

## Article

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Nicole C. Mueller, and Bernd Nowack

*Environ. Sci. Technol.*, **2008**, 42 (12), 4447-4453 • DOI: 10.1021/es7029637 • Publication Date (Web): 09 May 2008Downloaded from <http://pubs.acs.org> on December 8, 2008

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# Exposure Modeling of Engineered Nanoparticles in the Environment

NICOLE C. MUELLER AND  
BERND NOWACK\*

Technology and Society Laboratory, Empa - Swiss Federal  
Laboratories for Materials Testing and Research  
Lerchenfeldstrasse 5, CH - 9014 St. Gallen, Switzerland

Received November 27, 2007. Revised manuscript received  
March 12, 2008. Accepted March 17, 2008.

The aim of this study was to use a life-cycle perspective to model the quantities of engineered nanoparticles released into the environment. Three types of nanoparticles were studied: nano silver (nano-Ag), nano TiO<sub>2</sub> (nano-TiO<sub>2</sub>), and carbon nanotubes (CNT). The quantification was based on a substance flow analysis from products to air, soil, and water in Switzerland. The following parameters were used as model inputs: estimated worldwide production volume, allocation of the production volume to product categories, particle release from products, and flow coefficients within the environmental compartments. The predicted environmental concentrations (PEC) were then compared to the predicted no effect concentrations (PNEC) derived from the literature to estimate a possible risk. The expected concentrations of the three nanoparticles in the different environmental compartments vary widely, caused by the different life cycles of the nanoparticle-containing products. The PEC values for nano-TiO<sub>2</sub> in water are 0.7–16 µg/L and close to or higher than the PNEC value for nano-TiO<sub>2</sub> (<1 µg/L). The risk quotients (PEC/PNEC) for CNT and nano-Ag were much smaller than one, therefore comprising no reason to expect adverse effects from those particles. The results of this study make it possible for the first time to carry out a quantitative risk assessment of nanoparticles in the environment and suggest further detailed studies of nano-TiO<sub>2</sub>.

## Introduction

The increase in the production and use of engineered nanoparticles (NP) makes exposure of the natural environment to these compounds more and more likely (1). The risks emanating from NP are determined by their potential hazards (such as toxicity), as well as by the extent the material will come into contact with an organism (2, 3). The basis for a sound risk assessment of a possibly hazardous substance is thus a comparison between the exposure (concentration in the environment) and the toxic effects of the substance (dose–response relationship). So far, no measurements of engineered NP in the environment have been available due to the absence of analytical methods able to quantify trace concentrations of NP. A recent study reports the identification of natural nanosized TiO<sub>2</sub> particles in river water affected by mining-wastes (4). Much more information is available about the fate of ultrafine particles (UFP) in air (5).

Usually the concentration of a new substance in the environment is not known at the time of the assessment.

Therefore, expected concentrations have to be modeled with the help of extrapolations and analogies (6). The value derived from such modeling, the PEC (predicted environmental concentration), is compared to the PNEC (predicted no effect concentration), which extrapolates (based on toxicological studies) the concentration at which no adverse effect on organisms (and ecosystems) is to be expected. An ingredient is judged to be environmentally compatible if the PEC/PNEC ratio is smaller than one.

A recent study modeled the Ag emissions from nano Ag (nano-Ag) containing biocidal products and compared the expected concentrations in the environment with a reference emission (7). In this study, nano-Ag only served as Ag<sup>+</sup> source and no particulate Ag emissions were considered.

Two of the most widely used NP in consumer products are Ag and TiO<sub>2</sub>. nano-Ag is one of the most promising NP for future applications (8) due to its antimicrobial, antifungal and partially antiviral properties (9). nano-TiO<sub>2</sub> is produced on a large scale for applications in paints and coatings (self-cleaning, antifouling, and antimicrobial properties) (10) and in cosmetics as a UV-absorber. In Australia alone there are more than 300 registered sunscreen products containing nanoscaled titanium dioxide (11).

Carbon nanotubes (CNT) have applications in electronics and the polymer industry, the energy sector and the consumer goods industry are doing research with this unique material (12). CNT integrated into polymers (13) and lithium ion secondary batteries (14) promise interesting applications.

