an effect can be observed on the selected endpoint. In many cases, the concentration of ENMs released from a product will be too low to observe an effect in the organism, and it might be sensible to produce simulated aged products or ENMs, thus mimicking the

transformations expected to occur at a certain use stage or the end-of-life of the nano-enabled product in question (Nowack et al., 2016). Nonetheless, when it comes to investigating potential ENM release from nanowaste, information about the expected changes to the ENM whilst being manufactured into product, its use and disposal is essential. For instance, Dulger et al. (2016) studied the potential leaching of nano-TiO₂ from a fresh municipal solid waste matrix spiked with pristine nano-TiO₂ ENMs at different pH and ionic strength. It was concluded that the individual components of the waste (organic, glass, textile, paper and metal) all contributed to the retention of nano-TiO₂ and that the release potential of the ENM was low. Although it is valuable to understand how a waste matrix retains ENMs, the results do not seem useful in the context of understanding their release from waste, since the opposite phenomenon, i.e. retention or adsorption, is actually being quantified. Nano-enabled products will release ENMs that differ from the pristine form (e.g. Mackevica et al., 2017 and Al-Kattan et al., 2014), and therefore studies like Dulger et al. (2016) may have limited application when it comes to assessing potential environmental exposure associated with nanowaste products.

In terms of the set-up for investigating waste from nano-enabled products, another consideration could be whether the nanoproduct should be aged before performing the test, in order to perform a realistic assessment of ENM release. In Heggelund et al. (2017 – Paper III), the nano-enabled product under investigation was not aged or weathered artificially before testing. This might have affected the results, since the particles are located on the surface of the tiles, and may have been more prone to release if the surface had been partly damaged or decomposed, as it has been mentioned for waste incineration residues (Mitrano et al., 2017). However, in the preliminary study with wood protection paint containing nano-CuO (Section 4.4.2), there was no major difference in particle releases between the sanded and non-sanded (fresh) samples (c.fr. Figure 4.12 and 4.13).

5.4 Applicability of standardised batch leaching tests on nanowaste

Since nanowaste characterisation is still an emerging research field, the waste characterisation tests applied to ENMs or nano-enabled products, to date, have been largely simple batch tests performed under laboratory conditions (e.g. Dulger et al., 2016). These tests are used primarily for compliance testing of waste prior to landfilling (EU Commission, 2002), and they cannot be extrapolated to determine a material's leaching behaviour under environmental conditions in a real landfill. However, batch tests are used often and are well described for many materials. In addition, they are applied in regulation to establish landfill acceptance criteria, which makes them a sensible starting point for nanowaste characterisation. At a later stage, more in-depth characterisation tests in different pH conditions, as well as more long-term testing, would be very relevant for nanowaste testing, since it might reveal fundamental differences in release kinetics between ENMs and their natural counterparts. As a first step, batch tests could be modified to provide more information. For example, Bossa et al. (2017) prolonged a batch test at L/S 100 L/kg with nano-enabled cement for seven days, with leachate sampling at ten different time points. This enabled a study of release kinetics and mechanisms from the material. However, Bossa and co-workers performed the leaching test using ultrapure water, which is not representative of aquatic environmental media.

In some cases, as in Heggelund et al. (2017 – Paper III), nano-specific characterisation methods only provided information with regards to the non-detection of ENMs in leachate. However, they are necessary to include in batch leaching tests for waste characterisation, because ENMs are already used in significant quantities and annual production volumes are increasing in which case nanowaste amounts are bound to increase as well. Hence, we need methods to assess possible exposure from these products, and the only way to verify properly the presence or absence of the ENMs is to apply nano-specific characterisation methods, which have to be validated by testing different ENMs and product matrix combinations in different environmental conditions. Moreover, it is necessary to develop standardised methods for determining detection limits and data quality criteria. Still, a significant amount of work is needed both to establish reliable analytical methods and to conclude on whether EMN release poses a risk.

