Summary

Engineered nanomaterials (ENMs) can potentially be released during all waste treatment processes and can accumulate in residual materials, scrap materials, secondary raw materials or composts. Nonetheless, only few studies are available on the fate and behavior of ENMs during recycling and disposal. In Austria more than half of the waste produced by households is collected separately and undergoes further treatment as recoverables, biogenic waste, hazardous household waste or as waste electrical and electronic equipment. The remainder is processed either in waste incineration facilities or in mechanical-biological waste treatment facilities. Initial studies in waste incineration facilities show that thermally stable ENMs (metal oxides) accumulate mostly in the solid residues (slag, flue dust). In Austria, these are largely disposed of in residual waste landfills. ENMs can also be released again during the recycling of products (for example quantum dots from LEDs of waste electrical and electronic equipment or CNTs made of composite materials). During recycling, nanosilver apparently negatively affects the mechanical properties of plastics. ENMs can be disposed of directly as production waste, as components of “nano-products” or as secondary wastes such as ENM-containing sewage sludge or combustion residues. Worldwide, an estimated 60 to 86% of the most commonly used ENMs end up in landfills. Currently, no generalized statements can be made because ENMs are applied in very diverse sectors and their fates in the environment can differ considerably.

Introduction

The preceding NanoTrust Dossiers already broadly treated the potential disposal routes of “nano-products” (see1) and the environmental behavior of ENMs (engineered nanomaterials) during wastewater treatment (see2). ENMs can potentially be contained in all waste streams because they are used in a very wide range of consumer products. The application sectors of ENMs currently range from construction materials to cosmetics and textiles to electronic devices (see3). Assessing potential releases calls for differentiating whether ENMs are integrated into a product (e.g. CNTs in plastics) or present in unbound form (e.g. TiO2 in sunscreen lotions). As soon as ENMs enter urban wastewater systems, sewage sludges represent an important “barrier” prior to any release into the environment. The disposal of these secondary wastes differs considerably from country to country, whereby in Austria the vast majority are currently thermally treated in fluid bed incinerators (see4). Waste management processes such as wastewater disposal and waste treatment (biological, mechanical, chemical or thermal) can transform ENMs into dissolved ions, sulfates or oxides. After these processes, the question arises whether these forms (chemical species) still retain nanomaterial size (1–100 nm) and nanospecific properties. Thus, the prevailing environmental conditions in wastewater treatment pathways of solid wastes. The treatment pathways of solid wastes from households and similar infrastructures are presented in Figure 1 as a material flow diagram. The following chapters describe how ENMs can behave during solid waste treatment.

How do ENMs behave during waste incineration?

Vejerano et al.6 investigated the behavior of nano-TiO2, -nickel oxide (NiO), -silver (Ag), -ceroxide (CeO2) and -iron oxide (Fe2O3) as well as of CdSe/ZnS quantum dots and fullerences (C60) during thermal processing on the laboratory scale. In order to simulate the incineration of medical wastes and lab residues at the laboratory scale, paper waste, polyethylene terephthalate (PET) and polyvinylchloride (PVC) were admixed with selected ENMs in various mass fractions and incinerated. These experiments were designed to more closely study the effect of ENMs on the incineration process itself as well as on fine particle formation. These lab studies revealed that the fine particle formation was not significantly affected by the applied ENM amounts, i.e. there was no increased development of fine particles. A significant change in the number size distribution or a shift in ranges with smaller particle diameters was determined only at unrealistically high ENM dosages. The incineration of ENMs composed of metal oxides even reduced the formation of volatile polycyclic aromatic hydrocarbons (PAH), which represent an undesired toxic by-product of incineration processes. The stronger catalytic effect of these ENMs (CeO2, Fe2O3, 

* Corresponding author
NIo and TiO$_2$ potentially reflects the increased oxidative properties of the particle surfaces as well as the oxidation state of the metals and their specific features. In contrast, CdSe quantum dots can lead to elevated PAH emissions. The authors suspect that the size of the nano-CeO$_2$ (e.g. nano-Fe$_2$O$_3$, -TiO$_2$) and thus their toxicity. The authors underline that large-scale tests should be conducted in order to draw more definitive conclusions.