The goal of this study was to model the expected concentrations of nano-Ag, nano-TiO<sub>2</sub>, and CNT in the environment. The risk assessment was carried out for the three environmental compartments water, air, and soil for Switzerland. Based on this model, a first assessment of the potential risk posed by the three mentioned NP was conducted by comparing the PEC to the PNEC.

## Materials and Methods

**Model Background.** The modeling was based on established methods to assess the exposure of chemicals to the environment (6). In the absence of sufficiently detailed data, initial exposure assessments based on worst-case assumptions were considered acceptable (6). A realistic and a high exposure scenario (RE- and HE scenario) were developed due to the high uncertainty of the data. The RE-scenario was based on the most realistic information received. The worst-case scenario relied on estimations that would lead to higher concentrations in the environment.

The calculation of the predicted environmental concentration (PEC) was based on a substance flow analysis (Figure S1, Supporting Information). The flows of the NP from the products to the environment, waste incineration plants (WIP), landfills, and/or sewage treatment plants (STP) were quantified. The predicted no observed effect concentration (PNEC) was derived from ecotoxicological data such as the No Observed Effect Concentration (NOEC). An extrapolation-factor of 1 thousandth was used, as the accuracy of the data was low (6).

**Production and Product Distribution.** The worldwide production volume was allocated to Switzerland by means of the population of the industrialized world (EU, U.S., Japan, South Korea, 10% of China) compared to Switzerland (factor 0.0068). The allocation of the NP volume to the product categories was based on two weighting factors. The weighting factor “article” describes the distribution of the total NP production to different product categories and was determined by combining three sources: (i) the inventory of the

\* Corresponding author phone: +41 (0)71 274 76 92; fax: +41- (0)71-274 78 62; e-mail: nowack@empa.ch.

Woodrow Wilson Institute (15), (ii) a search of the www.products.ec21.com database, and (iii) a web search (see Tables S1 and S3, Supporting Information). The weighting factor “weight” describes the amount of NP in each product category and was derived from the estimated average weight of the product multiplied with the estimated average NP-concentration in the product (Tables S2 and S4, Supporting Information). The product of the two factors was scaled to 100% to yield the distribution of NP to the respective product categories. Percentages were rounded to the nearest 5% because the uncertainty was relatively high. Numbers not reaching 5% were rounded to the nearest percent.

**Substance Flows.** The primary compartments air, soil, and water were considered to be homogeneous and well mixed as suggested for modeling the regional PEC (6). For the reason of simplicity, it was further assumed that the system was in a steady state. In the case of steady state, the transfer coefficients between compartments can be used to estimate the concentration in each compartment. It was assumed that the substance flow rates between the different environmental compartments were the same for all NP unless otherwise specified. Secondary compartments (sediment and groundwater) were not considered. Two flows relevant for other countries were not considered: STP to landfill and STP to soil (sludge application to soil has been prohibited in Switzerland since 2006; all sludge is burned).

**Behavior during Waste Incineration.** WIP in Switzerland are equipped with different types of filters, but all have a multistage flue gas cleaning system consisting of electrofilters, a flue gas scrubber, a catalytic NO<sub>x</sub>/furan/dioxin removal, and possibly a fabric filter. The concentration of particles smaller than 100 nm is lowered by around 99.9% and in the subsequent wet filter by another 95% (16). There is not much information about the behavior of NP during waste incineration. It is unknown what NP fraction stays in the slag and what percentage becomes airborne. In the case of CNT, theoretically all particles should be burned in a WIP, as the temperature (about 850 °C) is higher than the ignition temperature of CNT (about 600 °C) and the waste is incinerated in the presence of oxygen. However, CNT may survive when not exposed to oxygen such as in the interior of a steel can (e.g. battery) (12).

In this study, the following coefficients were assumed in the RE-scenario: The fraction of incombustible nanoparticles (nano-Ag, nano-TiO<sub>2</sub>) becoming airborne and therefore transported to the filters during the incineration process was assumed to be 50%. For CNT, it was assumed that 50% were burned, 25% survived in the slag, and 25% became airborne. The suspended particles were caught to 99.9% in the WIP filters leaving 0.1% to enter the atmosphere. In the high HE-scenario it was assumed that 100% of all particles (nano-TiO<sub>2</sub>, nano-Ag) become airborne during the incineration process and 1% of the volatile particles are released to the atmosphere. CNT were assumed to burn (25%), stay in the slag (25%), and become airborne with 1% of the latter 50% being released to the atmosphere.

