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Nano and Environment – Part II: Hazard potentials and risks

Summary

There is currently no clear evidence that engineered nanoparticles (ENPs) pose a significant threat to the environment. Nonetheless, major gaps in our knowledge exist:

Environmental analytics: Suitable methods to determine nanoparticle concentrations and properties in complex environmental media such as water, soil, sediment or sewage sludge, as well as in organisms, remain to be developed.

Fate and behavior in natural environmental compartments: The special properties of artificial nanomaterials complicate predictions. The current dearth of data is a major stumbling block in comprehensively assessing the fate and behavior of nanomaterials in the environment.

Ecotoxicology: Research is concentrated primarily on controlled laboratory studies using cell cultures or model organisms. One of the major critiques here is the use of unrealistically high doses. No detailed ecotoxicological studies are available that can explain the mechanisms of uptake, distribution, metabolism and excretion of nanoparticles.

Environmental exposure: The most probable entry pathways of nanomaterials into the environment are via sewage water and wastes, but to date no quantitative exposure data are available for nanoparticles. The available studies are based exclusively on model calculations and estimates, which considerably hampers comprehensive risk assessment.

Overall, no definitive conclusions can be drawn on whether environmental damage can be expected or not.

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Introduction

Some products and applications involving nanomaterials promise advantages in the environmental and climate protection sectors – this topic is treated in [Dossier 026en](#). Nonetheless, determining the hazard potentials and possible risks posed by the special physical and chemical properties of engineered nanoparticles (ENPs) requires more detailed study. On one hand, there is currently no evidence that ENPs pose a significant threat to the environment; on the other hand, many gaps in our knowledge remain with regard to ENP ecotoxicity. The lack of evidence should by no means be interpreted to imply that environmental damage cannot occur.

At present, ecotoxicological research focuses primarily on controlled laboratory studies involving cell cultures or model organisms. One of the major critiques here is the use of unrealistically high dosages¹. Such “overdoses” are often necessary to trigger any kind of effect at all. In lab studies, however, they can lead to analytical artifacts. This is because some ENPs form large aggregates that can alter the bioavailability and thus the toxicity of a material. The concentrations used often lie far above realistic exposure scenarios. Risk assessments for nanosilver, for example, show that maximum concentrations in waters are currently probably about 0.1 µg/liter. Despite this, most ecotoxicological studies use nanosilver in concentrations in the mg/liter range¹.

Laboratory studies follow test protocols originally developed for conventional chemicals such as pesticides and do not consider the specific properties of nanomaterials. Moreover, natural ecosystems are considerably more complex than a petri dish, limiting the interpretability of lab results. Fortunately, no accidents involving major releases of ENPs into the environment have been documented to date; this also means that there have been no opportunities to directly study the impact of such an event under natural conditions¹.

The present dossier illustrates the problems in the field of *environmental analytics*, presents the current state of knowledge on the *fate and behavior of ENPs in various environmental compartments* and provides an overview of the preliminary results from *ecotoxicological research* and from model calculations of *exposure assessments*.

Environmental analytics

A number of methods are available to determine, measure or characterize nanoparticles in simple media. These include microscopy, chromatography, spectroscopy, centrifugation, filtration and related techniques². The choice of a particular approach depends on the type of sample and the nanomaterial, the desired information, the time constraints and the available funds. Some methods can only confirm the presence of nanoparticles, others provide information on the amounts, the size distribution or the surface area size³. A combination of several methods is often required to fully investigate a specific issue.

Suitable analytical methods remain to be developed to determine nanoparticle concentrations and properties in complex environmental media such as water, soil, sediment or sewage sludge, as well as in organisms. The difficulties facing environmental analyses are manifold and start with the sampling procedure and treatment, which can produce artifacts. Distinguishing between natural and artificial nanoparticles is also difficult. Finally, sample preservation and storage can create problems because chemical changes can occur⁴.

To date, no scientific publications are available on methods to quantify carbon nanotubes (CNTs) in the environment⁵. Unpublished results from a study at Duke University (USA) show that the presence of “Sin-

gle-Walled Carbon Nanotubes" (SWCNTs) can be demonstrated using special spectroscopic methods, although the isolation of the nanomaterial from the sample matrix is problematic⁶. Moreover, no publications exist on quantitative or qualitative measurements of synthetic nanomaterials in the air, with the exception of measurements at workplaces⁷. Only few studies have been able to demonstrate the presence of ENPs that have entered the environment through a specific application: one study, for example, showed that 20-300-nm-sized TiO₂ particles were washed out from facade paints by rain and entered natural waters⁸. Another study reported small amounts of 4-30-nm-sized TiO₂ nanoparticles that had been released into the environment from the run-off of wastewater treatment facilities⁹.

