

Dynamic Probabilistic Modeling of Environmental Emissions of Engineered Nanomaterials

Tian Yin Sun,^{†,‡,||} Nikolaus A. Bornhöft,^{†,§} Konrad Hungerbühler,[‡] and Bernd Nowack^{*,†}

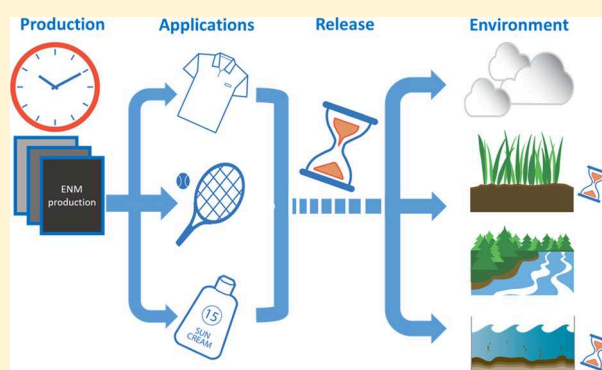
[†]Empa – Swiss Federal Laboratories for Materials Science and Technology, Technology and Society Laboratory, Lerchenfeldstrasse 5, CH-9014 St. Gallen, Switzerland

[‡]Institute for Chemical and Bioengineering, ETH Zürich, CH-8093 Zürich, Switzerland

[§]Department of Informatics, University of Zurich, Binzmühlestrasse 14, 8050 Zurich, Switzerland

S Supporting Information

ABSTRACT: The need for an environmental risk assessment for engineered nanomaterials (ENM) necessitates the knowledge about their environmental concentrations. Despite significant advances in analytical methods, it is still not possible to measure the concentrations of ENM in natural systems. Material flow and environmental fate models have been used to provide predicted environmental concentrations. However, almost all current models are static and consider neither the rapid development of ENM production nor the fact that many ENM are entering an in-use stock and are released with a lag phase. Here we use dynamic probabilistic material flow modeling to predict the flows of four ENM (nano-TiO₂, nano-ZnO, nano-Ag and CNT) to the environment and to quantify their amounts in (temporary) sinks such as the in-use stock and (“final”) environmental sinks such as soil and sediment. Caused by the increase in production, the concentrations of all ENM in all compartments are increasing. Nano-TiO₂ had far higher concentrations than the other three ENM. Sediment showed in our worst-case scenario concentrations ranging from 6.7 µg/kg (CNT) to about 40 000 µg/kg (nano-TiO₂). In most cases the concentrations in waste incineration residues are at the “mg/kg” level. The flows to the environment that we provide will constitute the most accurate and reliable input of masses for environmental fate models which are using process-based descriptions of the fate and behavior of ENM in natural systems and rely on accurate mass input parameters.



INTRODUCTION

Concerns about the potential environmental risks induced by the exposure to engineered nanomaterials (ENM) are growing. An environmental risk by ENM might occur when the exposure to these materials exceeds an ecotoxicological limit concentration in environment.¹ Therefore, knowing the current levels of ENM in environment is a fundamental step to assess the environmental risk of these materials. To date, the quantification of ENM in environmental samples, especially in solid samples such as soil and sediment, is still not possible.^{2,3} On the one hand, ENM are in most cases not directly detectable by analytic methods due to their very low concentration; on the other hand, even if detected, there are still major difficulties to differentiate the naturally occurring nanomaterials from the ENM.⁴ In order to perform a proactive environmental risk analysis, currently the only way to obtain information on existing levels of ENM in the environment is to model predicted environmental concentrations (PEC).^{2,5} Several modeling studies have presented quantitative estimations of the environmental concentrations of ENM.^{2,6–12} Mechanistic models specifically considering agglomeration and sedimentation reactions of ENM have also been developed.^{13,14}

However, all the material flow models published so far are static and do not consider time-dependent processes with respect to the use and release of ENM. The current models consider only the input by production, manufacturing and consumption (PMC) into the system that occurs in one year and subsequently distribute the mass over the entire system in the same year. The models also assume that all ENM produced are released to waste streams and environmental compartments in the same year in which they enter the system and no in-use stocks are considered. With these two oversimplifications of the true situation, the static models do not represent the actual ENM flows to environmental compartments under conditions where a rapid increase in production of ENM is taking place¹⁵ and when they are entering in-use stocks. Moreover, the static models cannot predict concentrations in environmental sinks, such as soil or sediment, because these compartments accumulate inputs over many years.

Received: November 26, 2015

Revised: March 1, 2016

Accepted: April 4, 2016

Published: April 4, 2016

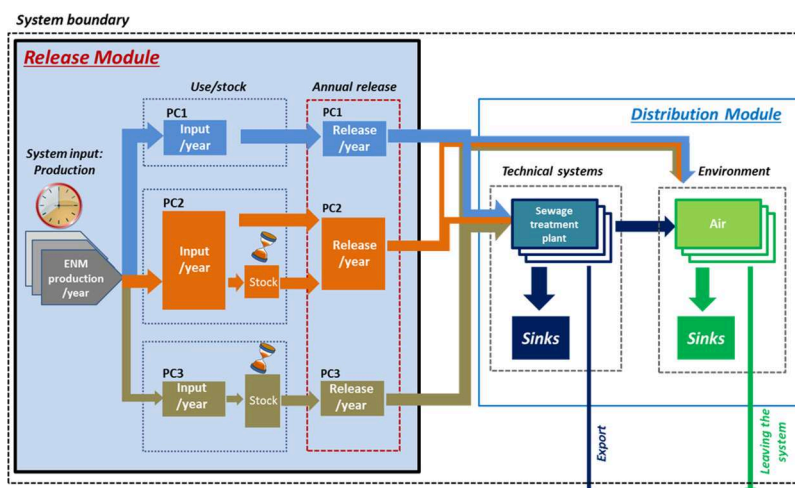


Figure 1. Schematic of the probabilistic dynamic material flow model for ENM. It consists of two modules, the “Release Module” and the “Distribution Module”. The “Release Module” focuses on dynamic system behavior, describing both the input dynamics and the release dynamics. The “Distribution Module” describes ENM distributions within and between technical and environmental systems after they are released out of the use phase. PC: Product Category; **Technical systems:** landfills, sewage treatment plants, waste incineration, recycling, and export; **Environment:** air, soil (natural and urban soil and sewage sludge treated soil), surface water, sediment; **Stock** indicates the mass stocked for both “Use release” and “EoL release” which are further explained in the following section “Release dynamics”.

First attempts in considering accumulation in environmental sinks have been made by Gottschalk et al.⁹ who used a very simplistic model to scale the input in different years to calculate final concentrations in soil and sediment. Sun et al. made a spatiotemporal prediction of mass-flows and concentrations for five ENM in biosolids amended soil in South Australia over a period between 2005 and 2012.¹⁶ However, both studies only considered one aspect of the dynamic nature of the system, the periodic production inputs into the system. The delayed ENM release from in-use stock was not covered at all so far.

A more realistic prediction of ENM flows to the environment therefore requires a dynamic material-flow analysis model (MFA). Unlike the static models, the dynamic MFA takes a reasonable time frame as the temporal system boundary and tracks the flows over many years; it also no longer needs the simplified assumption that all ENM are immediately released from all applications when they are produced. Dynamic MFA is a well-established modeling technique. Müller et al.¹⁷ performed a review on dynamic material flow modeling methods and studied whether and how uncertainty is treated by these methods. More than half of the methods covered by this review did not consider uncertainty at all; while there are some that use sensitivity analysis (37%), Gaussian error propagation (6%), or parameter ranges (5%), but none supports a full uncertainty representation with probability. The probabilistic dynamic MFA (DP-MFA) method developed by Bornhöft et al.¹⁸ fills this knowledge gap. This model treats all the uncertainty with probabilistic approaches. It constitutes the fundamental platform based on which the dynamic materials flow model of ENM is built.

The aim of this work was to build a customized dynamic probabilistic material flow model (DP-MFA) based on the method recently developed by Bornhöft et al.¹⁸ This new model predicts the former, current and future mass-flows of four ENM - nano-TiO₂, nano-ZnO, nano-Ag, and CNT - to technical and environmental compartments and the resulting concentrations in these compartments over time.

