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# Comprehensive probabilistic modelling of environmental emissions of engineered nanomaterials



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# ABSTRACT

Concerns about the environmental risks of engineered nanomaterials (ENM) are growing, however, currently very little is known about their concentrations in the environment. Here, we calculate the concentrations of five ENM (nano-TiO<sub>2</sub>, nano-ZnO, nano-Ag, CNT and fullerenes) in environmental and technical compartments using probabilistic material-flow modelling. We apply the newest data on ENM production volumes, their allocation to and subsequent release from different product categories, and their flows into and within those compartments. Further, we compare newly predicted ENM concentrations to estimates from 2009 and to corresponding measured concentrations of their conventional materials, e.g. TiO<sub>2</sub>, Zn and Ag. We show that the production volume and the compounds' inertness are crucial factors determining final concentrations. ENM production estimates are generally higher than a few years ago. In most cases, the environmental concentrations of corresponding conventional materials are between one and seven orders of magnitude higher than those for ENM.

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# 1. Introduction

The rapid increase in the production and use of ENM makes it likely that increasing environmental exposure to them will occur (Gottschalk and Nowack, 2011). Release of ENM into the environment may occur throughout their entire life cycle: from their production to the fabrication of ENM-containing products, to the use and end of life phase of those products. Risks from ENM emissions may emerge if both exposure (due to the presence of ENM in the environment) and hazard (in the form of toxic effects) are observed (Aschberger et al., 2011). Therefore, understanding environmental exposure and the toxicity of ENM provides the basis for assessing the environmental risks posed by these compounds. Knowledge on the hazard side is increasing exponentially (Klaine et al., 2008; Scown et al., 2010); however, there are currently almost no specific trace analytical methods available to quantify ENM in environmental samples, e.g. water, wastewater or biosolids (Kim et al., 2012; von der Kammer et al., 2012). Currently, to perform a proactive environmental risk analysis, the only way to obtain information on existing levels of ENM in the environment is to model predicted environmental concentrations (PEC). To derive these, we

0269-7491/\$ - see front matter © 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.envpol.2013.10.004 particularly need information on the flows of ENM into the environment. Material-flow modelling, which predicts and quantifies flows and stocks of materials or substances in a well-defined system, is an established method of deriving flows of materials to the environment (Baccini and Brunner, 2012). It is used at different spatial and temporal scales accounting for material flows within and between anthropogenic and connected ecosystems.

To date, only a few modelling studies have presented quantitative estimations of the environmental concentrations of ENM (Blaser et al., 2008; Boxall et al., 2007; Gottschalk et al., 2013, 2009; Hendren et al., 2013; Johnson et al., 2011; Keller et al., 2013; Mueller and Nowack, 2008). Furthermore, most of these studies only targeted one or two ENM and focused on scenarios considering just a few applications, e.g. nano-TiO<sub>2</sub> use in sunscreens (Arvidsson et al., 2011; Musee, 2011). These scenario-based models, therefore, cannot be representative of the total real levels of ENM currently in the environment. Data on environmental concentrations using a material-flow model of ENM were published in 2008 (Mueller and Nowack, 2008) and 2009 (Gottschalk et al., 2009), but these were necessarily based on the limited information available at that time on the behaviour of ENM in technical and natural systems. The recently published study by Keller et al. (2013) provided the first global assessment of the likely ENM emissions to the environment for ten most produced ENMs applications by combining ENM market information and material flow modelling. However, the



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production and use input data of the whole study relied solely on one single market report, and it is thus not transparent as to how the information was compiled. Because of this it is difficult to access the amount of uncertainty in the dataset itself, which therefore leads to unknown uncertainty of all their results. Mechanistic models specifically considering agglomeration and sedimentation reactions of ENMs have also been developed in Arvidsson et al. (2011). Praetorius et al. (2012). Modelled results may rapidly change due to the fast development of ENM production and applications; what is more, the availability and quality of published information on fate and behaviour have increased enormously in the last few years and thus we have a much better understanding of the behaviour of ENM in the environment. These two factors call for a more comprehensive and up-to-date prediction of ENM flows to the environment (surface water, soil, sediment, air), which is the main aim of this study. The new modelling effort is necessary to identify possible trends in production and concentrations and with the current knowledge a much more robust and comprehensive understanding of the flows is possible.