6 Conclusions and recommendations

This PhD thesis set out to investigate and analyse different aspects of nanowaste characterisation. Specifically, the potential occurrence, distribution and treatment of ENMs in waste from consumer products was characterised using an online product inventory and by developing a new analysis tool for nanowaste treatment. Direct experimental characterisation was performed on selected nano-enabled products to gain more knowledge regarding the potential release of ENMs from nanowaste.

By performing a mapping of nanoproducts available in the market, it was found that nano-Ag is the most used nanomaterial in terms of number of products, while “Health and Fitness” is the largest product application for nanoproducts, expanding by around 15% in just 2 years. Utilising the same nanoproduct inventory, The Nanodatabase, a method was developed for analysing the distribution of ENMs in waste. This involved estimating ENM fate in selected waste treatments based on their main matrix material. This information was included on The Nanodatabase to enable the online analysis of different waste treatment scenarios. The waste treatment analysis performed herein revealed that recycling may be the most likely waste treatment for nano-enabled products, and that nano-Ag will be present across all waste treatments. However, the recycling process does often not constitute the final end-of-life for an ENM. The online product inventory, The Nanodatabase, which was used to perform these analyses, is the most frequently updated inventory available; however, its main limitation is the fact that it does not include information regarding ENM mass or the number of particles in a product. An exposure framework to include this information was presented by Boldin et al. (2013), but it will not be possible to perform a quantification of ENM exposure unless more information regarding their presence in nanoproducts is made publicly available. Therefore, to assist the quantitative exposure assessment of ENMs from nanowaste, it is recommended that it is made mandatory to disclose their use in consumer products. Furthermore, the use of the word “nano” should be restricted to applications where products are in fact enabled by nanotechnology, since this would provide more clarity in the nanoproduct market and be a better starting point for assessing potential nanowaste generation.

On a global scale, it is expected that a significant amount of ENMs will end up in landfills, either directly in the original product or as a part of a secondary waste treatment process, such as in waste incineration ashes or sewage sludge. To gain more knowledge about the behaviour of ENMs in a landfill scenario, two nano-enabled products were tested using a standardised batch leaching test, which is often used for compliance testing waste prior to landfilling. On these grounds, the release of selected ENMs from two nano-enabled products was investigated using a standardised waste characterisation test. Nano-TiO₂ is used in many consumer applications, and its potential environmental exposure is expected to be high. The study of ceramic tiles with a nano-TiO₂ coating generally showed a very low release of total titanium ($\sim 0.1\mu\text{g/g}$). At least for this material and methods applied in this type of experimental set-up, the release of engineered nano-TiO₂ was also expected to be minor, and the quantification of particle release was challenging due to significant interference. Another ENM, nano-CuO, used in wood protection paint, was investigated using a similar set-up. Here, the presence of nano-Cu particles was confirmed using sp-ICP-MS, albeit these findings are associated with uncertainty, and so additional tests, including a larger number of samples, are needed to assess quantitatively the nano-CuO release from this material. While these two examples showed limited release, it cannot be excluded that other matrices and ENMs may be involved in more significant releases.

An important achievement was to identify, address and overcome some of the challenges involved in characterising ENMs in waste systems. A main challenge relates to the complexity of the waste matrix and varying environmental conditions, the combination of an ENM and a product matrix and the high presence of natural particles, which, until recently, could not be separated from the ENMs. In order to assess the potential release of ENMs from waste, it is important that future studies shape their experimental set-up to focus on discharged ENMs from nano-enabled product or their waste under different conditions. Studies of artificially spiked waste matrices are not able to take into account the transformations of the ENM that occur during the product life cycle, which is essential for gaining a realistic understanding of ENM release from waste. To enable these investigations, analytical methods still have to be developed and optimised to detect very low ENM concentrations or use fingerprinting or other tracer techniques. It is recommended that research into different nanowaste characterisation methods should be tested to

validate and standardise a way to assess ENMs in waste. Furthermore, there is a need for including nano-specific characterisation in waste characterisation tests, since ENMs are considered possible contaminants of waste that requires the level of contamination to be established in order to dispose of it safely.

