Engineered nanomaterials in rivers – Exposure scenarios for Switzerland at high spatial and temporal resolution

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Abstract

Probabilistic material flow analysis and graph theory were combined to calculate predicted environmental concentrations (PECs) of engineered nanomaterials (ENMs) in Swiss rivers: 543 river sections were used to assess the geographical variability of nano-TiO₂, nano-ZnO and nano-Ag, and flow measurements over a 20-year period at 21 locations served to evaluate temporal variation. A conservative scenario assuming no ENM removal and an optimistic scenario covering complete ENM transformation/deposition were considered. ENM concentrations varied by a factor 5 due to uncertain ENM emissions (15%–85% quantiles of ENM emissions) and up to a factor of 10 due to temporal river flow variations (15%–85% quantiles of flow). The results indicate highly variable local PECs and a location- and time-dependent risk evaluation. Nano-TiO₂ median PECs ranged from 11 to 1 ng L⁻¹ (conservative scenario) and from 2 to 1618 ng L⁻¹ (optimistic scenario). The equivalent values for nano-ZnO and nano-Ag were by factors of 14 and 240 smaller.

1. Introduction

Production and application quantities of engineered nanomaterials (ENMs) are growing and it has to be expected that ecosystems will be exposed to significant levels of such materials (Wiesner et al., 2006, 2009; Nowack and Bucheli, 2007; Alvarez et al., 2009; Battin et al., 2009). Scientific awareness has been particularly focussed on aquatic pollution (Boxall et al., 2007; Battin et al., 2009; Farre et al., 2009; Perez et al., 2009). Battin et al. (2009) showed that nano-TiO₂ at ambient UV radiation levels and realistic nano-TiO₂ concentrations can have relevant impacts on natural microbial aquatic communities. ENMs are also envisaged for applications in environmental remediation techniques (Vaseashta et al., 2007; Baun et al., 2008) that lead to direct release of such material into aquifers (Zhang, 2003). Industrial and domestic products and wastes containing ENMs tend to end up in water: either they are released directly into rivers and lakes, e.g. from outdoor use of sunscreens, or indirectly via surface run-off, domestic or industrial wastewater (Moore, 2006).

Unfortunately, the quantitative detection of ENMs in the environment and the distinction between engineered and naturally occurring nanomaterial is still extremely limited (Tiede et al., 2008; Hassellöv and Kaegi, 2009). Thus, modeling the ENMs’ release to and fate in the environment is essential to estimate environmental exposure. Such estimations have to cover diffuse emissions from a large number of relevant ENM containing products and lifecycle stages. These include but are not limited to ENM release into the environment from ENM production, ENM incorporation into products and storage, use, waste generation and disposal of such products. Once released into the environment, this material will to some extent agglomerate, associate with suspended solids or sediments, potentially accumulate in organisms and enter the food chain or drinking water sources (Boxall et al., 2007).

Mass balance partitioning models have already been used to assess aquatic exposure to ENM. Boxall et al. (2008) proposed simplistic algorithms to predict concentrations of ENMs in water, soil, and air by means of a specified but non-comprehensive range of ENM applications. Blaser et al. (2008) calculated the flow of silver in the environment including dissolved silver released from nano-Ag in textiles and biocidal plastics. However, biocidal plastics and textiles were seen to account only for up to 15% of the total silver release into water. Water and sediment concentrations were estimated based on a river box model developed by Scheringer et al.
(1999), where each box was subdivided into a compartment of moving water, a compartment of stagnant water and a sediment compartment. Recently, ENM release and concentrations in the environment were predicted by analyzing the complete lifecycle of ENM and ENM containing products (Mueller and Nowack, 2008; Gottschalk et al., 2009). In these studies predicted environmental concentrations (PECs) and predicted no effect concentrations (PNECs) revealed risk quotients (PEC/PNEC) at regional (national) level indicating that at least risks to aquatic organisms from nano-TiO₂, nano-Ag and nano-ZnO in undiluted sewage treatment plant (STP) effluents cannot be excluded. O’Brien and Cummins (2010) predicted relative concentrations in surface water for environmental release of ENM from selected single products. Arvidsson et al. (2011) modeled particle number concentrations in aquatic environments by considering continuous ENM release and by focusing on possible particle agglomeration kinetics.

