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Dynamic Model for the Stocks and Release Flows of Engineered Nanomaterials

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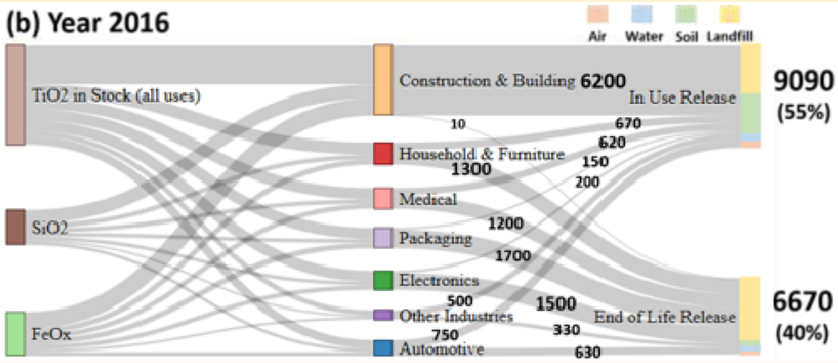
Supporting Information



ABSTRACT: Most existing life-cycle release models for engineered nanomaterials (ENM) are static, ignoring the dynamics of stock and flows of ENMs. Our model, nanoRelease, estimates the annual releases of ENMs from manufacturing, use, and disposal of a product explicitly taking stock and flow dynamics into account. Given the variabilities in key parameters (e.g., service life of products and annual release rate during use) nanoRelease is designed as a stochastic model. We apply nanoRelease to three ENMs (TiO_2, SiO_2 and FeO_x) used in paints and coatings through seven product applications, including construction and building, household and furniture, and automotive for the period from 2000 to 2020 using production volume and market projection information. We also consider model uncertainties using Monte Carlo simulation. Compared with 2016, the total annual releases of ENMs in 2020 will increase by 34−40%, and the stock will increase by 28−34%. The fraction of the end-of-life release among total release flows will increase from 11% in 2002 to 43% in 2020. As compared to static models, our dynamic model predicts about an order of magnitude lower values for the amount of ENM released from this sector in the near-term while stock continues to build up in the system.

INTRODUCTION

Engineered nanomaterials (ENMs) used in various applications can improve the performance of many consumer and industrial products, for example in paints and coatings,[1] solar power,[2] water treatment[3,4] and medicine.[5] The production volume of ENMs has increased rapidly over the past decades due to increasing new applications.[6] The growing use of ENMs has raised concerns about their potential implications to the environment and human health.[7] Over the past decade, increasingly more information has become available regarding the potential environmental implications of ENMs, including the estimates of the release of ENMs from products;[8−10] the fate-and-transport of ENMs between different environmental compartments after release;[11−16] the long-term behavior of ENMs in environment compartments and organisms;[17,18] the toxicity of different ENMs;[19,20] the sensitivity of different species to ENMs;[21] potential human exposure to ENMs and their behavior in the human body.[22,23] There are also a few predictive models for the bioactivity and life cycle impacts of ENMs and organic chemicals.[24,25]

Several previous studies have estimated the life-cycle releases of ENMs, using static models. For example, Gottschalk et al. predicted the environmental concentration of ENMs composed of TiO_2, ZnO, Ag, as well as carbon nanotubes (CNT) and fullerenes in different regions using material flow analysis.[26] Köhler et al. studied the possible release of carbon nanotubes and found that significant release may occur during the use and disposal phase within their life-cycle.[27] Keller et al. estimated the global life-cycle release of the ten most widely produced ENMs into air, surface water, soil and landfills using market data and product release estimates from peer-reviewed literature.[9] Keller and Lazareva refined this model and estimated the local life-cycle release of ENMs.[10] These release studies, along with others,[28−30] have provided the basis for environmental fate-and-transport studies of ENMs. Gottschalk

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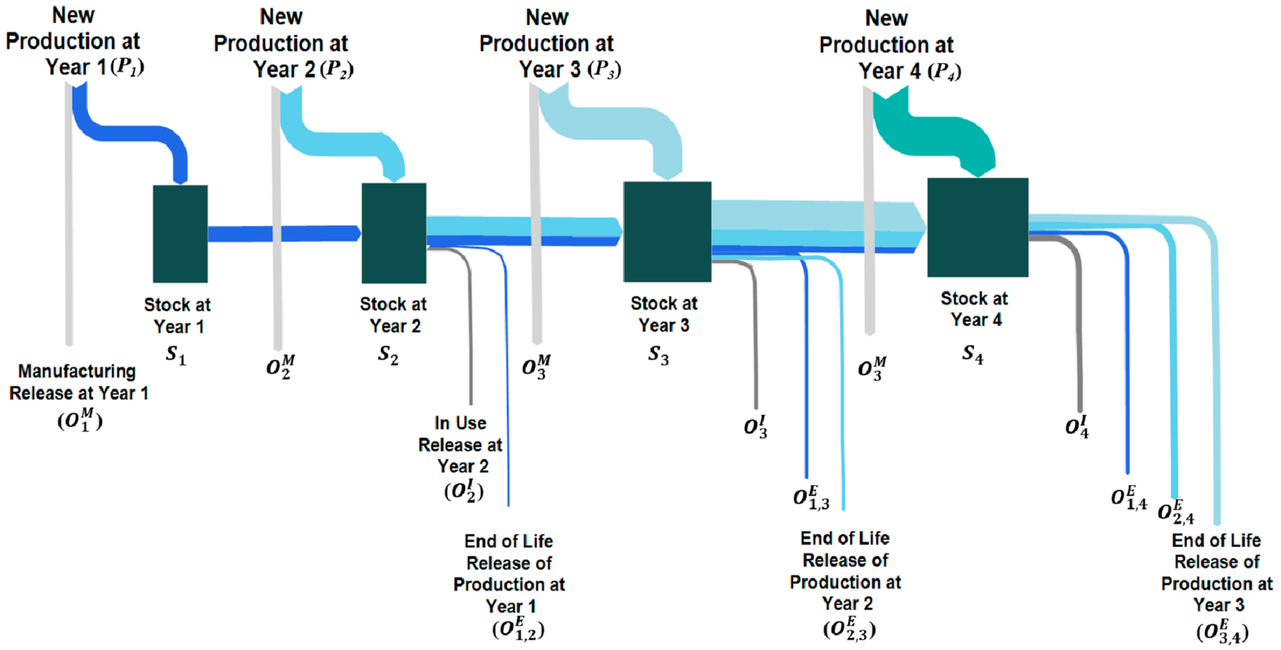

Figure 1. Conceptual framework of the nanoRelease model. Manufacturing (O_t^M) and in-use release (O_t^I) are constant fraction of new production (P_t) and stock size (S_t) at each year, respectively. Since retiring products have different ages every year, the end-of-life release consists of the ENMs produced in every previous year before retirement ($O_{n,t}^E$, where n is the year of one production, and t is the current modeling year, the final end-of-life release of year t O_t^E is the sum of the end-of-life release come from every production year before year t (see eq 3)).

and Nowack reviewed the current ENMs release models and pointed out the importance of mathematical modeling of ENMs release and the need to consider a life-cycle perspective.[8]

However, to date, most product-based ENM release models have assumed that the entire annual production of ENMs will be released in the year they are produced. While that may be a reasonable assumption for a few applications where there is minimal in-use stock, in most applications a significant fraction of the ENMs go into a stock, with a gradual release over time because of product aging or the retirement of ENM-enabled products at the end-of-life. For example, ENMs used in the personal care products or pharmaceuticals are likely to be released into the environment immediately after the use phase, with minimal stock accumulated over their life-cycle.[31] However, ENMs used in paints and coatings are likely to remain as in-use stock for years or even decades, and retire in some cases only when the building is eventually demolished or the automobile is crushed for recycling. The length of a product's in-use phase is generally stochastic in nature.