7 References

Andersen, L., Christensen, F.M., Nielsen, J.M., 2014. Nanomaterials in waste: Issues and new knowledge. The Danish Environmental Protection Agency, Project no. 1608, 2014, pp. 978–987, ISBN no-93283-10-7.

Asmatulu, E., Twomey, J., Overcash, M., 2012. Life cycle and nano-products: end-of-life assessment. *J. Nanopart. Res.* 14, 720.

Al-Kattan, A., Wichser, A., Zuin, S., Arroya, Y., Golanski, L., Ulrich, A., Nowack, B. 2014. Behavior of TiO₂ Released from Nano-TiO₂-Containing Paint and Comparison to Pristine Nano-TiO₂. *Environ. Sci. Technol.*, 2014, 48, 6710-6718.

Baalousha, M., Nur, Y., Roemer, I., Tejamaya, M., Lead, J. R. 2013. Effect of monovalent and divalent cations, anions and fulvic acid on aggregation of citrate-coated silver nanoparticles. *Science of the Total Environment*, 2013, 454, 119-131.

Bitragunta, S.P., Palani, S.G., Gopala, A., Sarkar, S.K., Kandukuri, V.R. 2017. Detection of TiO₂ Nanoparticles in Municipal Sewage Treatment Plant and Their Characterization Using Single Particle ICP-MS. *Bull Environ. Contam. Toxicol.* (2017) 98, 595–600.

Boholm, M. and Arvidson, R. 2016. *Nanoethics* (2016) 10:25–40. Doi: 10.1007/s11569-015-0249-7.

Boldrin, A., Heggelund, L., Hundebøll, N., Hansen, S.F. 2016. Guidelines for safe handling of waste flows containing NOAA. Deliverable report 7.6 for SUN – Sustainable Nanotechnologies, Grant Agreement Number 604305, October 2016. Available online: http://www.sun-fp7.eu/wp-content/uploads/2017/01/SUN_Deliverable_7_6.pdf

Boldrin, A., Heggelund, L., Hansen, S.F. 2015. Report on methods for characterizing of the composition and physical properties of NOAA-containing waste. Deliverable report 3.5 for SUN – Sustainable Nanotechnologies, Grant Agreement Number 604305. September 2015. Available online: http://www.sun-fp7.eu/wp-content/uploads/2017/01/SUN_Deliverable_3_5.pdf

Boldrin, A., Hansen, S.F., Baun, A., Hartmann, N.I.B., Astrup, T.F., 2014. Environmental exposure framework for nanoparticles in solid waste. *J. Nanopart. Res.* 16, 2394.

Bolyard, S.C., Reinhart, D.R., Santra, S., 2013. Behavior of engineered nanoparticles in landfill leachate. *Environ. Sci. Technol.* 47 (15), 8114–8122.

Bossa, N., Chaurand, P., Levard, C., Borschneck, D., Miche, H., Vicente, J., Geantet, C., Aguerre-Chariol, O., Michel, F.M., Rose, J. 2017. Environmental exposure to TiO₂ nanomaterials incorporated in building material. *Environmental Pollution*, 2017, 220, 1160-1170.

Buha, J., Mueller, N., Nowack, B., Ulrich, A., Losert, S., Wang, J. 2014. Physical and Chemical Characterization of Fly Ashes from Swiss Waste Incineration Plants and Determination of the Ash Fraction in the Nanometer Range.

Caballero-Guzman, A., Sun, T., Nowack, B., 2015. Flows of engineered nanomaterials through the recycling process in Switzerland. *Waste Manage.* 36, 33–43.

CEN - European Committee for Standardization, 2002. Characterization of waste – Leaching – Compliance test for leaching of granular waste materials and sludges - Part 1: One stage batch test at a liquid to solid ratio of 2 l/kg for materials with a high solid content and with particle size below 4mm (without or with size reduction) (2002).

