

# Modeled Environmental Concentrations of Engineered Nanomaterials (TiO<sub>2</sub>, ZnO, Ag, CNT, Fullerenes) for Different Regions

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Engineered nanomaterials (ENM) are already used in many products and consequently released into environmental compartments. In this study, we calculated predicted environmental concentrations (PEC) based on a probabilistic material flow analysis from a life-cycle perspective of ENM-containing products. We modeled nano-TiO<sub>2</sub>, nano-ZnO, nano-Ag, carbon nanotubes (CNT), and fullerenes for the U.S., Europe and Switzerland. The environmental concentrations were calculated as probabilistic density functions and were compared to data from ecotoxicological studies. The simulated modes (most frequent values) range from 0.003 ng L<sup>-1</sup> (fullerenes) to 21 ng L<sup>-1</sup> (nano-TiO<sub>2</sub>) for surface waters and from 4 ng L<sup>-1</sup> (fullerenes) to 4 μg L<sup>-1</sup> (nano-TiO<sub>2</sub>) for sewage treatment effluents. For Europe and the U.S., the annual increase of ENMs on sludge-treated soil ranges from 1 ng kg<sup>-1</sup> for fullerenes to 89 μg kg<sup>-1</sup> for nano-TiO<sub>2</sub>. The results of this study indicate that risks to aquatic organisms may currently emanate from nano-Ag, nano-TiO<sub>2</sub>, and nano-ZnO in sewage treatment effluents for all considered regions and for nano-Ag in surface waters. For the other environmental compartments for which ecotoxicological data were available, no risks to organisms are presently expected.

## Introduction

Engineered nanomaterials (ENM) are applied in many commercially available consumer products such as in cosmetics, textiles, and paints. Due to the increasing production volumes, an environmental exposure to ENMs is likely (1). Whereas toxic effects of nanomaterials on different organisms have already been described (2, 3), measurements of environmental concentrations of ENMs are almost completely absent. The first study in this field reported the detection of nano-TiO<sub>2</sub> in water leaching from exterior facades (4). Despite the fact that the release of ENM from products is a very important entry pathway for ENMs into the

environment, studies examining this process are very rare (5). One recent study quantified the release of silver ENM from socks during washing (6).

Because of the nearly absent information about environmental concentrations of ENMs, modeling of predicted environmental concentrations (PEC) currently constitutes a necessary and valuable substitute for measurement studies. ENMs may reach the environment during production of the material, incorporation into products or during the use-phase of such nanotechnology based goods (5). Only a few studies (7–9) have predicted environmental ENM concentrations. For instance, Mueller and Nowack (7) found that nano-TiO<sub>2</sub> may currently pose a threat to organisms living in the aquatic environment, whereas the current concentrations of nano-Ag and CNT seem nonhazardous. But a major drawback for assessing the risk of ENM is not only the lack of information about fate and behavior but also the inconsistency of the available data (1). Mueller and Nowack (7) have modeled two scenarios to address this lack of available data. Still, some important environmental compartments such as sediments were not included in their study, and consideration of the three nanomaterials (TiO<sub>2</sub>, CNT, Ag) analyzed was limited to the geographical boundaries of Switzerland.

Probabilistic methods of environmental exposure analysis (10–13) allow one to account for the inconsistency and variability of model input parameters by using probability (or density) distributions. Those input distributions may be constructed based on empirical data, on expert judgment or on a combination of these sources. Compared to a scenario analysis, this probabilistic/stochastic approach is not restricted to the use of single input values, but aims at considering all possible model inputs covering also extreme events. It provides in contrast to scenario estimations also an insight into the frequency probability of each simulated outcome. Such a probabilistic modeling approach (14) has been used to describe nano-TiO<sub>2</sub>, CNT, and nano-Ag flows in Switzerland (15).

The aim of this paper was to use the probabilistic material flow analysis proposed by Gottschalk et al. (14) to model the environmental concentrations of nano-TiO<sub>2</sub>, nano-ZnO, nano-Ag, CNT, and fullerenes for the U.S., Europe, and Switzerland, considering all environmental compartments including sediments. To assess the risks posed by the ENMs, the simulated PEC was compared to the predicted no effect concentration (PNEC) based on toxicity data for the corresponding environmental compartment.

## Materials and Methods

**Model Information.** The modeling was performed based on a probabilistic material flow analysis approach developed by Gottschalk et al. (14). This mass balance and multicompartment model allows one to treat all parameters throughout the modeling as probability distributions. Thus, the model outcome represents an ENM flow system, depicted by probability (or density) distributions. Model input and output distributions were derived from Monte Carlo (MC) and/or Markov Chain Monte Carlo (MCMC) simulations programmed and executed in R (16), an open source and open development software for statistical computing. For each region, the corresponding geographic boundaries were used as the spatial system boundary. The system was described by 11 boxes which represented environmental compartments (water, air, soil, sediment, and groundwater) and technical compartments (production, manufacturing, and consumption (PMC), sewage treatment plant (STP), waste incineration plant (WIP), landfill, and recycling processes). The environ-

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mental compartments were considered homogeneous and well mixed as suggested for modeling the regional PEC (17). Deposition and elimination/degradation of ENM within the compartments were modeled as constant annual flows into a subcompartment of each box considered. The derivation of the sizes of the air, water, soil, and sediment compartments is given in the Supporting Information (SI) (section A). These volumes were used to calculate the respective concentrations of the ENMs in these compartments.

The worldwide annual production amounts of the studied ENMs were scaled to regional production volumes in proportion of the population of the high income countries to the total population of a particular region (18). Then, log-normal distributions were modeled based on logarithmic means and standard deviations derived from these data. For allocating ENM production volumes to the different products, the same method as described in Gottschalk et al. (15) was used. The details are given in the SI (section B). ENM containing products were grouped into different categories according to similarities in life-cycle by means of Internet based research for each ENM.