Fate and behavior of nanomaterials in the environment

Ecological research on the behavior of ENPs can rely on numerous studies from the geosciences that have examined the behavior of naturally occurring nanoparticles in the environment. Nonetheless, ENPs differ in certain respects from those occurring naturally. While natural nanoparticles are randomly structured and diffusely distributed in the environment, industrially produced suspensions or powders contain pure nanomaterials of very uniform size, shape and structure. Such nanomaterials have unique properties such as the high tensile strength of CNTs or the photocatalytic activity of nano-TiO₂, which make them interesting for novel products and applications. Precisely these special features make it so difficult to predict the fate and behavior of ENPs in the environment¹.

In the environment, nanomaterials can undergo a range of chemical processes (see info box) that depend on many factors (e.g. pH value, salinity, concentration differences, the presence of organic or inorganic material). The characteristics and properties of a nanomaterial also play a major role. Bio-availability is decisive in determining potential toxicity. This depends strongly on whether nanoparticles remain stable in an environmental medium or are removed from the respective medium through agglomeration and deposition, or are transformed into a form that organisms cannot take up.

Potential environmental processes that can influence the behavior and the properties of nanomaterials (after⁷):

Dissolution: A solid nanomaterial dissolves in a solvent, yielding a chemical solution.

Precipitation/Sedimentation: Nanomaterials are separated from a suspension or solution.

Speciation: Formation of chemical variants (species) of a nanomaterial that are in a reaction equilibrium with one another.

Binding to biotic or abiotic particles: Nanomaterials interact with other living or non-living materials in the environment, for example in the form of adhesion or sorption.

Transformation: A nanomaterial undergoes a biological or chemical transformation.

Agglomeration/Disagglomeration: Nanomaterials combine into larger units or are separated again.

Mineralization: Transformation of a carbon-containing nanomaterial into an inorganic state through biotic and abiotic decomposition.

Diffusion: Transport of a nanomaterial from a zone of high concentration into one with a lower concentration through random (Brownian) molecular movement.

Deposition: Deposition of a nanomaterial, for example from the air into the water.

Resuspension: Renewed distribution of an insoluble nanomaterial in a liquid or a gas (for example from a surface into gas or from sediment into water) after it was previously separated through precipitation.

The current lack of data prevents a comprehensive picture of the fate and behavior of nanomaterials in the environment. Moreover, the available studies are poorly comparable because different nanomaterials with different properties (for example surface functionalization – see below) are used, and because both the methodology and the duration of the studies also often differ considerably. The research results on the potential impacts of ENPs on the environment and human health were recently compiled in the framework of an EU project⁷. The following account briefly summarizes our current state of knowledge on the fate and behavior of ENPs in the environmental compartments air, water, soil and sediment based on that report.

Air

When nanoparticles enter the atmosphere, they move from zones of higher concentration to zones of lower concentration (diffusion). Air currents distribute the particles rapidly; these can migrate great distances from their original source. Nonetheless, nanoparticles tend to aggregate into larger structures (agglomeration). Detecting nanoparticles in the air is very difficult because simple measurements of size distributions can hardly distinguish such agglomerates from natural particulates. The speed with which particles in the air are deposited on the ground, in the water or onto plants (deposition) depends on particle diameter. Nanoparticles from the air are deposited much slower than larger particles due to their smaller diameters.

Water

The general rule is that nanoparticles distributed in the water behave much like colloids, which are well described in the chemical literature. Colloids are droplets or particles that are finely distributed in a medium; they are relatively unstable because they rapidly adhere to one another due to electrostatic attractive forces and then sink as a result of gravity. Natural water bodies typically contain dissolved or distributed materials, including natural nanomaterials. As expected, synthetic nanomaterials that enter a natural water body bind themselves to such natural materials. The fate and behavior of nanomaterials in the water, however, are also influenced by factors such as pH, salinity (ionic strength) and the presence of organic material. Naturally present organic material (NOM) can lead to the decomposition of C60 fullerenes or of their aggregates and thus alter particle size and shape. A NOM such as humic acid can stabilize certain carbon nanotubes (MWCNT) in the water and thus prevent their settlement. Some CNTs are also deliberately produced through special surface changes so that they do not aggregate. The type of such functionalization helps determine whether CNTs can be removed from a natural water body through sedimentation. As CNTs are very polymorphic, it is usually impossible to provide generally valid statements about their fate and behavior in the environment. A strong influence of the surrounding environment on behavior, in particular the presence of NOM, has also been determined for other nanomaterials such as metals or metal oxides¹⁰.