We must also remember that ENM constitute only a portion of the nanomaterials existing on earth and conventional materials produced in high volumes (such as TiO<sub>2</sub> pigment) may contain a nano-sized fraction (Weir et al., 2012). Also, several studies (Akaighe et al., 2011; Glover et al., 2011) have reported that metallic silver nanoparticles can be generated under environmental conditions from sources such as silver wire or jewellery. Therefore, an additional aim of this work was to compare the environmental concentrations of ENM with that of their corresponding conventional materials.

We modelled for nano-TiO<sub>2</sub>, nano-ZnO, nano-Ag, CNT and fullerenes. These materials were selected because either they are used in large amounts (nano-TiO<sub>2</sub>, nano-ZnO), are contained in many products (nano-Ag), or because a relatively large amount of information is available about their properties (CNTs and fullerenes). The material flows of TiO<sub>2</sub> pigment were modelled as the conventional counterpart to nano-TiO<sub>2</sub>. The modelled concentrations of nano-Ag and nano-ZnO were compared to the measured concentrations of total Ag and Zn metal in the different environmental compartments.

#### 2. Methods

#### 2.1. Model structure, system boundary and assumptions

Fig. 1 presents the general material-flow model. The basis for the modelling is knowledge about the total use of certain ENM in a defined region (in our present model, the EU and Switzerland) and the distributions of their mass to different product categories. Product life-cycles then determine any possible releases of ENM into the environment. Apart from releases during their production and incorporation into products, the majority of the releases of ENM into the environment take place during the use and disposal phases. The model grew from the approach developed by Gottschalk et al. (2010), but with a more comprehensive description of the processes in technical systems, for example, sewage treatment plants (STP) and waste incineration plants (WIP). The model applies a stochastic approach to computing probability distributions of mass flows and PEC, by means of Monte Carlo simulations and Markov Chain Monte Carlo (MCMC) (Martin et al., 2011) modelling. This allows the model to cope with the uncertainties and inherent variability of its parameters (ENM production volumes, transfer coefficients etc.).

The material flows of ENM can be used to predict averaged concentrations of ENM in technical and environmental systems. This was achieved by calculating the total input flows into compartments using the material-flow calculation and then dividing the amounts remaining in each compartment by the volumes of the respective compartments. For air and surface water, a retention time of 10 (Anastasio and Martin, 2001) and 40 (ECB, 2003) days were used, therefore 10/365 and 40/365 of the total input flows into these compartments were considered as the fraction of ENM remaining in the two compartments. Different compartmental volumes were calculated based upon ECHA's technical guidance (ECHA, 2010), as explained in detail in Gottschalk et al. (2009), with environmental concentrations assuming well-mixed, homogeneous compartments. A summary of the calculated compartment volumes is shown in Supplementary Table S-6. The concentrations calculated are therefore average values. For surface water the concentrations correspond to a no-



**Fig. 1.** General structure of the material-flow model. The model's principle is to track ENM flows throughout the entire life cycle: ENM production; incorporation into products; ENM release from products during use; transport and fate of ENM between and within STP, WIP, landfill and recycling processes (technosphere); transfer from technosphere to air, soil, water and sediments (ecosphere); and transport within environmental compartments. The amounts of ENM in the compartments provide the basis for calculating the overall environmental concentrations of ENM.

sedimentation scenario which means no fate of ENM in water was considered, representing the initial concentration after mixing of surface water and wastewater effluents. Sediment concentrations on the other hand reflect the full-sedimentation scenario, representative of the sediment concentrations over the long-term with complete sedimentation (Gottschalk et al., 2011). The method used to estimate the masses of solid waste, bottom ash and fly ash in WIP can also be found in the Supplementary Information.

The modelling for the EU considers average data for the European Union, for example the household wastewater connection rate to wastewater treatment plants, the percentage of waste going to landfill or incineration. It thus represents an "averaged EU". The numbers are based on the standard risk assessment of chemicals as performed according to REACH (2007), so these parameters are generally accepted to represent an averaged region in material-flow and environmental fate modelling. Transfer factors from one compartment to another were estimated, incorporating the current knowledge on fate and behaviour in these compartments. Details about the mathematical model, the system equations, the modelling of distributions and the Monte Carlo simulations are given in Gottschalk et al. (2010).