CIEL, ClientEarth and BUND. 2012. High time to act on nanomaterials. A proposal for a “nano patch” for EU regulation. Available online, last accessed 4/7-2017: http://www.ciel.org/wp-content/uploads/2014/10/Nanopatch_EU_Nov2012.pdf.

Cupi, D., Hartmann, N.B., Baun, A. 2015. The influence of natural organic matter and aging on suspension stability in guideline toxicity testing of silver, zinc oxide, and titanium dioxide nanoparticles with *Daphnia Magna*. *Env. Tox. and Chemistry*, 2015, 34, 497-506.

Dulger, M., Sakallioglu T., Temizel, B., Demirel, B., Coptu, N. K., Onay, T. T., Uyguner-Demirel, C. S., Karanfil, T. 2016. Leaching potential of nano-scale titanium dioxide in fresh municipal solid waste. *Chemosphere*, 2016, 144, 1567-1572.

EU Commission, 2012. Commission staff working paper – Types and uses of nanomaterials, including safety aspects. Final version: 3/10-2012 Available online, last accessed 3/7-2017: <http://eurlex.europa.eu/LexUriServ/LexUriServ.do?uri=SWD:2012:0288:FIN:EN:PDF>.

EU Commission, 2011. Commission recommendation of 18 October 2011 on the definition of nanomaterial. 2011/696/EU. Available online, last accessed 4/7-2017: <http://eurlex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32011H0696>.

EU Commission, 2010. Commission staff working document accompanying the communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions on the Thematic Strategy on the Prevention and Recycling of Waste. Available online, last accessed 4/7-2017: <http://ec.europa.eu/environment/waste/pdf/Commission%20Working%20Doc.pdf>

EU Commission, 2002. Council decision 2003/33/EC of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of Annex II to Directive 1999/31/EC. Available online, last accessed 3/7-2017: http://eur-lex.europa.eu/legal-content/HR/TXT/?uri=uriserv:OJ.L_.2003.011.01.0027.01.ENG.

Eurostat, 2017. Available online, last accessed 3/7-2017: <http://ec.europa.eu/eurostat/web/waste>.

Filipe, V., Hawe, A., Jiskoot. 2010. Critical Evaluation of Nanoparticle Tracking Analysis (NTA) by NanoSight for the Measurement of Nanoparticles and Protein Aggregates. *Pharmaceutical Research*, 27, 5, 2010. Doi:10.1007/s11095-010-0073-2.

Gottschalk, F., Sonderer, T., Scholz, R.W., Nowack, B., 2009. Modeled Environmental Concentrations of Engineered Nanomaterials (TiO₂, ZnO, Ag, CNT, Fullerenes) for Different Regions. *Environ. Sci. Technol.* 43, 9216–9222.

Gottschalk, F. and Nowack, B. 2011. The release of engineered nanomaterials to the environment. *J. Environ. Monit.* 13, 1145-1155.

Hansen, S.F., Heggelund, L.R., Besora, P.R., Mackevica, A., Boldrin, A., Baun, A. 2016. Nanoproducts – What is Actually Available to European Consumers? *Environ. Sci.: Nano*, 2016, 3, 169. – Paper I

Hansen, S. F., Larsen B. H., Olsen S. I., Baun A., 2007. Categorization framework to aid hazard identification of nanomaterials. *Nanotoxicology*, 2007, 1 (3), 243-250.

Hansen, E., England, I.G., Sørensen, P.L., Nilsson, N.H. 2013. Hazardous substances in plastic materials. Available online, last accessed 7/7-2017: <http://www.miljodirektoratet.no/old/klif/publikasjoner/3017/ta3017.pdf>

Heggelund, L., L., Hansen, S.F., Astrup, T.F., Boldrin, A. Semi-quantitative analysis of solid waste flows from nano-enabled consumer products in Europe, Denmark and the UK – abundance, distribution and management. *Waste Management* 56 (2016) 584-592. – Paper II

Hennenbert, P., Avellan, A., Yan, J., Aguerre-Chariol, O. 2013. Experimental evidence of colloids and nanoparticles presence in 25 waste leachates. *Waste Management*, 33 (2013), 1870-1881.

