ÖAW ITA
Institute of Technology Assessment
of the Austrian Academy of Sciences

nano trust dossiers
No. 040en • August 2014

"Nanowaste" Nanomaterial-containing products at the end of their life cycle

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Summary

Based on their special chemical and physical properties, synthetically produced nanomaterials are currently being used in a wide range of products and applications. At the end of their product life cycle, nanomaterials can enter waste treatment plants and landfills via diverse waste streams. Little, however, is known about how nanomaterials behave in the disposal phase and whether potential environmental or health risks arise. There are no specific legal requirements for a separate treatment of nanomaterial-containing wastes. Virtually no information is available about the nanomaterials currently in use, their form and composition, or about their amounts and concentrations. The current assumption is that stable nanoparticles (e.g. metal oxides) are neither chemically nor physically altered in waste incineration plants and that they accumulate especially in the residues (e.g. slag). These residues are ultimately dumped. The disposal problem in the case of stable nanoparticles is therefore merely shifted to the subsequent steps in the waste treatment process. Carbon nanotubes (CNT) are almost completely combusted in incineration plants. Filter systems seem to be only partially efficient, and a release of nanoparticles into the environment cannot be excluded. Incinerating nanomaterials contained in products can also promote the development of organic pollutants as undesired by-products. Only few studies are available on the behavior of nanomaterials in landfills. Moreover, recycling such products could release nanomaterials, most likely when these are shredded and crushed.

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Introduction

Based on their special chemical and physical properties, synthetically produced nanomaterials (engineered nanomaterials, ENMs) are currently being used in a wide range of products and applications. The Nanomaterial Databank of "Nanowerk"[1] currently lists nanomaterials composed of 28 different elements as well as of carbon (fullerenes, CNT, graphene), quantum dots consisting of several semi-conductor materials, a large number of simple nanoparticulate compounds (oxides, carbonates, nitrides) and those made up of complex compounds containing several components. On the one hand, the application of nanomaterials promises reduction potentials and sustainability effects for the environment, for example through resource and material savings (see[2]). On the other hand, we know very little about the behavior of nanomaterials or about environmental and health risks when these products enter various waste streams at the end of their life cycles. A better understanding of the risks in the so-called End-of-Life-Phase (EOL) calls for considering the different disposal pathways and potential transformation processes that nanomaterials undergo in waste treatment plants. In the disposal phase no consideration is being given to either the special properties of nanomaterials or to potential recovery and re-use.[3]

There is no special legal framework in place for a separate treatment of nanomaterial-containing wastes (see[4]) or the monitoring of the processes. A prerequisite for such a framework would be exact knowledge about the nanomaterials being used, their form (species) and composition, potential transformation processes as well as about amounts and concentrations. Such information, however, is not available, and virtually no studies have been conducted on the EOL phase of products containing nanomaterials. Very little is known about how nanomaterial-containing wastes behave in thermal, biological or mechanical-biological waste treatment plants or in landfills.[5]

What is "nanowaste"?

Nanomaterials can potentially be released into the environment along the entire product life cycle through mechanical and/or chemical effects. According to a proposal by Boldrin et al.[6], nanomaterials that enter the environment from diffuse sources can be classified as potential "nanopollutants" (for example titanium dioxide nanoparticles released from sunscreen lotions in surface waters). Accordingly, the term "nanowaste" is first applicable when nanomaterials come into contact with solid wastes and can be collected separately.

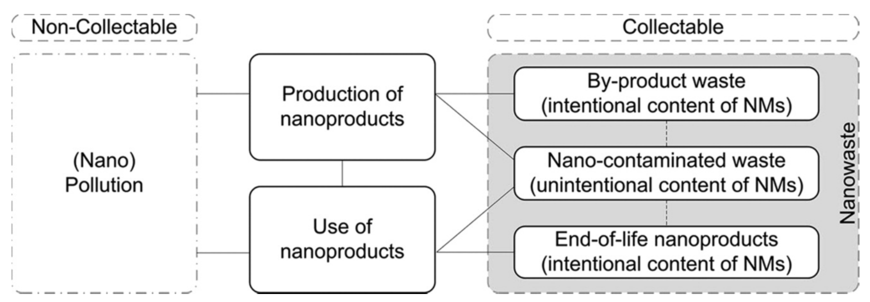


Figure 1: Differentiation between "nanopollutant" and "nanowaste", i.e. solid waste that contains nanomaterials[7]

Titanium dioxide nanoparticles therefore become waste only when they are for example eliminated in wastewater treatment plants after the biological purification phase. Nanomaterial-containing sludge which requires further treatment according to the Austrian Waste Management Act (Abfallwirtschaftsgesetz; AWG) is termed "nanowaste". Nanomaterial-containing wastes from production processes and households (e.g. production rejects or „nanoproducts") are also classified as "nanowaste" (Fig. 1).