In order to overcome one of the main limitations of such PEC calculations at regional scale – i.e. the assumption of homogeneous material distribution within aggregated environmental compartments – the modeling of concentrations at higher spatial and temporal resolutions at a local level is required (ECB, 2003). As a consequence, to evaluate local, specific ENM concentrations in rivers, the following refinements are necessary: (i) the total (national) ENM emission should be distributed geographically, e.g. according to spatial population density; (ii) geographical and temporal variation of flow rates in rivers have to be considered; and (iii) the transport and fate of ENMs within the system – i.e. the real river network – need to be studied in more detail. The modeling framework presented in this study comprehensively addresses all three points mentioned above. The systems analysis enables a clear distinction between model input uncertainty (ENM emission and transport in rivers) and spatial and temporal variability, which is expected to be influenced by the geographical position in the river network.

Since previous results predicted the highest concentrations and risk coefficients in surface water for nano-TiO₂, nano-Ag, and nano-ZnO (Gottschalk et al., 2009), our study aims to calculate local PECs for these materials. Such concentrations are modeled along all rivers in Switzerland at base flow. This enables us to identify river sections where PECs are expected to exceed PNECs at minimum dilution. Additionally, for selected river sections complete hydrological information will allow us to expand the geographic evaluation by including temporal differentiation in the estimation of PECs and potential risks for aquatic organisms exposed to ENMs.

2. Materials and methods

2.1. ENM emission

The total annual and regional (national) amount of ENM (nano-ZnO, nano-Ag) discharged to rivers was taken from Gottschalk et al. (2009). The emission of nano-TiO₂ was computed by using new data on ENM production volumes (Robichaud et al., 2009) and the same lifecycle-based Monte Carlo (MC) method (Gottschalk et al., 2010). The modeled emissions reflect direct release of ENM during the whole lifecycle of these compounds and the products containing them (consumption and disposal phases), indirect emissions of these materials e.g. through STPs and entry of them via other natural compartments (atmosphere, soils, sediments). The data basis for modeling such emissions is represented by a comprehensive inventory and/or quantification of ENM production quantities, and commercially available ENM containing products categorized on the basis of their ENM content and potential for ENM release. The MC simulations consider the ENM emission uncertainties at each stage of the compounds’ lifecycle. In order to separate emission uncertainties from spatial and temporal variability in the results, the subsequent evaluations with the geo-referenced model were carried out with the modal (most frequent) emission value of these MC simulations.

2.2. Geographical distribution of ENM emission

For a local distribution of the regional ENM emission a segmentation of the regional STP box – and other relevant emission sources (e.g. the boxes for consumption of ENM containing products and those for natural compartments) – at high spatial resolution is necessary. In Switzerland over 97% of the population are connected to STPs. More than 700 STPs represent the local distribution of the population and define the discharge locations of treated wastewater. In a previous study a model was developed to calculate realistic pollutant loads originating from all these STPs (Ort et al., 2009). Only a minimum of input data was used: i) annual regional sales data for compounds of interest and ii) linear transfer coefficients – i.e. transformation of compounds during application and average elimination in STPs. Assuming a constant per capita consumption throughout the year resulted in a distribution of the emitted loads directly proportional to the population in the catchments of the STPs. With site-specific measurements environmental fluxes of several recalcitrant micropollutants in Swiss rivers have been demonstrated to directly correlate with the sum of people connected to STPs in the corresponding river catchments. In this study we apply the same concept and model structure to predict the distribution of ENMs. It is a fair assumption that the ENM consumption and emission are proportional to the population in the STP catchments, as they are for other pollutant loads in domestic wastewater. Determining local concentrations with this approach will lead to a range of environmental ENM concentrations close to what may be expected. Any evidence contrasting with a more or less homogeneous, constant ENM per capita emission will result in a wider range.

