NanoDialogue
Of the German Government

Nanomaterials and Nanotechnologies in the aquatic environment

BMUB report including the
discussion results of the expert dialogue
“Nanotechnologies and the aquatic environment“

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1 Introduction

Water is an essential precondition to all life on earth. Therefore, its availability in sufficient amounts and quality is of crucial importance. Several measures have been implemented to protect the aquatic environment in this regard, such as different legislation setting requirements on the emission of pollutants or the construction and improvement of municipal or industrial wastewater treatment plants.

Nanotechnologies are understood as the technical use of nanomaterials[1] and structures in nanometre size. As nanomaterials are new "types" of substances and they may be released into the environment one can question, as has been done for other substances in the past, if the aquatic environment is sufficiently protected from potential risks. The potential risks from nanomaterials should be viewed together with the potential opportunities to protect the resource water by using nanomaterials.

The objective of this report is to provide basic information on the topic to support interested readers in developing their opinions. The report is based on the contents and discussions of the expert dialogue "Nanotechnologies and the aquatic environment", which was held in the context of the nanodialogue of the German government in May 2014 in Berlin[2].

1.1 What are nanotechnologies?

Nanotechnologies are generally understood as the use of technological processes in the size range of 1-100 nanometres[3] (nm). They can be differentiated into the use of:

- nanomaterials; according to a EU Commission recommendation[4] these are materials containing particles of which at a minimum of 50% should have at least one dimension in the nanometre range. It is not relevant if and how these particles are chemically or physically bound.[5]. Due to their size, nanomaterials

[1] Nanomaterials are chemical substances, which as primary particles have nanosize in one, two or three dimensions. This if further explained in Chapter 2.1.

[2] The presentations and documents of the expert dialogue are available at http://www.oekopol.de/de/themen/chemikalienpolitik/nanodialog/nanofachdialoge-2013-2015/fachdialog-aquatische-umwelt/

[3] A nanometre is one millionth of a meter (10^{-9}). Chemical molecules are a few nanometres big and the size of bacteria is in the micrometre range. There is no common definition of nanomaterials. In the EU and in the context of the OECD a size range of 1 to 100 nm is normally used.

[4] COMMISSION RECOMMENDATION of 18 October 2011on the definition of nanomaterial; http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2011:275:0038:0040:EN:PDF

[5] The exact wording of the definition is: '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. In specific cases and where warranted by

may have particular properties; for example they may have a higher reactivity than the materials they originate from.

- Nanostructured materials: these are materials, which have an inner structure in nanosize, for example foams or nanoporous filters.

Discussions on the risks of nanotechnologies usually relate to the use of nanomaterials because they may be hazardous to humans and the environment and may be released from products and industrial processes. Nanostructured materials usually do not have hazardous properties.

1.2 Hazardousness of nanomaterials

Some nanomaterials may cause harm[6] to humans and the environment, such as inflammations of the respiratory system, cancer or reduced motilities of aquatic organisms.

Whether or not a nanomaterial is hazardous to health and/or the environment, among others, depends on its chemical composition. Many nanomaterials have the same hazardous properties as the substances in their "normal" form. One example for this is some metals[7]. However, the larger specific surface area may cause a higher reactivity of the nanomaterials as compared to the "normal" form.

Further aspects which may be relevant regarding the hazardousness of nanomaterials for humans and the environment are among others:

- Coating: viele Nanomaterialien haben eine Beschichtung, die ihnen bestimmte Eigenschaften verleiht, zum Beispiel eine hohe Stabilität. Das sogenannte Coating kann die Gefährlichkeit eines Nanomaterials erhöhen oder verringern und es kann sich im Laufe des Lebenszyklus verändern oder ablösen.
- Form: nanomaterials exist in different number size distributions[8] and forms (for examples spheres or rods); also the form of nanomaterials can influence their harmfulness to man and/or the environment.
- Interactions: nanomaterials can be converted due to interactions with the environment, with organisms or reactions among them (aggregation and agglomeration) or with other molecules (heteroagglomeration). They can react

concerns for the environment, health, safety or competitiveness the number size distribution threshold of 50 % may be replaced by a threshold between 1 and 50 %.