In Switzerland, a large-scale experiment was conducted in a waste incineration plant with an annual capacity of 200,000 $\text{t}$. The aim was to more closely examine the fate and the mass flows of nano-CeO$_2$ under real conditions. In the first trial, 10 kg nano-CeO$_2$, suspended in water, were directly applied to ca. 7 $\text{t}$ residual waste. In the second trial, 1 $\text{kg}$ of these tracer nanoparticles were sprayed directly in the combustion chamber of the grate furnace plant. Subsequently, the concentrations of cerium (Ce) were determined using mass spectrometry methods (ICP-MS) in the slag, filter ash, process water, as well as in the cleaned flue gases. This helped calculate a mass balance for nano-CeO$_2$. The schematic flow diagram of the incineration facility and the respective sampling points are presented in Figure 2. The large-scale tests by Walser et al. revealed that 81 % and 53 % of the added tracer amounts were detected in the slag (trial 1 and trial 2, respectively), 19 % and 45 % in the flue ash, 0.02 % and 1.7 % in the process water; and only 0 % and 0.0004 % in the cleaned flue gas. Additional analyses showed that nanoparticulate CeO$_2$, which adhered to the surface of other combustion residues, was not present in bound form. The authors suggested that no chemical or physical changes had occurred.

In Germany, Liesen et al. investigated the behavior and thermal stability of nano-CeO$_2$ in the framework of a large-scale study in a hazardous waste incineration facility. There, 1 g/L CeO$_2$ (suspended in water) was injected directly in the flame of the combustion chamber and the particle number concentration as well as the number size distribution were determined using an aerosol measuring instrument (SMPS) and electron microscopy (SEM). The investigations showed that, in the flame, nano-CeO$_2$ can be transformed into smaller, individual primary particles (through de-agglomeration or sublimation), to larger clusters (through agglomeration), or to aggregates (through sintering). After the subsequent flue gas cleaning, more than 99.9 % of these tracer nanoparticles were separated out. Accordingly, an air-side diffuse release via the furnace is negligible (note: as long as an adequate flue gas cleaning technology is applied).

### Treatment of wastes from households and similar infrastructures

In Austria, in 2009, about 43 % of the wastes arising from households and similar institutions were sent either to waste incineration or mechanical-biological waste treatment plants. After separation of the high-caloric value fraction during mechanical-biological waste treatment, this fraction is subsequently thermally treated. The low-caloric value fraction from mechanical-biological waste treatment is initially treated biotechnically (e.g. decomposed) and then dumped. About 57 % of the waste collected from households and similar institutions are collected separately and sent for scrap material reclamation (e.g. plastic recycling) or biotechnical processing (e.g. composting or biogas production). Hazardous waste and waste electrical or electronic equipment (WEEE) are also collected separately and processed in hazardous waste treatment facilities. Overall, about 44.8 % of the total amount are lost as mass during thermal and biotechnical treatment (e.g. through conversion to CO$_2$ or steam). 38.9 % of the overall volume from households and similar institutions are recovered or recycled, only 13.8 % dumped, and 2.5 % are sent to hazardous waste treatment facilities. During the waste treatment processes, ENMs can potentially be released through mechanical, chemical or thermal forces (unintentionally) or accumulate in certain waste streams such as slags or secondary raw materials from recycling.