2.3. Water flow

In order to calculate local PECs, the expected ENM loads were divided by the corresponding local water flow. Base flow conditions were used to assess geographically variable dilution. Q₉₅ is the flow reached or exceeded in 95% of the time. Since this represented minimum dilution and maximal environmental risk (worst-case), Q₉₅ were available from previous studies: measured Q₉₅-values were taken from Aschwanden et al. (1999) and values for Q₉₅ at locations without measurements were estimated according to Staub et al. (2003). River sections without an estimate for the Q₉₅ only received treated wastewater from small STPs, overall serving approximately 5% of the total population. However, their ENM loads, as well as STPs discharging directly into lakes, were included in the simulations, but no concentrations could be calculated directly downstream from these STPs. This evaluation will identify river sections where high ENM concentrations can be expected. Twenty-one river sections – for which long-term discharge information was available – were used to assess temporal variability and exposure in more detail. With the evaluation of measured daily flow rates over a 20-year period (1988–2007) we intend to quantify the effect of temporal flow variations and not to assess historic ENM concentrations, since today’s ENM emissions were used. The historic flow variations are assumed to represent realistic variations to be expected in the near future.

2.4. Transport scenarios in rivers

Due to the absence or ambiguity of available data on ENM dissolution behavior or agglomeration/sedimentation rates and due to the fairly short residence time (<24 h) (Ort et al., 2009) of water in Swiss rivers between reservoirs (lakes), two “extreme” transport scenarios were considered: (i) a conservative scenario (Sₑ) without any ENM transformation/deposition in rivers and (ii) an optimistic scenario (Sₒ) with rapid (complete) ENM removal.

All the rivers were segmented into river sections that were treated as ‘closed units’, which were not further divided into subsections. Therefore, the modeled concentrations reflect in each case one single result for one single location (river section). For both scenarios and all locations these results represent the ENM concentration right after mixing sewage treatment effluent and river water. ENM decay after being emitted into river water was complete for Sₑ and zero for Sₒ. Complete in the sense that emitted ENM into a river section was removed from the liquid phase before reaching river water of the following section (infinitiesmally small concentrations). For modeling this, Sₒ considers for each river section only the ENM release via the sewage treatment effluent at the beginning of a corresponding river section. In contrast, Sₑ includes such ENM release at the beginning of a particular section as well as release from all upstream sewage treatment effluents. These two scenarios cover the whole possible spectrum of physical, chemical and biological processes ENMs may undergo after being discharged to receiving water bodies (agglomeration/disagglomeration, settling and sedimentation/resuspension, dissolution, interaction with molecular and ionic dissolved material or with biotic and abiotic suspended particles etc.).
midlands or near urban centers. The calculated values in rural, alpine and pre-alpine areas were negligibly small. Exceptions are river sections in the area of large tourist destinations in the Alps, where the PECs were comparable to the values of urban areas. Modeled PECs of all river sections for both scenarios (Sc and So) are summarized in box plots in Fig. 2. For Sc the simulations produced median values of 0.43 $\text{m g L}^{-1}/C_0^1$, for So 0.14 $\text{m g L}^{-1}/C_0^1$ nano-TiO$_2$. The corresponding min-max values showed differences by factors of 28'900 (Sc) and 122'000 (So), ranging from 0.27 ng L$^{-1}$–7.8 $\mu$g L$^{-1}$ and 0.05 ng L$^{-1}$–6.6 $\mu$g L$^{-1}$ nano-TiO$_2$. All corresponding concentrations for nano-ZnO and nano-Ag were smaller due to lower emissions (factor 14 (nano-ZnO) and 240 (nano-Ag), see also Fig. S1 in the Support Information). Obviously, the concentrations are generally higher for Sc compared to So. At the beginning of a river, impacted only by one STP, there is no difference between the two scenarios (217 river sections), whereas farther downstream, the scenarios differ from less than a factor of 2 (76 river sections) to over 100 (55 river sections) with a maximum of over 6'000 and a median of 6.