MATERIALS AND METHODS

General Principle. The new DP-MFA model for the four ENM is distinguished from all previous static models by the following two aspects: (1) time scope consideration of a period rather than a single year; (2) time dependent ENM release from products over the life-cycle of the products rather than simply assuming complete ENM release from products in one year when they are produced. We call the first point input dynamics in the context of this study, and the latter release dynamics. The input dynamics describe the annual production of ENM as inflows into the system within a given period. The release dynamics describe the time-dependent ENM release kinetics from a specific product category over the entire life-cycle.

Following a life-cycle concept, the model tracks the ENM mass-flows from ENM production to incorporation into the commercial products and finally from the products to technical and environmental compartments during/after their use and disposal.¹⁹ Probabilistic methods are employed for all the parameters used in the modeling processes to address the inherent uncertainty in the raw data used.²⁰ This means data from varied sources, with inherently different reliability, are combined into an appropriate probability density distribution. The input data for the model are the annual production amounts of ENM in the EU, the estimated shares of ENM applied onto product categories, the process-based transfer coefficients within and among the technical systems and the transfer coefficients between environmental compartments. All these parameters are treated as appropriate probability distributions depending on the data available. For each of the parameters, 100 000 random iterations are made to represent the comprehensive picture of the probability density distribution as described in a previous study.²⁰

The scheme of the DP-MFA is shown in Figure 1. It consists of two modules: the “Release Module” and the “Distribution Module”. The “Release Module” addresses the input and release dynamics. It describes the annual ENM production/consumption entering the system, the estimated share onto product categories, the flows from product categories by

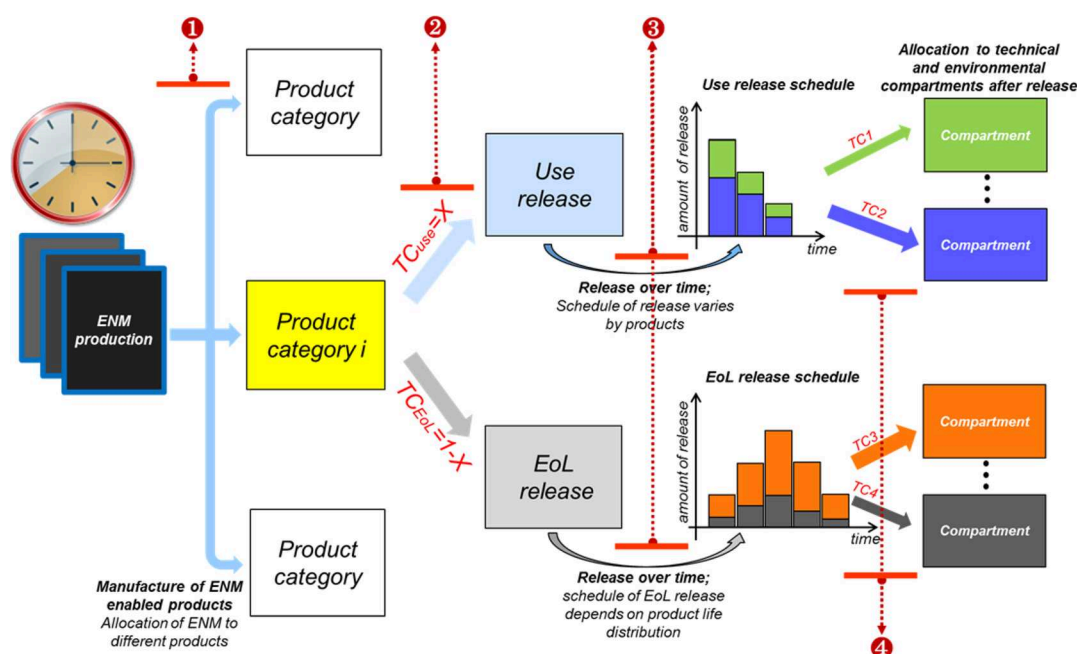


Figure 2. Schematic visualization of the time dependent ENM release dynamics. For ENM contained in a product category, the first step ① is the allocation of total produced ENM to different products. The second step ② is the division of the total ENM-content between the “Use release” and “EoL release”. The ENM contained in a product category allocated to “Use release” is the fraction supposed to be released during its use phase; the part allocated to “EoL release” is the fraction supposed to be remaining in the product and be released once the products come to their end of life. The third step ③ is the definition of the duration of the “Use release” and the “EoL release” as well as the release schedule; in other words in how many years the release events take place for one product category and how much of the fraction is released each year. The “EoL release” depends on the lifetime distributions of each product category; here normal distributions are assumed. The fourth step ④ is the allocation of the released ENM from the scheduled “Use release” and “EoL release” to technical and environmental compartments. TC: Transfer Coefficient; EoL: End of Life.

immediate release or into in-use stocks and finally the release from in-use stocks. The total annual release of ENM is then transferred to the compartments of the “Distribution Module”. The “Distribution Module” is built upon the previous static model,¹¹ which describes the ENM transfers within and between technical and environmental compartments. The transfer coefficients for the “Distribution Module” summarized from Sun (2014)¹¹ are listed in the [Supporting Information \(SI\) Table S5](#).

System Boundary. The geographical focus of this study is the European Union (EU) due to the abundant information available. But modeling for other regions can be easily expanded once data needed are provided. The technical compartments included in this study are landfills, sewage treatment plants (STP), waste incineration plants (WIP), recycling and export. The environmental compartments considered are atmosphere, natural and urban soil, sewage sludge treated soil, surface waters, and sediment. Among these compartments, landfills, soil, and sediment are defined as sink compartments. From sink compartments no downstream flows are modeled. A study by Caballero et al.²¹ was included providing an explicit description of ENM fate during and after recycling processes.

In this study we track the mass of the initial ENM. Transformed ENM (in our definition particles which lose their nano features i.e. by incineration, dissolution, or chemical reactions) will be viewed as loss of the ENM and flow to a virtual compartment called “Elimination”.

Input Dynamics. We considered in our model a time frame from 1990 to 2020. Explanations of the definition of the time frame are given in the [SI](#). The estimation of production of ENM over time is made by multiplying the base year

production (2012) with retrospective and prospective scaling factors. The production of the four ENM in 2012 is based on the probability distributions provided by Sun et al.¹¹ updated with newly available data. [SI Table S1](#) shows the raw data used for building the probability distribution of the ENM production in 2012. The scaling factors for each individual year are based on ENM market projections, nanotechnology patent analysis, and direct information on ENM production.¹⁵ We use the assumption that the development of ENM production is proportional to nanotechnology development with respects to, for example, patents registrations, funding, etc. A summary of all the data used for estimating probability distributions of the scaling factors are summarized in [SI Table S2](#). The probability distribution of ENM production in 2012 and the probability distributions of scaling factors are multiplied to obtain the probability distribution of ENM production for the period from 1990 to 2020. Production data in 2012 are used as the reference because they are available in Sun et al.¹¹

For nano-Ag, an additional estimation of the production development for a period from 1900 to 2020 has been made. This longer time period is founded in the historic applications of “silver colloids” that are in fact nano-Ag.²² Detailed information on how this was done can be found in the [SI](#).

Release Dynamics. “Release” in our definition refers to ENM that leave the production, manufacturing, and consumption phase and are transferred to technical or environmental compartments. The total ENM production is assigned to different nanoenabled product categories in shares based on the information provided by a previous study.¹¹ This allocation of ENM to product categories is assumed to remain constant over the time considered in this study. [Figure 2](#) shows the scheme of how time dependent ENM release from products is

Table 1. Summary of Parameters for the Release Dynamics Used in the Model for Nano-Ag; the Respective Information for Nano-TiO₂, Nano-ZnO and CNT Is Provided in SI Table S6^c