Depending on the ENM-containing product, different release pathways of ENMs to the environment were assumed during the products life-cycle. Section C in the SI gives a complete overview of the transfer coefficients (TC) used to model the ENM emission flows from PMC to other system compartments. For composites and plastics, complete disposal was assumed. For glass and ceramics and light bulbs, the main pathway was also disposal. For cosmetics, coatings, and cleaning agents and dietary supplements, the major release of ENM to the environment was via sewage treatment plants. Released ENMs from paints were assumed to end up in STP, landfill, soil, and surface waters. Metals, batteries and capacitors, filter aggregates, textiles, and consumer electronics were considered as either recycled or discharged to waste incineration plants or to landfills. Furthermore, some of these recycled products were also exported abroad. For textiles, abrasion, and emissions during the washing process were considered. The release of nanoparticles from Ag containing textiles was modeled using data from an experimental study (6). The dissolution of nano-ZnO and nano-Ag was modeled as elimination within the different compartments. For nano-ZnO the dissolution was modeled as elimination and calculated by means of a uniform distribution, which ranged from 0 to 100%. It has been shown that under natural conditions readily soluble minerals can be protected from dissolution by a corrosion layer (19, 20). Dissolution of nano-Ag was quantified based on information given in Blaser et al. (9) for the release of Ag from biocidal plastics and in Benn and Westerhoff (6) for release from textiles. No continuous dissolution was considered for natural waters, as little quantitative information was available. It has been shown that nano-Ag dissolves by less than 1% in various natural waters (21).

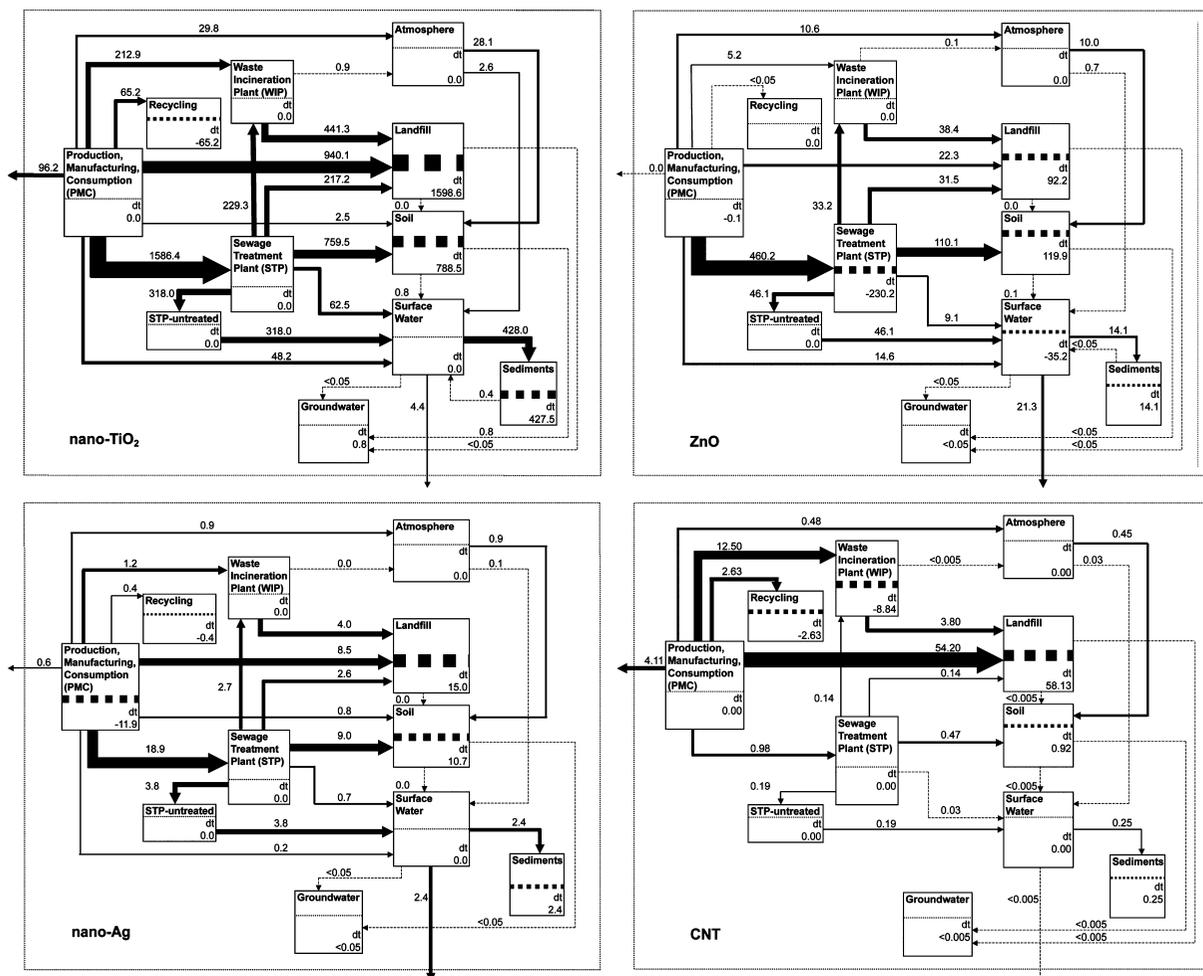
The sedimentation rate of nano-TiO<sub>2</sub> in water was derived using the sedimentation curves in Fang et al. (22) as measurement data to run MCMC iterations, which produced a distribution for the sedimented fraction with a minimum of 0.29 and a maximum of 1. Although a lot of research has been conducted to understand the behavior of fullerenes in aquatic systems or suspensions (23), most of the results were not applicable to our purpose because they yielded qualitative rather than quantitative data. We assumed almost complete dispersion (90–100%) for derivatized fullerenes and almost complete sedimentation (90–99.99%) for nonderivatized fullerenes based on a paper by Terashima et al. (24) in which fullerenes were added to water containing different amounts of humic acids. This range of sedimentation covers also the results provided by Li et al. (25). For CNT the MCMC sampling to calculate a posterior distribution of the deposited fraction

was carried out from data presented in Kennedy et al. (26) and Hyung et al. (27). A range of sedimentation between 79 and 99.9% was modeled. For nano-ZnO sedimentation, a constant probability distribution was chosen with a lower and upper boundary of 6 and 74%, respectively, based on a study in which nano-ZnO was flocculated by MgCl<sub>2</sub> (28). No sedimentation studies were available for nanosized silver and thus a uniform distribution from 0 to 100% was assumed.