Bornhöft et al. developed a framework for dynamic probabilistic material flow (DPMFA) modeling and used it to estimate the stock and release flows of CNTs in Switzerland.[32] Using the same model structure, Sun et al. estimated the dynamic release flows for four ENMs ($nTiO_2$, nZnO, nAg and CNT) for the European Union from 1990 to 2020, considering 14 broad ENM applications, including paints and coatings.[33] Sun et al. also estimated the future trend of ENM release using the same model structure.[34] Their model considers the release during production and consumption, as well as end-of-life management. For $nTiO_2$ used in the paint market, only 1% is assumed to be released during use, with 99% going to end-of-life, whereas we assume that there is a continuous release of ENMs from painted surfaces until the product is disposed of. For $nTiO_2$ used in coatings and for nZnO in paints and coatings, Sun et al. assume 35% is released during the use phase, and 65% at end-of-life. For both ENMs, Sun et al. assume that 90% of the in-use release occurs in year 1, and that paints last 7 years and coatings last 10 years. Although the model considers 14 broad applications, there is no differentiation within the paint application as to whether the paint (or coating) is used in buildings, automobiles, packaging, or other product sectors, as proposed in this study. Our consideration of the product sector lifetime accounts in a more realistic manner for the growth of stocks. Thus, although both models consider dynamic material flows, there are significant differences in assumptions, scope and results.

Building on the stock-and-flow models that consider product lifetime,[35−42] we present a stochastic dynamic model, nanoRelease. Although the model is general for any ENM, here we apply the model to estimate the global life-cycle releases of three ENMs: nanotitanium dioxide ($nTiO_2$), nanosilicon dioxide ($nSiO_2$) and nanoiron oxides ($nFeO_x$) for the period from 2000 to 2020 for the paint and coating market. These ENMs are widely applied to paint and coating products. For example, due to its photocatalytic properties, $nTiO_2$ is a very effective ingredient in self-cleaning and antifogging paints and coatings.[1,43,44] We collected production volumes and market use information for these three ENMs. Then we estimated the manufacturing, in-use and end-of-life releases of these ENMs from paints and coatings in seven different product groups: construction and building, automotive, household and furniture, medical, electronics, packaging, and other. Finally, we conducted an uncertainty analysis to better understand the key factors controlling ENM releases, which can serve to design focused experiments to collect data to inform the model. Based on our model, the amounts of annual releases for the three selected ENMs were estimated along with an uncertainty range. We present the dynamics of release flows from 2000 to 2020 and the trend in manufacturing, in-use and end-of-life releases. The results of nanoRelease are compared to a previous static

Table 1. Product Sector Information for ENMs used in Coatings and Paints

	paints and coatings used in product sector[66]	product lifetime range (years)	repainting frequency (years)	average lifetime	source of average lifetime
construction and building	45%	20−100	10	60	Davis et al. 2007[36]
household and furniture	14%	2−25	0	15	USEPA 2014[65] and estimated
medical	13%	5−25	0	15	estimated
other industries	10%	5−35	0	20	Davis et al. 2007[36]
packaging	6%	1−6	0	1.5	estimated
electronics	6%	2−8	0	5	USEPA 2014[65] and estimated
automotive	6%	1−16	0	13	Davis et al. 2007[36]

model. Limitations, recommendations and outlook of nanoRelease are also discussed. The model outputs can then be linked to detailed environmental fate-and-transport models to determine human exposure and environmental concentration of ENMs in various compartments.

■ MATERIALS AND METHODS

Model Framework. ENMs can be released during the manufacturing, in-use and end-of-life phases of nanoenabled products (NEPs). In our model, these three types of releases are calculated as a function of many factors including the annual production volume, size of accumulated stock, and in-use release rates of ENMs. ENM stock refers to the amount of ENMs that are incorporated in all product applications currently in the system. The model framework is presented in Figure 1.

The manufacturing release is assumed to be a constant fraction, m, of the annual production volume $P_{a,t}$:

$$O^{M}_{a,t} = P_{a,t} \times m \tag{1}$$

Where $O^{M}_{a,t}$ is the manufacturing release of ENM a for year t.

The annual in-use release, $O^{I}_{a,t}$, is the amount of ENMs that is released immediately (i.e., within the first year) during initial application, (e.g., the releases during painting and washing brushes and rollers), plus the amount of ENMs that is released from products during use, each year until the product reaches its end of life. The in-use release is given by

$$O^{I}_{a,t} = P_{a,t} \times \theta + \sum_{n=1}^{N} r_n \times S_{a,n,t-1} \tag{2}$$

where θ is the release fraction during the initial application, r_n is the annual in-use release fraction of product sector n; $S_{a,n,t-1}$ is the stock of ENM a in product sector n at year $t-1$. While we recognize that the in-use release rate may vary as the product ages, there are no tangible experimental values that match all the applications in this study. In addition, the results of different studies vary considerably; thus, we use a constant in-use release rate overtime, but also explore increasing and decreasing release rates. We assume there is no stock at $t = 0$.

The end-of-life release $O^{E}_{a,t}$ is the mass of ENM remaining in an Nano-Enabled Product (NEP) by the time it is disposed of. The product service lifetime varies significantly among NEPs (e.g., nanoenabled paints and coatings), which are taken into consideration in the model. The annual end-of-life release of ENMs depends on the age and the expected lifetime of the product group in which ENMs are used. For example, when estimating ENMs released in 2016, ENMs produced and incorporated in buildings in 2010 are less likely to be released compared to ENMs produced in 2000, since the building sector has an average lifetime of more than 50 years.[36] In nanoRelease, the end-of-life release of an ENM at year t is given by

$$O^{E}_{a,t} = \sum_{x=0}^{t-1} \sum_{n=1}^{N} S_{a,x,n,t-1} W_n(t - x, \lambda_n, \beta) \tag{3}$$

Where $S_{a,x,n,t-1}$ is the stock of ENM a in year $t-1$ produced in year x and used in product group n; W_n is the stochastic distribution function that approximates the probability of product (in product group n) retiring in year t; $t-x$ is the age of the product when it retires; λ_n is the average product lifetime of product sector n and β is the shape parameter of the probability distribution. The end-of-life release at year t is the sum of the end-of-life release of ENMs that produced every year before t.