[6] Harmful effects of substances (including nanomaterials) are called „hazardousness" in expert terms. The properties of material which cause the hazardousness are called hazardous properties. In this report the terms hazardousness and harmfulness are used as synonyms.

[7] One example is silver, which has an antibacterial effect in its „normal" form and as nanomaterials (the effect mechanism is based on silver ions which are released independent of the sizes of the original substances).

[8] The production of nanomaterials normally yields particles of various sizes within one production batch.

with other molecules which may cause the loss of the nanoscale or the particle form. Depending on the type of interaction a particle's hazardousness to humans and the environment may change.

A nanomaterial's hazardous properties are normally determined in acute tests in the laboratory. Laboratory tests showed that for some nanomaterials they do not cause harm but for others possible hazardous effects were detected. Information on their harmful effects is not available for all nanomaterials on the market.

Relevant information gaps on the hazardous properties of nanomaterials regard long-term effects. Data is missing on the effects from continuous exposures of humans and the environment. Furthermore, there is little information on how nanomaterials are changed in the environment and what consequences these changes have on their harmfulness.

The hazardousness of nanomaterials not only depends on the factors listed above but also on the media they are contained in. Therefore, a general evaluation of the hazardousness of nanomaterials is not possible and their properties need to be determined in relation to the respective conditions of exposure.

Due to the large amount of technically produced nanomaterials which are already on the market and the high diversity of their modifications, the efforts to identify their hazardousness - in particular regarding the environmental effects – would be enormous. Therefore, several approaches are being developed to group nanomaterials and to conclude on the properties of nanomaterials based on the testing results of representative materials in the group.

As a general evaluation of the nanomaterials' hazardous properties is not possible, it is also not possible to make a general statement on the risks potentially related to their use. Therefore, risks and opportunities of "the nanotechnologies" should not be discussed in a global manner but should be related to specific nanomaterials and specific uses.

2 Emissions of nanomaterials to the aquatic environment

2.1 The „aquatic environment"

The "aquatic environment" comprises surface waters, such as rivers, lakes and oceans as well as groundwater. The elements of the aquatic environment are connected via the global hydrological cycle. This report focuses on two areas where human activities intervene with the hydrological cycle: the discharge of (treated) wastewater into rivers and the use of groundwater and partly also surface water as drinking water.

2.2 Detection of nanomaterials in the environment

It is difficult to detect "the" nanomaterials in the environment with analytical measurements or determine their amounts or concentrations, respectively. This is, among others, due to the following:

- There are many different nanomaterials in several sizes and with different forms and surface modifications (c.f. Chapter 1.2).
- It is likely that nanomaterials occur only in very low concentrations in the environment.
- Measurement methods do not exist for certain materials, are not sensitive enough (c.f. bullet point above) or are very expensive.
- Nanomaterials may be converted in the environment and may partition to the different media (soil, water, air).

Therefore, the occurrence and/or the concentrations of nanomaterials in the aquatic environment are hardly ever measured. Instead, calculation models are applied to estimate the emission amounts and the resulting environmental concentrations. Estimations on production volumes and the amounts of nanomaterials used in products as well as their release rates from these products are used as input to these models. From the estimated release amount the environmental concentrations are estimated using information on the nanomaterials' properties relevant for their partitioning between water, soil and air.[9]

2.3 Release of nanomaterials from products and processes

In principle, nanomaterials can be released into the aquatic environment during their entire lifecycle, which means from their production, use in the manufacture of different products[10] as well as during the product use and disposal (see Figure 1).

Information on the contents of nanomaterials in products is currently scarce. On the one hand labelling requirements exist only for a few product types (cosmetics and biocide products and from autumn 2014 also food)[11]. There is also no industry

[9] Frequently the production volumes, the amounts in the different applications and the release rates from products and processes are provided as ranges (minimum and maximum) or as probabilities. Therefore minimum (best case) or maximum (worst case) concentrations or probabilistic distributions of the environmental concentrations are derived. The models cannot predict real concentrations but they can give orientation about potential concentrations and their trends in the environmental media.