A further pathway for nanomaterials to enter the environment is through the air via flue gas cleaning of waste incineration plants. For the efficiency of these filter systems, we used measurements on the removal of ultrafine particles during flue gas cleaning (29), which suggest a cleaning efficiency for nanoparticles between 99.6 and 99.9%. Combustible ENMs (i.e., CNT and fullerenes) should theoretically be completely burned unless they have no contact with oxygen, such as in batteries which may be intact in the bottom ash (5, 30). Therefore, a triangular probability function for elimination was chosen between 0 and 100% with a peak at 98% according to a typical carbon mass flow for incineration plants (31). The remaining part was then distributed randomly either to the slag or to the flue gas cleaning. Incombustible nanoparticles (i.e., nano-Ag, nano-TiO<sub>2</sub>, and nano-ZnO) were randomly distributed either to the slag or to the flue gas cleaning but without elimination. Expecting only small differences in the efficiency of waste incineration plants due to the highly developed technology commonly used, processes leading to nanoparticle outputs were modeled similarly for each region with the sole exception of Switzerland, which exports about 80% (32) of the filter ash. The EU and the U.S. were assumed to landfill all their incineration residues.

For nano-Ag, nano-TiO<sub>2</sub>, nano-ZnO, a removal efficiency during wastewater treatment between 90.6 and 99.5% (uniform distribution) was used based on Limbach et al. (33). For CNT, a removal between 96.3 and 99.7% (uniform distribution) was assumed based on settling studies in water containing 100 mg L<sup>-1</sup> NOM (26, 27). Because of the different types (functionalizations) of fullerenes, a quantification of treatment efficiency was not possible. Therefore, a distribution with constant probability from 0 to 100% was taken to account for this lack of knowledge. During and after heavy rainfall, untreated wastewater is discharged into surface water. For the EU and U.S., 20% stormwater overflow was assumed (17), and a uniform distribution between 3 and 16% (15) was used for Switzerland. Sewage sludge is used in different ways in the studied regions. In Switzerland it ends up entirely in waste incineration plants, whereas the majority of it is applied to soils in the EU and U.S. (EU: 55% (9), U.S.: 63% (34)). The remaining fraction is incinerated (EU: 25% (9) U.S.: 19% (34)) or landfilled (EU: 20% (9), U.S.: 18% (34)). Application of sewage sludge to soil is only relevant for 1% (35) of the agricultural area. The percentage of sources connected to sewage treatment facilities is 80% for the EU (17), 71% for the U.S. (36) and 100% as for Switzerland. The treatment efficiency and ultimate fate of the sludge from other treatment systems such as septic tanks was assumed to be the same as for sewage treatment plants. For calculating the water volume in the effluent, a daily water consumption per inhabitant of 200 L for Switzerland and the EU was assumed (17); for the U.S. 388 L (37).

Due to the deposition of nanomaterials in soils and sediment, the simulation results for these two compartments show annual increases in the nanomaterial concentrations. In order to obtain current concentrations in these compartments, the time course of the annual deposition needs to be known. Based on estimations of both public sector expenditures to promote nanotechnology (38) and the worldwide market value for products incorporating nanosized materials (39) for the period 2001–2012, the modeled increase (base year 2008) of ENM concentrations in sludge treated soil and



**FIGURE 1.** Simulation results (mode values >0.0005 t/a) of the material flow for the ENMs TiO<sub>2</sub>, ZnO, Ag, and CNT for the United States in t/year. The thickness of the arrows indicates the proportions of the ENM flows, the thickness of the horizontal line within the compartments the proportional magnitude of the removal or accumulation.

sediment was scaled to calculate annual increases of these concentrations for each year within the indicated period. No market and thus zero deposition of ENM was assumed for the year 2000.

**Toxicity Assessment.** Calculations of the predicted no effect concentration (PNEC) were based on ecotoxicological data from literature and were conducted according to established procedures on risk assessment (17). Due to the low accuracy of available data, an assessment factor of 1000 was applied to the lowest concentration for calculating the appropriate PNEC values that are listed in section D in the SI. The risk quotient (RQ) was calculated according to the European approach by dividing the PEC (mode value of the PEC density distribution) by the PNEC. If the RQ was greater than or equal to 1, further testing was required; less than 1 meant that no risk was currently posed to the environment and therefore further testing or risk reduction measures were not needed (17).

## Results

**Material Flow.** In Figure 1, the calculated material flows for nano-TiO<sub>2</sub>, nano-ZnO, nano-Ag, and CNTs for the system boundary of the U.S. are shown in t per year and as mode values of the simulation output distributions. Flows leaving the system describe the export of ENMs abroad. ENMs may be accumulated or eliminated (indicated as “dt”) within each compartment. For CNTs, the most prominent flows were from PMC to the waste incineration plant and to the landfill. For nano-ZnO, the flows from PMC to the sewage treatment

plant and the application of sewage sludge to soil were the most important. The STP influent, the application of sewage sludge to soil, and the flow from PMC to the landfill were by far the predominant flows in the cases of nano-TiO<sub>2</sub> and nano-Ag. The most prominent flows for fullerenes (not shown) were from products to landfill and STP and from STP to WIP and surface waters; all flows, however, were less than 1 t/a.