We also considered in nanoRelease the effect of repainting. For the product sector construction and building, there will be repainting by an amount $R_{a,t,n}$ at year t, with the same amount of ENMs as in the initial painting process. The repainting frequency is assumed to be 10 years for construction and building, and zero for the others (Table 1). Repainting will also affect the stock at year t as follows:

$$S_{a,t,n} = S_{a,t-1,n} - O^{I}_{a,t-1} - O^{E}_{a,t-1} + R_{a,t,n} \tag{4}$$

The mass of ENMs in repainting, R, will be deducted from ENM production $P_{a,t}$ that is available for new products at year t.

Thus, the total release of ENM a at year t willbe

$$O^{t}_{a} = O^{M}_{a,t} + O^{I}_{a,t} + O^{E}_{a,t} \tag{5}$$

Manufacturing Release. Manufacturing release happens due to fugitive emissions and imperfect manufacturing material use efficiency. Detailed data are lacking on this type of release for different ENMs. Previous studies have estimated that the mass of ENMs released during the manufacturing process ranges from 0.1% to 2% of total production.[8,26,30,45] This indicates that manufacturing releases are smaller than most other releases during the ENM product life. We used 2% as the manufacturing release rate m in the case study.

In Use Release. Several studies have shown that ENMs used as coating materials can have considerable amount of release during use, either through mechanical abrasion or photooxidative processes,[46−51] and end up in either water or directly emitted into air as aerosols.[28] Previous experimental studies and expert judgment indicated that the release rate during use of ENMs in paint and coatings could range from 10% to 90% in mass over the useful lifetime of the product.[9] However, this indicates that the annual release rate during use is small.[52] In our study, we consider 0.1% and 5% of the previous stock as the low and high estimates of the annual release rate in the uncertainty analysis, and use 3% as the mean value for outdoor applications (construction and building and automotive), and 1% for other indoor applications.

Previous studies have indicated that the ENM release rate from paints during the use phase varies depending on the environmental conditions, such as UV-illumination, pH and weathering.[46,47,53] Currently there is no experimental data on the long-term release of ENMs. In our study, two additional models were created and presented in the Supporting Information (SI). One model considers a high initial release rate, in each product category, decreasing over time (starting from 5% annual release and decreasing 20% every year), and the other considers a lower initial release rate and increasing over time (starting from 0.5% annual release and increasing 20% every year).

End of Life Release. Previous studies showed that the year of product retirement can be approximated by statistical distributions. This theory was first applied in the chemical engineering field to account for the distribution of the residence time of a chemical in a flow system.[54] It was then introduced into the field of Material Flow Analysis (MFA) as a way to estimate the product lifetime distribution and failure rate in many other industries, including iron, vehicle and plastic manufacturing industries.[35,55−59]

Weibull and log-normal distributions have been widely used as the approximation functions for the product lifetime distribution.[55,60,61] Several studies have shown that there is no substantial difference between these two distributions in terms of the simulated product lifetimes.[38,55,62] In nanoRelease we used a two-parameter Weibull distribution to approximate the lifetime distribution of products that use ENMs in paints and coatings. The probability density function (PDF) of the two-parameter Weibull distribution is given by[63]

$$E(t) = \frac{\beta}{\eta}\left(\frac{t}{\eta}\right)^{\beta-1}\exp\left[-\left(\frac{t}{\eta}\right)^{\beta}\right] \tag{6}$$

where t is the year when the probability of retirement is estimated ($t \geq 0$); η is the scale parameter; and β is the shape parameter. The scale parameter η is determined by the average lifetime $\overline{t}$ of each product sector:

$$\eta = \frac{\overline{t}}{\exp\left(\Gamma\left(1 + \frac{1}{\beta}\right)\right)} \tag{7}$$

where Γ is the gamma function:[64]

$$\Gamma(\alpha) = \int_0^{\infty} x^{\alpha-1}\exp(-x)dx \tag{8}$$

SI Figure S1 illustrates the probability distribution function of Weibull distribution for average product lifetimes of 1, 2, 4, and 8 years (β).

The stochastic approach to estimate the end-of-life releases relies on the average lifetime $\overline{t}$ for each product sector. The seven product sectors selected for this study cover the major uses of ENMs in paints and coatings and they have quite different average lifetimes. Previous studies have collected average lifetime information for some of the product sectors.[31,43,47] The U.S. Environmental Protection Agency (USEPA) also collected the average lifetimes for some durable goods include consumer electronics and furniture.[65] We combined our estimates with the USEPA estimates to obtain release estimates for the product sectors in our study. For other product sectors (medical and packaging) in our study, no references were found for their actual product lifetimes. Hence, our estimates are based on expert judgment for these product sectors. To account for uncertainty, we considered a range of lifetimes for each product sector and conducted a Monte Carlo analysis. The seven selected product sectors, their market share in the paint and coatings market, and lifetime range are presented in Table 1 along with the source of information.

Conservative production rates of TiO_2, SiO_2, and FeO_x ENMs from 2002 to 2016 were collected from a market report.[67] We extrapolated the data to the range from 2000 to 2020 assuming an 8% annual growth rate, which is the average rate of increase reported for the three ENMs. The conservative production volume was used to create the baseline model in this study due to the higher reliability of the data. The optimiztic production data from 2000 to 2020 was extrapolated based on the reported production data of 2011 in the same market report, using the same annual increase rate as in the conservative estimates. Other estimates are available in the literature but unfortunately there is no means of validating current production estimates reliably.[68−70] While it is likely that most of these ENMs were already in production before 2000, there is little information on the ENMs fraction used in various applications of these materials, and may represent a small fraction of the current stock. We also collected market application information on paints and coatings from a separate market report that provides the market share of ENMs in paints and coatings in the seven selected product sectors.[66] The detailed annual production data, along with the market share information for each of the three selected ENMs are presented in SI Figure S3.

Releases into Environmental Compartments. The fraction of ENMs released into various environmental compartments (e.g., air, water, soil, and landfill) during the various life-stages were based on previous estimates, with some adjustments as summarized in Table 2.[9] The end-of-life management strategies we considered are landfill and incineration.

Table 2. Release (Fraction by Weight) From Paints into Different Environmental Compartments[a]

	to air	to water	to soil	to landfill
manufacturing release	10%	0.1%	0.1%	89.8%
in-use release	1%	1%	48%	50%
end-of-life release	1%	1%	5%	93%

[a] The estimates are based on the study in Keller et al.[9].

Uncertainty Analysis. The model parameters that we considered in the uncertainty analysis were the in-use release rate r_n, the average product lifetime and the annual production volumes, which were assumed to have triangular distributions. Triangular distributions have been widely applied when the upper, lower, and common values of data are estimated, but there is no information to consider another distribution.[71,72] For in-use release rates, the uncertainty range is 0.1−5%. For the average product lifetime, the uncertainty ranges were specified in Table 1 for each product sector, respectively. The conservative and the optimiztic production data were used as the lower and upper bounds for the production volume in uncertainty analysis.

