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(Nano)-Titanium dioxide (Part III): Environmental effects

Summary

Nano-titanium dioxide (nano-TiO_2) is the nanomaterial produced in the greatest amounts and is already a component in many products, both in its regular and nano-scale size. This also makes it the best-investigated nanoparticle. Many in-vivo and in-vitro studies have been conducted to test for potential environmental risks. Nonetheless, the possible long-term effects remain unknown. Short-term exposures to high doses showed damage both in aquatic and in terrestrial ecosystems. No specific regulations for nano-TiO_2 are currently in place.

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Introduction

Titanium dioxide (TiO_2) has been industrially produced and used for over 100 years (see NanoTrust Dossier 033en); this makes nano-titanium dioxide (nano-TiO_2) the best investigated of all nanomaterials. Its abundance also raises the question of risks to the environment from TiO_2 both in its regular and nano-form. Numerous in-vivo and in-vitro studies have been conducted to determine the environment-related risks. This dossier provides a brief overview. Details, compilations of studies as well as in-depth risk assessments are available from a number of international bodies (EU, IARC, OECD, FDA, CDC).

Environmental effects of nano-TiO_2

As already reported in detail in the Dossier Environment[1], the impacts of nano-TiO_2 are the best investigated among nanomaterials. Many animals and plants as well as the media water and soil (aquatic, terrestrial) have been studied. One criticism is that the results of the studies are not comparable because the respective NPs (and therefore their properties) vary from manufacturer to manufacturer[2]. Moreover, the presence and distribution of synthetic nanoparticles in the environment are almost completely unknown[3], with the exception of a few modeling studies in which environmental concentrations were calculated[4; 5]. Nonetheless, experimental approaches provide evidence for harmful effects both in aquatic and terrestrial ecosystems, although such impacts were demonstrable only at very high doses. An industrial accident, however, could release such concentrations of nano-TiO_2 and pose a risk to algae, plankton and fishes[6]. The US Environmental Protection Agency EPA[7] has compiled an overview of research results on TiO_2-NPs on the aquatic environment[8; 9]:

- For **algae**, which serve as the basis of marine food chains, values exceeding 30 mg/l are harmful. 30 mg/l photocatalytic and 90 mg/l photostable nano-TiO_2 impede growth.
- For **water fleas** (*Daphnia magna*, Figure 1), which are accepted test organisms and indicators for environmental impacts, damage was caused by photocatalytic particles at concentrations from 5.5 to 10 mg/l (LC_{50} see also[10]). For coated nano-TiO_2, an LC_{50}-value of 100 mg/l was determined.
- For **fish** (rainbow trout, *Oncorhynchus mykiss* as an aquatic test organism) an LC_{50}-value of 100 mg/l photostable TiO_2-NPs was determined. In the case of chronic exposure to photocatalytic particles, a value of 0.1 mg/l already led to oxidative stress and altered organ structure. The accumulation in the organs, however, apparently does not impair their function (see also[11; 12]).

Figure 1:
The water flea (Daphnia magna)[17]

One study experimentally simulated a running water system and added photocatalytic nano-TiO_2 (5 mg/l water) in order to investigate the effects on the microbial communities under natural conditions[13]. Both TiO_2-NPs as well as larger natural agglomerates significantly damaged the microorganisms. The authors concluded that the microbial communities reacted very sensitively to NP concentrations that can be expected in the environment. The resulting impacts on the ecosystem itself remain unknown.

A further study reported on the effect of UV light on the toxicity of photoactive nano-TiO_2(1 mg/l)[14]. Laboratory measurements showed that even the very low UV intensities that occur near the ocean surface can trigger significant toxic damage to aquatic organisms (phytoplankton). The authors therefore identify the need to consider the photoactive (toxic) properties of nanomaterials.

It remains unknown how TiO_2-NPs behave along food chains. Does a transfer of the particles take place from animal to animal or from plant to animal through food uptake? A first study shows that this is experimentally possible. Daphnia fed with TiO_2-NPs were subsequently fed to zebra fishes *(Danio rerio)* and the particles were found in the fishes. The long-term effect of such particles on these fishes and on other food chains is not known.