Practical considerations dictate distinguishing between "nanowaste" and "nanopollutant" because quantifying ENMs in waste streams is a precondition for determining potential limit values. A distinction is also necessary in order to be able to differentiate the definition of "waste" in the waste legislation framework from other environmental laws. Accordingly, wastes are first subject to the Waste Management Act when there is, resp. was, an intention to discard or when their collection, storage, transportation and treatment is necessary in the public interest.

European and Austrian waste legislation currently contain no nano-specific regulations[8]. Additional studies – in particular regarding the persistence of and changes undergone by nanomaterials in waste – will be required to be able to draw conclusions about whether nano-specific limit values might become necessary in the future.

Nanomaterials in waste streams

Austria generates more than 50 million tons of waste per year. Materials that arise from digging or excavating the soil or subsoil make up the largest proportion (Fig. 2). Such excavated material could be contaminated with nanomaterials via several pathways, for example through nanomaterial-containing building materials. No studies are available on this issue. Ash and slag from thermal waste treatment plants can also contain nanomaterials, as can construction wastes (see further below) or household wastes. In principle, nanomaterials can be present in all waste categories.

"Nanowaste" can already arise in ENM production and use by industry and trade, for example in the form of faulty batches, production wastes, filter residues, of wiping cloths or solvents contaminated with nanoparticles, but also as residues produced by research and development facilities.

According to a working group commissioned by the Swiss Bundesamt für Umwelt (BAFU; Federal Department of the Environment), companies that produce or process synthetic nanomaterials should in particular take the following measures in dealing with "nanowastes":[10]

- reduce waste volumes.
- if possible treat the resulting nanomaterial-containing wastes directly at the point of origin with appropriate methods such that they lose their nano-features (for example by dissolving metallic nanomaterials in suitable acid baths or sintering at high temperatures).
- develop waste management schemes that ensure that nanowastes are separately collected, documented, packaged and further directed to disposal, whereby these work steps should proceed with consistent quality.
- minimize nanomaterial emissions (dust or aerosols) into the environment. Nanowastes should, to the extent possible, not be collected and transferred as powdered preparations but rather as dispersions, pastes, granulates, etc.

Currently, too little is known about the behavior of ENMs in waste incineration plants. This leads to the recommendation not to dispose large quantities of nanowastes from industry and trade in such facilities.[10] This, however, raises the question of viable alternatives, such as chemo-physical treatment methods.

The special application of ENMs in industrial processes (e.g. filter or catalyst technologies) enables ENMs to be collected in unmixed form. Their use in consumer products such as cosmetics, textiles, paints and varnishes, etc., however, leads to a diffuse distribution. This considerably complicates separate collection.[3]

Waste treatment in Austria

The European Waste Framework Directive[11], which has been implemented in the Austrian Waste Management Act (AWG 2002)[12], is based on the following hierarchy:

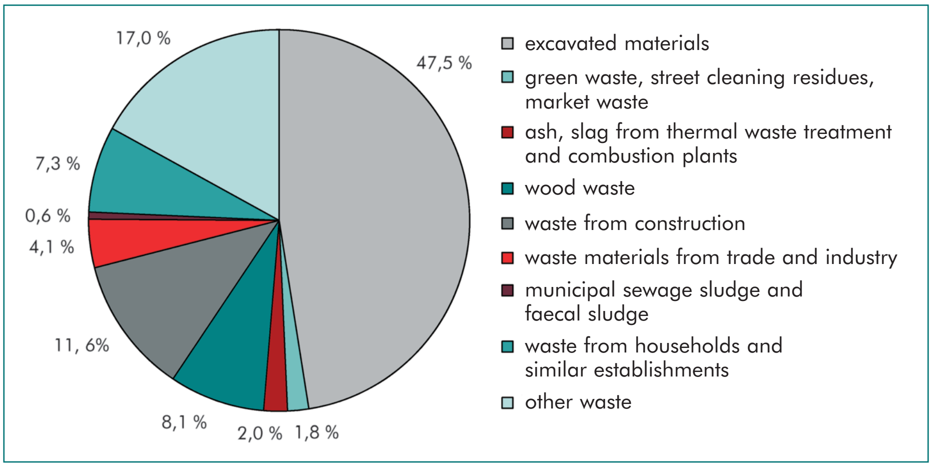
1. waste prevention
2. preparation for re-use
3. recycling
4. other utilization (e.g. energy recovery)
5. disposal.