#### 2.2. Input data preparation

All the model input parameters were treated as probability distributions; the methodologies for these probability distributions were chosen by analysing the raw data. Raw data – obtained from published papers and reports, but also from experts - were classified according to a degree of belief (DoB) scale (80% for high and 20% for low DoB are used, respectively). The DoB of the data were judged according to their reliability: e.g. for ENM production volumes, a high DoB was assigned to data from peer reviewed papers explicitly investigating this topic, with detailed, clear descriptions of how data were obtained. First hand commercial market information via personal communication also scored a high DoB. Surveys of companies also received a high DoB. Data from reports or presentations where only numbers were available, without further reference or explicit explanations as to their sources, scored a lower DoB. For transfer coefficients, like STP removal efficiency, the highest DoB was assigned to experimental results from full-scale STP, a medium DoB was given to data from pilot STP, and the lowest DoB was assigned to results from laboratory scale or batch reactor experiments. Complete data on ENM production volumes and STP removal efficiency, together with their DoB, are summarized in Supplementary Tables S-1 and S-3. DoB was reflected in the Monte Carlo modelling by assigning more or fewer samples (proportional to their DoB) to the corresponding input data. For example, if in total there are three data sources for one parameter are available and they are assigned DoBs of 20%, 30% and 50%. If the total simulation for this parameter is 100,000 times, we will assign 20,000, 30,000 and 50,000 samples respectively for these data sources to express their likelihood and differentiate their reliability. MCMC, as a combination of Bayes inference and Monte Carlo method, is considered to include data with different DoB from different sources and to produce a normal distribution (Gottschalk et al., 2010) e.g. for nanomaterial production and use (see section on Characterization of production volume of ENM).

In many cases we have only a single data point for a certain parameter; in such cases this single value is deviated  $\pm 50\%$  and a triangular distribution is obtained. This approach was applied for the major part of the parameters in our modelling, e.g. ENM release rate from product to disposal or environment (*see* Supplementary Table S-2), connection rate of wastewater to STP, or STP sludge disposal. For all the parameters where minimal, mode (mean) and maximal values were available, such as for the allocation of ENM to product categories, triangular distributions were also applied.

Many data were available in the form of a range or pair of values. For these data a general uniform distribution was used to produce the input distributions. Examples are the filter removal efficiency of WIP, or TC from soil to surface water. For parameters exhibiting uncertainty and variability, and where there were many different data sources – such as STPs' ENM removal efficiency (Supplementary Table S-3) – a simple random Monte Carlo sampling of empirical raw data, combined with a uniform distribution (ranging from 0 to 1 by the inherence of these parameters), was used to produce probability distributions for these parameters. The distribution generated includes all the information contained in these data and at the same time is able to represent the inherent variability of these Transfer Coefficients (TC) (the inhomogeneity of the same type of ENM can lead to a variety of TC for the same process). Our modelling also used a standard normal distribution for overflow rates, for example, for which both mean value and standard deviation were known (Staufer, 2012).

#### 2.3. Characterization of ENM production volumes

Production volume is an important input parameter for any material-flow model. We therefore screened all the available publications and studies published after 2008 reporting information on ENM production or use (data sources and raw data are summarized in Supplementary Table S-1). Global and regional (e.g. U.S.A.) production or use data were extrapolated to Europe and Switzerland in proportion to Gross Domestic Product; detailed principles are given in Supplementary Information "Production volume of ENM". The production/use probability distributions were obtained by feeding these data into simple MCMC algorithms (Martin et al., 2011) that produce for each ENM studied a sample from the posterior distribution of a normal likelihood with known variance and a normal prior (see Fig. 2). Prior mean and variance values (derived from the 20% weighting factor data, see Supplementary Table S-1) were combined with newer evidence on central tendency and spread (derived from the 80% weighting factor data), so as to benefit from Bayes inference and compute the joint posterior distributions. In the EU, the most produced/used ENM of the five studied is nano-TiO<sub>2</sub>, with an annual production of about 10.000 tonnes (t); followed by nano-ZnO with a production of around 1600 t; then CNT, around 400 t; nano-Ag, around 30 t; and finally fullerenes, with about 20 t



**Fig. 2.** Yearly ENM production distribution and mode values in the EU (t) in 2012. Raw data of ENM production or use (see Supplementary Table S-1) were classified into groups according to their degree of belief (DoB), which, according to Huber (2009) formally represent the strength with which we believe in the truth of various propositions, e.g. data from peer-reviewed studies received a higher DoB than values extracted from reports without information on the methods used to obtain them. DoB was reflected in the modelling by assigning more or less samples (in proportion to their DoB) to the corresponding input data. These data were treated with MCMC(Martin et al., 2011) to obtain annual probability distributions of the production/ use amounts in the EU for the five ENM investigated.

per year. The full probability curves were used as input into the material-flow modelling described below.