[10] Due to different release rates of substances it is useful to differentiate between chemical products (mixtures) and articles (objects). Examples of chemical products are paints, cleaning agents or sun lotions.

[11] Even if a general labelling requirement existed, no information would be available on the amounts and types of nanomaterials used. However, the general information basis on the occurrence of nanomaterials in final products would be improved.

reporting requirement on the use of nanomaterials either as raw material intended to remain in a product or as a processing auxiliary.

The authorities are partially aware of the use of nanomaterials in industrial installations[12]. This information is however not publicly accessible. The existing databases on nanomaterial containing products are fairly incomplete because they were established on a voluntary basis or through market research of scientific institutes or non-governmental organisations[13].

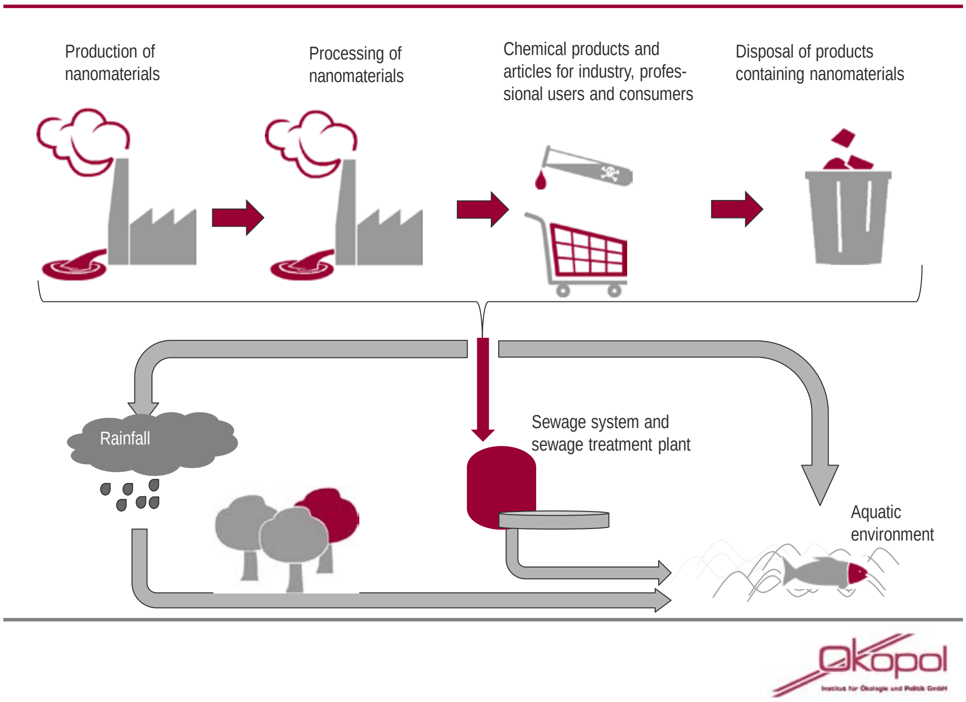

Figure 1: Lifecycle of nanomaterials and emission sources to the aquatic environment

[12] The installations producing nanomaterials are usually known. In addition there is a requirement to provide an inventory of raw materials to obtain an installation permit. The inventory is to include hazardous substances and mixtures. As the nanoscale of raw materials is no distinct characteristic it is not recorded.

[13] There are nano databases run by environmental NGOs and scientific institutes. They are based on market information and the product information of the manufacturers. These databases are voluntary and therefore incomplete.
France and Denmark established national reporting obligations for nanomaterials in products. Belgium plans a similar requirement for 2016. Further Member States are discussing the introduction of a reporting requirement. The topic of nano databases was subject of an expert dialogue of which the background information is accessible at: http://www.bmub.bund.de/themen/gesundheit-chemikalien/nanotechnologie/details-nanotechnologie/artikel/tagungsdokumente-des-2-fachdialogs-nanotechnologien/?tx_ttnews[backPid]=569.