1		2	3					4				2	3	4				
Priority (share of the total nano-Ag application) ^(a)	nano-Ag (product categories)	Use release	Use release duration (years)	Use release schedule					Allocation after use release ^(b)				EoL release	Lifetime distribution (normal) Note: σ is the standard deviation	Allocation after EoL release			
		X		Y1	Y2	Y3	Y4	...	Waste water	Air	Surface water	Soil	1-X		Landfill	WIP	Recycling	Export
38.1%	Electronics & Appliances	0.30 ^(b)	8 ^(c)	1/8 ^(d)					1.00				0.70 ^(b)	mean=8; $3\sigma=8^{(c)(d)}$	0.09 ^(e)	0.06 ^(e)	0.65 ^(f)	0.2 ^(g)
25.1%	Textiles	0.60 ^(h)	3 ⁽ⁱ⁾	0.7 ^(h)	0.2 ^(h)	0.1 ^(h)		0.80	0.20			0.40 ^(h)	mean=3; $3\sigma=2^{(i)}$	0.31 ⁽ⁱ⁾	0.07 ⁽ⁱ⁾	0.28 ⁽ⁱ⁾	0.34 ⁽ⁱ⁾	
10.2%	Cosmetics	0.95 ^(b)	2 ^(d)	0.9 ^(d)	0.1 ^(d)			0.90		0.10		0.05 ^(b)	Y1=0.90, Y2=0.10 ^(d)	0.35 ^(e)	0.25 ^(e)	0.40 ^(k)		
6.6%	Foods	0.90 ^(d)	1 ^(d)	1.0 ^(d)				1.00				0.10 ^(d)	Y1=1.0 ^(d)	0.6 ^(e)	0.4 ^(e)			
6.0%	Cleaning agents	0.95 ^(b)	1 ^(d)	1.0 ^(d)				1.00				0.05 ^(b)	Y1=1.0 ^(d)	0.35 ^(e)	0.25 ^(e)	0.40 ^(k)		
3.6%	Medtech	0.05 ^(d)	1 ^(d)	1.0 ^(d)				1.00				0.95 ^(d)	Y1=1.0 ^(d)	1 ^(d)				
3.3%	Plastics	0.80 ^(d)	8 ^(d)	1/8 ^(d)					1.00			0.20 ^(d)	mean=8; $3\sigma=5^{(d)}$	0.35 ^(e)	0.25 ^(e)	0.40 ^(k)		
3.0%	Paints	0.35 ^(j)	7 ^(m)	0.9 ^(j)	0.1*(1/6) ^{(d)(j)}			0.50	0.25		0.25	0.65 ^(j)	mean=80; $3\sigma=20^{(n)}$	0.3 ^(e)		0.7 ^(e)		
2.4%	Metals	0.05 ^(b)	20 ^(d)	1/20 ^(d)					1.00			0.95 ^(b)	mean=20; $3\sigma=5^{(d)}$	0.03 ^(e)	0.02 ^(e)	0.95 ^(j)		
0.6%	Glass & Ceramics	0.35 ^(j)	10 ^(d)	0.9 ^(j)	0.1*(1/9) ^{(d)(j)}			1.00				0.65 ^(j)	mean=10; $3\sigma=5^{(d)}$	0.20 ^(e)	0.10 ^(e)	0.7 ^(e)		
0.6%	Soil remediation	0.98 ^(d)	1 ^(d)	1.0 ^(d)							1.00	0.02 ^(d)	Y1=1.0 ^(d)	0.6 ^(e)	0.4 ^(e)			
0.3%	Filter	0.30 ^(d)	8 ^(m)	1/8 ^(d)					0.80	0.20		0.70 ^(a)	mean=8; $3\sigma=8^{(m)}$	0.09 ^(e)	0.06 ^(e)	0.65 ^(f)	0.2 ^(g)	
0.2%	Diapers	0.05 ^(d)	1 ^(d)	1.0 ^(d)				1.00				0.95 ^(d)	Y1=1.0 ^(d)	1 ^(d)				
0.1%	Paper	0 ^(d)										1.00 ^(d)	mean=5; $3\sigma=4^{(d)}$	0.07 ^(e)	0.03 ^(e)	0.7 ^(a)	0.2 ^(g)	

^aSun et al. 2014.¹¹ ^bRevised based on Sun et al. 2014.¹¹ ^cSWICO report.²⁴ ^dExpert opinion.²⁴ ^eBakas et al. 2011.²⁹ ^fKiddee et al. 2013.³⁰ ^gEEA 2012.³¹ ^hPers. com, P. Limpitprakan. ⁱWebpage.³⁸ ^jFOE 2013.³² ^kEEA Web site.³³ ^lKaegi et al. 2010.²⁶ ^mATD Home inspection.²⁸ ⁿHischier et al. 2015.²⁷ ^oEEA 2009.³⁹ ^pGlass International.³⁴ ^qERPC.³⁵ ^rColumns ①, ②, ③ and ④ correspond to the four allocation steps shown in Figure 2. The column "Priority" or ① is based on the share of nano-Ag applied in the different product categories. Values of X in the column "Use release" in step ② indicate the fraction of nano-Ag contained in a product released during the use phase; values of 1-X in the column "EoL release" indicate the fraction of nano-Ag released at the product's end of life (EoL). "Use release duration" in step ③ means the estimated number of years during which release takes place; "Use release schedule" in step ③ describes during the use phase how much nano-Ag is released from a product each year; in step ③ the lifetimes of the products categories are assumed to be normally distributed. Average lifetime and standard deviations are either based on literature if available or estimated based on expert judgment; 3σ is used to show the whole span of the lifetime. "Allocation after use release" and "Allocation after EoL release" in step ④ contains information about the transfer coefficients defining the nano-Ag allocation to different compartments after release; Note: Yn = year n, e.g., Y1 = year 1.

expressed in the model. It proceeds in four steps: allocation of total ENM to different products ①, separation of ENM allocated to one product category into the "Use release" and "End of Life (EoL) release" ②, scheduling of "Use and EoL release" ③, allocation of ENM to technical and/or environmental compartment after "Use release" and "EoL release" ④. Scheduling in this context indicates the allocation of ENM mass released over the time.

Table 1 depicts the dynamic release parameters for nano-Ag as an example. The respective data for the other ENM are given in the SI. This table demonstrates the allocation of nano-Ag shares to different products, the division of the release between "Use release" and "EoL release", the release schedule over time and the allocation to different compartments after release. As Table 1 shows, important products categories such as "Electronics and Appliances", "Medtech", and "Paints" have the major part of nano-Ag remaining in the product and it is released when it reaches the end of life. In contrast, product categories like "Textiles", "Cosmetics", "Foods", "Cleaning agents", and "Plastics" have their nano-Ag component released mainly during the use phase.

Product life times are often independent of the ENM application, therefore they are either well-known or can be easily estimated. The release kinetics of ENM is specific to which ENM is applied to and how the material is bound to a product. This information is based preferably on experimental data when it is available or estimated on the basis of expert judgment. The use of realistic data compared to worst-case assumptions^{7–12,23} ensures a realistic modeling effort.

The product categories "Electronics & Appliances", "Plastics", "Paints", "Metals", and "Filters" have lifetimes normally longer than 5 years. With 20 years of use release, "Metals" is the product category with the longest use release. "Electronics and Appliances", the most important product

category for nano-Ag, has an average lifetime of 8 years.²⁴ Fast release is found in nondurable product categories for instance "Cosmetics", "Foods", "Cleaning agents", and "Medtech". For these, we have estimated general use release durations of 1–2 years. Experimental studies indicated that the majority of nano-Ag release takes place in the early stage of their lifetime.^{25,26} Therefore, in the Use release schedule release is mostly allocated to the first year. Most nano-Ag released during use release end up in wastewater, which was evaluated on the basis of a previous study.¹¹

In our approach, the "EoL release schedule" of ENM for a product category is represented by its lifetime distribution, i.e. the time it takes until the products are discarded. The longest EoL release is estimated for "Paints". Although "Paints" have an average use release duration of 8 years, the EoL release duration is in average 80 years, governed by the lifetime of the buildings on which they are applied to.^{27,28} Majority of the release in the first year of use is assumed for product categories with fast use release, such as "Foods", "Cleaning agents" and "Medtech". Distribution of nano-Ag to landfill, WIP, recycling and export after EoL releases are made according to solids waste management statistics in the EU for general solid waste²⁹ and specific waste.^{30–35}

Calculation of Concentrations. Concentrations are calculated by using standard volumes of environmental compartments (based on the REACH guidance³⁶). There are either flow-through compartments (e.g., water, air) without accumulation and sinks (e.g., soil, sediment) with accumulation. Additionally, for air and surface water, a retention time of 10 (Anastasio and Martin, 2001³⁷) and 40 (ECB, 2003³⁶) days were used, therefore 10/365 and 40/365 of the yearly input flows into these compartments were considered as the fraction of ENM remaining in the two compartments. The value for air is not particle specific but represents an average residence time