#### 2.4. Characterization of model parameters

Our model tracks ENM release throughout the entire life cycle of the products containing them, therefore knowing how much ENM is incorporated into which products is essential. Information from various sources was combined to allocate ENM to different products. A company survey by Piccinno et al. (2012) provided direct distribution data for various ENM. These data were complemented using publicly available nano-product inventories that were analysed and summarized so as to make them ready for modelling purposes: the inventory of the Woodrow Wilson Centre for Scholars' Project on Emerging Nanotechnologies; (WWI, 2012) the ANEC/BEUC Inventory (ANEC/BEUC, 2010); the BUND inventory (BUND, 2011); a summary of recent nanotechnology patents (Lem et al., 2012) and a comprehensive nano market report (Future Markets, 2011). We also conducted an internet search using Google, Yahoo and EC21 for counting the numbers of products for wide variety of applications available on the market. The information obtained from these sources was either the share of ENM in certain applications (which can be used directly) or product numbers that were used to obtain product shares as described by Gottschalk et al. (2009) Each product category was assigned relative shares according to different sources. Minimal, maximal and average values were calculated from these assigned shares for each product category and form the basis for building triangular distributions, see Supplementary Table S-7. Supplementary Figure S-2 shows the mean percentages of ENM allocated to different product categories. calculated from the sources mentioned above, which were used as modes for generating triangular distributions.

The next important modelling step was to define during which life cycle stages ENM release occurs and how much is released into which technical or environmental compartments. Supplementary Table S-2 shows the transfer factors for ENM released from products into these compartments. These transfer factors were estimated based on published release studies, for example for textiles (Geranio et al., 2009; Lorenz et al., 2012) and paints (Kaegi et al., 2008; Kaegi et al., 2010); fate studies in STP (Kaegi et al., 2011; Lombi et al., 2012) and WIP (Walser et al., 2012). Release can occur onto technical compartments, e.g. wastewater treatment plants or directly into the environment, e.g. from bathing in natural waters after application of sunscreen.

Our modelling is based on transfer factors that summarize the overall transport behaviour from one compartment to another. For sedimentation from air for example we base the transfer factor on the known life-time of ultrafine particles because no data about ENM in the atmosphere are available (Anastasio and Martin, 2001). However, we don't use one single value for these transfer coefficients but produce probability distributions that consider variability between different studies and uncertainty based on the available knowledge. As stated above, our primary source of data are studies that are able to deliver an overall transfer factor. Top soils are treated as final sinks and thus no fate processes are modelled. Also the sedimentation in natural waters was not modelled in this work because empirical data describing the important heteroagglomeration process are not yet available (Praetorius et al., 2012). The flow from surface water into sediments was therefore predicted based on two extreme scenarios; no sedimentation and complete sedimentation. Dissolution, phase transformation, degradation, incineration and other removal processes were modelled as flows going into an "elimination" compartment. CNT and fullerenes, for example, can be burned in WIP (Mueller et al., 2013); the majority (85%-100%) (Kaegi et al., 2011) of nano-Ag is transformed into silver sulphide in STP; and nano-ZnO can be completely transformed into other non-nano forms during the anaerobic digestion process in STP (Lombi et al., 2012). The fate and behaviour of the ENM relevant for transfer between the compartments is described in detail in the Supplementary Information. All transfer factor are given in the Supplementary Table S-2.

#### 3. Results

#### 3.1. ENM flows

Flows of the five ENM, from production and use through release into all the compartments, were modelled by combining the modelled production volumes, product distributions and transfer factors between all the compartments. The material-flows calculated for nano-TiO<sub>2</sub>, nano-ZnO, nano-Ag, CNT and fullerenes in the EU are shown in Fig. 3. The corresponding material-flows for Switzerland can be found in Supplementary Fig. S-3. Flows leaving the system describe ENM flows out of the system boundary considered, e.g. export or river flow into the sea. ENM might be transformed or degraded before they end up in environment. Nano-Ag and nano-ZnO can be transformed into other forms in the anaerobic phase in a STP or be dissolved in the acid washing



PMC: Production, Manufacture and Consumption; N&U soil: natural and urban soil; ST soil: sludge treated soil

process in a WIP. Carbon-based ENM can be completely destroyed through the combustion processes in WIP (Mueller et al., 2013). All these processes are regarded as ENM elimination and the corresponding flows lead to a virtual elimination compartment representing the loss of these materials. ENM can also accumulate in landfills, soils and sediments, as indicated by the black squares in Fig. 3, with a yearly increment.