Figure 1: Processing and disposal of wastes from households and similar institutions in 2009. ENMs can potentially be released during all waste treatment processes as well as accumulate in residues, scrap materials (secondary raw materials) or composts.
Thus, thermally stable ENMs such as nano-CeO$_2$, -TiO$_2$, -NiO, -CeO$_2$ and -Fe$_2$O$_3$ accumulate largely in the solid residues of waste incineration facilities (e. g. slag, flue dust or solid flue gas scrubbing products). In Austria, most such residues are dumped in so-called residual-waste landfills. Combustion residues with minimal contamination can also be recovered as secondary construction materials (e. g.: for road construction). No specifications and limit values for specific nanoparticles in wastes, residual products or secondary raw materials are currently in force in Europe or in Austria’s waste management laws. Nonetheless, a release of ENMs from recycling construction materials and other secondary raw materials cannot be excluded.

How do ENMs behave during recycling?

Very little is currently known about the behavior of ENMs during material recovery or recycling. From the worker protection perspective, only very few studies have been conducted in waste treatment facilities. Those ENMs firmly integrated in a product matrix can be released only through mechanical, chemical or thermal processes (see13). Thus, quantum dots in LED backlighting can be released again when recycling waste electrical and electronic equipment. Liu et al.14 studied the release behavior of CdSe/ZnS quantum dots used in lighting systems (LEDs or TVs) or solar modules and that were integrated into a solid matrix there. In laboratory experiments the quantum dots were subjected to leaching processes with acidic solvents. In this case only relatively low concentrations of highly toxic cadmium ions (Cd$^{2+}$) leached out. Accordingly, the risk arising from these substances during the use of lighting systems and solar modules containing quantum dots is very low. Nonetheless, it remains completely unknown whether quantum dots made of gallium nitride (GaN), indium phosphide (InP), cadmium selenide (CdSe) or cadmium telluride (CdTe) can be unintentionally released again when processing such waste electrical and electronic equipment.

A Swiss research team15 developed potential emission scenarios for composite materials containing carbon nanotubes (CNTs). The authors suggest that a CNT release during production is unlikely (e. g. when plastic is extruded). During the use phase, however, CNTs can be released for example from

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**Figure 2:** Detection of CeO$_2$ tracer particles in solid and liquid combustion residues.

*Figure 2a:* nano-CeO$_2$ was sprayed directly into the pre-chamber of the combustion chamber (Case 1) or in the flue gas stream directly above the combustion chamber (Case 2). Sampling points I-VI before and after addition of nano-CeO$_2$.

*Figure 2b:* Electron microscope images of crystalline nano-CeO$_2$ (10 – 50 nm) from different sampling points.

*Figure 2c:* Schematic representation of the expected residence times of nano-CeO$_2$ in the flue gas stream (the lighter the blue arrows, the purer the gas).8
CNT-containing automobile tires or textiles through abrasion. Nowack et al.\textsuperscript{12} consider an unintentional release during the recycling of CNT-containing products such as wind turbines, automobile tires, textiles, sports- or electronic equipment to be entirely possible.

Sánchez et al.\textsuperscript{16} examined the influence of nanomaterials and nanoparticulate calcium carbonate (CaCO\textsubscript{3}), silver (Ag), as well as zinc oxide (ZnO) on the recycling of plastic foils. They tested foils made of polyethylene (PE), polypropylene (PP) and polyethylene terephthalate (PET) with and without ENMs for their mechanical as well as optical properties. With regard to durability, no significant difference was determined between conventional recycled plastics and those admixed with ENM-containing plastics. The exception was ENM-containing PET packaging foils, where nano-Ag had a negative effect on the mechanical properties. An excessive ENM dose or accumulation in recycled plastics, however, can reduce the transparency of the packaging foils. The decision on using recycled plastics generally depends on whether the strict hygienic and technical standards for packaging materials can be fulfilled and on the purpose for which these are applied (e.g. for food- or construction material packaging).