Soil and sediment

Unfortunately, the data for this environmental compartment are insufficient to draw general conclusions. Considerably fewer studies are available for this sector than for water or air. There is, however, comprehensive literature on the mobility of natural colloids in the soil and groundwater, which helps draw conclusions about nanomaterial behavior. Accordingly, nanomaterials in the soil and in sediments are assumed to bind themselves to solids. The generally very low concentrations of particles in the groundwater support this notion. The bioavailability – and therefore the potential toxicity – of a nanomaterial for soil organisms apparently depend strongly on whether it binds to NOM. The bioavailability of nanosilver in complex media such as soil is considerably lower than in water because the reactive silver ions can bind to components in the soil (e.g. NOM)¹¹. The co-transport of pollutants in the soil with ENPs has only been poorly studied, but is probably not relevant for most pollutants and ENPs due to the extremely low ENP concentrations in soils¹².

Environmental toxicity

Nanoparticles have been naturally present in the environment since the origin of earth, for example as the result of combustion processes (forest fires), in volcanic ash, in most natural waters, or as dust in the air due to weathering and erosion. Organisms produce various substances in nanoform (for example proteins, DNA) in their cells or are themselves only several nanometers large, such as viruses. During their evolution, all living organisms have adapted to an environment that contains nanoparticles, some of which can also be toxic (e.g. volcanic ash). This adaptation is a function of exposure, dose and the speed with which habitats change¹³. These natural nanoparticles in the environment are now accompanied by those that have been released unintentionally due to human activities such as household heating, industry, slash-and-burn clearance, transport and, most recently, through the industrial application of various, extremely polymorphic synthetic nanoparticles in unknown amounts. This additional burden on humans and the environment has taken place over a very short period (from an evolutionary standpoint). To what degree can organisms deal with such artificial nanoparticles without suffering damage?

Most data on acute toxicity as well as on sub-lethal effects are available for freshwater organisms (e.g. water fleas, fishes). More studies on marine and terrestrial invertebrates are also necessary to determine potential toxicities, as are further studies on amphibians, reptiles, birds or plants, bacteria and in particular microorganisms. To date, no ecotoxicological studies are available that could explain in detail the mechanisms of uptake, distribution, metabolization and excretion of nanoparticles¹³.

In an overview of the relevant scientific literature compiled in 2010, only 12 studies were identified that can actually be classified as ecological studies (i.e. that more or less consider the complexity of natural ecosystem). These few studies on the effects of ENPs on ecological communities failed to detect significant increases in mortality rates or changes in their compositions¹.

The following paragraphs briefly summarize the results of ecotoxicological studies on selected nanomaterials (for a comprehensive review see⁷).

Carbon nanotubes (CNTs)

The ecotoxicity of CNTs has been treated in only a few studies, and in some cases the results are highly contradictory. While some studies were unable to determine any negative effects on test organisms, others clearly did, for example in the case of fishes and amphibian larvae. The reason for this is the great variability of CNTs: they differ considerably in length, structure, surface charge, surface chemistry, agglomeration behavior and purity (see also^{14; 15}). Moreover, investigating the toxicity of CNTs for aquatic organisms is very difficult because CNTs are very poorly soluble in water, have different sizes and diameters, and form complex aggregates⁵. CNTs are often surface functionalized so that their fine distribution in water remains very stable and they do not sediment to the bottom. Such surface changes, however, promote the tendency of CNTs to accumulate heavy metals, which can influence their transport in water bodies or even in biological systems¹⁶.

Nano-TiO₂

Titanium dioxide nanoparticles are among the most frequently investigated nanomaterials. A range of standardized tests are already available for fishes, crustaceans and algae. Nano-TiO₂ has a photocatalytic effect, i.e. under UV radiation, reactive oxygen species (ROS) develop that can damage

the cell membrane of microorganisms. Studies have been conducted to simulate the conditions in natural running waters at the laboratory scale (so-called aquatic microcosms). They show that TiO₂ nanoparticles and low concentrations of larger, naturally developed agglomerates can both significantly damage the cell membranes of microorganisms. Microorganisms are very sensitive to nano-TiO₂ – the precise effect on ecosystem function, however, remains unknown¹⁷. Preliminary results show that aquatic organisms such as small crustaceans (which play an important role as zooplankton in aquatic food chains) are not damaged by the photocatalytic effect of nano-TiO₂. Nonetheless, the nanoparticles can attach themselves to the chitinous exoskeleton of the animals and hinder molting, which is necessary for growth in juveniles. This can kill such animals. This effect was determined at concentrations of 0.24 mg/liter of water; nano-TiO₂ proved to be twice as toxic as the larger form¹⁸.

Nanosilver

Silver ions from silver compounds or those that develop from nanosilver particles through contact with water are highly toxic to microorganisms such as bacteria, fungi and algae (see also¹⁹). Soil microorganisms can be affected when, for example, sewage sludge contaminated with nanosilver is spread on fields. Nanosilver particles show negative effects on fishes and crustaceans already at low concentrations; in mammals, this material is toxic only at very high concentrations. Few studies on plants are available, but a more recent paper shows an impact of nanosilver particles on the growth of grass seedlings due to cell damage²⁰. A plausible primary entry pathway of nanosilver is via water because nanosilver can be washed out of special textiles (see also²¹) or is an ingredient in cosmetics and cleaning agents. Nanosilver in waste water has therefore been identified by an international group of researchers from different scientific disciplines as one of 15 areas of concern that can threaten biological diversity²².