The most prominent flows for nano-TiO<sub>2</sub> and nano-ZnO were from production, manufacturing, and consumption (PMC) to wastewater (and further to STP), for both the EU and Switzerland. This is due to the fact that the major applications for these two ENM are in cosmetics (Supplementary Fig. S-2 shows shares for all ENM applications). In the case of TiO<sub>2</sub> pigment, the dominant flows were from PMC to landfills. For nano-Ag, the major flows were from PMC to recycling and to wastewater. The most prominent flows for carbon-based ENM (CNT and fullerenes) were from PMC to recycling and to WIP, and from there to further elimination. Initially ENM flows going through STP would mainly be captured and settled in STP sludge, and further transported to WIP and landfill (in Switzerland), and some of ENM end up in soil from the part of STP sludge that is used as fertilizer (in the EU, but not in Switzerland). In our modelling we track the mass of the primary particles. Agglomeration plays a role in transferring particles from one compartment to another (e.g. from water to sediment), but does not affect the total mass of the primary particles.

### 3.2. ENM concentrations in technical and environmental systems

Table 1 shows the predicted ENM concentrations in STP effluent. surface water, STP sludge, air, solid waste, WIP bottom ash and WIP fly ash, as well as yearly incremental concentration increases in sediments, soils, and STP sludge treated soils (only for the EU). The values presented are the most probable values (mode values) and their 15th and 85th percentiles ( $Q_{0.15}$  and  $Q_{0.85}$ ) from each distribution. No concentrations in sludge-treated soil were calculated for Switzerland since sewage sludge is not applied to soils; instead it goes to waste incineration plants or is used as solid fuel in cement plants. In general, all the ENM showed their highest concentrations in STP sludge, followed by concentrations in solid waste, WIP bottom ash and WIP fly ash. Among the environmental compartments (soil, surface water, air and sediments), sediments had the most considerable concentrations, followed by STP-sludge treated soil (in the case of EU), then untreated soil and surface water, followed by air, with the lowest concentration of ENM overall. This appears quite reasonable due to the low release of ENM into the air and their short persistence time there. For soils and sediments, the simulations provided the annual amount of ENM deposited in these compartments in recent years.

In all the considered compartments, nano-TiO<sub>2</sub> had far higher concentrations than the other four ENM modelled; it was followed by nano-ZnO. This reflects on the one side the correlation between the total input production volume and the consequent concentration in different compartments but also the allocation to product groups with similar release pathways to the environment (for both groups cosmetics are major uses). Significant flows of nano-TiO<sub>2</sub>

and nano-ZnO were found going into wastewater and then from STP to landfill, WIP and soil (only for EU). For nano-Ag, the major part coming from PMC went to recycling, which is believed to be due to its use in various consumer products with antibacterial effects; a quite considerable amount also went to wastewater and this part is assumed to originate from nano-Ag applied to textiles and released during washing. For CNT and fullerenes, the flows from PMC to WIP, landfill and recycling were of similar magnitude.

Sediments, where most ENM entering surface water end up, showed concentration increases ranging from 0.4  $\mu$ g/kg·per year (fullerenes) to nearly 2000  $\mu$ g/kg·per year (nano-TiO<sub>2</sub>). In most cases the concentrations in WIP materials (solid waste, WIP bottom ash and WIP fly ash) were at the "mg/kg" level, exceeding concentrations in sediments.

Although in reality there may well be ENM in landfill leachates, our model did not take into account this possibility due to the insufficient existing quantitative information on this process. Furthermore, we did not track the fate of ENM during and after recycling, again due to the limited understanding of the behaviour of ENM associated with different products during recycling.

Compared to the results of Gottschalk et al. (2009), the newly predicted concentrations of ENM were in general 1–70 times higher, mainly due to the larger production in our new evaluation, well matching the rapid development of nanotechnology. For nano-TiO<sub>2</sub>, newly predicted concentrations were 1 (in STP sludge) to 5 (in STP effluent) times higher. This equated to an increase from 140 mg/kg to a newly predicted concentration of 170 mg/kg in STP sludge, and from 3.5  $\mu$ g/L in 2009 to a predicted concentration of 16  $\mu$ g/L in STP effluent. For CNT the new values were 2 (in STP sludge) to 3 times higher (in soil).