In Austria the targeted recycling of separately collected waste fractions (paper, metals, plastics, glass) from municipal wastes is well established.[13] In 2009, 63% of the wastes were collected for processing and recycling. The residual waste (from households and similar institutions) undergoes either mechanical-biological waste treatment (24.4%; basis 2009) or thermal waste treatment in incineration plants (70.5%; basis 2009).[14]

In Austria the wastes must be pre-treated or recycled, and only very small amounts are directly disposed. The residues from the waste treatment plants (e.g. slag after incineration) as well as construction and demolition waste are dumped. In many other EU countries, however, municipal wastes are largely or entirely disposed in landfills without pre-treatment (Fig. 3.).

Many products that are re-used in **recycling processes** (for example electrical and electronic equipment, metals, plastics, paper, clothing, etc.) can contain nanomaterials and these can potentially be released. At least four different processes could lead to releases during recycling:[16]

Figure 2:
Percentages of selected waste categories in 2010 (Basis: 51.72 million tons)[9]



1. **dust-like abraded material**, which can disperse in the air as airborne particulate matter, can develop especially during transport, during shredding and crushing, as well as when tipping.
2. if the wastes are initially cleaned or certain components dissolved or detached (for example a nano-coating on PET bottles), then **nanomaterials** might enter the **liquid media** and ultimately collect in the cleaning- and wastewater. The same holds true for the cleaning of facilities, equipment and floors, in which the dusts are captured in cleaning cloths and cleaning water.
3. when incinerating products with nanomaterial-containing substances, it cannot be excluded that **nanomaterials** enter the **flue-gases**.
4. in readily soluble or strongly heated media, an **evaporation of nanomaterials** is also theoretically possible.

Experts from the "Hans Böckler Stiftung" of the Deutschen Gewerkschaftsbundes (German Trade Union Federation) therefore made an important recommendation in their working paper on the significance of nanomaterials in waste recycling[16]: future research efforts on the risk potentials of nanomaterials should be devoted to treatment processes for potentially nanomaterial-containing consumer products. The individual material streams in the recycling chains should be examined in detail regarding the types and amounts of nanomaterials being used. This would help estimate the degree of potential risks.

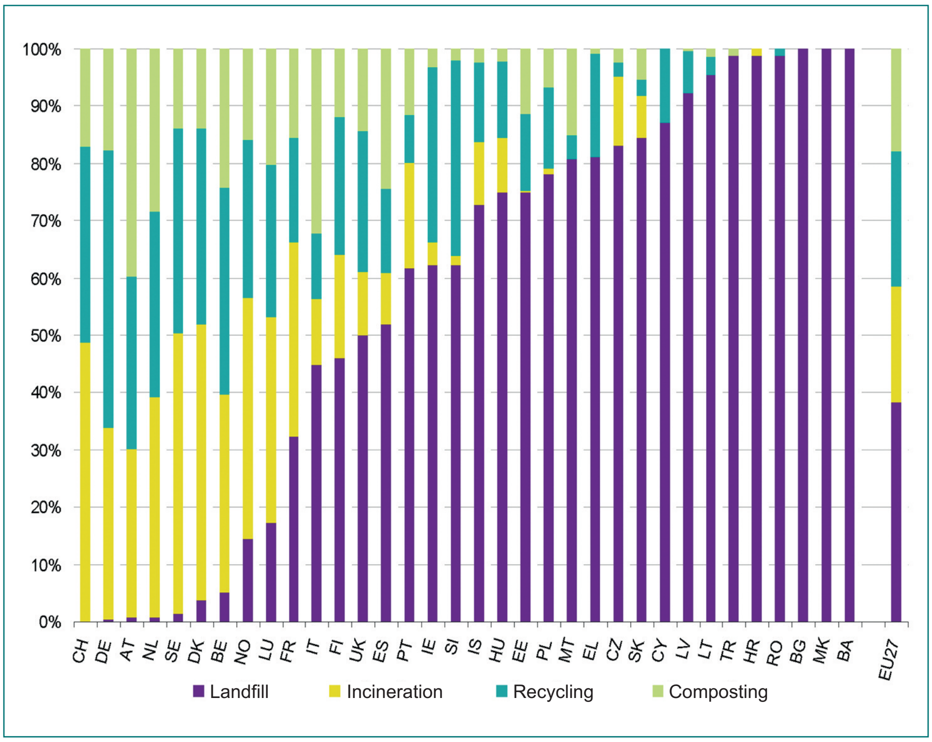


Figure 3: Municipal wastes according to treatment categories – inner-EU comparison[15]