**Environmental Concentrations.** The main purpose of the model was to calculate the PEC for environmental compartments. Table 1 shows the predicted ENM concentrations for air, surface water, STP effluent, and sewage sludge for each region and the increase of ENM concentration per year (base year 2008) for soil, sludge-treated soil, and sediment. No concentrations in sludge-treated soil were calculated for Switzerland since, contrary to Europe and the U.S., sewage sludge is not applied to soil, but is instead incinerated in waste incineration plants or used in cement plants as solid fuel. All results are shown as simulated mode (the most frequent value) and as range of the lower and upper quantiles,  $Q_{0.15}$  and  $Q_{0.85}$ . On average, the highest concentrations of ENM for Europe and U.S. were found in sludge-treated soil or in the sediment; for Switzerland in the sediment or in sewage treatment plants’ effluent. Among the ENMs considered, nano-TiO<sub>2</sub> showed the highest concentrations in general for all regions.

For soils and sediments, the simulations provided the ENM amount deposited in these compartments in 2008. Using estimations of the worldwide market evolution for

**TABLE 1. Simulation Results of the Predicted Environmental Concentrations Shown As Mode (Most Frequent Value) and As Range of the Lower and Upper Quantiles ( $Q(0.15)$  and  $Q(0.85)$ )<sup>a</sup>**

	Europe			U.S.			Switzerland			
	Mode	$Q_{0.15}$	$Q_{0.85}$	Mode	$Q_{0.15}$	$Q_{0.85}$	Mode	$Q_{0.15}$	$Q_{0.85}$	
<b>nano-TiO<sub>2</sub></b>										
soil	1.28	1.01	4.45	0.53	0.43	2.13	0.28	0.21	1.04	$\Delta\mu\text{g kg}^{-1}\text{y}^{-1}$
sludge treated soil	89.2	70.6	310	42.0	34.5	170				$\Delta\mu\text{g kg}^{-1}\text{y}^{-1}$
surface water	0.015	0.012	0.057	0.002	0.002	0.010	0.021	0.016	0.085	$\mu\text{g L}^{-1}$
STP Effluent	3.47	2.50	10.8	1.75	1.37	6.70	4.28	3.50	16.3	$\mu\text{g L}^{-1}$
STP sludge	136	100	433	137	107	523	211	172	802	$\text{mg kg}^{-1}$
sediment	358	273	1409	53	44	251	499	426	2382	$\Delta\mu\text{g kg}^{-1}\text{y}^{-1}$
air		<0.0005			<0.0005		0.001	0.0007	0.003	$\mu\text{g m}^{-3}$
<b>nano-ZnO</b>										
soil	0.093	0.085	0.661	0.050	0.041	0.274	0.032	0.026	0.127	$\Delta\mu\text{g kg}^{-1}\text{y}^{-1}$
sludge treated soil	3.25	2.98	23.1	1.99	1.62	10.9				$\Delta\mu\text{g kg}^{-1}\text{y}^{-1}$
surface water	0.010	0.008	0.055	0.001	0.001	0.003	0.013	0.011	0.058	$\mu\text{g L}^{-1}$
STP effluent	0.432	0.340	1.42	0.3	0.22	0.74	0.441	0.343	1.32	$\mu\text{g L}^{-1}$
STP sludge	17.1	13.6	57.0	23.2	17.4	57.7	21.4	16.8	64.7	$\text{mg kg}^{-1}$
sediment	2.90	2.65	51.7	0.51	0.49	8.36	3.33	3.30	56.0	$\Delta\mu\text{g kg}^{-1}\text{y}^{-1}$
air		<0.0005			<0.0005			<0.0005		$\mu\text{g m}^{-3}$
<b>nano-Ag</b>										
soil	22.7	17.4	58.7	8.3	6.6	29.8	11.2	8.7	41.2	$\Delta\text{ng kg}^{-1}\text{y}^{-1}$
sludge treated soil	1581	1209	4091	662	526	2380				$\Delta\text{ng kg}^{-1}\text{y}^{-1}$
surface water	0.764	0.588	2.16	0.116	0.088	0.428	0.717	0.555	2.63	$\text{ng L}^{-1}$
STP effluent	42.5	32.9	111	21.0	16.4	74.7	38.7	29.8	127	$\text{ng L}^{-1}$
STP sludge	1.68	1.31	4.44	1.55	1.29	5.86	1.88	1.46	6.24	$\text{mg kg}^{-1}$
sediment	952	978	8593	195	153	1638	1203	965	10184	$\Delta\text{ng kg}^{-1}\text{y}^{-1}$
air	0.008	0.006	0.02	0.002	0.0020	0.0097	0.021	0.017	0.074	$\text{ng m}^{-3}$
<b>CNT</b>										
soil	1.51	1.07	3.22	0.56	0.43	1.34	1.92	1.44	3.83	$\Delta\text{ng kg}^{-1}\text{y}^{-1}$
sludge treated Soil	73.6	52.1	157	31.4	23.9	74.6				$\Delta\text{ng kg}^{-1}\text{y}^{-1}$
surface water	0.004	0.0035	0.021	0.001	0.0006	0.004	0.003	0.0028	0.025	$\text{ng L}^{-1}$
STP effluent	14.8	11.4	31.5	8.6	6.6	18.4	11.8	7.6	19.1	$\text{ng L}^{-1}$
STP sludge	0.062	0.047	0.129	0.068	0.053	0.147	0.069	0.051	0.129	$\text{mg kg}^{-1}$
sediment	241	215	1321	46	40	229	229	176	1557	$\Delta\text{ng kg}^{-1}\text{y}^{-1}$
air	0.003	0.0025	0.007	0.001	0.00096	0.003	0.008	0.006	0.017	$\text{ng m}^{-3}$
<b>Fullerenes</b>										
soil	0.058	0.057	0.605	0.024	0.024	0.292	0.026	0.019	0.058	$\Delta\text{ng kg}^{-1}\text{y}^{-1}$
sludge treated soil	2.2	2.1	22.2	1.01	1.0	12.2				$\Delta\text{ng kg}^{-1}\text{y}^{-1}$
surface water	0.017	0.015	0.12	0.003	0.0024	0.021	0.04	0.018	0.19	$\text{ng L}^{-1}$
STP effluent	5.2	4.23	26.4	4.6	4.49	32.66	3.82	3.69	25.1	$\text{ng L}^{-1}$
STP sludge	0.012	0.0088	0.055	0.01	0.0093	0.068	0.0107	0.0101	0.068	$\text{mg kg}^{-1}$
sediment	17.1	6.22	530	2.5	1.05	91.3	20.2	8.2	787	$\Delta\text{ng kg}^{-1}\text{y}^{-1}$
air		<0.0005			<0.0005			<0.0005		$\text{ng m}^{-3}$