Hincapié, I., Caballero-Guzman, A., Hiltbrunner, D., Nowack, B. 2015. Use of engineered nanomaterials in the construction industry with specific emphasis on paints and their flows in construction and demolition waste in Switzerland. *Waste Management*, 43 (2015), 398-406.

Kaegi, R., Voegelin, A., Sinnet, B., Zuleeg, S., Hagendorfer, H., Burkhardt, M., Siegrist, H. 2011. Behavior of Metallic Silver Nanoparticles in a Pilot Wastewater Treatment Plant. *Environ. Sci. Technol.* 2011, 45, 3902-3908.

Kaegi, R., Ulrich, A., Sinnet, B., Vonbank, R., Wichser, A., Zuleeg, S., Simmler, H., Brunner, S., Vonmont, H., Burkhardt, M., Bollner, M. 2008. Synthetic TiO₂ nanoparticle emission from exterior facades into the aquatic environment. *Environ. Pollution* 156 (2008) 233-239.

Keller, A.A., Vosti, W., Wang, H., Lazareva, A., 2014. Release of engineered nanomaterials from personal care products throughout their life cycle. *J. Nanopart. Res.* 16, 2489.

Keller, A.A. and Lazareva, A., 2014. Predicted releases of engineered nanomaterials: from global to regional to local. *Environ. Sci. Technol. Lett.* 1, 65–70.

Kjeldsen, P., Barlaz, A.M., Rooker, A.P., Baun, A., Ledin, A., Christensen, T.H. 2002. Present and Long-Term Composition of MSW Landfill Leachate: A Review. *Critical Reviews in Environmental Science and Technology*, 32(4):297–336.

Kjølholt, J., Gottschalk, F., Lützhøft, H.C.H., Hartmann, N.B., Nowack, B., Baun, A. 2015. Environmental assessment of nanomaterial use in Denmark Environmental, project No. 1788, 2015

Lee, W.C., Lee, B.T., Lee, S., Hwang, Y.S., Jo, E., Eom, I.C., Lee, S.W., Kim, S.O. 2016. Optimisation, evaluation and application of asymmetrical flow field-flow fractionation with single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) to characterise silver nanoparticles in environmental media. *Microchemical Journal*, 129, 2016, 219-230.

Mackevica, A.; Olsson, M.E. and Hansen, S.F. 2017. The release of silver nanoparticles from commercial toothbrushes. *J. Hazard. Mater.* 2017, 332, Issue Part A, 270-275.

Mackevica, A. and Hansen, S.F. 2016. Release of nanomaterials from solid nanocomposites and consumer exposure assessment—a forward-looking review. *Nanotoxicology*, 2016, 10(6), 641-653.

Massari, A., Beggio, M., Hreglich, S., Marin, R., Zuin, S. 2014. Behavior of TiO₂ nanoparticles during incineration of solid paint waste: A lab-scale test. *Waste Management*, 34 (2014), 1897-1907.

Maurer, F., Christl, I., Fulda, B., Voegelin, A., Kretzschmar, R. 2013. Copper Redox Transformation and Complexation by Reduced and Oxidized Soil Humic Acid. 2. Potentiometric Titrations and Dialysis Cell Experiments. *Environ. Sci. Technol.* 2013, 47, 10912-10921.

Mehrabi, K., Nowack, B., Dasilva, Y.A.R., Mitrano, D.M. 2017. Improvements in Nanoparticle Tracking Analysis To Measure Particle Aggregation and Mass Distribution: A Case Study on Engineered Nanomaterial Stability in Incineration Landfill Leachates. *Environ. Sci. Technol.* 2017, 51, 5611-5621.

Mitrano, D. M., Mehrabi K., Dasilva, Y. A. R., Nowack B. 2017. Mobility of metallic (nano)particles in leachates from landfills containing waste incineration residues. *Environ Sci.: Nano*, 2017, 4, 480.