Use of nanomaterials in products

Various nanomaterials are increasingly being employed in products for industry, trade, and consumers. The online database of the American Woodrow Wilson Center currently encompasses 1798 "nanoproducts" that are available on the international market.[17] A study on the Austrian market identified 450 "nanoproducts" between late 2007 and April 2009. The most entries are in the categories "cosmetics" and "textiles", which according to voluntary manufacturer information contain a number of nanomaterials (see[18]). The actually incorporated amounts of nanomaterials are unknown. Estimates of production volumes are available, but these often differ considerably from one another (Tab. 1). Accordingly, SiO_2 and TiO_2 are the nanomaterials with the highest production volumes worldwide and are probably the most common in products as well.

Several past NanoTrust Dossiers have dealt with the various applications of nanomaterials. The following therefore only briefly summarizes several product categories.

Textiles, for example for the outdoor sector, socks and underwear, can be impregnated with nanosilver to achieve an antimicrobial effect. Impregnation with nanoparticulate TiO_2 or ZnO acts as a UV filter, and SiO_2 has dirt- and water-repellent properties (see[20]). When these textiles are washed, nanomaterials can collect in sewage plants via wastewater. Studies on the behavior of nanomaterials during the washing process are available only for silver, whereby the released amounts vary considerably (see[21]). If textiles are chemically cleaned, then the produced wastes, including lint, can also contain nanomaterials. No studies have been conducted on nanoparticle releases during this process.[22] Although used clothing is collected separately in Austria, nanomaterial-containing textiles are also partially disposed of via the municipal solid waste stream in incineration plants.

Cosmetics can contain carbon black (black pigment), TiO_2, ZnO, SiO_2 in their nanoform, or in certain cases also fullerenes as radical scavengers. These nanomaterials can enter household waste in incompletely emptied canisters and then be combusted in waste incineration plants, or enter wastewater during washing or showering. In particular, the nanoparticulate UV filter TiO_2, which is a common component in sunscreen lotions (see[23]), can be released into the water when people bath or swim. No information is available on the exact amounts released, and only few studies have been conducted on potential negative ecological effects; these studies provide inconclusive evidence (see[24]).

In **paints and varnishes**, nanosilver, TiO_2, ZnO, SiO_2 or Al_2O_3 (aluminum oxide) are used as biocides, as UV protection or to improve scratch- and abrasion resistance (see[25]). Containers with remnant contents are discarded as household waste, as hazardous waste or as construction wastes. Moreover, nanomaterials can also leach out of facade paint and enter the soil and waterbodies via rainwater, or enter sewage treatment plants through the sewer system.[26]

Cement-bound **building materials** (e.g. concrete) can also contain nanomaterials, for example SiO_2 as aggregates to improve strength and stability, or TiO_2 based on its photocatalytic "self-cleaning effect" or its ability to remove air pollutants (see[27]). Special sun protection glazing for windows or electrochromic (automatically adjusting) window glass to darken room interiors with nanoscale coatings of silver or wolfram oxide are still niche products in the construction busi-

Table 1: Estimated global production volumes of different nanomaterials[19]

Nanomaterial	Production volumes (in tons p.a.)	Year
SiO_2	1,590,000	2009
TiO_2	700-61,000 50,000 44.000 (only USA) 1,450 (only Japan)	2007/2008 2010 2008 2019
ZnO	20-10.000 480 (only Japan)	2007/2008 2009
CeO_2	10,000	2010
Al oxides	100	2003
ZrO_2	2,500	2010
Metals	20	2007
Silver	4-560	2005/2008
Quantum dots	< 100 kg	2001

ness, but could find wider use in the future. Nanoparticles could be released with the dust produced when demolishing buildings. Such materials could also be released into the air during temporary storage, during the treatment process or when disposed in landfills. They could also enter the groundwater through wastewater or by leaching.[28] No information is available on these processes.