Monte Carlo simulation is one of the approaches to assessing model uncertainty.[73−75] Many studies in the environmental and risk assessment field have also applied Monte Carlo to account for model uncertainties,[30,76,77] including a study that used the Monte Carlo method for the life-cycle environmental emissions of different products.[72,78] In this study, we used 10 000 iterations to estimate the range of annual releases of ENMs. In each iteration, a set of model parameters was randomly selected based on their distributions. The mean and 2.5−97.5% range for the releases are reported for each ENM.

Comparison with Static ENM Release Model. Keller et al. investigated the global static life-cycle releases of ten ENMs from varies market and product applications in year 2010.[9] We compared the results of the dynamic nanoRelease model vs the static model,[9] considering only the estimates of $nTiO_2$, $nSiO_2$ and FeO_x from paints and coatings in 2010.

■ RESULTS AND DISCUSSION

Based on the results of 10,000 iterations of Monte Carlo simulations, the median values (solid lines) and the range for upper (97.5%) and lower (2.5%) bounds of the annual life-cycle releases of $nTiO_2$, $nSiO_2$ and $nFeO_x$ from paints and coatings between 2000 and 2020 (dash lines) are presented in Figure 2. The shaded areas in Figure 2 are made by 10 000 lines for each ENM, which are the results of the MCS. NanoRelease estimates that in 2016, the worldwide annual release of $nTiO_2$ (light pink color in Figure 2) from the paints and coatings market was in the range of 8200 to 13 200 t, whereas the annual release of $nSiO_2$ (dark yellow) and $nFeO_x$ (green) in 2016 ranged from 3000 to 4900 and 3800 to 6000 tons, respectively. With the increasing production of ENMs since 2000, their release has grown significantly. NanoRelease predicts that by 2020, the annual releases of $nTiO_2$, $nSiO_2$ and $nFeO_x$ will increase by 34%, 37%, and 40%, compared with 2016, respectively. In the same time, the stocks of these three EMNs will grow by 29%, 28%, and 34% compared with 2016, respectively (SI Figure S2). Among these three ENMs, $nTiO_2$ has the highest absolute annual release and stock, due to its high production volume.

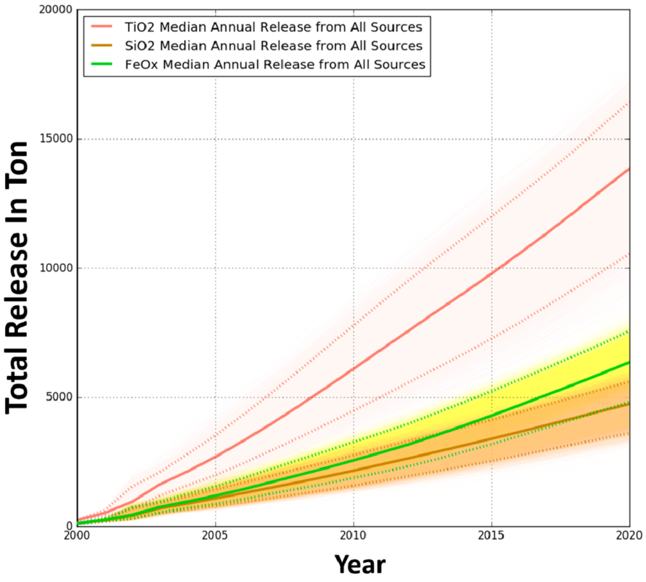

Figure 2. Total annual release of TiO_2, SiO_2, and FeO_x ENMs from paints and coatings from 2000 to 2020 with their uncertainty ranges. The dash lines represent the upper (97.5%) and lower (2.5%) bounds for the releases of each corresponding ENM. The solid lines represent the median releases. The shaded areas are made by the results of 10 000 Monte Carlo runs for each ENM.

The uncertainty analysis in Figure 2 indicates that the uncertainty range increases over time, from almost 0% in year 2000 to 20−30% from the median value in 2020 for TiO_2, SiO_2 and FeO_x ENMs. In nanoRelease, the model uncertainty is a function of three factors: uncertainty in production, in in-release rate, as well as in product lifetime distribution. As the stocks and end-of-life releases increase over time, this drives the range of emission estimates, increasing the uncertainty range.

Figure 3 provides the total releases of $nTiO_2$, $nSiO_2$ and $nFeO_x$ by product sectors from paints and coatings, considering the conservative production estimates, 1−3% annual in-use release rate and mean average product lifetimes. In 2016, the construction and building product sector contributed about 38% (6210 tons) of the total releases, followed by household and furniture, packaging, and medical sectors, which contributed about 12% (1970 tons), 11% (1,850 tons), and 11% (1820 tons), respectively. By 2020, the construction and building product sector will contribute about 35% (8440 tons) of the total releases. The household is still the second-largest contributor, reaching 13% (3150 tons) of the total releases, followed by medical and packaging sectors, which will contribute about 12% (2900 tons) and 9% (2200 tons) of the total annual releases, respectively. There are peaks in the releases from packaging and electronics product sectors around 2002 and 2005. This is due to the relatively short average lifetime of these two product sectors. Therefore, the ENMs produced in the first year are released within a short time from the packaging and electronics sectors, mostly at the end-of-life disposal from these two sectors. The probability distribution of the end-of-life release flows of each product sector can be found in the SI as well.

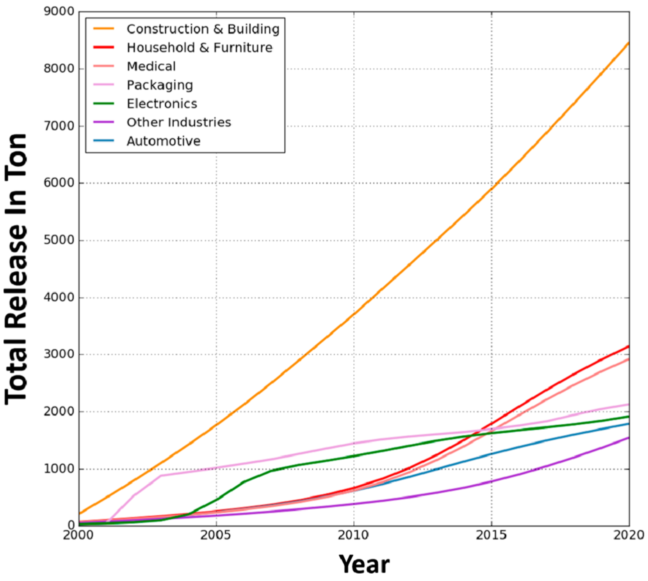

Figure 3. Releases estimates of all three ENMs ($nTiO_2$, $nSiO_2$ and $nFeO_x$) from each product sector in paints and coating market from 2000 to 2020. Assuming 1−3% annual in-use release rate, conservative production estimates and average product lifetime.