**Behavior during Wastewater Treatment.** Connection to a sewage treatment plant (STP) is nearly 100% for wastewater in Switzerland. The fate of NP in wastewater treatment plants has not yet been studied. The ability to immobilize the particles by the processes in a STP will depend on the characteristics of the particles and the residence time in the STP. Particles <0.1 μm are effectively removed (97%) in packed-bed filters (17). The average removal efficiency for suspended particles during treatment is 97–99% (18, 19). For modeling it was assumed that 97% of the particles are cleared in the RE-scenario and 90% in the HE-scenario.

The overflow discharge during heavy rain strongly varies between STPs. Values between 2 and 10% of the total inflow were reported (20). It was assumed that the particle con-

centration in the overflow discharge is equal to the concentration in the inflow. The average overflow discharge for the RE- and HE-scenarios was assumed to be 5 and 10%, respectively.

**Deposition from Air.** It was assumed that eventually all particles in the air are deposited (dry deposition) or washed out (wet deposition) on water or soil. This leads to a double count of all airborne particles (first in the air compartment and second in the soil/water compartments). The particle deposition to water (3%) and soil (97%) is proportional to the land area covered by water/soil (6). To obtain the concentration in air, the relevant air volume for terrestrial ecosystems of 1 km (6) was multiplied with the total area of Switzerland to yield 41 285 km<sup>3</sup>.

**Water Compartment.** The aquatic compartment is defined as surface water (lakes, rivers) excluding groundwater. The concentration of NP in water was calculated by multiplying the relevant mixing depth of 3 m (6) with 3% (6) of the total area of Switzerland, resulting in a relevant water volume of 3.7 km<sup>3</sup>.

**Soil Compartment.** The average concentration of NP in the soil was calculated as follows: The soil mixing depth depends on the type of soil and is 0.2 m for agricultural soil and 0.05 m for natural and urban soil (6). The fraction of the country area agriculturally used is 0.27, 0.6 is natural ground, and 0.1 urban ground (6). These numbers lead to a relevant soil volume of 3.7 km<sup>3</sup>. A soil density of 1.5 kg L<sup>-1</sup> was taken.

## Results

**Production Volumes.** The best guess for the worldwide production of nano-Ag is 500 t/a worldwide (Table S5, Supporting Information) and it was used in the RE-scenario. According to (21), 25 620 t of silver are used per year in jewelry, photography, and industry, representing 95% of the total silver consumption. The remaining 5% approximate 1230 t of silver. This represents the maximum amount of silver that could be processed to nanoparticles and is used in the HE-scenario. The value for the RE-scenario of nano-TiO<sub>2</sub> is derived from the worldwide production volume of nano-TiO<sub>2</sub> (5000 t/a) estimated by ref 22 (Table S6, Supporting Information). The production volume of 10 companies in Switzerland (400 t/a) was taken for the HE-scenario (Table S6, Supporting Information). The best guess for CNT is 350 t/a worldwide (RE-scenario) for the year 2007/2008 (Table S7, Supporting Information). The HE-scenario assumes 500 t/a.

**Allocation of the Production Quantities to the Categories.** The NP-containing products were grouped into categories with a similar release of particles and a similar lifecycle (Table 1). There was almost no information on the concentration of nano-TiO<sub>2</sub> in the products. The concentrations underlying the weighting were thus assumed to be similar to nano-Ag if no other information was found. In the case of CNT, a quantitative allocation of the production volume to the categories turned out to be very difficult due to a lack of information of products containing CNT. In order to model the PEC<sub>CNT</sub>, we made a rough estimation which must be considered as a first attempt to approach the PEC<sub>CNT</sub>. We assumed that 50% of the produced CNT is incorporated into plastics and 50% into electronics.