3.2. Temporal variation of nano-TiO$_2$ concentrations

A whole range of “typical cases” is represented with the 21 locations we analyzed: small to large rivers (highly variable to more attenuated flow rates) and predominantly alpine to urban catchments (low to high ENM emission). The range of temporal PEC variations for nano-TiO$_2$, based on daily flow rates in rivers over a 20-year period, is charted in Fig. 3. The concentrations were in agreement to the results obtained at base flow ($Q_{95\%}$) — significantly higher in urban regions (locations S,T,U) than in rural and alpine areas (A,B,C). Median nano-TiO$_2$ concentrations for Sc ranged from 11 ng L$^{-1}$ to 1'623 ng L$^{-1}$ and from 2 ng L$^{-1}$ to 1'617 ng L$^{-1}$ for

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**Fig. 1.** Predicted environmental concentrations (PEC) for nano-TiO$_2$ in 543 Swiss rivers at base flow conditions $Q_{95\%}$ (river discharge/flow reached or exceeded in 95% of the time) and categorized in different ranges of magnitude. A: conservative scenario without any removal of ENM from the water phase. B: optimistic scenario with rapid ENM transformation/sedimentation.

**Fig. 2.** Ranges reflecting all the predicted environmental concentrations (PEC) calculated for 543 river sections at base flow conditions $Q_{95\%}$ (river discharge/flow reached or exceeded in 95% of the time) (see also Fig. 1) for nano-TiO$_2$, nano-ZnO, and nano-Ag as well as for a fixed unitless (hypothetically assumed to be known) and nonspecified engineered nanomaterial (ENM) emission. White box: conservative scenario without any removal of ENM from the water phase. Gray box: optimistic scenario with rapid ENM transformation/sedimentation.
Minimum to maximum values at a given location differed approx. from a factor of 10 (locations L, J) to a factor 1'100 (location U). Varying differences were also observed for the two ENM transport scenarios at a given location. River sections impacted only by a few STPs at the beginning of a river showed negligibly small differences in the ENM concentrations between Sc and So. In 80% of the cases this difference was smaller than a factor of 10. Higher variation between the PECs for the two scenarios was modeled only for single sections located at the end of long rivers.

For the alpine Rhine after STP Rueun (location A) the smallest concentrations were simulated: the PECs varied approx. by a factor 170 ranging from 0.9 ng L\(^{-1}\)-144 ng L\(^{-1}\) nano-TiO\(_2\) for the conservative scenario. They were almost zero for the optimistic scenario (only in dry years up to 12–17 ng L\(^{-1}\) for a few days). Some of the highest concentrations were observed within a lowland river section of the Ergolz after the STP Liestal (location T). The PECs varied by a factor of 540, ranged from 27 ng L\(^{-1}\)-14.5 µg L\(^{-1}\) (Sc) and 10 ng L\(^{-1}\)-5.5 µg L\(^{-1}\) nano-TiO\(_2\) (So). All the corresponding concentration values for nano-ZnO and nano-Ag were again smaller approximately by factors of 14 and 240.

### 3.3. Risk potential estimation

In order to evaluate the potential risk caused by environmental exposure to the investigated materials, we compared our modeled PECs to currently available PNECs. The highest PECs were found for nano-TiO\(_2\). In 34% of the river sections a current PNEC of 1 µg L\(^{-1}\) \((\text{Gottschalk et al., 2009})\) would be exceeded at base flow conditions for Sc and in 23% of all cases for So (pink, purple and black dots in Fig. 1). The corresponding values for nano-ZnO were 45% and 30% and for nano-Ag 75% and 48%, the respective PNECs 40 ng and 75 ng. As shown in Figs. 1 and 3 (Figs. S1 and S2 in the Supporting Information) critical concentrations for all three metals were almost exclusively found in urban areas. In rural regions the modeled PECs were mostly far below the corresponding PNECs even when considering minimal dilution (base flow conditions).

The PEC/PNEC comparison for 21 river sections based on historic river flow data (median flows) led to similar results. For all three metals some river sections in urban/industrial areas showed PEC values higher than the PNECs for both ENM transport scenarios. Between 8% (location M) and 68% (location U) of the time the simulated nano-TiO\(_2\) values exceeded the PNEC for surface water. The equivalent percentages for nano-ZnO were 5 (location K) and 85 (location U), those for nano-Ag 5 (location E) and 98 (location U).

In contrast the ENM concentrations in almost all the rural rivers did not exceed such PNECs even for Sc (no ENM removal from liquid phase). Hence, currently no significant risks are posed by these ENMs to aquatic organisms in non-urban rivers. However, significant exposure in urban water bodies to these metals is possible and, therefore, needs more detailed investigations.