Figure 4 shows the detailed release flows in 2016, with the same model parameters used for Figure 3, of all three ENMs in the seven product sectors, including new production and stocks. The stocks comprise ENMs embedded in paints and

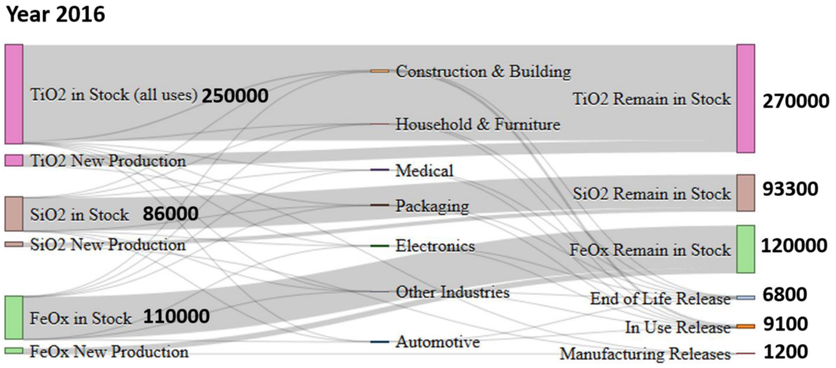

Figure 4. Release flows and stocks (in tons) for TiO_2, SiO_2 and FeO_x ENMs in 2016, assuming 1−3% annual in-use release rate, conservative production estimates and average product lifetime.

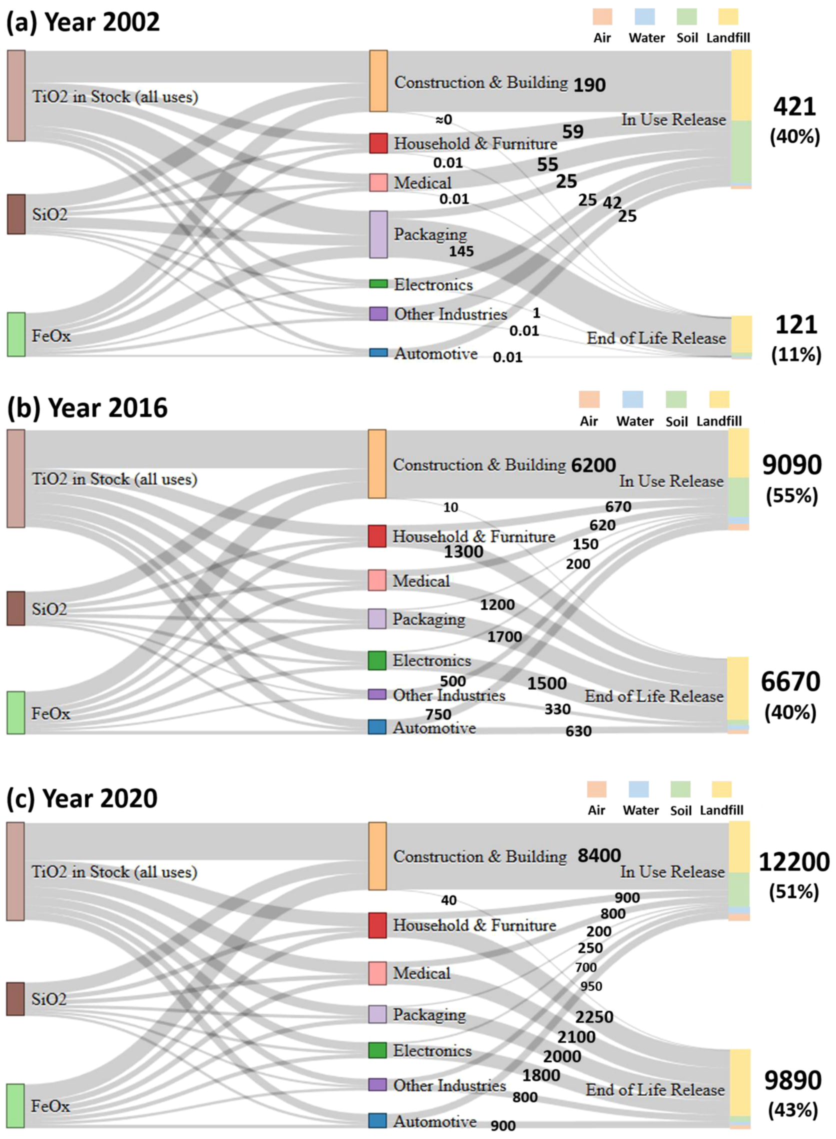

Figure 5. Analysis of the in-use and end-of-life releases (in tons) of TiO_2, SiO_2 and FeO_x ENMs from each sector in year 2002 (a), 2016 (b), and 2020 (c), along with the fraction of ENMs entering the environmental compartments of air, water, soil, and landfill. Assuming a 1− 3% annual in-use release rate, conservative production estimates and average product lifetime.

coatings applied previously in each of the seven product sectors. According to the prediction from nanoRelease, at the beginning of 2016 the stocks were 250 000 t for $nTiO_2$, 86 000 tons for $nSiO_2$, and 110 000 tons for $nFeO_x$. By the end of 2016, the stock sizes increased to 270 000 for $nTiO_2$, 93 300 for $nSiO_2$, and 120 000 tons for $nFeO_x$. The ENMs released in 2016 were about 1200 tons from manufacturing, 9100 tons from in-use, and 6800 tons from the end-of-life phase.

A closer inspection of the material flows from stocks to in-use and end-of-life releases (without manufacturing release) for 2002, 2016, and 2020 is presented in Figure 5, along with the fraction of the in-use and end-of-life releases entering water, air, soil and landfill compartments. NanoRelease estimates that in 2016 (Figure 5b) about 6200 tons of ENMs ($nTiO_2$, $nSiO_2$ and $nFeO_x$) were released from paints and coatings previously applied to buildings during the use phase, which is the highest in-use release among all product sectors. Only 10 tons of ENMs were disposed at the end-of-life of buildings in 2016. This reflects the large volume of ENMs used in construction and building sector (45%) and very long residence time of ENMs in buildings (60 years). On the other side, in 2016 only 150 tons of ENMs were released from packaging during the use phase, whereas the end-of-life release reached 1700 tons, due to the short typical residence time (1.5 years) and smaller market size (6%). The color bar on the right side of Figure 5 indicates the fraction of releases entering the environment compartments of air, water, soil and landfill. As indicated in Table 2, most of the ENMs releases end in landfill (50% for in-use release and 93% for end-of-life release).

Figure 5 also shows that the fraction of the end-of-life releases increases over time. In 2002 (Figure 5a), the fraction of end-of-life release among all releases was only about 11%, whereas in-use release contributed about 40%, and the rest was manufacturing release. As more products are retired, by 2020 (Figure 5-c) end-of-life release will contribute more than 43% of the total release flows, and the share from manufacturing release will decrease to less than 10%. A detailed example is the end-of-life release from the household and furniture sector. The average lifetime for furniture considered in the model is 15 years. In 2002, the end-of-life release from the household sector was almost zero (0.01 tons). However, by 2020 a significant fraction of the ENM-coated furniture will reach its end-of-life stage, releasing 2,250 tons of ENMs. As more products retire, we can expect increasing ENM releases in the future.