<sup>a</sup> For air, surface water and sewage treatment plant effluents, the results illustrate current (2008) ENM concentrations, for soil, sludge treated soil and sediments the annual increase of ENM concentration. The results for nano-Ag, CNT, and nano-TiO<sub>2</sub> for Switzerland were taken from Gottschalk et al. (15).

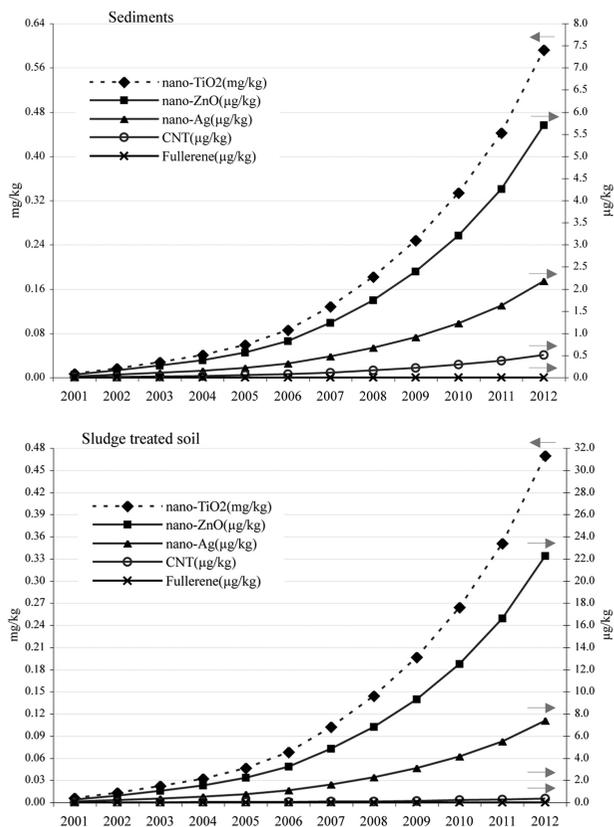
products containing ENMs for the period 2001–2012 (38, 39) and assuming zero concentrations in 2000 we scaled the deposition of ENM in 2008 to roughly estimate deposition amounts and ENM concentrations for each year of the period considered. (Figure 2). The concentrations in sediments (U.S.) will presumably rise between 2008 and 2012 from 0.2 to 0.6 mg/kg for nano-TiO<sub>2</sub>, from 1.8 to 5.7  $\mu\text{g/kg}$  for nano-ZnO, from 0.7 to 2.2  $\mu\text{g/kg}$  for nano-Ag, and from 0.2 to 0.5  $\mu\text{g/kg}$  for CNT. In the case of fullerenes, the concentrations remain close to zero. The concentrations in sludge-treated soil increase from 0.1 to 0.5 mg/kg for nano-TiO<sub>2</sub>, from 6.8 to 22.3  $\mu\text{g/kg}$  for nano-ZnO, from 2.3 to 7.4  $\mu\text{g/kg}$  for nano-Ag, and from 0.1 to 0.4  $\mu\text{g/kg}$  for CNT. In a manner similar to that of concentrations in sediments, no meaningful concentrations were observed in sludge-treated soil for fullerenes.

**Risk Estimation.** Although several reports assessed toxic effects for different ENMs to organisms in environmental compartments (2, 3), difficulties in quantifying these effects still remain due to the lack of standardization in testing. However, toxicity data was available for some ENMs and environmental compartments (SI Table 4), and risk quotients

(RQ) could thus be calculated (Table 2). For the carbon based ENM fullerenes and CNTs, the RQs were below 1. For the inorganic ENMs (Ag, TiO<sub>2</sub>, ZnO), the RQs were greater than 1 for sewage treatment effluent, but below (TiO<sub>2</sub>, ZnO) this critical value for the other environmental compartments. However, with the exception of the U.S., the RQs for nano-Ag in water bodies were around one. Unfortunately, due to the lack of available studies, it was not possible to calculate RQs for soil and sediment for some materials.

## Discussion

Of all the ENMs considered, nano-TiO<sub>2</sub> generally showed the highest concentrations for all compartments, followed by nano-ZnO. This reflects the worldwide production volumes of the ENMs. Therefore, it seems obvious that production volumes of ENMs are crucial input factors. The uncertainty about ENM production volumes is very high and, hence, the range of the available data is very broad. Thus, reducing the great uncertainties in the quantification of the total production volumes and the allocation of these volumes



**FIGURE 2. Predicted nanomaterial concentrations (U.S.) in sediment and sludge treated soil for nano-TiO<sub>2</sub> in mg/kg (left side axis ←) and for nano-ZnO, nano-Ag, CNTs, and fullerene in µg/kg for the period 2001–2012.**