**Paths of Particle Release.** The amount of nanoparticles released by the different processes depends on several factors: the nanoparticle stock in the article, the article's lifetime, the way NP are incorporated in the material and the actual use/usage of the article (12). Articles with a long lifetime, a loose incorporation of the NP and/or an intense use (e.g., through frequent cleaning) will most likely not contain NP anymore at the time of disposal. On the other hand, factors such as short lifetime, low usage, and strong fixation of NP increase the likelihood that particles will not be released until disposal (23).

**TABLE 1. Calculation of the Categories' Relative Share from the Total Volume of Nano-Ag and Nano-TiO<sub>2</sub> for the RE- and HE Scenario Used in Switzerland with the Two Weighting Factors (WF) "Weight" and "Article"<sup>a</sup>**

		WF "article"	WF "weight"	product of WFs	scaled (%)	rounded (%)	amount per category (RE- scenario) (t)	amount per category (HE- scenario) (t)
nano-Ag	textiles	0.17	0.018	0.0030	11	10	0.37	0.91
	cosmetics/ supplements	0.16	0.044	0.0069	24	25	0.84	2.06
	sprays/ cleaning agent	0.11	0.044	0.0049	17	15	0.60	1.47
	metal products	0.17	0.0044	0.0008	3	5	0.09	0.23
	plastics	0.38	0.0088	0.0033	12	10	0.41	1.00
	paint/ sealings	0.01	0.88	0.0098	34	35	1.20	2.94
nano-TiO <sub>2</sub>	sporting goods/ plastics	0.30	0.004	0.0013	2	2	0.7	8.2
	cosmetics	0.13	0.28	0.036	59	60	20.5	235
	coatings/ cleaning agents	0.32	0.004	0.0014	2	2	0.8	8.8
	metals	0.21	0.001	0.0002	1	1	0.1	1.5
	energy production/storage	0.02	0.35	0.0075	12	10	4.3	48.9
	paint	0.02	0.71	0.0151	24	25	8.6	97.8

<sup>a</sup> The derivation of the weighing factors is given in the Supporting Information.