Wastes that originally contained no ENM can, however, also be utilized as secondary raw material for the targeted production of nanomaterials. For example, carbon-containing ENMs such as graphene\textsuperscript{17} or CNTs\textsuperscript{18} can be gained from biogenic wastes or old plastic bags. In the future, an increased use of plastic waste as an “ENM source” could become a commercially viable recycling opportunity. Note in this connection that mechanical and chemical processes can transform plastic wastes that bypass legitimate waste collection systems and inadvertently enter the environment into nanoscale particles (nanoparticulate emissions). These, in turn, can impact the environment\textsuperscript{19}.

How do ENMs behave in landfills?

 Generally, ENMs can be disposed of directly as production wastes or as a component of “nano-products”. The disposal of secondary wastes represents an indirect input (e.g. of sewage sludges, combustion residues, etc.). Material flow models\textsuperscript{20} have shown that, in the future, the largest ENM amounts will accumulate in landfills. A key factor in this respect is the broad application of ENMs in many products and sectors along with the often very country-specific disposal systems (see\textsuperscript{21}).

Keller et al.\textsuperscript{17} therefore estimated that, worldwide, between 60 and 86 % of the most commonly used ENMs\textsuperscript{22} end up in landfills. A material flow modelling approach based on the Swiss disposal system revealed that less than 100 kg CNT, 51 t ZnO- and Ag- as well as 150 t TiO\textsubscript{2}-ENM land in dumps every year\textsuperscript{23}. Of this, the greatest mass fraction is deposited as residual materials after thermal waste treatment; a small proportion is directly dumped as construction waste. Müller et al.\textsuperscript{19} underline that we currently know only very little about the behavior of ENMs in landfills.

A French study\textsuperscript{27} has already detected nanomaterials and larger particles that have leached from landfills and wastes. That investigation, however, was unable to definitively distinguish between nanoparticulate emissions that stem from non-nanomaterial-containing wastes (and that can develop unintentionally), and ENMs. A study in the U.S.A\textsuperscript{28} more closely examined the behavior of CNTs in landfills. The experiments, conducted under laboratory conditions, showed that CNTs remain colloidal in landfill leachate and are thus mobile as long as dissolved humic acids are present. Ion strength is an equally decisive factor for potential ENM mobility in leachates. Bolyard et al.\textsuperscript{29} examined the role and impact of ENMs (nano-ZnO, TiO\textsubscript{2} and Ag) on biological decomposition processes occurring in real leachates. These lab experiments, using relatively high ENM concentrations (0.1 – 100 mg/L), detected no significant changes in the selected landfill parameters\textsuperscript{30}. Another U.S. study\textsuperscript{31} examined the effects of nano-Ag on microbial processes in landfills containing a high fraction of organic wastes. An inhibition of methane gas formation was recorded only at unrealistically high ENM concentrations (≥ 10 mg/kg)\textsuperscript{32}.

In the U.S.A. most wastes are directly dumped without prior treatment (waste incineration, recycling, etc.). Wastes also continue to be directly dumped in several EU member states (see\textsuperscript{23}). Only a few more detailed studies are available on the behavior and fate of ENMs in landfills under European conditions. In Austria, the mobility behavior of colloidal stable ENMs – under the prevailing landfill conditions – is currently being examined in more detail\textsuperscript{34}. Using surface-modified CdTe/ZnS quantum dots as tracers, the researchers are attempting to establish baseline information regarding the colloidal stability and mobility of ENMs under landfill conditions. In the framework of an EU-funded study\textsuperscript{26}, diffusion experiments are being conducted on ENMs in order to assess the permeability of landfill base sealants and bottom liners.

ENMs not only represent a potential pollution load in the environment, but can also be used to remediate contaminated sites or purify drinking water. An ongoing EU research project\textsuperscript{37}, for example, is investigating the use of zerovalent nano-iron to remove pollutants from contaminated sites. The aim of this project is to develop a cost-effective remediation method for contaminated areas such as industrial sites or landfills. Nano-iron can be used to remediate groundwater contaminated with organic or inorganic pollutants (e.g. halogenated methane, polychlorinated hydrocarbons or heavy metals)\textsuperscript{38}.