However, nano-ZnO and nano-Ag were exceptions by showing lower concentrations in some compartments in the new modelling: lower predicted concentrations of nano-Ag in wastewater resulted from lower production estimates based on more reliable data than was previously available. The comprehensive consideration of transformation reactions (e.g. of nano-Ag and nano-ZnO in STP) resulted in much lower estimated releases into natural waters and into STP sludge, and thus much lower environmental concentration estimates than in 2009, despite higher production of nano-ZnO. The newly predicted increment in nano-ZnO concentration in sludge-treated soil was 0.01 µg/kg·per year, versus 3 µg/kg·per year in 2009. For nano-Ag, the newly predicted incremental increase in concentrations in soil and sludge-treated soil were 1.2 ng/ kg and 110 ng/kg·per year respectively; the corresponding increments for 2009 were 23 ng/kg and 1580 ng/kg·per year - very much higher. This comparison shows that the knowledge gained in the last years on behaviour of ENM in technical systems such as wastewater treatment plants that was not available in 2009, especially about the transformation reactions of ENM that lead to their destruction, can have a very strong influence on the mass flows and the concentrations in the environmental compartments.

The ranges presented in Table 1 include both the uncertainty in some of the parameters as well as the variability that is caused by our approach, which considers all different forms of an ENM (e.g. coatings, functionalization) and thus provides information for a

**Fig. 3.** Modelled results (mode values) of material flows for nano-TiO<sub>2</sub>, TiO<sub>2</sub> pigment, nano-ZnO, nano-Ag, CNT and fullerenes in the EU in t for 2012. In the model, technical compartments (e.g. PMC, STP, WIP, landfill, recycling and elimination) and environmental compartments (air, soil, water and sediments) are expressed as boxes; flows between these processes and compartments are expressed as arrows, the thickness of these arrows indicates the magnitude of the flows. Dotted arrows between surface water and sediments/export indicate two different scenarios with either complete ENM sedimentation or 100% of ENM remain in surface water with 0% sedimentation. The flows are determined by transfer coefficients (TC) that describe the exchange of ENM between and within these boxes. The mathematical structure of the material-flow model describes the processes by rates of changes of stocks and flows by TC; the model is a stationary input–output system consisting of set *n* linear equations containing *n* unknowns. Matrix algebra is embedded in Monte Carlo algorithms for material flows and solutions are found by computing inverse matrices. For details refer to Gottschalk et al. (2010). All the ENM mass-flows are computed regardless of their agglomerated and aggregated form, therefore tracking the mass of the primary particles. Degradation (e.g. combustion of CNT and fullerenes in WIP) and transformation (e.g. nano-Ag transformation in STP and nano-ZnO transformation in the STP anaerobic digestion process) are treated as disappearance entering into an "elimination" box. All the values are rounded to three significant numbers; therefore the balance between input and put flows from one compartment might not be 100% closed.

#### Table 1

Predicted ENM concentrations in different technical and environmental compartments shown as mode (most frequent value) and as a range of lower and upper percentiles ( $Q_{0.15}$  and  $Q_{0.85}$ ). Black values designate concentrations; grey values designate yearly increases in concentrations. ENM concentrations in surface water and sediments represent no and complete sedimentation, respectively.