### 3.4. Emission uncertainty versus geographical and temporal variability

Table 1 gives more insight into the question as to which of the investigated parameters has the most significant influence on the prediction of PECs for these materials: i) the ENM emission uncertainty, ii) the geographical flow variation among locations, iii) temporal variation at a given location, or (iv) the ENM transport scenario (with or without ENM transformation/deposition). In order to facilitate the comparison of model input uncertainty and natural variability, we ran simulations with one hypothetical uncertainty value. This value was determined such that the smallest concentration was 1 (unitless, see also Fig. 2). We evaluated and report both 15%–85% ranges of modeled PECs and in brackets minimum to maximum concentrations. Uncertain ENM emissions from Monte Carlo-simulations \((\text{Gottschalk et al., 2009})\) yielded a concentration variation of a factor 5 (min–max: \(1.6 \times 10^3\)). Temporal variation of dilution (analyzed by considering measured flow rates over a 20-year period) revealed PEC variation for a particular river section of up to a factor 10 (min–max: \(1 \times 10^2\)). A factor 5 (min–max: 200) would e.g. be observed at location K, the highest just mentioned factors at location S. For two thirds of the river sections the range of such temporally variable dilution was higher than the one caused by the uncertainty of ENM emission (see Fig. 3). Regardless of the evaluation range the two different ENM transport scenarios produced PEC values that differed e.g. approx. by a factor 2 for location K (river stretch in the upper part of a river course influenced by only a small number of STPs) and by a factor 30 for location S (river stretch at the end of a river course influenced by the discharge of many STPs). However, for most locations the influence of such factors on the modeled PECs was much smaller than the one caused by ENM emission uncertainty (15%–85% quantiles). 50% of all simulated PECs varied less than a factor 6 between these two scenarios (not shown in Table 1). Geographical variation, assessed at base flow \(Q_{0.95}\) for 543 river...
sections, yields differences of concentrations among locations of up to a factor of 370 (min–max: 1.2 × 10^3). These results show that by far the greatest influence on the ENM PECs in rivers could be allocated to a combination of geographical distribution of the ENM release and spatially variable dilution. Dilution due to temporal river flow variations has for most river stretches the second highest influence. The effect of dilution on the modeled PECs is at least as high as the one of ENM emission uncertainty. Finally, our analysis showed that the influence of the ENM transport scenarios on the PECs is lower than spatial and temporal variability of dilution in rivers.

### 4. Discussion

In order to model realistic PECs of ENM in rivers it is essential to i) account for realistic local dilution (data available, but not considered in fate models), ii) reduce uncertainty on ENM release (gather more detailed input data independent of model complexity: geographically resolved information on ENM production and use as well as empirical information on the ENM release from products containing these materials) and iii) consider the fate and behavior of these compounds in the liquid phase in detail.

i) Dilution: As already shown for the constant entry of pharmaceuticals (Ort et al., 2009) and then revisited for estrogens and phosphate (Johnson, 2010), natural flow variations considerably influence contaminant concentrations in rivers. These variations make it impossible to indicate individual values as relevant environmental concentrations; a concentration distribution or range is more appropriate. This also holds true for ENM in a particular river even when assuming a constant per capita emission. Whenever the ENM emission is not constant and varies among individuals or among different STP catchments, this range is even higher.

ii) ENM emission: The total ENM emission into rivers in our work was distributed to each individual river section based only on the population each STP served. This is reasonable as long as the studied ENM are used mostly in household products like cosmetics, coatings, cleaning agents and textiles (Gottschalk et al., 2009). Such a geographical allocation should be refined e.g. whenever the industrial ENM emission is known to be dominant in a certain catchment. Direct industrial emissions such as e.g. release into rivers from ENM production and incorporation into products or from ENM transport processes may occur as well. However, an almost complete lack of data to such direct emissions makes these ENM release calculations very difficult. If one wanted to improve this part of the model, a distinction would be necessary among the quantities of ENM produced, imported and exported. Ensuring that such data from industry (apart from commercially confidential information) becomes publicly available would be crucial for improving the simulations of ENM environmental concentrations and the subsequent risk assessment.