Exposure

Whether ENPs pose a risk to the environment depends not only on the toxicity of the respective material but also on exposure, i.e. on the amount released into the environment. Unfortunately, no quantitative data are

available for even a single nanomaterial. This is because there is no obligatory registration of nanomaterials, and companies are very reticent about divulging production volumes²³. Only very few studies have dealt with the environmental exposure to nanomaterials. These are based on rough estimates of production volumes and releases as well as on model calculations, which do not allow comprehensive risk assessments.

Thus, a recently published study²³ estimates the annual production volume of nano-TiO₂ in the USA at 7800 to 38,000 t, followed by CNTs at 55 to 1101 t and nano-cerioxide at 35 to 700 t. The production volume of nano-silver is estimated to be 2.8 to 20 t per year. Knowledge about production volumes alone is insufficient to estimate potential environmental risk: the actually released amounts must be known.

To date, the assumption has been that nanomaterials that are tightly embedded in a matrix pose no or only minimal environmental risk. This holds true for example for CNTs that are incorporated into plastics or for nano-TiO₂ in permanent photocatalytic coatings. Nonetheless, only very few studies have examined the release of ENPs from consumer products. Nanosilver, both in the form of particles as well as ions, can be released when such treated textiles are washed; the release rate depends strongly on the type of production process²⁴. TiO₂-particles can also be washed out of facade paints and enter the environment⁸.

For Europe, the USA and Switzerland, the concentrations of five nanomaterials expected in the environment ("Predicted Environmental Concentrations", PEC) were estimated based on model calculations. The highest concentration in all environmental compartments was found for nano-TiO₂, followed by nano-zinc oxide. These values were compared with concentrations of the studied nanomaterials for which no negative environmental effects are expected ("Predicted No-Effects-Concentration", PNEC). The results revealed a potential risk for aquatic organisms through nano-TiO₂, nanosilver and nano-zinc oxide in wastewater of sewage treatment plants. The PEC of CNTs and fullerenes was classified as so low that no environmental risk is currently to be expected²⁵.

The most likely entry pathways of nanomaterials into the environment are sewage water and wastes. Wastes that contain nanomaterials can arise either during the production of the raw materials, the manufacture of products with nanomaterials, as well as at the end of the products' lifecycles. The cur-

Conclusions

Little is known about the fate and behavior of synthetic nanomaterials in the environment, and suitable methods to detect them in complex environmental media are only in the development stage. Model calculations on exposure alone are insufficient for comprehensive risk assessments. This calls for developing methods to monitor nanomaterials in the environment. Ecotoxicological investigations show a certain hazard potential of some nanomaterials. Even though scientific uncertainties still exist, the precautionary principle should be applied in the sense of preventive risk minimization. Environmental inputs should be avoided to the extent possible. Ecotoxicological research should increasingly focus on the environmental relevance of the materials and consider the complexity of natural systems. Long-term studies would be necessary to determine delayed impacts of environmental exposure to ENPs and to help determine potential adaptive mechanisms. More studies on bioaccumulation in the food chain are also necessary, as are studies on the interaction of ENPs with other pollutants in the environment. Under certain conditions, ENPs might change the transport and effects of such pollutants.

rent legal framework contains no specific regulations for treating wastes containing nanomaterials²⁶. A release of ENPs into the environment from wastes is possible, although virtually no studies have been conducted on this aspect. The assumption is that ENPs are efficiently removed by filters during waste incineration²⁷.

LEDs contain nano-scale coatings of the semiconductor materials arsenic, gallium, phosphorus and their compounds. They therefore belong to the waste category requiring special treatment or monitoring. In particular the semiconductor material gallium arsenide is problematic because, in the absence of atmospheric oxygen and water, a very thin layer can develop on the surface of the material. This is highly toxic and could create environmental damage in a normal landfill²⁸.

Nanosilver can enter wastewater via various pathways, for example when washing special textiles, through cosmetics or cleaning agents. About 90 % of the nanosilver is apparently removed from waste water in sewage treatment plants and is then contained in the sewage sludge²⁹. If this is spread on fields as fertilizer, this nanomaterial enters the environment, whereby damage to soil microorganisms cannot be excluded (see also¹⁹).

An additional open question is the recyclability of products that contain nanomaterials. Plastic bottles made of polyethylene terephthalate (PET) can be recycled as long as they do not contain coloring agents or additives. Coatings of nanocomposite materials, which reduce gas permeability or provide light protection, create recycling problems³⁰.

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