**TABLE 2. Substance Flow Analysis for the Release of Nano-Ag, Nano-TiO<sub>2</sub> and CNT from Products**

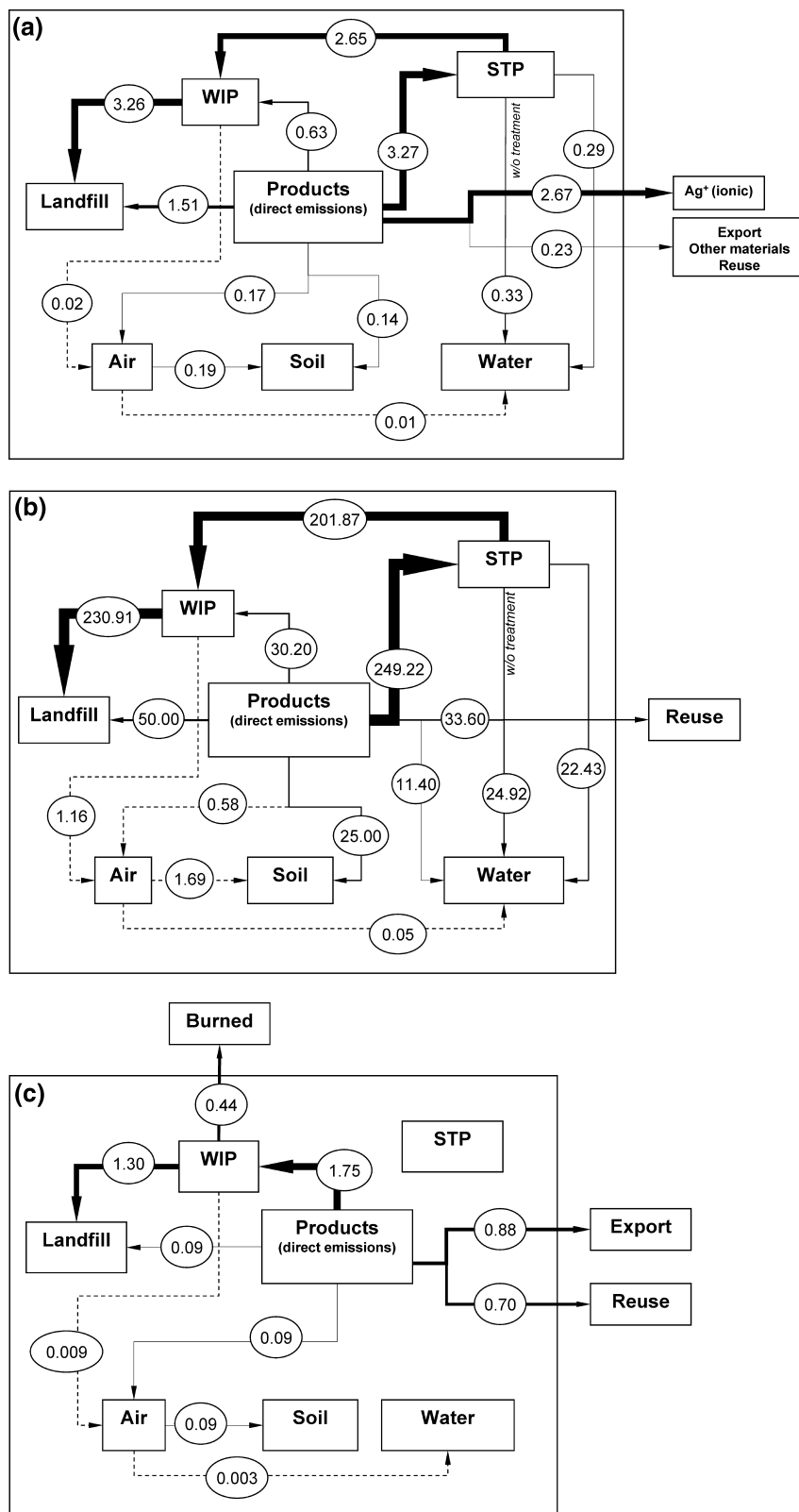
NP	product category	% of total amount	release	%	release
nano-Ag	textiles	10	abrasion during use	5	air
			abrasion during washing	5	STP
			disposal (WIP)	2.5	WIP
			recycling	0.5	leaving system
			export	2	leaving system
			dissolution	85	leaving system
	cosmetics	25	application	95	STP
			disposal	5	WIP
	sprays, cleaning agents	15	application	95	air (10%), STP (85%), soil (5%)
			disposal	5	WIP
	metal products	5	abrasion	5	STP
			recycling	47.5	leaving system
			disposal	2.5	WIP
			dissolution	45	leaving system
	plastics	10	abrasion	5	STP
			disposal	50	WIP
			dissolution	45	leaving system
			run off	5	soil (50%), STP (50%)
	paint	35	dissolution	45	leaving system
			disposal	50	disposal site
nano-TiO <sub>2</sub>	plastics	2	abrasion	5	air (50%), STP (50%)
			disposal	95	WIP
	cosmetics	60	application	95	STP (95%), water (5%)
			disposal	5	WIP
	coatings	2	application	95	STP (95%), air (5%)
			disposal	5	WIP
	metals	1	abrasion	5	STP
			recycling	90	leaving system
			disposal	5	WIP
	energy storage/ production	10	disposal	25	WIP
			recycling	75	leaving system
	paint	25	runoff	50	STP (50%), soil (50%)
			disposal	50	disposal site
CNT	plastics, sporting equipment	50	abrasion	5	air
			disposal	95	WIP
	electronics, batteries	50	recycling	40	leaving system
			disposal	10	WIP (50%), disposal site (50%)
			export	50	leaving system

Ag is also released in ionic form from nanoparticles, and this was considered to be the major process of Ag release from plastics and textiles (7). The release of nano-TiO<sub>2</sub> from coatings on wood, polymer, and tile were the highest from coated tile, and UV-light increased the release of particles (24).

CNT in consumer products are almost exclusively bound into materials such as polymers or integrated in closed compartments such as in computers and batteries that are not intended to be opened by the consumer. Release of CNT

during the application is unlikely except for CNT in clothing. Release from textiles is to be expected during tailoring and finishing and also during use (12). The release rates used in this study are summarized in Table 2. They are based as far as possible on actual information on product life-cycles and disposal in Switzerland.