Mitrano, D.M., Motellier, S., Claaguera, S., Nowack B. 2015. Review of nanomaterial aging and transformations through the life cycle of nano-enhanced products. *Environment International*, 77 (2015), 132-147.

Mitrano, D.M. and Nowack, B. 2017. The need for a life-cycle based aging paradigm for nanomaterials: importance of real-world test systems to identify realistic particle transformations. *Nanotechnology*, 28 (2017). doi: 10.1088/1361-6528/28/7/072001.

Nowack, B., Boldrin, A., Caballero, A., Hansen, S.F., Gottschalk, F., Heggelund, L., Hennig, M., Mackevica, A., Maes, H., Navratilova, J., Neubauer, N., Peters, R., Rose, J., Schäffer, A., Scifo, L., von Leeuwen, S., von der Kammer, F., Wohlleben, W., Wyrwoll, A., Hristozov, D. 2016. Meeting the needs for Released nanomaterials required for further testing – the SUN approach. *Environ. Sci. Technol.*, 2016, 50 (6), pp 2747–2753.

Nowack, B., Ranville, J.F., Diamond, S., Gallego-Urrea, J.A., Metcalfe, C., Rose, J., Horne, N., Koelmans, A.A., Klaine, S.J., 2012. Potential scenarios for nanomaterial release and subsequent alteration in the environment. *Environ. Toxicol. Chem.* 31 (1), 50–59.

OECD, 2016. *Nanomaterials in Waste Streams: Current Knowledge on Risks and Impacts*. OECD Publishing, Paris Available online, last accessed 23/5-2016: <http://www.oecd-ilibrary.org/environment/nanomaterials-in-waste-streams_9789264249752-en>.

Pace, H.E., Rogers, N.J., Jarolimek, C., Coleman, V.A., Higgins, C.P., Ranville, J.F. 2011. Determining Transport Efficiency for the Purpose of Counting and Sizing Nanoparticles via Single Particle Inductively Coupled Plasma Mass Spectrometry. *Analytical Chem.* 2011, 83, 9361-9369.

Part, F., Zaba, C., Bixner, O., Zafiu, C., Mann, S., Sinner E.K., Huber-Humer, M. 2016. Traceability of fluorescent engineered nanomaterials and their fate in complex liquid waste matrices. *Env. Pollution* 214 (2016), 795-805.

Part, F., Zecha, G., Causon, T., Sinnern, E., Huber-Humer, M., 2015. Current limitations and challenges in nanowaste detection, characterization and monitoring. *Waste Manage.* 43, 407–420.

PEN CPI, 2017. Project for Emerging Nanotechnologies – Consumer product inventory. Available online, last accessed 4/7-2017: <http://www.nanotechproject.org/cpi/>.

Praetorius, A., Gundlach-Graham, A., Goldberg, E., Fabienke, W., Navratilova, J., Gondikas, A., Kaegi, R., Günther, D., Hotmann, T., von der Kammer, F. 2017. Single-particle multi-element fingerprinting (spMEF) using inductively-coupled plasma time-of-flight mass spectrometry (ICP-TOFMS) to identify engineered nanoparticles against the elevated natural background in soils. *Environ. Sci.: Nano*, 2017, 4, 307.

Reihlen, A. and Jepsen, D. 2015. Nanotechnologies and Waste. Report by the Ministry of the Environment. January 2015. Available online, last accessed 4/7-2017: http://www.bmub.bund.de/fileadmin/Daten_BMU/Download_PDF/Nanotechnologie/nanodialog_4_fd3_bericht_en_bf.pdf

Reinhart, D.R., Berge, N.D., Santra, S., Bolyard, S.C. 2010. Emerging contaminants: Nanomaterial fate in landfills. *Editorial / Waste Management* 30 (2010) 2020–2021.

Ruud, P., Herrera-Rivera, Z., Undas, A., vander Lee, M., Marvin, H., Mouwmeester, H., Weigel, S. 2015. Single particle ICP-MS combined with a data evaluation tool as a routine technique for the analysis of nanoparticles in complex matrices.