Figure 6 presents the comparison between the static model and the dynamic model in terms of the total releases of TiO_2, SiO_2, and FeO_x ENMs in 2010. In 2010, the static model estimated the total release of $nTiO_2$ from paints and coatings was 39 600 tons, while the dynamic model estimates a range of 4200 to 6100 tons for $nTiO_2$ in the same year. This highlights the importance of considering dynamic models for release estimates. Given the differences in scope (global vs European Union, 14 applications vs 1 with 7 product sectors), it was not possible to make a valid comparison between the results of Sun et al.[33] and the current model.

SI Figure S2 presents the stock size of TiO_2, SiO_2, and FeO_x ENMs in paints and coatings from 2000 to 2020. Compared with 2000, the total stock size of these three ENMs in 2020 increased by 2,800% due to the large volume of ENMs in new products over the last two decades. These growing stocks, and the eventual release of ENMs, need to be considered by solid-waste managers and product manufacturers.

To test the influence of a constant annual release rate, we considered two separate scenarios with an increasing or decreasing annual release rate during use (SI Figures S4−S6). There are noticeable differences, both in the shape of the release curves for different product groups, as well as the eventual release at a given year. For example, the "low-and-increasing" model predicts about 2900 tons of $nTiO_2$ will be released from the construction and building sector by 2020, while the "high-and-decreasing" model predicts that about 3700 tons of $nTiO_2$ will be released from the same sector by 2020. It will be important to generate more experimental release estimates from various product groups, and to consider longer-term experimental studies, to establish a better basis for modeling these releases.

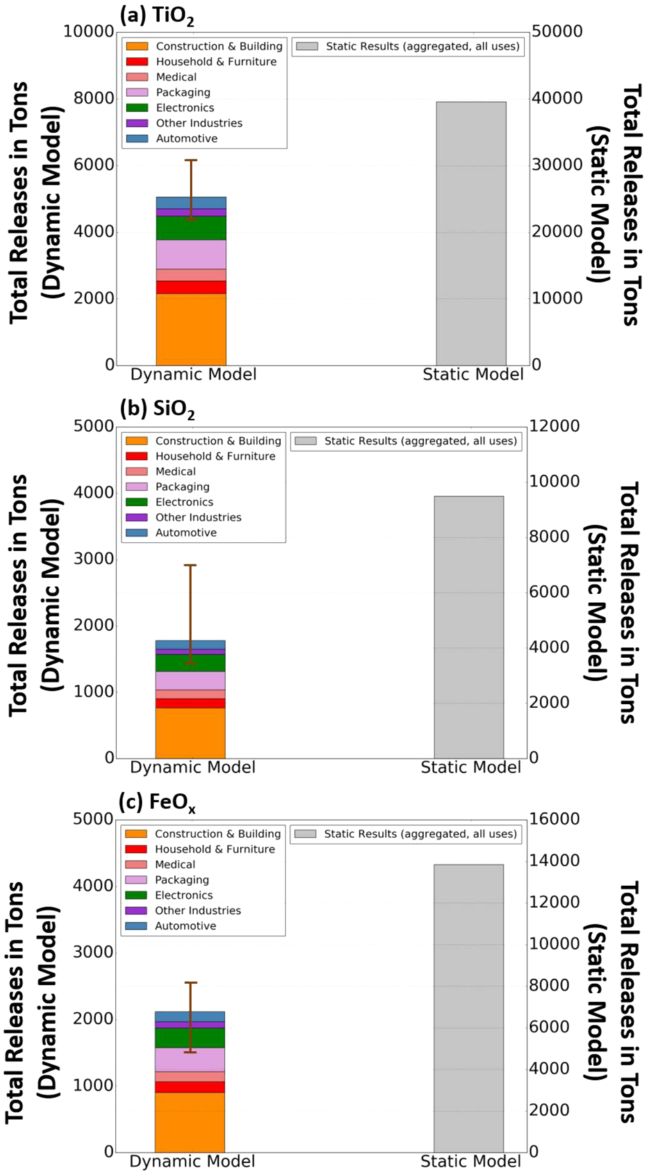

Figure 6. Comparison between the dynamic nanoRelease model and a static release model[9] for TiO_2 (a), SiO_2 (b), and FeO_x (c) ENMs in year 2010. The *y*-axis of the three subgraphs are in different scales.

In future studies, we intend to expand the dynamic model to the entire ENM market on global scale, so that more comprehensive release flows can be estimated, and more reliable information can be used by modelers. However, this will require better estimates of the input data and parameters. The predictions of nanoRelease depend strongly on the estimated annual in-use release rate (e.g., 1−3% of ENMs released from the product during its use phase every year) and the modeled lifetimes. Currently there are few studies that report this information, and no data to validate the models. The overall material flows are also very dependent on the quality of ENMs production volumes, which have only been roughly estimated by various researchers using diverse methods with

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widely different levels of accuracy. The model can be easily updated with more accurate production estimates as these become available. Moreover, in our study, the probability of product retirement at each year was estimated using a two-parameter Weibull distribution. We assumed that the product retirement rate increases overtime, therefore the shape parameter β was set to be larger than one. Future studies could also consider the effect of a different shape parameter, for example by investigating the retirement rate of ENM-enabled products over time. NanoRelease considers release estimates at a global level. For a local (e.g., country or city) release estimate, details on local manufacturing processes should be considered (e.g., open vs close manufacturing, or flame production).

Environmental Significance and Outlook. In this study, we introduced a stochastic dynamic model, nanoRelease, to estimate the life-cycle release of ENMs over time, which consists of the manufacturing, in-use and end-of-life release material flows. We considered the multiyear time lag between ENM production and release, with an increasing stock size of ENMs in different product groups. Our results showed that consideration of stock, product lifetime and release delay makes a significant difference in ENMs release estimates, which has been observed previously.[33,34] Our study focused on an ENM application (paints and coatings) in which the combination of ENM stock and release to the environment make it particularly clear that dynamic modeling is important. Compared to the dynamic models, previous static models may overestimate the total release of ENMs by almost an order of magnitude, since static ENM release models do not consider stocks, and simply integrate the emissions into a single time frame (e.g., one year of production). Thus, consideration of time lag and stock between production and release have a significant effect on the release estimates of ENMs. The results of nanoRelease and the Sun et al. model (which consider a different spatial scale and ENM applications than this study) can provide a more concrete basis for future studies that consider environmental and human health impacts of ENMs.[34]

Policy makers and waste managers can use these results to better understand the potential future releases and disposal of ENMs, and take them into consideration in their policies and design of waste management. It may also serve to motivate means for recycling more of these ENM mass flows.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b01907.

> Model input data, model parameters, stock size, detailed model output and additional analysis results with dynamic in use release rate (PDF)

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■ REFERENCES

(1) Khanna, A. S. Nanotechnology in high performance paint coatings. *Asian J. Exp. Sci.* **2008**, *21* (2), 25−32.

(2) Serrano, E.; Rus, G.; García-Martínez, J. Nanotechnology for sustainable energy. *Renewable Sustainable Energy Rev.* **2009**, *13* (9), 2373−2384.

(3) Huang, Y.; Keller, A. A. Magnetic Nanoparticle Adsorbents for Emerging Organic Contaminants. *ACS Sustainable Chem. Eng.* **2013**, *1* (7), 731−736.