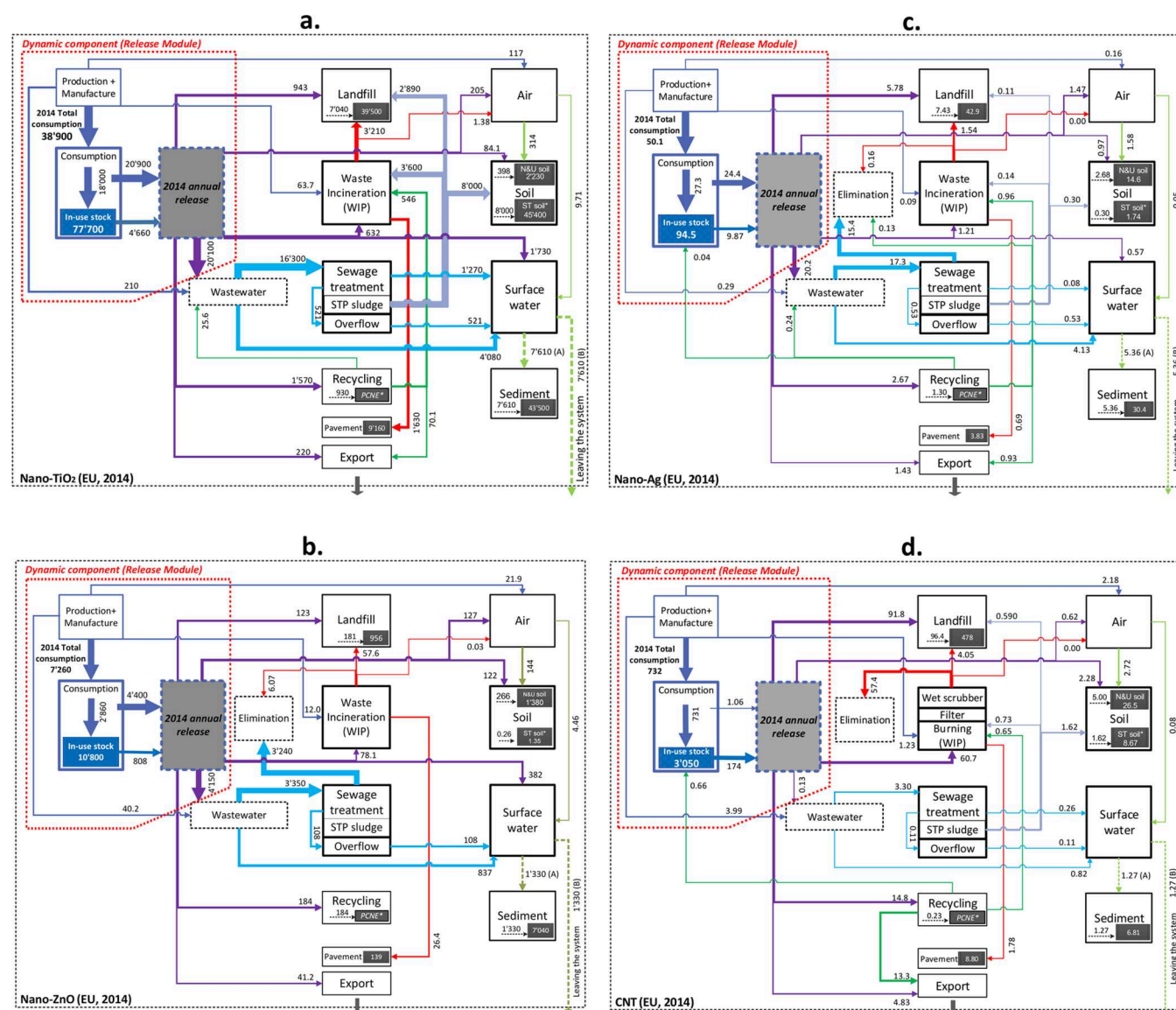


Figure 3. Mass-flows and stocks of the dynamic modeling of (a) nano-TiO₂, (b) nano-ZnO, (c) nano-Ag, and (d) CNT in the EU for the year 2014 in ton/year (for flows) and ton (for stocks). The nano-Ag flowchart displays the 1990–2020 scenario. The values for flow quantities are mean values from the respective probability distributions and are rounded to three significant digits. The thickness of the arrows reflects the quantities of flows; the blue/black squares in some compartments represent stocks in these compartments, for example, in-use stock, landfill, soil, and sediment. Values in these stocks are given to represent the current status of ENM accumulation in 2014. Colors of flow arrows are used only differentiating flows. The dynamic component, the “Release Module”, is highlighted with the red dashed circle. The dashed lines from “Surface water” to “Sediment” or leaving the system indicate two worst case scenarios: (A) full sedimentation and (B) no sedimentation, where ENM are fully stable in water and are carried by water out of the system boundary. PCNE: “Product Categories Not Evaluated” in the recycling compartment refers to materials in processes not covered by Caballero-Guzman (2015), which forms the basis of the recycling processes modeled; NU Soil: natural and urban soil. ST Soil: Sludge treated soil, for values of ENM annual inflows and accumulations to/in ST soil, only the amount carried by sludge is accounted here. Pavements: where waste is used as road pavements, is modeled here as a separately from recycling, because the data for this is directly available.

of particles smaller than 100 nm in air. Over the time scale of the modeling (1 year) in principle all particles settle out of the atmosphere. This value is therefore not a very critical one in our model and using an average value is therefore reasonable. A summary of the volumes of the compartments is given in SI Table S7.

RESULTS AND DISCUSSION

Mass-Flows of the Four ENM. Flows of the four ENM from production and use to release into all compartments were modeled by combining the modeled production volumes, shares of ENM applied in products and transfer factors between

all the compartments for the year 2014, incorporating the dynamics of the system from 1990 to 2014, as shown in Figure 3. The mean total productions of nano-TiO₂, nano-ZnO, CNT, and nano-Ag estimated for EU in 2014 were 39 000, 7300, 730, and 50 tons, respectively. Depending on the products applying these materials, different shares of amounts currently produced are entering into in-use stock or are released into technical and environmental compartments. For nano-TiO₂, nano-ZnO and nano-Ag, about half of the year’s total input into the system enters the in-use stock and the rest is directly released during the same year. With respect to CNT, less than 1% (1 out of 730 tons) is directly released and nearly 100% is allocated to the in-