Nanomaterials composed of carbon, such as CNTs, fullerenes or graphene, are – according to manufacturer specifications – incorporated into the synthetics used in **sports equipment**. In tennis rackets, for example, they can help increase tensile strength (see[29]). When disposed of in household waste, the majority of such products is incinerated in Austria. CNTs most likely burn completely in such facilities, but it cannot be excluded that small fractions enter the environment through flume gases or solid residues (see[30]). In Austria, household wastes must be pre-treated, but in other countries they are directly disposed in landfills (compare Fig. 3). A study in the USA shows that CNTs – when these come into contact with other wastes in landfills – are partially bound or retain their stability.[31] Leaching of CNTs and other “nanowastes” depends strongly on the respective landfill conditions. No information is available on the behavior of fullerenes or graphene.

Nanoparticulate crystals made of semi-conductor materials, so-called quantum dots, are increasingly being applied in the **electronics industry**. Examples include modern televisions with LED backlighting but also the production of lamps (LED) and in highly efficient thin-film solar cells. Based on their potential content of arsenic, cadmium, europium, gallium, indium, tellurium, etc., LEDs should be collected as “problematic waste” (hazardous waste) and not be discarded in household garbage. The semi-conductor gallium arsenide is particularly problematic due to the toxicity of arsenic. This is because, in the absence of atmospheric oxygen and water, a very thin oxide layer can form on the surface of the material; it is highly toxic and could damage the environment. Quantum dots can contain numerous rare-earth metals, and resource policy considerations dictate that these should be recycled. The recycling processes, for example for LEDs, are currently still under development and very expensive.[32] As provided for by the EU guidelines on waste electrical and electronic appliances, LEDs must be taken back by the traders or manufacturers and properly disposed of.

Behavior of nanomaterials in waste incineration plants

Little information is currently available about how nanomaterials behave in waste incineration plants or in landfills. Studies have been conducted on only a few materials, for example on ceroxide nanoparticles that were experimentally introduced into an incineration plant. The results show that these were neither chemically nor physically altered by the incineration process, but that they were effectively retained in the facility’s filters. Nanoparticles that bond with the solids in the facility, however, ultimately end up with the combustion residues in landfills. Thus, the disposal problem in the case of stable ENMs is merely shifted to the subsequent steps in the waste treatment process.[33]

Studies in Switzerland show that only a tiny fraction (on average ca. 0.00079 percent by weight) of the filter dust of incineration plants is present in the form of nanoparticles and that these make up less than 10% of the total particle counts. Model calculations revealed that most of the nanoparticles (nanosilver, TiO_2, ZnO) in the wastes (residual wastes, wood, sludge) are present in form of bottom ash[34] and end up in landfills. In contrast, CNTs are almost completely combusted (94%)[35].

The behavior of nanomaterials in waste incineration plants can currently be summarized as follows:[36, 37]

- When incinerated, nanomaterials can either be destroyed, converted into other nanomaterials (e.g. oxides, chlorides) or be released unchanged.
- Nanomaterials in the size class 100 nm and larger are most efficiently removed in the filters of waste gas purification systems.
- Nanomaterials smaller than 100 nm are only partially retained by filters. An estimated up to 20% can be released.
- Incinerating nanomaterials can accelerate the formation or destruction of undesired by-products (e.g. polycyclic aromatic hydrocarbons).
- Nanomaterials can be retained in the solid wastes (ash, slag, filter residues) produced by waste incineration plants. A leaching of nanomaterials from such wastes, for example when subsequently dumped in a landfill, should be avoided (landfill base sealing, leachate treatment, surface sealing etc.).

Conclusions

Various nanomaterials are currently being incorporated in a wide range of products. It remains largely unknown whether these can pose an environmental or health risk when they end up in waste treatment plants or in landfills via various waste streams at the end of their life cycle. In a precautionary approach, several experts and organizations have therefore formulated first recommendations designed to minimize nanomaterials in wastes. Future research efforts should increasingly focus on the disposal phase of „nanoproducts“ in order to better estimate potential risks.

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MASTHEAD:

Owner: Austrian Academy of Sciences; legal person under public law (BGBl 569/1921; BGBl I 130/2003); Dr. Ignaz Seipel-Platz 2, A-1010 Vienna

Editor: Institute of Technology Assessment (ITA); Strohgasse 45/5, A-1030 Vienna; www.oeaw.ac.at/ita

Mode of publication: The NanoTrust Dossiers are published irregularly and contain the research results of the Institute of Technology Assessment in the framework of its research project NanoTrust. The Dossiers are made available to the public exclusively via the Internet portal "epub.oeaw" : epub.oeaw.ac.at/ita/nanotrust-dossiers

NanoTrust-Dossier No. 040en, August 2014: epub.oeaw.ac.at/ita/nanotrust-dossiers/dossier040en.pdf

ISSN: 1998-7293