(4) Su, Y.; Adeleye, A. S.; Huang, Y.; Sun, X.; Dai, C.; Zhou, X.; Zhang, Y.; Keller, A. A. Simultaneous removal of cadmium and nitrate in aqueous media by nanoscale zerovalent iron (nZVI) and Au doped nZVI particles. *Water Res.* **2014**, *63*, 102−111.

(5) West, J. L.; Halas, N. J. Engineered Nanomaterials for Biophotonics Applications: Improving Sensing, Imaging, and Therapeutics. *Annu. Rev. Biomed. Eng.* **2003**, *5* (1), 285−292.

(6) Future Markets, Inc. *The Global Market for Nanomaterials 2002−2016: Production Volumes, Revenues and End Use Markets*, 2012; pp 371.

(7) Colvin, V. L. The potential environmental impact of engineered nanomaterials. *Nat. Biotechnol.* **2003**, *21* (10), 1166−1170.

(8) Gottschalk, F.; Nowack, B. The release of engineered nanomaterials to the environment. *J. Environ. Monit.* **2011**, *13* (5), 1145.

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

(10) Keller, A. A.; Lazareva, A. Predicted Releases of Engineered Nanomaterials: From Global to Regional to Local. *Environ. Sci. Technol. Lett.* **2014**, *1* (1), 65−70.

(11) 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.

(12) 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.

(13) Garner, K. L.; Keller, A. A. Emerging patterns for engineered nanomaterials in the environment: a review of fate and toxicity studies. *J. Nanopart. Res.* **2014**, *16* (8), 2503.

(14) Garner, K. L.; Suh, S.; Keller, A. A. Assessing the Risk of Engineered Nanomaterials in the Environment: Development and Application of the nanoFate Model. *Environ. Sci. Technol.* **2017**, *51* (10), 5541−5551.

(15) Keller, A. A.; Adeleye, A. S.; Conway, J. R.; Garner, K. L.; Zhao, L.; Cherr, G. N.; Hong, J.; Gardea-Torresdey, J. L.; Godwin, H. A.; Hanna, S.; et al. Comparative environmental fate and toxicity of copper nanomaterials. *NanoImpact* **2017**, *7*, 28−40.

(16) P. Tsang, M.; Li, D.; L. Garner, K.; A. Keller, A.; Suh, S.; W. Sonnemann, G. Modeling human health characterization factors for indoor nanomaterial emissions in life cycle assessment: a case-study of titanium dioxide. *Environ. Sci.: Nano* **2017**, *4*, 1705.

(17) Liu, Z.; Davis, C.; Cai, W.; He, L.; Chen, X.; Dai, H. Circulation and long-term fate of functionalized, biocompatible single-walled

carbon nanotubes in mice probed by Raman spectroscopy. *Proc. Natl. Acad. Sci. U. S. A.* **2008**, *105* (5), 1410−1415.

(18) Adeleye, A. S.; Conway, J. R.; Perez, T.; Rutten, P.; Keller, A. A. Influence of Extracellular Polymeric Substances on the Long-Term Fate, Dissolution, and Speciation of Copper-Based Nanoparticles. *Environ. Sci. Technol.* **2014**, *48* (21), 12561−12568.

(19) Peralta-Videa, J. R.; Zhao, L.; Lopez-Moreno, M. L.; de la Rosa, G.; Hong, J.; Gardea-Torresdey, J. L. Nanomaterials and the environment: A review for the biennium 2008−2010. *J. Hazard. Mater.* **2011**, *186* (1), 1−15.

(20) Reidy, B.; Haase, A.; Luch, A.; Dawson, K. A.; Lynch, I. Mechanisms of Silver Nanoparticle Release, Transformation and Toxicity: A Critical Review of Current Knowledge and Recommendations for Future Studies and Applications. *Materials* **2013**, *6* (6), 2295−2350.

(21) Garner, K. L.; Suh, S.; Lenihan, H. S.; Keller, A. A. Species Sensitivity Distributions for Engineered Nanomaterials. *Environ. Sci. Technol.* **2015**, *49* (9), 5753−5759.

(22) Hansen, S. F.; Michelson, E. S.; Kamper, A.; Borling, P.; Stuer-Lauridsen, F.; Baun, A. Categorization framework to aid exposure assessment of nanomaterials in consumer products. *Ecotoxicology* **2008**, *17* (5), 438−447.

(23) Li, D.; Emond, C.; Johanson, G.; Jolliet, O. Using a PBPK model to study the influence of different characteristics of nanoparticles on their biodistribution. *J. Phys.: Conf. Ser.* **2013**, *429* (1), 012019.

(24) Puzyn, T.; Rasulev, B.; Gajewicz, A.; Hu, X.; Dasari, T. P.; Michalkova, A.; Hwang, H.-M.; Toropov, A.; Leszczynska, D.; Leszczynski, J. Using nano-QSAR to predict the cytotoxicity of metal oxide nanoparticles. *Nat. Nanotechnol.* **2011**, *6* (3), 175−178.

(25) Song, R.; Keller, A. A.; Suh, S. Rapid Life-Cycle Impact Screening Using Artificial Neural Networks. *Environ. Sci. Technol.* **2017**, *51* (18), 10777−10785.

(26) 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* (24), 9216−9222.

(27) Köhler, A. R.; Som, C.; Helland, A.; Gottschalk, F. Studying the potential release of carbon nanotubes throughout the application life cycle. *J. Cleaner Prod.* **2008**, *16* (8−9), 927−937.

(28) Nowack, B.; Ranville, J. F.; Diamond, S.; Gallego-Urrea, J. A.; Metcalfe, C.; Rose, J.; Horne, N.; Koelmans, A. A.; Klaine, S. J. Potential scenarios for nanomaterial release and subsequent alteration in the environment. *Environ. Toxicol. Chem.* **2012**, *31* (1), 50−59.

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

(30) Gottschalk, F.; Sonderer, T.; Scholz, R. W.; Nowack, B. Possibilities and limitations of modeling environmental exposure to engineered nanomaterials by probabilistic material flow analysis. *Environ. Toxicol. Chem.* **2010**, *29* (5), 1036−1048.

(31) Keller, A. A.; Vosti, W.; Wang, H.; Lazareva, A. Release of engineered nanomaterials from personal care products throughout their life cycle. *J. Nanopart. Res.* **2014**, *16* (7), 2489.

(32) Bornhöft, N. A.; Sun, T. Y.; Hilty, L. M.; Nowack, B. A dynamic probabilistic material flow modeling method. *Environ. Model. Softw.* **2016**, *76*, 69−80.

(33) Sun, T. Y.; Bornhöft, N. A.; Hungerbühler, K.; Nowack, B. Dynamic Probabilistic Modeling of Environmental Emissions of Engineered Nanomaterials. *Environ. Sci. Technol.* **2016**, *50* (9), 4701−4711.

(34) Sun, T. Y.; Mitrano, D. M.; Bornhöft, N. A.; Scheringer, M.; Hungerbühler, K.; Nowack, B. Envisioning Nano Release Dynamics in a Changing World: Using Dynamic Probabilistic Modeling to Assess Future Environmental Emissions of Engineered Nanomaterials. *Environ. Sci. Technol.* **2017**, *51* (5), 2854−2863.