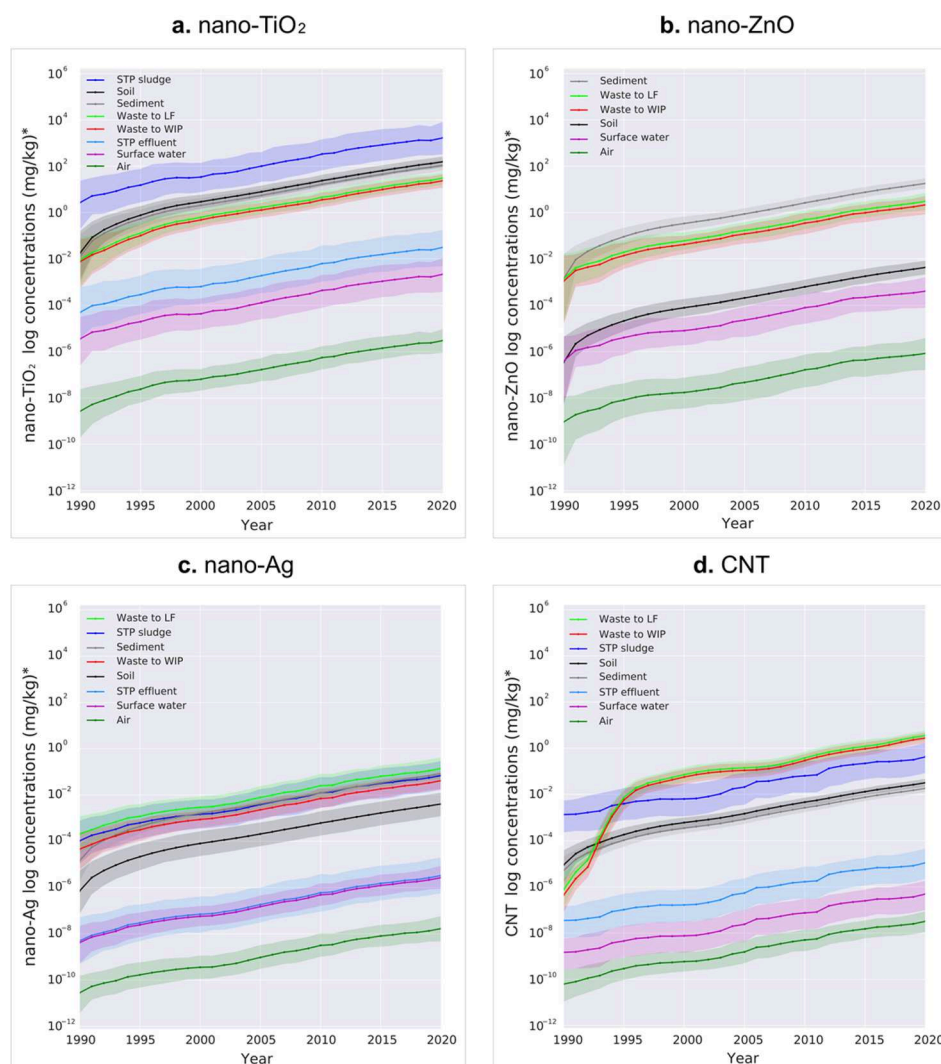


Figure 4. Modeled mean (dotted lines) and 15% and 85% quantiles (colored bands) evolution of concentrations of a) nano-TiO₂, b) nano-ZnO, c) nano-Ag and d) CNT in the EU from 1990 to 2020 (for nano-Ag an additional scenario from 1900 to 2020 is provided in SI Figure S2). Concentration values shown here are the mean and quantile values taken from probability distributions and are shown on a log scale. Concentrations are predicted for eight technical and environmental compartments: solid waste delivered to landfill, solid waste delivered to waste incineration, STP sludge, STP effluent, STP sludge treated soil, surface water, sediment, and air. No information on STP sludge and effluent is given for nano-ZnO because after STP processes no primary nano-ZnO survives as indicated in an earlier study.¹⁶ LF = Landfill, WIP = waste incineration plant, STP = sewer treat plant, Soil = STP sludge treated soil. *Unit for STP effluent and Surface water is mg/L, and unit for Air is mg/m³.

use stock. The amount in the in-use stock up to 2014 for nano-TiO₂, nano-ZnO and nano-Ag is in general around two times of their input in 2014; for CNT it is four times because the majority is stocked. Releases from in-use stock together with the immediate release from 2014's input constitute the total release in 2014. Compared to the immediate release, the release from stocks (previous year's input into the system) is in most cases much smaller, being about 15–30% of the total annual release. The one exception are CNT, for which more than 99% of the annual release in 2014 is coming from in-use stock, again showing their particular application in polymer nanocomposites which result in little immediate release.

This importance of releases from in-use stocks justifies the need for a dynamic modeling of ENM. Because flows into a certain product category are split into stocked and released amounts, it is not possible to compare the new results to those of static models such as from Sun (2014) or Keller (2014).^{10,11,23} In these models the production in one year was completely distributed to the environment, an assumption

that our dynamic modeling has clearly shown to be not representative for the ENM investigated.

The most prominent flows for nano-TiO₂ and nano-ZnO after release were from production, manufacturing, and consumption (PMC) to wastewater (and further to STP). This is due to the fact that the major applications for these two ENM are in cosmetics (the priority columns in Table 1 and SI Table S6 show the shares for all ENM applications). For nano-Ag, the major flows are from PMC to landfill and to wastewater. The most prominent flows for CNT were from PMC to landfill, followed by the flow to WIP, and from there to elimination. This can be explained by the fact that most of these materials are applied in polymer composites. ENM flows through the STP are mainly captured in STP sludge, and further transported to WIP and landfill, and some ENM end up in soil from sludge application. After wastewater treatment processes, nano-ZnO is transformed into different chemical forms such as ZnS, Zn sorbed to iron oxides and Zn₃(PO₄)^{40,41} and thus allocated to the virtual elimination compartment. As

mentioned above, after passing through wastewater treatment, most of the metallic nano-Ag is transformed to Ag sulfides and is therefore also ending up in the elimination compartment (thus left the system because the metallic nano-Ag property was lost).

With respect to recycling, we were able to include the fate of ENM during recycling based on a recent modeling study of ENM flows during recycling.²¹ We were therefore able to follow the majority of the mass flowing to recycling on their way to subsequent compartments.

One of the reasons to conduct a dynamic modeling endeavor is to calculate the ENM loads in compartments that accumulate ENM. With the dynamic model we are able to provide the accumulated mass of ENM in landfills, soil and sediment, with the values shown in black squares in Figure 3. All these three compartments are important sinks of ENM. In general, the accumulated masses are about five times larger than the contemporary input flows in 2014. For nano-TiO₂ sludge treated soil (with 45 000 tons) is found to be the largest accumulator, followed by sediment (with 44 000 tons) and landfills (with 40 000 tons). For nano-ZnO, sediments accumulate the most (with 7000 tons), followed by natural and urban soil (with 1400 tons) and landfill (1000 tons). Nano-Ag finds its most significant accumulations in landfills (40 tons) and sediment (30 tons). In the case of CNT, landfills dominate the list with almost 500 tons, whereas the accumulated masses in other sinks are less than 30 tons. These differences again highlight the varied life-cycles of the different products in which these ENM are applied.

Both Figure 1 and Figure 3 highlight the release module, which drives the model dynamics. In the release module there are two dynamic aspects: the time-dependent annual input and the time-dependent ENM release from products. These two then result in a dynamic behavior in all the following processes and compartments. In sink compartments there is an accumulation over time, which constitutes an additional important dynamic aspect of our model.

Concentrations. One reason to conduct a dynamic modeling endeavor is to describe the former and predict the future development. Figure 4 shows the modeled mean and 15% and 85% quantiles concentrations evolution of nano-TiO₂, nano-ZnO, nano-Ag, and CNT in the EU from 1990 to 2020 (for nano-Ag an additional scenario from 1900 to 2020, provided in SI Figure S2). The compartments for which concentrations of ENM are calculated are assumed to be well-mixed and homogeneous, although natural and urban soil and sewage sludge treated soil are differentiated. These concentrations are therefore representative for an average hypothetical region as defined in the REACH guidance.⁴² All details about the parameters used to calculate the concentrations are given in SI Table S7.

Triggered by the increase in production, the concentrations of all ENM in all compartments are increasing. Some of the compartments are flow-through compartments with no accumulation such as sludge, waste and wastewater effluent, others are accumulating sinks such as sediment and soil. Depending on the materials, the ranking order of concentrations differs, mainly caused by the different life-cycles of the products where these materials are applied. Regarding the development, nano-TiO₂, nano-ZnO and nano-Ag follow a similar pattern. On a logarithmical scale, all materials show initially larger increases of concentrations in sinks compared to flow-through compartments. The steepest increase in concen-

trations is observed for CNT in solid wastes. This can be explained again by the very different life-cycles of products applying CNT. A dominant majority of the products applying CNT are “durable” products, such as polymer composite that have almost no CNT release during use. Release takes place only when they come to the disposal phase. This leads the fact that most of CNT end up in solid waste over time, and further results in higher concentration there. Concentrations in air can be found always at the bottom indicating very low concentrations. However, it must be noted that the unit used here for air is mg/m³ which is different from the others. Therefore, these values cannot be directly compared with the concentrations in other compartments. The uncertainty in the concentrations are shown by the colored bands in Figure 4 (15–85% quantile), resulting from the combination of the uncertainties of all modeling parameters. Basically the sewage treatment plant related compartments (STP sludge, STP effluent and surface water) have a relatively high uncertainty range which can be partially explained by the large uncertainty involved in the STP removal efficiency. This parameter represents not only the uncertainty of the measured results but also the variety of a range of “generic ENM” that the model is targeting.

Table 2 shows the predicted ENM concentrations in STP effluent, surface water, STP sludge, air, solid waste entering landfill, solid waste entering WIP, WIP bottom ash, and WIP fly ash, as well as accumulated concentrations in sediment, soil, and STP sludge treated soil for the EU in 2014. The values presented are the mean values, mode values, median values and the 15% and 85% quantiles ($Q_{0.15}$ and $Q_{0.85}$) from each distribution. This feature of our results is unique compared to other deterministic models because it allows assessing the range and the likelihood of expected concentrations. In general, for all ENM (except nano-ZnO), the highest concentration is found in STP sludge, followed by solid waste, WIP bottom ash and WIP fly ash. Among the environmental compartments (soil, surface water, air and sediment), sediment had higher than other compartments, followed by STP-sludge treated soil, then untreated soil and surface water, followed by air, with the lowest concentration of ENM overall. For soil and sediment, the simulations provided the accumulative amount of ENM deposited in these compartments since 1990.