Behavior and transport of ENMs in environmental media:

A potential mobilization and transformation of ENMs are largely caused by hydrodynamic transport processes (leaching or deposition), dissolution, de- or adsorption as well as oxidation or reduction processes\textsuperscript{24}. The behavior and fate of ENMs, for example in a landfill, depend highly on the environmental conditions such as pH value, ion strength, total content of organic material, content of dissolved humic acids, as well as on the colloidal stability of ENMs. The prevailing conditions, in turn, vary with the type and age of a landfill along with its mode of operation. It cannot be excluded that certain ENMs can penetrate artificially deployed barriers against ENMs such as landfill bottom liners\textsuperscript{25}. Once ENMs have entered the groundwater or surface waters, then they can – as also can naturally present nanomaterials – additionally serve as “carrier substances” for other contaminants\textsuperscript{26}. The environmental monitoring of ENMs and associated contaminants represents a major challenge because differentiating between naturally present and ENMs is very complicated at very low environmental concentrations.
Notes and References

1 NanoTrust Dossier Nr. 040en.
2 NanoTrust Dossier Nr. 043en.
3 NanoTrust Dossier Nr. 041
   [only available in German].
4 NanoTrust Dossier Nr. 043en.
5 Illustration based on the Federal Waste Management Plan 2011 (Volume 1), Page 42, BMLFUW.
8 Walser, Tobias, et al., 2012, Persistence of engineered nanoparticles in a municipal solid-waste incineration plant, Nat Nano 7(8), 520-524. http://dx.doi.org/10.1038/nnano.2012.64.
9 ICP-MS … Inductively coupled plasma mass spectrometry (e. g. for determination of mass concentration).
11 SMPS … Scanning Mobility Particle Sizer for determination of particle concentration and particle number distribution of aerosols and ultrafine particles.
12 Transmission electron microscopy to determine the particle size, particle size frequencies and particle shape.
13 NanoTrust Dossier Nr. 040en.
17 Suryawanshi, Anil, et al., 2014, Large scale synthesis of graphene quantum dots (GQDs) from waste biomass and their use as an efficient and selective photoluminescence on-off probe for Ag+ ions, Nanoscale 6(20), 11664-11670. http://dx.doi.org/10.1039/C4NR02494J.

Conclusions

The material flow modelling efforts in various international studies show that the end-of-life-phase of “nano-products” can play a key role in the potential release of ENMs. Currently, however, little is known about the behavior and fate of ENMs in waste streams, especially in landfills. In the future, additional studies must be conducted in order to draw more general conclusions about ENM behavior in waste streams and landfills. Currently, many questions remain open regarding the fate (“sink effect”) and potential release of nanoparticle emissions in the various waste treatment processes (for example during recycling). The same holds true for the behavior and transport of ENMs in residual materials in landfills. In particular, the measuring techniques need to be (further) developed in order to detect and characterize ENM-containing wastes and nanoparticulate emissions such as ultrafine particles in waste treatment facilities or dissolved nanoparticles in landfill leachates. Thus, ENMs can be released when recycling waste electrical and electronic equipment, construction materials or plastics. At the same time, nanoparticulate emissions can also occur inadvertently from conventional products (without ENMs). Nonetheless, more detailed studies with suitable measuring techniques are currently not available for recycling processes. In the future, reliable environmental monitoring will be crucial in order to be able to assess (long-term) environmental impacts of ENMs during and after their use phase.


30 In the U.S. biological oxygen demand after 5 days (BSB5) and biochemical methane potential (BMP) can be used to evaluate biological degradation processes of landfill leachates.


32 In comparison with estimates based on Müller et al., in Switzerland, a maximum of ca. 1 mg nano-Ag per kg in slogs is predicted.

33 NanoTrust Dossier Nr. 040en.