	EU			Switzerland			
	Mode	<b>Q</b> <sub>0.15</sub>	<b>Q</b> <sub>0.85</sub>	Mode	<b>Q</b> <sub>0.15</sub>	<b>Q</b> <sub>0.85</sub>	
		N	ano-TiO				
STP Effluent	16	13	110	32	26	220	µq/L
Surface water	0.53	0.40	1.4	0.67	0.54	3.0	µg/L
Sediment	1.9	1.4	4.8	2.3	1.9	10	mg/kg·y
STP sludge	170	150	540	320	250	950	mg/kg
Natural and urban soil	0.13	0.09	0.24	0.57	0.39	1.0	µg/kg∙y
Sludge treated soil	1200	940	3600				µg/kg∙y
Air	0.001	0.000	0.001	0.002	0.002	0.004	µg/m³
Solid waste	12	8.3	20	19	14	32	mg/kg
WIP bottom ash	120	82	230	210	150	410	mg/kg
WIP fly ash	150	110	310	280	200	560	mg/kg
		N	ano-ZnO				
STP Effluent	2.3	1.7	21	5.3	3.7	45	µg/L
Surface water	0.09	0.05	0.29	0.12	0.07	0.61	µg/L
Sediment	0.32	0.18	1.0	0.41	0.26	2.1	mg/kg∙y
STP sludge	24	17	110	45	31	200	mg/kg
Natural and urban soil	0.01	0.01	0.03	0.06	0.03	0.13	µg/kg∙y
Sludge treated soil	0.01	0.01	0.03				µg/kg∙y
Air	< 0.001	<0.001	<0.001	<0.001	<0.001	<0.001	µg/m³
Solid waste	0.89	0.47	2.4	1.6	0.73	3.7	mg/kg
WIP bottom ash	3.5	1.9	11	5.1	2.9	16	mg/kg
WIP fly ash	2.8	2.7	22	4.8	4.1	33	mg/kg
		1	Vano-Ag				
STP Effluent	0.17	0.06	16	0.32	0.08	23	ng/L
Surface water	0.66	0.51	0.94	0.45	0.37	0.73	ng/L
Sediment	2.3	1.8	3.3	1.6	1.3	2.6	µg/kg∙y
STP sludge	0.02	0.01	0.08	0.04	0.02	0.16	mg/kg
Natural and urban soil	1.2	0.91	1.8	5.1	3.9	7.4	ng/kg∙y
Sludge treated soil	0.11	0.09	0.65				µg/kg∙y
Air	0.003	0.003	0.004	0.01	0.01	0.02	ng/m³
Solid waste	0.06	0.05	0.08	0.05	0.04	0.07	mg/kg
WIP bottom ash	0.23	0.18	0.36	0.21	0.17	0.33	mg/kg
wiP ny ash	0.30	0.24	0.65	0.33	0.22	0.77	тід/кд
			CNT				
STP Effluent	4.0	3.6	12	5.5	4.9	16	ng/L
Surface water	0.23	0.17	0.35	0.35	0.27	0.56	ng/L
Sediment	0.79	0.61	1.2	1.2	0.95	2.0	µg/kg∙y
STP sludge	0.15	0.12	0.23	0.27	0.21	0.40	mg/kg
Natural and urban soli	5.1	3.7	1.0	22	17	32	ng/kg·y
Sludge treated soll	0.99	0.76	0.02	0.00	0.07	0.12	µg/kg·y
All Solid waste	1.7	1.3	2.6	3.0	23	4.0	ng/m² ma/ka
WIP hottom ash	0.23	0.21	2.0 1.4	0.30	0.36	23	mg/kg
WIP fly ash	0.36	0.33	29	0.00	0.55	47	ma/ka
	0.00	-		0.00	0.00		
	47	Fi	ullerenes	0.4	0.0	40	
SIP Emilient	1.7	1.3	/	3.4	2.3	13	ng/L
Surrace water	0.11	0.07	0.28	0.13	0.08	1.33	ng/L
Seament STD chudao	0.37	0.24	0.99	0.40	0.27	0.34	µy/kg·y
Natural and urban coll	0.09	0.05	0.22	0.10	0.09	0.34	ng/kgw
Sludge treated coll	0.10	0.07	1.5	U. 10	0.10	0.00	ug/kg-y
Δir	0.001	0.000	0.001	0.001	0.000	0.001	ng/m <sup>3</sup>
Solid waste	0.07	0.04	0.13	0.08	0.04	0 14	ma/ka
WIP hottom ash	0.01	0.04	0.07	0.00	0.01	0.08	ma/ka
WIP fly ash	0.01	0.01	0.14	0.01	0.01	0.16	mg/kg

generic ENM, e.g. "nano-TiO<sub>2</sub>". The concentrations in the technical compartment, e.g. wastewater, sludge or bottom ashes, may be used as input values to more sophisticated environmental fate models incorporating a mechanistic description of fate processes, e.g. agglomeration and sedimentation. Praetorius et al. for example used the mass flow to natural waters from Gottschalk et al. (2009) as

input to their mechanistic river fate modelling of nano- $TiO_2$  (Praetorius et al., 2012), also Gottschalk et al. (2011), used the release from wastewater as input for a local modelling study with high spatial resolution of ENM within the Swiss river network. In a next step the new material flow model will be coupled with the mechanistic environmental fate model provide realistic concentrations in natural waters and sediments.

We also have to consider that our modelling did not take into account accidental releases but only the standard handling and use of ENM and ENM-containing products. During major accidents locally elevated concentrations may be present, however, such events are normally not considered during risk assessment of chemicals but are part of process risk analysis and covered by accident regulations (Krug, 2013).