In all the compartments considered, nano-TiO₂ had far higher concentrations than the other three ENM. This reflects the correlation between the total input production volume and the consequent concentration in different compartments. Sediment, where most ENM entering surface water end up in our worst-case scenario, showed accumulated concentration ranging from 6.7 µg/kg (CNT) to about 40 000 µg/kg (nano-TiO₂). In most cases the concentrations in WIP materials (solid waste to WIP, WIP bottom ash, and WIP fly ash) are at the “mg/kg” level.

Comparing the results for the concentrations of nano-Ag based on the two scenarios with different time scope, the results of the scenario with the time frame “1900–2020” are only slightly higher than the results of the scenario “1990–2020”. For most compartments the difference is less than a factor of 2. Larger differences are found in the accumulated amounts in sludge treated soil and sediment. There, the concentrations from the scenario “1900–2020” are a factor of 5 higher than those of the scenario of depicting “1990–2020”. Here, certainly the longer accumulation effect plays a role, although historic

Table 2. Predicted (Accumulated) Concentrations of Nano-TiO₂, Nano-ZnO, Nano-Ag, and CNT in Waste Streams and Environmental Compartments in the EU in 2014^a

		EU (2014)				
		Mean	Mode	Median	Q _{0.15}	Q _{0.85}
Nano-TiO₂						
STP Effluent	44.4	13.7	16.3	2.77	76.1	µg/L
STP sludge	1.60	0.47	0.84	0.16	3.42	g/kg
Solid waste to Landfill	12.9	7.67	10.3	5.37	21.3	mg/kg
Solid waste to WIP	10.3	6.19	7.93	4.24	16.9	mg/kg
WIP bottom ash	395	161	237	93.6	729	mg/kg
WIP fly ash	543	238	327	129	979	mg/kg
Surface water	2.17	0.61	1.10	0.19	4.40	µg/L
Sediment	43.1	30.0	38.7	21.3	65.0	mg/kg
Natural and urban soil	2.94	1.86	2.57	1.44	4.53	µg/kg
Sludge treated soil	61.1	40.8	54.6	30.9	93.3	mg/kg
Air	2.05	0.86	1.24	0.43	3.98	ng/m ³
Nano-ZnO						
STP Effluent	0	0	0	0	0	µg/L
STP sludge	0	0	0	0	0	µg/kg
Solid waste to Landfill	1.69	0.96	1.21	0.52	2.64	mg/kg
Solid waste to WIP	1.27	0.64	0.86	0.34	2.04	mg/kg
WIP bottom ash	6.43	3.13	4.10	1.49	10.2	mg/kg
WIP fly ash	12.2	4.85	7.32	2.16	20.8	mg/kg
Surface water	0.38	0.16	0.23	0.05	0.64	µg/L
Sediment	6.97	4.95	6.26	3.64	10.5	mg/kg
Natural and urban soil	1.82	1.01	1.52	0.74	2.96	µg/kg
Sludge treated soil	1.82	1.01	1.52	0.74	2.96	µg/kg
Air	0.94	0.39	0.48	0.08	1.67	ng/m ³
Nano-Ag (1990-2020)						
STP Effluent	2.65	0.71	1.04	0.16	4.57	ng/L
STP sludge	61.3	20.2	32.9	7.41	113	µg/kg
Solid waste to Landfill	79.0	35.4	51.0	18.7	139	µg/kg
Solid waste to WIP	19.7	10.6	14.7	6.87	33.5	µg/kg
WIP bottom ash	170	111	141	75.4	267	µg/kg
WIP fly ash	340	169	259	114	582	µg/kg
Surface water	1.51	0.63	1.01	0.40	2.78	ng/L
Sediment	30.1	23.8	27.8	18.3	43.3	µg/kg
Natural and urban soil	0.02	0.02	0.02	0.01	0.03	µg/kg
Sludge treated soil	2.31	0.73	1.83	0.47	4.29	µg/kg
Air	0.01	0.00	0.01	0.00	0.02	ng/m ³
Nano-Ag (1900-2020)						
STP Effluent	2.60	0.59	1.06	0.18	4.52	ng/L
STP sludge	63.3	23.7	37.4	7.88	117	µg/kg
Solid waste to Landfill	82.3	42.6	54.9	27.7	146	µg/kg
Solid waste to WIP	24.8	14.4	19.6	11.6	40.0	µg/kg
WIP bottom ash	287	205	260	149	437	µg/kg
WIP fly ash	571	335	474	223	934	µg/kg
Surface water	1.50	0.76	1.05	0.49	2.71	ng/L
Sediment	164	163	162	127	201	µg/kg
Natural and urban soil	0.07	0.06	0.06	0.05	0.09	µg/kg
Sludge treated soil	13.7	3.81	12.1	2.84	24.7	µg/kg
Air	0.01	0.00	0.01	0.00	0.02	ng/m ³
CNT						
STP Effluent	8.58	6.50	7.00	0.92	15.6	ng/L
STP sludge	326	273	277	33.9	593	µg/kg
Solid waste to Landfill	1.26	0.72	1.08	0.54	1.99	mg/kg
Solid waste to WIP	0.98	0.60	0.83	0.42	1.60	mg/kg
WIP bottom ash	0.43	0.17	0.30	0.09	0.79	mg/kg
WIP fly ash	0.92	0.30	0.54	0.14	1.74	mg/kg
Surface water	0.36	0.28	0.30	0.04	0.65	ng/L
Sediment	6.74	6.34	6.46	4.32	9.24	µg/kg
Natural and urban soil	35.0	33.8	33.9	23.6	46.2	ng/kg
Sludge treated soil	11.7	10.2	11.1	7.42	15.8	µg/kg
Air	0.02	0.01	0.02	0.00	0.03	ng/m ³

^aMean, mode, median, and 15% and 85% quantiles are shown. Values are rounded to three significant digits. Results for nano-Ag are presented for both the time intervals of the 1900-2020 and 1990-2020.

nano-Ag uses were modeled to be much lower than current ones.

Although in reality there may well be ENM in landfill leachates, our model did not take this into account due to the insufficient quantitative information that exists on this process. It also needs to be noted that the concentrations in surface water and sediment reflect worst-case scenarios for both compartments. No fate modeling was performed and the water concentrations assume no sedimentation or other losses while the sediment concentrations reflect complete sedimentation from water. However, our flow results can be used as input data for dedicated mechanistic fate models that all rely on accurate predictions of the input flows.

Due to the different dynamic and static modeling concepts applied, it is not really possible to draw a direct comparison between the newly predicted concentrations results with all previous studies.^{8–11,16,23} As stated in the mass flow section above, the previous models distributed the produced mass in one year to the whole system in that year while our dynamic modeling clearly revealed that in-use stocks and delayed releases are highly important and essentially define the system behavior. However, this does not necessarily lead to lower predicted concentrations because releases from previous years are also considered and in some cases may dominate the flows. Similar concentrations in 2014 predicted by static and dynamic models may therefore by chance have the same magnitude. Extending the simulation time will reveal larger and larger differences between the two approaches due to additional releases from stocks.

The values presented in Table 2 include both the uncertainty in some of the parameters as well as the variability that is caused by the representation of a range of different forms of an ENM (e.g., coatings, functionalization), which are subsumed under the label of a generic ENM, for example, nano-TiO₂. In our approach, single numbers are treated as distributions. Triangular, uniform, normal, and other distributions are used alone or combined in accordance to available data. This treatment of the available data allows us to consider for each parameter the knowledge that is available by including always the specific uncertainty associated with each parameter.

The major purpose of the dynamic modeling is to track the historical concentrations and project the future concentrations of ENM in accumulative compartments. Therefore, besides the ENM concentrations predicted for the year 2014, we also provide the concentrations in 2020 in SI Table S8. Additionally, the predicted evolution of ENM concentrations in major compartments is provided in Figure 4. These predictions are based on the combined estimates of different market research companies and are grounded in the increase in the market in the last years and are probably valid if the technology continues to develop as it does today. Full probability distributions of flow data for single years are available from the authors upon request.

Considerations for the Applicability of Model Results.