Sakallioğlu, T., Bakirdoven, M., Temizel, I., Demirel, B., Coptý, N. K., Onay, T. T., Uyguner Demirel C. S., Kranfil, T. 2016. Leaching of nano-ZnO in municipal solid waste. *J. Hazard. Mater.* 2016, 317, 319-326.

Schwirn, K., Tietjen, L., Beer, I. 2014. Why are nanomaterials different and how can they be appropriately regulated under REACH? *Environmental Sciences Europe* 26:4. Available online, last accessed 4/7-2017: <http://www.enveurope.com/content/26/1/4>.

Shaw, D.J. 1966. Introduction to colloid and surface chemistry. Chapter 7: Electrical properties. Butterworth –Heinemann, 1966. ISBN: 0585470642.

Sun, T.Y., Gottschalk, F., Hungerbühler, K., Nowack, B., 2014. Comprehensive probabilistic modelling of environmental emissions of engineered nanomaterials. *Environ. Poll.* 185, 69–76.

Synnott, D., Nolan, N., Ryan, D., Colreavy, J., Pillai, S.C. 2013. Self-cleaning tiles and glasses for eco-efficient buildings. Woodhead Publishing Limited, 2013. Doi: 10.1533/9780857098832.3.327.

The Nanodatabase, 2017. www.nanodb.dk. Available online, last accessed: 3/7-2017.

Tuoriniemi, J., Jürgens, M., Hassellöv, M., Cornelis, G. 2017. Size dependence of silver nanoparticle removal in a wastewater treatment plant mesocosm measured by FAST single particle ICP-MS. *Environ. Sci.: Nano*, 2017, 4, 1189.

Vejerano, E.P., Leon, E.C., Holder, A.L., Marr, L.C. 2014. Characterization of particle emissions and fate of nanomaterials during incineration. *Envir. Sci.: Nano*, doi: 10.1039/c3en0080j.

von der Kammer, F., Ferguson, L.P., Holden, P.A., Maisson, A., Rogers, K.R., Klaine, S.J., Koelmans, A.A., Horne, N., Unrine, J.M. 2012. Analysis of engineered nanomaterials in complex matrices (environment and biota): General considerations and conceptual case studies. *Env. Tox. and Chemistry*, Vol. 31, no. 1, pp 32-49, 2012.

von der Kammer, F., Wagner, S., Gondikas, A., Neubauer, E., Hofmann, T., 2014. Spot the Difference: Engineered and Natural Nanoparticles in the Environment – Release, Behavior, and Fate. *Ange. Chem. Int. Ed.* 2014, 53, 123998-12419.

Walser, T. and Gottschalk, F., 2014. Stochastic fate analysis of engineered nanoparticles in incineration plants. *J. Clean. Prod.* 80, 241–251.

Walser, T., Limbach, L.K., Brogioli, R., Erismann, E., Flamigni, L., Hattendorf, B., Juchli, M., Krumeich, F., Ludwig, K., Prokopsky, K., Rossier, M., Saner, D., Sigg, A., Hellweg, S., Günther, D., Stark, W.J. 2012. Persistence of engineered nanoparticles in a municipal solid-waste incineration plant. *Nature Nanotechnology Letters*, Vol. 7. Doi: 10.1038/NNANO.2012.64.

Wagner, S., Legros, S., Loeschner, K., Liu, J., Navratilova, J., Grombe, R., Linsinger, T.P.J., Larsen, E.H., von der Kammer, F., Hofmann, T. 2015. First steps towards a generic sample preparation scheme for inorganic engineered nanoparticles in a complex matrix for detection, characterization, and quantification by asymmetric flow-field flow fractionation coupled to multi-angle light scattering and ICP-MS. *J. Anal. Spectrom.*, 2015, 30, 1286.

WRAP (The Waste and Resources Action Programme), 2016. Plastics market situation report. WRAP: Banbury. Available online, last accessed 4/7-2017: http://www.wrap.org.uk/sites/files/wrap/Plastics_Market_Situation_Report.pdf

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