**TABLE 2. Risk Quotients (PEC/PNEC) for all ENM and Regions<sup>a</sup>**

compartment	Europe	U.S.	Switzerland
nano-TiO <sub>2</sub>			
surface water	0.015	0.002	0.02
STP effluent	3.5	1.8	4.3
air	<0.0005	<0.0005	<0.0005
soil	0.004	0.002	0.001
sludge treated soil	0.3	0.14	
nano-ZnO			
surface water	0.25	0.02	0.32
STP effluent	10.8	7.7	11
nano-Ag			
surface water	1.1	0.17	1.03
STP effluent	61.1	30.1	55.6
air	<0.0005	<0.0005	<0.0005
CNT			
surface water	<0.0005	<0.0005	<0.0005
STP effluent	<0.0005	<0.0005	<0.0005
sediment	<0.0005	<0.0005	<0.0005
air	<0.0005	<0.0005	<0.0005
soil	<0.0005	<0.0005	<0.0005
sludge treated soil	<0.0005	<0.0005	
Fullerenes			
surface water	<0.0005	<0.0005	<0.0005
STP effluent	0.026	0.023	0.019
soil	<0.0005	<0.0005	<0.0005
sludge treated soil	<0.0005	<0.0005	

<sup>a</sup> The quotients for soils and sediments reflect the current state of ENM accumulation as illustrated in Figure 2. The values for nano-Ag, CNT and nano-TiO<sub>2</sub> for Switzerland were taken from Gottschalk et al. (15).

to application quantities in relevant commercially available products is crucial for improving the model. However, apart

from worldwide production and application volumes, comparable environmental concentrations of nano-TiO<sub>2</sub> and nano-ZnO also reflect a similar distribution of the main product categories (cosmetics and coatings and cleaning agents) that both result in significant release into water. Water concentrations of CNTs or fullerenes might possibly increase as well if those materials were applied in product categories with relevant ENM emissions to water bodies.

Comparing the modeled regions, it is noteworthy that the ENM concentrations for a particular environmental compartment are in a similar range for all three regions. This may be due to the fact that ENM production volumes were scaled according to the number of inhabitants of the particular region. Regional distinctions regarding ENM applications would be needed to better model region-specific ENM flows from the production, manufacturing, and consumption processes to environmental and technical compartments. In order to incorporate these differences, it would be useful to build regional databases on products containing ENM. In addition to enhancing region-specific modeling of ENM emissions, it will also be important to follow the development of new products containing engineered nanomaterial to further improve the model. Products with novel ENM emission properties, which are not currently relevant and thus not considered in the product categories, could lead to significantly higher ENM emission volumes that, combined with unexpectedly high ENM application and production volumes, could turn upside down the simulation results of ENM emissions from the PMC process to environmental and technical compartments.

Due to a lack of the mentioned regional information in the presented modeling, the input parameters differed only by the total ENM production volumes and material disposal pathways between the considered regions. Thus, the simulated flows and environmental concentrations of the corresponding ENMs do not vary significantly between the modeled systems. The main difference between the regions is visible in the different approaches of handling sewage sludge. Countries with a high proportion of land-disposal will have to deal with increasing concentrations of ENMs in sludge-treated soil, while countries with complete incineration of sludge should not experience this problem.

Our model assumes homogeneous and well-mixed compartments on a country or continent-wide scale (17). In order to cover local conditions such as, e.g., those near ENM-producing factories, near sewage treatment outflows or for special release events such as accidents, further modeling has to be conducted which, once the data is available, will also be possible with the probabilistic approach.

For Europe and the U.S., relatively high concentrations of ENMs were found on soil treated with sewage sludge. Due to the very low fraction of soil to which sewage sludge is applied, the relevant volume for this compartment is very low. Therefore, it seems reasonable that these particular concentrations are much higher than for the soil compartment as a whole. Our model also includes sedimentation of ENMs in surface waters. Although information on aggregation and sedimentation of ENMs under natural conditions is sparse, we can expect that a relevant fraction of the ENMs will be removed from waters and settle into the sediment. The inclusion of this sedimentation process can explain the relatively large difference in the surface water concentrations of TiO<sub>2</sub> and nano-Ag compared to the previous study of Mueller and Nowack (7). For all regions, air shows the lowest PEC compared to the other environmental compartments; this is mainly due to its high volume and the short residence time (10 days) of ultrafine particles. ENMs reach the atmosphere either during the usage of products or via emissions from waste incineration plants at low percentages.

Additionally, they could agglomerate and/or be coated by organic and inorganic material on time scales shorter than 10 days.

In our modeling we did not distinguish between specific forms of ENMs, e.g., between single and multiwalled CNTs and the various forms of fullerenes (e.g., C60, C70). Due to the absence of data we also lumped together all the different modifications, functionalizations, and surface-coatings of the ENMs. ENMs may be technically altered to fit the purpose of the end product such as, e.g., being water-soluble or insoluble. With the probabilistic modeling, we included this uncertainty in some processes (e.g., the sedimentation behavior) by using transfer factors that include the behavior of both pristine and modified ENMs, e.g., CNT and fullerenes. Derivatized fullerenes are assumed to stay dispersed in water, whereas almost complete sedimentation is assumed for nonderivatized fullerenes. In such cases, bimodal distributions have to be modeled. For the soluble ENMs (e.g., nano-Ag and nano-ZnO), the dissolution rate in water is difficult to quantify; further studies are needed to fully understand their behavior and fate in natural water bodies and to quantify their release during usage or washing of ENM containing products. Slightly soluble materials such as, e.g., ZnO (at pH 7) may be protected from dissolution by a corrosion layer. Furthermore, ENMs may also be coated by other substances, such as silica, meaning that it is difficult to generalize the environmental fate of a particular ENM. Additional to such technically intended modifications in functionalization or coating characteristics, changes in the engineered nano-material properties induced by chemical and physical processes in the environment or by their reaction with natural compounds cannot be excluded. Besides this mentioned environmental fate and behavior, size and functionalization of ENMs could also influence the toxic effects of the particular ENM. However, due to a lack of data, a differentiation of toxicological data based on derivatization and functionalization of ENMs was not possible.