**System Flowcharts.** Figures 1a–c show the NP-flows from the products to the environmental compartments, STP, WIP, and the landfill for the HE-scenario. The data for the RE



**FIGURE 1.** nano-Ag (a), nano-TiO<sub>2</sub> (b), and CNT (c) flows from the products to the different environmental compartments, WIP, STP, and landfill (HE-scenario). All flows are in tons/year. The thickness of the arrows is proportional to the amount of silver flowing between the compartments. Dashed arrows represent the lowest volume.

scenario are given in Figure S2 (Supporting Information). In the case of nano-Ag and nano-TiO<sub>2</sub>, the most prominent flows are between the products and the STP (3.27 t/a, 249.22 t/a), the STP and the WIP (2.65 t/a, 201.87 t/a) and the WIP to the landfill (3.26 t/a, 230.91 t/a). Unlike nano-Ag and nano-

TiO<sub>2</sub>, the most prominent flow for CNT is between the products and the WIP (1.75 t/a) and from the WIP to the landfill (1.30 t/a). The reason is that CNT-containing material staying in Switzerland ends almost exclusively in the WIP if not recycled.



**Derivation of PNECs for the Three Environmental Compartments.** The only ecotoxicological data at hand for nano-Ag refer to bacterial toxicity. In a first attempt, the following considerations were used to approach a PNEC for nano-Ag. For the water compartment, threshold concentrations of 20 mg/L and 40 mg/L for *B. subtilis* and *E. coli* respectively were reported (25), which could be considered equivalent to a NOEC. With the suggested assessment factor of 1000 (6), the  $PNEC_{\text{nano-Ag}}(\text{water})$  is thus around 0.04 mg/L. No data for soil are yet available.

For nano-TiO<sub>2</sub> and aquatic organisms (algae, daphnia), <1 mg/L is the lowest value found (26). With an assessment factor of 1000 (6), the  $PNEC_{\text{nano-TiO}_2}(\text{water})$  is <0.001 mg/L. The  $PNEC_{\text{nano-TiO}_2}(\text{air})$  must be based on a (L)OEC of 10 mg/m<sup>3</sup> (5). The resulting  $PNEC_{\text{nano-TiO}_2}(\text{air})$  is 0.01 mg/m<sup>3</sup>.

According to (27), the occupational limit for CNT exposure should be no greater than 0.1 mg/m<sup>3</sup>. For organisms in water (fish, daphnia), a NOEC of <0.1 mg/L was the lowest value found. With an assessment factor of 1000 (6), the PNEC water is <0.0001 mg/L.

**Risk Characterization (RQ=PEC/PNEC).** The modeling suggests that currently nano-Ag poses little or no risk to soil organisms. The RQ water is less than one thousandth. Also in the HE-scenario, the modeling suggests that currently little or no risk is to be expected from nano-Ag in the soil compartment and the water in general.

The modeling suggests that nano-TiO<sub>2</sub> may pose a risk to water organisms with a RQ between >0.73 and 16. By contrast, the RQ air is smaller than one thousandth. Also in the HE-scenario, the expected concentration of nano-TiO<sub>2</sub> in water is critical (RQ between >15.83 and >3933.33), whereas the RQ air is very small (0.004).

The calculation indicates that currently CNT most probably pose little to no risk to air and water organisms. The RQ water and air are both very small. Also in the HE-scenario, the expected concentration of CNT in water and air are small. Ecotoxicological data on soil organisms are scarce and an evaluation is not yet possible.

## Discussion

The modeled concentrations of NP in the environment are only as good as the raw data. For nano-Ag and nano-TiO<sub>2</sub> the range between the estimations for the worldwide production is wide. In order to address the uncertainty of data in this thesis, two scenarios were modeled: a realistic exposure scenario based on the most reliable data and a high exposure scenario including the worst-case assumptions. A future scenario was not conducted, as the predictions for the development of the production volumes of the NP are too vague. It seems to be realistic, though, that the production volumes of all three substances will increase significantly in the coming years (22).

So far there has been no exhaustive inventory that lists all NP containing products and their nanoinredients. Scientific reports usually address the application areas only on an abstract level and do not mention concrete products. Furthermore only very little trustworthy information is given by companies. Many producers do not advertise nanocomponents. It can be expected that more data on the production and use of nanoparticles in consumer products will become available in a few years when ongoing governmental projects on nanomaterials are completed.