Nanomaterials contained in chemical products[14] are usually released on purpose and completely in order to fulfil the function in the product. Nanomaterials in articles[15] normally should remain in the product to fulfil their function, e.g. at the article surface. Therefore they are released only to a minor extent and unintentionally during the products‘ use. If and how nanomaterials reach the environment after the end of the products' service-life depends on the disposal technology. Products containing nanostructures, e.g. filters for waste water treatment normally do not release nanomaterials.

Nanomaterials are released into the aquatic environment either indirectly via a discharge to the sewer and a municipal waste water treatment plant or directly into the soil, air and surface waters.

2.3.1 Environmental emissions via the wastewater treatment plant

Nanomaterials in chemical consumer products as well as articles which come into contact with e.g. cleaning water (floor coverings, furniture et cetera) or through washings (textiles) reach the sewer system via the wastewater.

There are only a few studies examining the behaviour of nanomaterials in the sewage system. Studies from Switzerland[16] indicate that nanosilver is converted in the sewage system and is adsorbed to other substances in the wastewater. This reduces their hazardousness[17]. Many experts believe that this or a similar behaviour is also likely for other nanomaterials. However, there is no certainty if "all" nanomaterials behave this way.

Wastewater is cleaned in wastewater treatment plants by mechanical, physical and biological processes. The biological step includes the conversion and degradation of organic substances, which are collected as sludge at the bottom of the treatment basins. Several experts assume, based on studies related to several nanomaterials[18]

[14] These are products which are defined mainly by their chemical composition rather than their physical form. Examples are cleaning agents, lacquer sprays or lubricants.

[15] These are products the function of which is defined by their physical form rather than their chemical composition. Examples are tables, cars or pullovers.

[16] Kägi Ralf, Voegelin Andreas, Ort Christoph, Sinnet Brian, Thalmann Basilius, Krismer Jasmin, Hagendorfer Harald, Elumelu Maline and Mueller Elisabeth. Fate and transformation of silver nanoparticles in urban wastewater systems (2013). Water Research: doi 10.1016/j.watres.2012.11.060

[17] This is of lesser importance for humans and the environment but quite important for the sewage treatment plant. If higher concentrations of pollutants are discharged to the biological treatment step (active sludge basin) the microorganisms which biodegrade the substances can be harmed and lose the ability to carry out the degradation processes.

[18] For example the project UMSICHT: Abschätzung der UMweltgefährdung durch SIlber-Nanomaterialien: vom CHemischen Partikel bis zum Technischen Produkt der Universität Bremen; http://www.umsicht.uni-bremen.de/ (Estimation of the environmental risks from silver nanomaterial: from the chemical particle to the technical product of the University of Bremen)

that these adsorb to a large extent to the sewage sludge in the biological treatment step and are then removed from the wastewater with the sludge.

The sewage sludge is frequently treated in digestion towers; this leads to a (further) conversion of organic substances which is correlated in most cases to a lower hazardousness to humans and the environment. The sewage sludge is then either dried and incinerated or used as fertiliser on agricultural soils. The incineration of sludge destroys most substances, including adsorbed nanomaterials, due to the high temperatures.[19]

The fate of nanomaterials distributed on agricultural lands with the sewage sludge is hardly known. A study on nanosilver[18] showed that it remains adsorbed to the sludge also over a longer time period[20]. However, it was not examined what happens to the nanosilver after the organic components of the sewage sludge to which it is adsorbed are degraded.

Nanomaterials which are neither degraded in the treatment plant nor removed with the sewage sludge are discharged into the rivers with the wastewater of the treatment plant. It was shown for nanosilver that approximately 5 – 10% of the nanomaterials entering a sewage treatment plant leave it via the wastewater. Also, in this case experts assume that these study results can be transferred to other nanomaterials. If the nanomaterials finally emitted from the sewage treatment plant are converted and therefore also have a different hazardousness than the original nanomaterials is currently not known. In a further study a higher toxicity of nanosilver was identified[21] after it had passed the sewage treatment plant. The reason for this changed toxicity could not yet be identified.