The concentrations we provide for the technical compartments, for example, wastewater, sludge or bottom ashes and the ENM loads into environmental compartments such as surface water, soil, and air (see SI Table S9), can be used as input values for more sophisticated environmental fate models that incorporate a mechanistic description of fate processes, for example, agglomeration and sedimentation. These models then add another level of complexity with respect to dynamic modeling because they are considering the dynamics of physical and

chemical reactions not included in our flow models. Praetorius et al. for example used the ENM mass flow to natural waters from Gottschalk et al.⁹ as input to their mechanistic river fate modeling of nano-TiO₂.¹³ Also Gottschalk et al.⁴³ used the release from wastewater from the same source as input for a local modeling study with high spatial resolution of ENM within the Swiss river network. In another example using the same data set, Dumont et al.⁴⁴ calculated the spatial distribution of ENM in European watersheds. Meesters et al.⁴⁵ took the emission data to air, water, and soil from the Mueller (2008)⁸ mass-flow model as their SimpleBox4Nano model input. Liu et al.⁴⁶ used the ENM emission results from Gottschalk et al.⁹ and Keller et al.²³ as input data for their fate model. Dale et al.⁴⁷ used the US emission data for nano-Ag and nano-ZnO from Gottschalk et al.⁹ and included a modeling of the dynamics of water and sediment flows in streams and chemical transformations. This list exemplifies that the data provided by mass flow models are absolutely crucial for the fate models to come up with correct environmental concentrations as they all rely on mass inputs into one or several environmental compartments. The results of our dynamic model provide so far the most reliable and accurate results by incorporating ENM accumulation and release and they constitute the fundamental input information for predicting realistic concentrations results by environmental fate models. The use of dynamic MFA models is standard in assessing flows of materials in situations with rapid technological changes¹⁷ and our new dynamic MFA modeling of ENM is making use of this tool. Whereas the dynamic modeling requires more input data, we have shown that it is feasible to estimate the required data by combining information on technology development, release and fate processes in technical systems. In a situation with rapid increase in production and use of ENM, the modeling of environmental sinks needs to include historic uses that were much smaller (and future ones that might be much higher). The use of ENM in products with a long delay before any substantial release may occur (as is the case for ENM contained in polymers), is another strong argument for the use of a dynamic model that is able to capture the stocks of ENM contained in products.

We have to stress here that the concentrations reported in our work for environmental sinks such as soils and sediments do not consider any further chemical reaction such as dissolution or transformation, which will likely be very important for materials such as Ag and ZnO. To include these reactions into models will require the use of the above-mentioned environmental fate models. The results we provide are therefore worst-case assumptions on accumulated concentrations. Furthermore, because our model tracks the ENM release with a one year-based resolution, the release variability between seasons is not reflected in our study, for example, consumption of sunscreen only takes place massively during summer time. However, once data with better resolution are available, the model is able to calculate ENM release with a better temporal resolution.

The concentrations in natural compartments that we calculated nevertheless provide ecotoxicologists and risk assessors with crucial exposure data needed for first ecological risk assessments. As long as analytical chemists are not able to quantify ENM at the natural concentrations and distinguish them from the natural background particles, the modeled concentrations constitute the only source of environmental exposure information that we have available. The modeled concentrations have previously been used to compare the

exposure levels used in toxicological studies⁴⁸ or to perform a full environmental risk assessment based on the comparison of PEC values with NOEC values (no observed effect concentrations) extracted from the ecotoxicological literature.¹ These assessments rely on the provision of accurate environmental exposure data and our dynamic modeling is able to provide the most realistic and accurate numbers on flows and accumulated amounts in sinks. In the current situation a validation of modeled data for environmental ENM exposure is not possible as discussed in Nowack et al. (2015)⁴ but using the resulting data together in a mutually supportive way will advance the field of ENM risk assessment.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b05828.

Derivation of input dynamics. Details for release parameters for TiO₂, ZnO and CNT. Summary of volumes of technical and environmental compartments. Comparison of the modeled mean concentration evolution of nano-Ag from two different scenarios from 1990 to 2020 and from 1900 to 2020. Table with Predicted (Accumulated) concentrations of nano-TiO₂, nano-ZnO, nano-Ag and CNT in waste streams and environmental compartments in the EU in 2020 (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +41 (0)58 765 76 92; fax: +41 (0)58 765 78 62; e-mail: nowack@empa.ch.

Present Address

^{||}(T.Y.S.) Singapore-ETH Centre, Future Resilient Systems, 1 Create Way, #06-01 CREATE Tower, 138602, Singapore.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Prof. Dr. Martin Scheringer for valuable discussions on the manuscript. We also thank Dr. Denise Mitrano for reviewing the manuscript and improving the English. Tian Yin Sun was supported by project 406440_131241 of the Swiss National Science Foundation within the National Research Program 64. Nikolaus A. Bornhöft was supported by the European Commission within the Seventh Framework Programme (FP7; MARINA project - Grant Agreement No. 263215).

■ REFERENCES

- (1) Gottschalk, F.; Kost, E.; Nowack, B. Engineered nanomaterials in water and soils: A risk quantification based on probabilistic exposure and effect modeling. *Environ. Toxicol. Chem.* **2013**, *32* (6), 1278–1287.
- (2) Gottschalk, F.; Sun, T.; Nowack, B. Environmental concentrations of engineered nanomaterials: Review of modeling and analytical studies. *Environ. Pollut.* **2013**, *181* (0), 287–300.
- (3) von der Kammer, F.; Ferguson, P. L.; Holden, P. A.; Masion, A.; Rogers, K. R.; Klaine, S. J.; Koelmans, A. A.; Horne, N.; Unrine, J. M. Analysis of engineered nanomaterials in complex matrices (environment and biota): General considerations and conceptual case studies. *Environ. Toxicol. Chem.* **2012**, *31* (1), 32–49.
- (4) Nowack, B.; Baalousha, M.; Bornhöft, N.; Chaudhry, Q.; Cornelis, G.; Cotterill, J.; Gondikas, A.; Hasselov, M.; Lead, J.; Mitrano, D. M.; von der Kammer, F.; Wontner-Smith, T. Progress

towards the validation of modeled environmental concentrations of engineered nanomaterials by analytical measurements. *Environ. Sci.: Nano* **2015**, *2* (5), 421–428.

(5) Hendren, C. O.; Lowry, M.; Grieger, K. D.; Money, E. S.; Johnston, J. M.; Wiesner, M. R.; Beaulieu, S. M. Modeling Approaches for Characterizing and Evaluating Environmental Exposure to Engineered Nanomaterials in Support of Risk-Based Decision Making. *Environ. Sci. Technol.* **2013**, *47* (3), 1190–1205.

(6) Blaser, S. A.; Scheringer, M.; MacLeod, M.; Hungerbühler, K. Estimation of cumulative aquatic exposure and risk due to silver: Contribution of nano-functionalized plastics and textiles. *Sci. Total Environ.* **2008**, *390* (2–3), 396–409.

(7) Boxall, A. B. A.; Chaudhry, Q.; Sinclair, C.; Jones, A. D.; Aitken, R.; Jefferson, B.; Watts, C. *Current and Future Predicted Environmental Exposure to Engineered Nanoparticles*; Central Science Laboratory: Sand Hutton, UK, 2007.

(8) Mueller, N. C.; Nowack, B. Exposure modeling of engineered nanoparticles in the environment. *Environ. Sci. Technol.* **2008**, *42*, 4447–4453.

(9) Gottschalk, F.; Sonderer, T.; Scholz, R. W.; Nowack, B. Modeled environmental concentrations of engineered nanomaterials (TiO₂, ZnO, Ag, CNT, fullerenes) for different regions. *Environ. Sci. Technol.* **2009**, *43*, 9216–9222.

(10) Keller, A.; McFerran, S.; Lazareva, A.; Suh, S. Global life cycle releases of engineered nanomaterials. *J. Nanopart. Res.* **2013**, *15* (6), 1–17.

(11) Sun, T. Y.; Gottschalk, F.; Hungerbühler, K.; Nowack, B. Comprehensive probabilistic modelling of environmental emissions of engineered nanomaterials. *Environ. Pollut.* **2014**, *185* (0), 69–76.

(12) Johnson, A. C.; Bowes, M. J.; Crossley, A.; Jarvie, H. P.; Jurkschat, K.; Jorgens, M. D.; Lawlor, A. J.; Park, B.; Rowland, P.; Spurgeon, D.; Svendsen, C.; Thompson, I. P.; Barnes, R. J.; Williams, R. J.; Xu, N. An assessment of the fate, behaviour and environmental risk associated with sunscreen TiO₂ nanoparticles in UK field scenarios. *Sci. Total Environ.* **2011**, *409* (13), 2503–2510.