Another point is the necessity of integrating in the calculations time-dependent parameters for modeling the ENM emission into the environment. Such a temporal differentiation in the ENM emission should also account for unforeseen and possibly extreme ENM release events: accidents with ENM and products containing ENM, or e.g. new products on the market with high ENM release potential.

iii) Fate and behavior of ENM in rivers: As a comprehensive understanding of ENMs' fate in rivers is still far off, our scenario S_c of no ENM transformation/deposition, as well as the optimistic one S_o (full ENM removal from the river water), are only to be taken as approximations of the uncertainties and ambiguities of the potential ENM degradation and removal processes in water. As seen above, PECs at a given location differ to varying degrees between S_o and S_c: the effect of considering or not considering deposition/transformation processes in our model primarily depends on the size of the STP (local) and the number and size of STPs (upstream).

In the literature fast deposition rates leading to almost full sedimentation after 24 h were shown in Boncagni et al. (2009) e.g.
for commercially available aerogel P25 TiO₂. In contrast, for sol-gel synthesized porous anatase TiO₂ almost no sedimentation was observed. As these two types of nano-TiO₂ showed totally different deposition/agglomeration properties, the authors state that examining more types of this compound would be necessary to draw generic conclusions about the fate and behavior of this material in water. Battin et al. (2009) complemented the results of Boncagni et al. (2009) by studying effects of benthic biofilms on ENM exchange between water and streambed. Biofilms strongly affected the travel distance of two types of nano-TiO₂. Hombikat UV-100 and P25 nano-TiO₂ were predicted to travel without biofilm 10 and 12 km downstream before being removed from the liquid phase. However, biofilms in the flume reduced significantly such transfers. As the authors state, river water streambed roughness and hydrodynamic exchange could as well shorten the travel distance. Also contrary effects on ENM transport length due to ratios of flow velocity to streambed depth that differ from the experimental conditions could not be excluded. Microbial changes to ENM chemistry and biofilm detachment as a possible mechanism in the ENM fate in aqueous environments should be studied as well.

The comparison of the modeled PECs with ecotoxicological values reveals that risks to aquatic organisms for all three investigated ENM cannot be excluded. This evaluation (a simplified approach within a complex field of data uncertainty in risk analysis (Scholz et al., 1997)) does not mean that an immediate risk is present because the PNEC values include a safety factor of 1000, that these risk estimations definitely call for more chronic ecotoxicity data at environmentally realistic exposure concentrations of nano-TiO₂, nano-Ag and nano-ZnO. New knowledge on the environmental fate of ENM may also completely change this risk assessment. The risk analysis for Ag, for example, assumes that nano-Ag remains as zero-valent Ag particle in water; however, recent results indicate that in wastewater rapid transformation of nano-Ag into nano-silver-sulphides occurs (Kim et al., 2010; Nowack, 2010; Kaegi et al., 2011). This reaction would not affect our modeled PEC values but rather the choice of the PNEC and the form of the nano-Ag to be studied in natural waters.

5. Conclusions

This study differentiates for the first time between uncertainty of input parameters and effects of measurable, natural variability (for ENM and calculations at high spatial and temporal resolution). Geographical variation — caused by the local distribution of ENM emissions and spatially variable, local dilution — has by far the greatest influence on the modeled PECs revealing a factor of up to 300 (15%–85% quantiles) for the optimistic scenario with rapid ENM removal from water. In comparison, a variable dilution at a given location can cause concentration variations over time up to a factor 10 and the uncertain release of total annual ENM loads by a factor 5 (both 15%–85% quantiles). For most river stretches the different ENM transport scenarios have the smallest impact on the results.

Experimental validation of the calculations would be highly desirable, but it is still not possible to assess and quantify at trace concentrations the nano-sized fraction of a material in the environment (Hasseliov et al., 2008). Our modeling results provide, however, analytical method developers with improved estimates of expected environmental concentrations that a successful method needs to achieve.

Our results also provide ecotoxicologists with possible nano-Ag, TiO₂ and ZnO concentration ranges in rivers that can be used to design tests of acute and chronic toxicity and that aid in the evaluation of toxicity data. The data also gives hints as to which river stretches the highest concentrations should be expected, and thus where effects might be observed first on aquatic and benthic communities.

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Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.envpol.2011.08.023.

References