The flow coefficients were determined based on numbers found in the literature or expert estimations. It must also be noted that there was a general lack of data for the environmental flow coefficients. The behavior of nanoparticles in the environment as well as in the STP and WIP is largely unknown. In order to allow modeling, it was further necessary to assume equal distribution within the environmental

compartments, which may not be realistic. A space-oriented model is needed to simulate the regional concentration differences in the three environmental compartments; and emissions from production sites, handling and transport would need to be included. Transformation, degradation, and bioaccumulation of nanoparticles have been intentionally neglected in this paper, but they may play an important role.

In this study several flows between environmental compartments were not examined. Follow up studies are necessary taking into account secondary compartments (groundwater, sediments), surface erosion, and irrigation. Especially the water-sediment partitioning of NP should be studied, but currently no data are available which would allow one to do quantitative modeling. In order to extend the model to other countries, the application of sludge to the soil should also be considered. As the model assumes a more than 90% removal during wastewater treatment, the addition of sludge to agricultural land would pose a significant input of NP into soils. A rough calculation shows that this would result in an input of about 1 µg/kg<sup>3</sup> nano-Ag and 120 µg/kg<sup>3</sup> nano-TiO<sub>2</sub> per year if 50% of the agricultural land receives all sludge.

In the air compartment, the PEC for all three substances was very low, which is mainly due to the large volume of the air compartment. It was also found that nano-Ag and nano-TiO<sub>2</sub> are generally less likely to be released into the air than into water or soil, whereas CNT almost exclusively end up in the air and soil compartment. In the water compartment, the expected concentrations of nano-Ag are lower than the  $PEC_{\text{nano-TiO}_2}$  by a factor of 20 - 200. The continuous dissolution of nano-Ag in water, which would further decrease the amount of nanoparticulate silver in the water compartment, was not considered. The actual concentration of nano-Ag in water can, therefore, be expected to be even smaller.

When comparing the substance flowcharts of nano-Ag and nano-TiO<sub>2</sub>, it is obvious that the main particle flow takes place from the products to the STP, from there to the WIP and finally to the landfill (for nano-Ag around two-thirds and for nano-TiO<sub>2</sub> around three-quarters of the total particle volume). The particle flow from the WIP to the landfill turned out to be the predominant flow of all three substances due to the relatively high filtering efficiency of the wastewater treatment and the waste incineration plants. Leachate from landfills was neglected in this modeling, as the standard of landfills in Switzerland is high. But as the identified flows of NP to landfills are important, it will be necessary to study the possibility of leachate from landfills more closely.

It can be noticed that the PEC values for CNT are the lowest of the three NP in all environmental compartments. It has been stated that currently very little of these very expensive materials will find their way to contaminate the outdoor environment (27). Even within production facilities the concentrations measured in the air and on gloves were small (28). It has to be expected, though, that in the future—when the price of CNT falls and CNT application in consumer products becomes more widespread—the concentration in the environment will increase considerably. The system flowchart of CNT shows no particle flow to the STP (and the water compartment). In the current situation for Switzerland the particles are almost exclusively exported (leaving the system boundary) or transported to the WIP. Because CNT are partially burned in the WIP, the percentage of CNT in the landfill is lower than with the other two substances (one-fifth to about half of total particle volume). However, with an increasing variety of products that contain CNT, the CNT flows may change considerably.

The current lack of studies on the ecotoxicity of all substances in all compartments makes it difficult to evaluate the risks to organisms. Almost no studies for organisms in the soil compartment exist to date and the NOEC-values

**TABLE 3. Predicted Environmental Concentration (PEC) of Nano-Ag, Nano-TiO<sub>2</sub> and CNT in Air, Water, and Soil<sup>a</sup>**

	unit	nano-Ag		nano-TiO <sub>2</sub>		CNT	
		RE	HE	RE	HE	RE	HE
air	μg m <sup>-3</sup>	1.7 × 10 <sup>-3</sup>	4.4 × 10 <sup>-3</sup>	1.5 × 10 <sup>-3</sup>	4.2 × 10 <sup>-2</sup>	1.5 × 10 <sup>-3</sup>	2.3 × 10 <sup>-3</sup>
water	μg L <sup>-1</sup>	0.03	0.08	0.7	16	0.0005	0.0008
soil	μg kg <sup>-1</sup>	0.02	0.1	0.4	4.8	0.01	0.02

<sup>a</sup> RE: realistic scenario; HE: high emission scenario.

found in the literature vary substantially. For nano-TiO<sub>2</sub>, for example, the values differ by up to a factor of 1000, highlighting the fact that the methods/materials applied in the studies are not comparable and further research with standardized tests are needed.