(13) Praetorius, A.; Scheringer, M.; Hungerbühler, K. Development of Environmental Fate Models for Engineered Nanoparticles—A Case Study of TiO₂ Nanoparticles in the Rhine River. *Environ. Sci. Technol.* **2012**, *46* (12), 6705–6713.

(14) Arvidsson, R.; Molander, S.; Sanden, B. A.; Hasselöv, M. Challenges in Exposure Modeling of Nanoparticles in Aquatic Environments. *Hum. Ecol. Risk Assess.* **2011**, *17* (1), 245–262.

(15) Piccinno, F.; Gottschalk, F.; Seeger, S.; Nowack, B. Industrial production quantities and uses of ten engineered nanomaterials in Europe and the world. *J. Nanopart. Res.* **2012**, *14* (9), 1–11.

(16) Sun, T. Y.; Conroy, G.; Donner, E.; Hungerbühler, K.; Lombi, E.; Nowack, B. Probabilistic modelling of engineered nanomaterial emissions to the environment: a spatio-temporal approach. *Environ. Sci.: Nano* **2015**, *2* (4), 340–351.

(17) Müller, E.; Hilty, L. M.; Widmer, R.; Schluep, M.; Faulstich, M. Modeling Metal Stocks and Flows: A Review of Dynamic Material Flow Analysis Methods. *Environ. Sci. Technol.* **2014**, *48* (4), 2102–2113.

(18) Bornhöft, N. A.; Sun, T. Y.; Hilty, L. M.; Nowack, B. A dynamic probabilistic material flow modeling method. *Environmental Modelling & Software* **2016**, *76*, 69–80.

(19) Mitrano, D. M.; Motellier, S.; Clavaguera, S.; Nowack, B. Review of nanomaterial aging and transformations through the life cycle of nano-enhanced products. *Environ. Int.* **2015**, *77* (0), 132–147.

(20) Gottschalk, F.; Scholz, R. W.; Nowack, B. Probabilistic material flow modeling for assessing the environmental exposure to compounds: Methodology and an application to engineered nano-TiO₂ particles. *Environ. Modeling Software* **2010**, *25*, 320–332.

(21) Caballero-Guzman, A.; Sun, T.; Nowack, B. Flows of engineered nanomaterials through the recycling process in Switzerland. *Waste Manage.* **2015**, *36* (0), 33–43.

(22) Nowack, B.; Krug, H. F.; Height, M. 120 years of nanosilver history: implications for policy makers. *Environ. Sci. Technol.* **2011**, *45*, 1177–1183.

(23) Keller, A. A.; Lazareva, A. Predicted Releases of Engineered Nanomaterials: From Global to Regional to Local. *Environ. Sci. Technol. Lett.* **2013**, *1* (1), 65–70.

(24) SENS SWICO SLRS. *Fachbericht 2014*, 2014; p 18.

(25) Xu, H.; Shi, X.; Lv, Y.; Mao, Z. The preparation and antibacterial activity of polyester fabric loaded with silver nanoparticles. *Text. Res. J.* **2013**, *83* (3), 321–326.

(26) Kaegi, R.; Sinnet, B.; Zuleeg, S.; Hagendorfer, H.; Mueller, E.; Vonbank, R.; Boller, M.; Burkhardt, M. Release of silver nanoparticles from outdoor facades. *Environ. Pollut.* **2010**, *158* (9), 2900–2905.

(27) Hischier, R.; Nowack, B.; Gottschalk, F.; Hincapié, I.; Steinfeldt, M.; Som, C. Life cycle assessment of façade coating systems containing manufactured nanomaterials. *J. Nanopart. Res.* **2015**, *17* (2), 1–13.

(28) ATD Home inspection Average Life Span of Homes, Appliances, and Mechanicals. <http://www.atdhomeinspection.com/advice/average-product-life/>.

(29) Bakas, I.; Sieck, M.; Hermann, T.; Andersen, F. M.; Larsen, H. *Projections of Municipal Waste Management and Greenhouse Gases*; European Environment Agency: 2011.

(30) Kiddee, P.; Naidu, R.; Wong, M. H. Electronic waste management approaches: An overview. *Waste Manage.* **2013**, *33* (5), 1237–1250.

(31) EEA. *Movements of Waste Across the EU's Internal and External Borders*; European Environment Agency, 2012; ISSN 0013-936X.

(32) Friend of the Earth Europe *Less is More, resource efficiency through waste collection, recycling and reuse of aluminium, cotton and lithium in Europe*; 2013.

(33) EEA Website Municipal waste recycling rates in 32 European countries, 2001 and 2010. <http://www.eea.europa.eu/data-and-maps/figures/municipal-waste-recycling-rates-in>.

(34) Glass International EU glass recycling rate passes 70% mark. <http://www.glass-international.com/news/view/eu-glass-recycling-rate-passes-70-mark>.

(35) ERPC European paper recycling rates reach 70.4%. <http://www.regions4recycling.eu/News-and-events/News/european-paper-recycling-rates-reach-70>.

(36) ECB. *Technical Guidance Document on Risk Assessment*; European Chemicals Bureau; Institute for Health and Consumer Protection: Dublin, 2003.

(37) Anastasio, C.; Martin, S. T. Atmospheric nanoparticles. In *Rev. Mineral. Geochem.*; Banfield, J. F., Navrotsky, A., Eds.; **2001**; Vol. 44, pp 293–349.10.2138/rmg.2001.44.08

(38) Eastonstewartsvilledrycleaner36 The average life expectancy of clothing. <https://eastonstewartsvilledrycleaner36.wordpress.com/2010/11/30/the-average-life-expectancy-of-clothing/>.

(39) EEA. *EU as a Recycling Society Present recycling levels of Municipal Waste and Construction & Demolition Waste in the EU*; European Topic Centre on Sustainable Consumption and Production: Copenhagen, 2009.

(40) Ma, R.; Levard, C.; Judy, J. D.; Unrine, J. M.; Durenkamp, M.; Martin, B.; Jefferson, B.; Lowry, G. V. Fate of Zinc Oxide and Silver Nanoparticles in a Pilot Wastewater Treatment Plant and in Processed Biosolids. *Environ. Sci. Technol.* **2013**, *48* (1), 104–112.

(41) Lombi, E.; Donner, E.; Tavakkoli, E.; Turney, T. W.; Naidu, R.; Miller, B. W.; Scheckel, K. G. Fate of Zinc Oxide Nanoparticles during Anaerobic Digestion of Wastewater and Post-Treatment Processing of Sewage Sludge. *Environ. Sci. Technol.* **2012**, *46* (16), 9089–9096.

(42) ECHA. *Guidance on Information Requirements and Chemical Safety Assessment*, Chapter R.16; *Environmental Exposure Estimation*; European Chemicals Agency, 2012; p 81.

(43) Gottschalk, F.; Ort, C.; Scholz, R. W.; Nowack, B. Engineered nanomaterials in rivers – Exposure scenarios for Switzerland at high spatial and temporal resolution. *Environ. Pollut.* **2011**, *159* (12), 3439–3445.

(44) Dumont, E.; Johnson, A. C.; Keller, V. D. J.; Williams, R. J. Nano silver and nano zinc-oxide in surface waters – Exposure estimation for Europe at high spatial and temporal resolution. *Environ. Pollut.* **2015**, *196* (0), 341–349.

(45) Meesters, J. A. J.; Koelmans, A. A.; Quik, J. T. K.; Hendriks, A. J.; van de Meent, D. Multimedia Modeling of Engineered Nanoparticles with SimpleBox4nano: Model Definition and Evaluation. *Environ. Sci. Technol.* **2014**, *48* (10), 5726–5736.

(46) Liu, H. H.; Cohen, Y. Multimedia Environmental Distribution of Engineered Nanomaterials. *Environ. Sci. Technol.* **2014**, *48* (6), 3281–3292.

(47) Dale, A. L.; Lowry, G. V.; Casman, E. A. Stream dynamics and chemical transformations control the environmental fate of silver and zinc oxide nanoparticles in a watershed-scale model. *Environ. Sci. Technol.* **2015**, *49* (12), 7285–7293.

(48) Holden, P. A.; Klaessig, F.; Turco, R. F.; Priester, J. H.; Rico, C. M.; Avila-Arias, H.; Mortimer, M.; Pacpaco, K.; Gardea-Torresdey, J. L. Evaluation of Exposure Concentrations Used in Assessing Manufactured Nanomaterial Environmental Hazards: Are They Relevant? *Environ. Sci. Technol.* **2014**, *48* (18), 10541–10551.