It was concluded at the expert dialogue "Nanotechnologies and the aquatic environment" that there are some indications that only a small share of all nanomaterials that are discharged into the sewer system and the sewage treatment plant reaches the aquatic environment. There are however no unambiguous findings on whether or not this is true for all types of nanomaterials and how particularly the long-term risks of released nanomaterials can be evaluated.

[19] This is not applicable to metals and minerals; this are either retained from the waste gas of incineration plants by filters or remain in the slags / ashes and are disposed in landfills.

[20] The studies were conducted with activated sludge; which means sludge which was not treated anaerobically. Normally sludge used in agriculture is only used after an anaerobic digestion. Therefore, the results are not representative for all cases where sludge is used in agriculture.

[21] For example conducted at the Fraunhofer Institute; http://www.ime.fraunhofer.de/de/geschaeftsfelderAE/Chemikaliensicherheit/Nanomaterialien.html

2.3.2 Direct emissions to the environment

Nanomaterials can also be directly released into the environment, namely from products which are used outdoors, such as plant protection products, car care products, façade paints or lacquers for garden furniture. Here, nanomaterials can be emitted during the product use (application of chemical products) or leach from articles over time. Another, totally different emission source are nanomaterial based veterinary products[22], because they may be excreted by the animals.

Nanomaterials may also be used intentionally in the open environment to clean ground water or soils from polluting substances. The developers of such nanomaterial based processes hope for a more efficient and improved remediation of soils and groundwater compared to the conventional technologies. In most cases it is foreseen that the remediation method allows recollection of the nanomaterials from the environment or that mechanisms are in place that prevent a wide distribution.

3 Regulatory requirements on nanomaterial emissions

It is desirable to keep the emissions of nanomaterials as low as possible, as long as it is not clarified if nanomaterials cause risks to the environment (precautionary principle).

Currently, there is no legislation that limits the content of nanomaterials in chemical products. However, if nanomaterials are used in cosmetics a safety assessment must be conducted before marketing the cosmetic product. In addition, the content of nanomaterials in cosmetics, food and biocidal products must be indicated on the product labels. The use of nanomaterials in any type of articles is not restricted.

There are restrictions on the content of substances in chemical products, which have specific hazardous properties, such as carcinogens or mutagens. If nanomaterials have these properties, they are also covered by these provisions.

Large industrial installations normally need to have a permit of operation and the operators have to ensure that emission limit values for defined substances are met in the waste air and wastewater. Such emission limit values apply to chemical substances or substance groups in general and there is no differentiation for nanomaterials and non-nanoscale substances. Due to the lack of practical methods to control emission limit values for nanomaterials in industrial emissions, an introduction of such values is not regarded as useful.

[22] Currently no veterinary products containing nanomaterials are authorised in Germany.

The use of substances and the emissions from smaller, professional companies is not regulated with regard to nanoscale substances.

The regulation on drinking water specifies that drinking water should:

- be “fit for consumption and clean“
- not contain chemical substances in concentrations which could harm human health and
- be treated so that the concentration of pollutants is kept as low as possible (minimisation imperative).

These requirements also apply to nanomaterials but specific limit values do not exist.

All in all, the general legislation on chemical substances also applies to nanomaterials regarding marketed products as well as (emissions from) industrial installations and the quality of drinking water.

4 Nanotechnologies’ contribution to the protection of the resource water

Nanotechnologies are already used in several applications for the cleaning of drinking water and decontamination of groundwater. The use of nanotechnologies may lead to higher efficiencies and lower costs compared to conventional processes. It is also possible that pollutants which are not accessible to the conventional procedures (for example persistent organic substances) can be removed from water. If nanotechnologies are applied to the cleaning of drinking water and/or wastewater, particularly the high volume-surface ratio, the reactivity and the possibility to design nanomaterials with specific functions, are taken advantage of.