The wide range of values observed is mainly due to a difference in the methods applied and in the material used. Differences in size, shape, modification and purity may considerably influence the result (29, 30). It has been shown that hydrophobic coatings usually tend to lower the inflammatory response after inhalation or instillation (31, 32). A precise characterization of the particles used is thus necessary. In this study, it was not possible to consider particle differences due to the patchy base data, neither for the substance flow modeling nor for the toxicological evaluation. When analyzing the results, it should therefore be kept in mind that the size and the functionalization of NP will have a great influence on their effects. However, this has been partially taken into account by using the large assessment factor of 1000.

The EC<sub>50</sub>- and EC<sub>100</sub>-values for nano-Ag are much larger than the LC<sub>50</sub> value of ionic silver. EC<sub>50</sub>-values of 20–40 mg/L nano-Ag were found for the water compartment (25, 33), while the LC<sub>50</sub>-values of Ag<sup>+</sup> range between 0.0007 mg/L (algae) and 0.002 mg/L (daphnia) (7). In consideration of the fact that ionic silver (in water) is around 10 000 times more toxic than nanoparticulate silver (according to the data presently known), the release of silver in the form of nanoparticles is of subordinate importance compared to the release of ionic Ag from NP.

Based on the PEC-values received in this study, it is now possible to make a first estimation as to what substances and compartments may pose the highest risk. This evaluation, however, needs to be very critically examined and should only provide a rough approximation. A low risk quotient does not necessarily mean that this compartment is risk-free; instead, further detailed experimental and modeling studies should focus on all aspects. The modeling shows that the concentration of nano-TiO<sub>2</sub> in water may pose a risk to aquatic life (risk quotient >0.73 and >15.83 in the RE- and HE-scenario, respectively). In this case, the EU authorities state that the substance is of concern and ask that more data is gathered to validate the result (34). The behavior and ecotoxicity of nano-TiO<sub>2</sub> in water and especially wastewater should, therefore, be studied more closely.

The expected concentrations of CNT and nano-Ag probably pose little risk based on the data presently known. Assuming that the PNEC-values are accurate and the ways of release stay the same, the production volume of nano-Ag would need to increase 100 times in order for the risk quotient to rise to about 1. Please note that this calculation does not include the risk emanating from ionic silver. In the case of CNT the paths of release will change with an increasing variety of products that contain CNT. An extrapolation of the RQ<sub>CNT</sub> to the future is thus not possible. It has also to be considered that this study did not include emissions from production sites, and it assumed well mixed environmental compartments, which denotes that much higher concentrations could be found locally, e.g., around production sites.

**TABLE 4. Calculation of the Risk Quotient (PEC/PNEC) for Water, Air, and Soil<sup>a</sup>**

	nano-Ag		nano-TiO <sub>2</sub>		CNT	
	RE	HE	RE	HE	RE	HE
air	nd	nd	0.0015	0.004	1.5 × 10 <sup>-5</sup>	2.3 × 10 <sup>-5</sup>
water	0.0008	0.002	>0.7	>16	0.005	0.008
soil	nd	nd	nd	nd	nd	nd

<sup>a</sup> nd: not determined due to lack of ecotoxicological data.

### Supporting Information Available

Four Tables showing the derivation of the weighing factors “article” and “weight” for nano-Ag and nano-TiO<sub>2</sub>. Three Tables summarizing production volumes of nano-Ag, nano-TiO<sub>2</sub> and CNT. One Figure with an overview of the model compartments of the flow coefficients. One Figure with the material flow diagrams for the RE-scenario of nano-Ag, nano-TiO<sub>2</sub> and CNT. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ES7029637