For nano-Ag, nano-TiO<sub>2</sub>, and nano-ZnO, the RQ (PEC/PNEC) exceeded the critical value of one for sewage treatment plant effluents, meaning that further investigations are needed to evaluate the risk posed to aquatic organisms by these ENMs. This urgent need for further investigations is in addition emphasized by the fact that the RQ for nano-Ag in water is slightly above one (EU, Switzerland). For the other environmental compartments for which toxicological data was available, no risks to organisms are currently expected. However, it should also be emphasized here that the calculation of the RQ involves a safety factor of 1000. A RQ slightly above one does therefore not constitute an immediate risk but is an indication that further data are needed.

Although ENM concentrations in sediments and sludge-treated soil (U.S.) increase from 2008 to 2012, the RQs derived for CNTs in sediments and for nano-TiO<sub>2</sub>, CNTs and fullerenes in sludge-treated soil for 2012 are far below one. The only pronounced RQ (0.3) was calculated for nano-TiO<sub>2</sub> in sludge-treated soil. This parallels the modeled critical RQ for nano-TiO<sub>2</sub> in sewage treatment plant effluents and, given the implication that both nano-Ag and nano-ZnO show even higher RQs for sewage treatment plant effluents, the ecotoxicological effects in sludge-treated soils of these two ENMs need further investigation as well.

In order to validate results of modeled environmental concentrations as presented in this study, a comparison between our data and measurement data is necessary. Kiser et al. (40) measured 5–15 µg/L Ti (<0.7 µm) in STP effluents. This validates very well our calculations (mode values) of nano-Ti in STP effluents: EU 2.01 µg/L, U.S. 1.01 µg/L, Switzerland 2.48 µg/L. However, it has to be noted that in their study Kiser et al. used filtration with 0.7 µm and their value may thus also include part of the bulk Ti released into

STP. Blaser et al. (9) calculated total Ag concentrations in surface waters which were by a factor 10–100 higher than our simulation results for nano-Ag and they also concluded that nano-Ag contributes only 1–15% to the total Ag into the environment. First measurements (40) of Ti in STP sludge indicated concentrations which ranged from 1 to 6 g Ti/kg. Our simulations showed concentrations (mode values) of the same order of magnitude: EU and U.S. 0.1 g Ti/kg, Switzerland 0.12 g Ti/kg. These first measurements of ENM in the environment show concentrations in the same order of magnitude than our modeling results and thus allow a first validation of some aspects of our model.

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## Supporting Information Available

Description of the system compartments. ENM production volumes and allocation of these volumes to product categories. Table with worldwide production volumes for ENM. Table with product categories for each ENM with the modeled input distribution. Table with parameters for release of ENM from products. Table with considered ecotox studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## Literature Cited

- (1) Nowack, B.; Bucheli, T. D. Occurrence, behavior and effects of nanoparticles in the environment. *Environ. Pollut.* **2007**, *150*, 5–22.
- (2) Klaine, S. J.; Alvarez, P. J. J.; Batley, G. E.; Fernandes, T. F.; Handy, R. D.; Lyon, D. Y.; Mahendra, S.; McLaughlin, M. J.; Lead, J. R. Nanomaterials in the environment: Behavior, fate, bioavailability, and effects. *Environ. Toxicol. Chem.* **2008**, *27*, 1825–1851.
- (3) Baun, A.; Hartmann, N. B.; Grieger, K.; Kusk, K. O. Ecotoxicity of engineered nanoparticles to aquatic invertebrates: a brief review and recommendations for future toxicity testing. *Ecotoxicology* **2008**, *17*, 387–395.
- (4) Kaegi, R.; Ulrich, A.; Sinnet, B.; Vonbank, R.; Wichser, A.; Zuleeg, S.; Simmler, H.; Brunner, S.; Vonmont, H.; Burkhardt, M.; Boller, M. Synthetic TiO<sub>2</sub> nanoparticle emission from exterior facades into the aquatic environment. *Environ. Pollut.* **2008**, *156*, 233–239.
- (5) Koehler, A.; Som, C.; Helland, A.; Gottschalk, F. Studying the potential release of carbon nanotubes throughout the application life cycle. *J. Clean. Prod.* **2008**, *16*, 927–937.
- (6) Benn, T. M.; Westerhoff, P. Nanoparticle silver released into water from commercially available sock fabrics. *Environ. Sci. Technol.* **2008**, *42*, 4133–4139.
- (7) Mueller, N. C.; Nowack, B. Exposure modeling of engineered nanoparticles in the environment. *Environ. Sci. Technol.* **2008**, *42*, 4447–4453.
- (8) Boxall, A. B. A.; Chaudhry, Q.; Jones, A.; Jefferson, B.; Watts, C. D. *Current and Future Predicted Environmental Exposure to Engineered Nanoparticles*; Central Science Laboratory: Sand Hutton, UK, 2008.
- (9) Blaser, S. A.; Scheringer, M.; MacLeod, M.; Hungerbuehler, K. Estimation of cumulative aquatic exposure and risk due to silver: Contribution of nano-functionalized plastics and textiles. *Sci. Total Environ.* **2008**, *390*, 396–409.
- (10) Finley, B.; Paustenbach, D. The benefits of probabilistic exposure assessment: Three case studies air, water, and soil. *Risk Anal.* **1994**, *14*, 54–73.
- (11) McKone, T. E.; Bogen, K. T. Predicting the uncertainties in risk assessment—A California groundwater case-study. *Environ. Sci. Technol.* **1991**, *25*, 1674–1681.
- (12) van der Voet, H.; Slob, W. Integration of probabilistic exposure assessment and probabilistic hazard characterization. *Risk Anal.* **2007**, *27*, 351–365.
- (13) Macleod, M.; Scheringer, M.; Poday, H.; Jones, K. C.; Hungerbuehler, K. The origin and significance of short-term variability