Effects on sewage treatment plants

The issue of accumulation of TiO_2-NPs is relevant not only for the environment but also for sewage treatment plants, where an accumulation can actually take place. Two studies[4; 5] came to the conclusion that risks for aquatic organisms through nano-TiO_2 in waste streams in all regions considered (USA, Europe, Switzerland) could not be excluded. This pertained both to surface waters as well as to the wastewater in sewage treatment plants. The calculations are based on a scenario using current estimated values (no extrapolation into the future was undertaken because the uncertainty of such data was too high). The simulations involved both a realistic as well as a so-called „worst case scenario" based on generally accepted values (see Table 1). Since 2006 it is no longer permissible to spread sewage sludge on agricultural land. This has minimized soil contamination with nano-TiO_2. If this ban did not exist and sewage sludge was applied on 50 % of such land, this would yield the higher values (marked with KS)[4] in Table 1. The second study[5] simulated material flows for different regions (Europe, Switzerland and the US). The data for surface waters and for treated wastewater represent the actual values in 2008. In contrast, the data for soils consider the annual increase in the NP concentration and separately treat soils with (KS) and without (noKS) fertilization with sewage sludge. This makes the newer simulation more precise (Table 2). Interestingly, the concentrations of nano-TiO_2 in treated wastewater and in soils are lower than in the earlier study.

Another study investigated the purification effect of the sewage treatment facilities in greater detail. The results show that a good biological wastewater treatment retains more than 98 % of the TiO_2-NPs from the wastewater flows and that the use of microfiltration is more effective than the commonly used settling tanks[15]. The remaining concentration of Ti in the treated wastewater typically lies between 2 and 20 μg/l.

One study focused on the question of what effects TiO_2-NPs have on those bacterial colonies in sewage treatment plants that decompose nitrogen and phosphorus compounds. Over the short term (1 day), TiO_2 concentrations of 1 or 50 mg/l showed no effects. It required a long-term period (70 days) with a very high TiO_2 concentration (50 mg/l) to significantly reduce nitrogen decomposition from 80 % to 24 %. A more detailed DNA study of the bacterial strains showed that this was caused by a strongly reduced microbial diversity[16].

Effects on soils

Similar results were obtained in studies on soil samples from meadows (California, USA), where TiO_2-NPs were applied at different concentrations (0, 0.5, 1.0, and 2.0 mg/g soil) and times (15 days and 60 days) (see also[6]). The effects on the natural soil bacteria communities were investigated. The authors determined that both amount of microorganismic biomass and its diversity changed over time. The impacts were dose-dependent and already present at the lowest dose applied (0.5 mg/g soil). The authors point to model calculations[5] that predict the annual amount of TiO_2-NPs spread by sewage sludge to be 0.09 mg/kg soil, underlining the potential risks to the environment.

Table 1:
Different scenarios for
nano-TiO_2 concentrations in wastewater, sewage sludge and soil

Study	Concentration of nano-TiO_2		
	In treated wastewater (in μg/l)	In sewage sludge (in mg/kg)	In soil (in μg/kg)
MUELLER 2008[4]	0.7 $^{(rs)}$ to 16 $^{(ws)}$	no data	0.4 $^{(rs)}$ to 4.8 $^{(ws)}$, 120 $^{(KS)}$
GOTTSCHALK 2009[5]	3.5 (Europe)	136 (Europe)	Europe (annual input): 1.3 $^{(noKS)}$ to 89 $^{(KS)}$
	1.8 (USA)	137 (USA)	USA (annual input): 0.5 $^{(noKS)}$ to 42 $^{(KS)}$
	4.3 (Switzerland)	211 (Switzerland)	Switzerland (annual input): 0.3 $^{(noKS)}$

^{rs} *... realistic scenario*
^{ws} *... worst case scenario*
^{KS} *... with sewage sludge application*
^{noKS} *... without sewage sludge application*

Conclusions (Parts I to III)

TiO_2 is a widely distributed substance that is currently incorporated in many different products including sunscreens and foods. This explains why TiO_2 is so well studied, even if no long-term studies on nano-TiO_2 are available. In epidemiological studies, regular TiO_2 showed no TiO_2-specific effects related to cancer incidence. Nonetheless, based on animal experiments, international bodies have classified this material as “possibly carcinogenic in humans”. Although specific studies conducted by the FDA clearly point to an extremely low risk, the remaining uncertainties and discrepancies lead to the recommendation to use caution when applying nano-TiO_2-containing cosmetics to injured skin.

Many studies have been conducted to describe the potential environmental effects of nano-TiO_2. As most of these studies involved extremely high doses, any definitive statements on the environmentally relevant risks remain speculative. Nonetheless, the consensus is that small amounts represent a rather low risk to the environment, whereby the long-term effects with low doses of nano-TiO_2 remain unclear. There are currently no actually measured data on environmental exposure; another unclarified issue is how TiO_2-NPs behave in food chains. Whether a transfer of the particles takes place from animal to animal or from plant to animal through feeding also remains unclear. We have no information about the effects that the particles may exert over the long term on aquatic and terrestrial ecosystems. This calls for urgent and targeted research in this field.

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