In a report by the German Federal Environment Agency[23] the state of the art regarding the use of nanotechnologies in cleaning and disinfection of drinking water, wastewater and groundwater are presented. It describes that the following technologies are used:

- Filtration/Separation: In contrast to conventional techniques, nanoscale membranes can also retain dissolved organic and inorganic pollutants. Organic polymers and inorganic ceramics are used. Among others they can be optimized regarding the permeability and selectivity due to the high specific surface area, the high porosity of the materials and a narrow distribution of pore sizes.

[23] Umweltbundesamt: Untersuchung des Einsatzes von Nanomaterialien im Umweltschutz, Juni 2010 (German Federal Environment Agency: Use of nanomaterials in environmental protection; June 2010).

- Functionalization of surfaces: coated surfaces are among others used to remove pollutants from water (absorption, immobilisation) or to counteract fouling processes[24] or the sedimentation of inorganic materials on membranes.
- Sorption: nanomaterials and nanostructured surface areas can be used to separate pollutants from water. The high specific surfaces and the partially quite high sorption energies of nanomaterials and/or nanostructured materials enable an effective and specific binding of pollutants. Several technologies to adsorb heavy metals, endocrine disrupters or persistent substances are currently in the development phase.
- Nanocatalysts: a catalysis accelerates chemical processes such as oxidations, reductions or the degradation of substances. The catalyst is not changed in the reaction. Nanomaterials are good catalysts because on the one hand they (may) have a high reactivity and on the other hand their large surface area and/or potentially complex form and structure provide many starting points for chemical reactions. Nanocatalysts are already being used to remove heavy metals from groundwater and drinking water.
- Nanotechnologies are also used in analytics and measurement techniques. Some examples are the development of sensors for specific molecules, miniaturised test systems (“lab-on-a-chip) or continuous in-situ measurement techniques. Also, procedures for the detection of nanomaterials in the environment are being developed. The measurement techniques are relevant for the monitoring of water quality and nanotechnologies can contribute to the conduction of more and cheaper measurements, which may in turn lead to quicker reactions if contaminations are detected.

Nanotechnologies can also contribute to maintaining the resource water by substituting industrial processes that involve water pollution or processes which require the consumption of much water.

At present there are hardly any studies on the extent to which the use of nanotechnologies in the treatment of drinking water and wastewater as well as the clean-up of groundwater and soils causes less environmental burdens than conventional technologies. For example there are no lifecycle assessments or sustainability assessments available for the processes introduced at the expert dialogue “Nanotechnologies and the aquatic environment”. Economic evaluations exist for some processes which are already commercialized[25].

[24] Growth of algae and microorganisms on surfaces, which leads tot he formation of so called biofilms..

[25] The example of ceramic filters for the treatment of drinking water showed that the costs of nanotechnology based processes are significantly higher than for polymeric membranes. The costs could be reduced step-by-step and now almost reached the same level as conventional technologies, if the economic assessment is conducted for the long-term.

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5 Summary

The use of nanotechnologies to clean wastewater, drinking water and drinking water may enable the removal or immobilization of substances, which can either, not be removed with conventional technologies or only with a significantly higher technical and economic effort.

The benefits of nanotechnologies in the treatment of wastewater, drinking water and groundwater are counterbalanced by potential risks from the release of nanomaterials from products and processes. Here, the use of nanomaterials as such or in form of coatings is in the focus, because nanostructured materials normally do not have hazardous properties.

Studies on the behaviour of nanomaterials in wastewater treatment plants indicate that it is likely that a large share of the nanomaterials entering the treatment plant may be removed from the water and that only a small share reaches the aquatic environment via the plant wastewater. However, how the sludge, which normally contains the nanomaterials is treated is important for the assessment of the total risk as well as which toxicity remains with the nanomaterials in the discharged wastewater.

All in all the benefits of nanotechnologies used in the area of environmental technologies (for the treatment of water) appear to outweigh the risks. Nevertheless, this must be assessed case-by-case and depending on the material used and the application area.