No current analytical methods are able to distinguish and quantify ENM in environmental samples containing naturally occurring nanoscale materials (von der Kammer et al., 2012), thus a direct validation of our modelled results is impossible. However, there are some data available that might be used to provide an initial comparison. The concentration of Ti smaller than 700 nm was, for example, found to be  $5-15 \mu g/L$  in STP effluents in the USA (Kiser et al., 2009), therefore close to our predicted value. Using single-particle ICP-MS, a concentration of nano-Ag of 100 ng/L was found in one STP (Mitrano et al., 2012), including however, all forms of Ag, e.g. nano-Ag<sub>2</sub>S which was considered a transformed nano-Ag in our modelling. This compares well to the upper range of 16 ng/L for engineered nano-Ag in our model. As soon as more analytical data become available, better validations will be able to be performed. However, our modelled data provides analytical chemists with an indication of the expected concentrations that their methods will need to be able to detect in a certain compartment.

#### 3.3. Comparison with conventional materials

We made the same material-flow calculations for TiO<sub>2</sub> pigment as for nano-TiO<sub>2</sub> (material-flows of TiO<sub>2</sub> pigment, see Fig. 3) and we also searched for measured concentrations of TiO<sub>2</sub> for comparison and validation. For the measured environmental concentrations of total metals (silver and zinc), relevant publications and studies were screened and the results were summarised in Supplementary Table S-5. Despite the 150 times higher production of pigment-TiO<sub>2</sub>, the environmental concentrations are only about 1 order of magnitude higher, reflecting the prime importance of product allocation and release over the whole life cycle in determining the final concentrations. Fig. 4 shows the comparison between the modelled concentrations of ENM (green bar) and their conventional materials (orange bar) in sewage effluent, surface water, soil and sediments. In all compartments the modelled concentrations of TiO<sub>2</sub> pigment (yellow bar) are about one order of magnitude higher than those of nano-TiO<sub>2</sub>; the concentration of TiO<sub>2</sub> measured in sewage effluent is 1 and 2 orders of magnitude lower than that of modelled nano-TiO<sub>2</sub> and TiO<sub>2</sub> pigment, respectively. The concentrations of TiO<sub>2</sub> measured in sewage effluent were obtained by filtration at 700 nm (Kiser et al., 2009), 220 nm (Khosravi et al., 2012) or 100 nm (Westerhoff et al., 2011), and thus capture only a small fraction of the total modelled TiO<sub>2</sub> in that effluent. We also need to consider that a fraction of the pigment-TiO<sub>2</sub> has particles sizes below 100 nm (Weir et al., 2012) and thus not all TiO<sub>2</sub> particles below 100 nm are thus actually "engineered NM" but some may be unintentional by-products from pigment manufacturing. Weir et al. (2012) measured 36% of the particle number of a food-grade pigment sample to be below 100 nm. The measured concentration of TiO<sub>2</sub> in surface water was around the same levels as those modelled for TiO<sub>2</sub> pigment, which validates our modelled results well. Due to high background concentrations in sediments and soil,



**Fig. 4.** Box and Whisker plots for comparison between logarithmical concentrations of ENM predictions and their corresponding conventional materials in sewage effluent, surface water, soil and sediments in the EU; green bars indicate modelled concentrations of ENM, yellow bars indicate modelled concentrations of TiO<sub>2</sub> pigment and orange bars indicate measured concentrations of their conventional materials. The diagrams were generated based on the modelled concentration values of ENM and TiO<sub>2</sub> pigment and measured concentrations (see <u>Supplementary Table S-5</u>) of TiO<sub>2</sub> and total silver and zinc. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

measured  $TiO_2$  concentrations in these two compartments were 3– 4 orders of magnitude higher than those for modelled nano- $TiO_2$ and  $TiO_2$  pigment.

Total metal concentration levels for Ag and Zn were 1–3 orders of magnitude higher than for their corresponding ENM in sewage effluent, surface water and sediments. In soil, the total metal level concentrations were up to 7 orders of magnitude higher (e.g. for Zn) due to high natural background concentrations. Any assessment of ENM risks, e.g. nano-Ag in water or nano-ZnO in soils, therefore needs to consider these much higher total metal concentrations, which are of course also toxic at higher concentrations. Fig. 4 also highlights the "needle-in-a-haystack" problem: any analytical method needs to be able to be specific for very low concentrations of ENM in the presence of high background total metal concentrations, many of which are present in colloidal or particulate form (Hochella and Madden, 2005; Theng and Yuan, 2008), further complicating the analysis of ENM.

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# Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2013.10.004.

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