- of semivolatile contaminants in air. *Environ. Sci. Technol.* **2007**, *41*, 3249–3253.
- (14) Gottschalk, F.; Scholz, R. W.; Nowack, B. Probabilistic material flow modeling for assessing the environmental exposure to compounds: Methodology and an application to engineered nano-TiO<sub>2</sub> particles. *Environ. Model. Software*, **2009**, in press, DOI: 10.1016/j.envsoft.2009.08.011.
- (15) Gottschalk, F.; Sonderer, T.; Scholz, R. W.; Nowack, B. Modeling the environmental concentrations of engineered nanomaterials based on a probabilistic material flow analysis. *Environ. Toxicol. Chem.*, **2009**, submitted.
- (16) R Development Core Team R. *A Language and Environment for Statistical Computing*; R Foundation for Statistical Computing: Vienna, Austria, 2008.
- (17) ECB. Technical Guidance Document on Risk Assessment; European Chemicals Bureau; Institute for Health and Consumer Protection, European Commission: Dublin, 2003.
- (18) The World Bank Group. *World Development Indicators*; The World Bank: Washington, DC, 2008.
- (19) Birkefeld, A.; Schulz, R.; Nowack, B. In situ transformations of fine lead oxide particles in different soils. *Environ. Pollut.* **2007**, *145*, 554–561.
- (20) Gimbert, L. J.; Hamon, R. E.; Casey, B. P.; Worsfold, P. J. Partitioning and stability of engineered ZnO nanoparticles in soil suspensions using flow field-flow fractionation. *Environ. Chem.* **2007**, *4*, 8–10.
- (21) Gao, J.; Youn, S.; Hovsepian, A.; Llana, V. L.; Wang, Y.; Bitton, G.; Bonzongo, J. C. J. Dispersion and toxicity of selected manufactured nanomaterials in natural river water samples: Effects of water chemical composition. *Environ. Sci. Technol.* **2009**, *43*, 3322–3328.
- (22) Fang, J.; Shan, X.-q.; Wen, B.; Lin, J.-m.; Owens, G. Stability of titania nanoparticles in soil suspensions and transport in saturated homogeneous soil columns. *Environ. Pollut.* **2009**, *157*, 1101–1109.
- (23) Ju-Nam, Y.; Lead, J. R. Manufactured nanoparticles: An overview of their chemistry, interactions and potential environmental implications. *Sci. Total Environ.* **2008**, *400*, 396–414.
- (24) Terashima, M.; Nagao, S. Solubilization of [60]fullerene in water by aquatic humic substances. *Chem. Lett.* **2007**, *36*, 302–303.
- (25) Li, Q. L.; Xie, B.; Hwang, Y. S.; Xu, Y. J. Kinetics of C-60 fullerene dispersion in water enhanced by natural organic matter and sunlight. *Environ. Sci. Technol.* **2009**, *43*, 3574–3579.
- (26) Kennedy, A. J.; Hull, M. S.; Steevens, J. A.; Dontsova, K. M.; Chappell, M. A.; Gunter, J. C.; Weiss, C. A. Factors influencing the partitioning and toxicity of nanotubes in the aquatic environment. *Environ. Toxicol. Chem.* **2008**, *27*, 1932–1941.
- (27) Hyung, H.; Fortner, J. D.; Hughes, J. B.; Kim, J. H. Natural organic matter stabilizes carbon nanotubes in the aqueous phase. *Environ. Sci. Technol.* **2007**, *41*, 179–184.
- (28) Zhang, Y.; Chen, Y.; Westerhoff, P.; Hristovski, K.; Crittenden, J. C. Stability of commercial metal oxide nanoparticles in water. *Water Res.* **2008**, *42*, 2204–2212.
- (29) Burtscher H.; Zürcher M.; Kasper A.; Brunner M. Efficiency of Flue Gas Cleaning in Waste Incineration for Submicron Particles. *Proceedings of the International ETH Conference on Nanoparticle Measurement*, August 6-8, 2001.
- (30) Bunge, R.; Krebs, A.; Meyer, M. K. *Unkonventionelles Recycling*; Bafu: Illnau, February, 2008.
- (31) Baccini, P.; Brunner, P. H. *Metabolism of the Anthroposphere*; Springer-Verlag: Berlin, Heidelberg, New York, 1991.
- (32) KVA-Winterthur. Antrag für die Nachrüstung der Reststoffensorgung in der Kehrichtverbrennungsanlage; Winterthur, 1999.
- (33) Limbach, L. K.; Bereiter, R.; Müller, E.; Krebs, R.; Gälli, R.; Stark, W. J. Removal of oxide nanoparticles in a model wastewater treatment plant: Influence of agglomeration and surfactants on clearing efficiency. *Environ. Sci. Technol.* **2008**, *42*, 5828–5833.
- (34) Metropolitan Council U.S. Biosolids Scene. <http://www.metrocouncil.org/environment/Biosolids/BiosolidsUS.htm> (2008).
- (35) US EPA. Biosolids, Frequently Asked Questions. <http://www.epa.gov/owm/mtb/biosolids/genqa.htm> (2009).
- (36) *Environmental Data Compendium*; Organisation for Economic Co-operation and Development (OECD): Geneva, 2004; 2005.
- (37) Versar Center. *Exposure and Fate Assessment Screening Tool (E-FAST)*; U.S. Environmental Protection Agency Office of Pollution Prevention and Toxics Exposure Assessment Branch: Springfield, VA, 2007.
- (38) Luther, W.; Malanowski, N.; Bachmann, G.; Hoffknecht, A.; Holtmannspötter, D.; Zweck, A.; Heimer, T.; Sanders, H.; Werner, M.; Mietke, S.; Köhler, T. *Nanotechnologie als wirtschaftlicher Wachstumsmarkt, Innovations- und Technikanalyse*; VDI Report: Duesseldorf, 2004.
- (39) *Cientifica Nanotechnology Opportunity Report*; Cientifica: London, 2008.
- (40) Kiser, M. A.; Westerhof, P.; Benn, T.; Wang, Y.; Pérez-Rivera, J.; Hristovski, K. Titanium Nanomaterial Removal and Release from Wastewater Treatment Plants. *Environ. Sci. Technol.* **2009**, *43*, 6757–6763.

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