(35) Ruhrberg, M. Assessing the recycling efficiency of copper from end-of-life products in Western Europe. *Resour. Conserv. Recycl.* **2006**, *48* (2), 141−165.

(36) Davis, J.; Geyer, R.; Ley, J.; He, J.; Clift, R.; Kwan, A.; Sansom, M.; Jackson, T. Time-dependent material flow analysis of iron and steel in the UK: Part 2. Scrap generation and recycling. *Resour. Conserv. Recycl.* **2007**, *51* (1), 118−140.

(37) Chen, W.; Shi, L.; Qian, Y. Substance flow analysis of aluminium in mainland China for 2001, 2004 and 2007: Exploring its initial sources, eventual sinks and the pathways linking them. *Resour. Conserv. Recycl.* **2010**, *54* (9), 557−570.

(38) 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.

(39) Kagawa, S.; Nansai, K.; Kondo, Y.; Hubacek, K.; Suh, S.; Minx, J.; Kudoh, Y.; Tasaki, T.; Nakamura, S. Role of Motor Vehicle Lifetime Extension in Climate Change Policy. *Environ. Sci. Technol.* **2011**, *45* (4), 1184−1191.

(40) Kagawa, S.; Hubacek, K.; Nansai, K.; Kataoka, M.; Managi, S.; Suh, S.; Kudoh, Y. Better cars or older cars?: Assessing CO2 emission reduction potential of passenger vehicle replacement programs. *Glob. Environ. Change* **2013**, *23* (6), 1807−1818.

(41) Nakamura, S.; Kondo, Y.; Kagawa, S.; Matsubae, K.; Nakajima, K.; Nagasaka, T. MaTrace: Tracing the Fate of Materials over Time and Across Products in Open-Loop Recycling. *Environ. Sci. Technol.* **2014**, *48* (13), 7207−7214.

(42) Nakamura, S.; Kondo, Y.; Matsubae, K.; Nakajima, K.; Tasaki, T.; Nagasaka, T. Quality- and Dilution Losses in the Recycling of Ferrous Materials from End-of-Life Passenger Cars: Input-Output Analysis under Explicit Consideration of Scrap Quality. *Environ. Sci. Technol.* **2012**, *46* (17), 9266−9273.

(43) Kwon, C. H.; Shin, H.; Kim, J. H.; Choi, W. S.; Yoon, K. H. Degradation of methylene blue via photocatalysis of titanium dioxide. *Mater. Chem. Phys.* **2004**, *86* (1), 78−82.

(44) Gaya, U. I.; Abdullah, A. H. Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems. *J. Photochem. Photobiol., C* **2008**, *9* (1), 1−12.

(45) Lazareva, A.; Keller, A. A. Estimating Potential Life Cycle Releases of Engineered Nanomaterials from Wastewater Treatment Plants. *ACS Sustainable Chem. Eng.* **2014**, *2* (7), 1656−1665.

(46) Allen, N. S.; Edge, M.; Ortega, A.; Sandoval, G.; Liauw, C. M.; Verran, J.; Stratton, J.; McIntyre, R. B. Degradation and stabilisation of polymers and coatings: nano versus pigmentary titania particles. *Polym. Degrad. Stab.* **2004**, *85* (3), 927−946.

(47) Kaegi, R.; Ulrich, A.; Sinnet, B.; Vonbank, R.; Wichser, A.; Zuleeg, S.; Simmler, H.; Brunner, S.; Vonmont, H.; Burkhardt, M.; et al. Synthetic TiO2 nanoparticle emission from exterior facades into the aquatic environment. *Environ. Pollut.* **2008**, *156* (2), 233−239.

(48) 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.

(49) Al-Kattan, A.; Wichser, A.; Zuin, S.; Arroyo, Y.; Golanski, L.; Ulrich, A.; Nowack, B. Behavior of TiO2 Released from Nano-TiO2-Containing Paint and Comparison to Pristine Nano-TiO2. *Environ. Sci. Technol.* **2014**, *48* (12), 6710−6718.

(50) Al-Kattan, A.; Wichser, A.; Vonbank, R.; Brunner, S.; Ulrich, A.; Zuin, S.; Nowack, B. Release of TiO 2 from paints containing pigment-TiO 2 or nano-TiO 2 by weathering. *Environ. Sci. Process. Impacts* **2013**, *15* (12), 2186−2193.

(51) Benn, T. M.; Westerhoff, P. Nanoparticle Silver Released into Water from Commercially Available Sock Fabrics. *Environ. Sci. Technol.* **2008**, *42* (11), 4133−4139.

(52) Al-Kattan, A.; Wichser, A.; Vonbank, R.; Brunner, S.; Ulrich, A.; Zuin, S.; Arroyo, Y.; Golanski, L.; Nowack, B. Characterization of materials released into water from paint containing nano-SiO2. *Chemosphere* **2015**, *119*, 1314−1321.

(53) Adeleye, A. S.; Oranu, E. A.; Tao, M.; Keller, A. A. Release and detection of nanosized copper from a commercial antifouling paint. *Water Res.* **2016**, *102*, 374−382.

(54) Danckwerts, P. V. Continuous flow systems. *Chem. Eng. Sci.* **1953**, *2* (1), 1−13.
(55) Melo, M. T. Statistical analysis of metal scrap generation: the case of aluminium in Germany. *Resour. Conserv. Recycl.* **1999**, *26* (2), 91−113.
(56) Hatayama, H.; Daigo, I.; Matsuno, Y.; Adachi, Y. Outlook of the World Steel Cycle Based on the Stock and Flow Dynamics. *Environ. Sci. Technol.* **2010**, *44* (16), 6457−6463.
(57) B. Müller, D. Stock dynamics for forecasting material flows—Case study for housing in The Netherlands. *Ecol. Econ.* **2006**, *59* (1), 142−156.
(58) Kleijn, R.; Huele, R.; van der Voet, E. Dynamic substance flow analysis: the delaying mechanism of stocks, with the case of PVC in Sweden. *Ecol. Econ.* **2000**, *32* (2), 241−254.
(59) Brunner, P. H.; Rechberger, H. *Practical Handbook of Material Flow Analysis*; Springer, 2004.
(60) Xie, M.; Lai, C. D. Reliability analysis using an additive Weibull model with bathtub-shaped failure rate function. *Reliab. Eng. Syst. Saf.* **1996**, *52* (1), 87−93.
(61) Chen, Z.; Zheng, S. Lifetime distribution based degradation analysis. *IEEE Trans. Reliab.* **2005**, *54* (1), 3−10.
(62) Dahlström, K.; Ekins, P.; He, J.; Davis, J.; Clift, R. Iron, steel and aluminium in the UK: material flows and their economic dimensions. *London Policy Stud. Inst.* 2004.
(63) Papoulis, A.; Pillai, S. U. *Probability, Random Variables, And Stochastic Processes*; Tata McGraw-Hill Education, 2002.
(64) Suhir, E. *Applied Probability for Engineers and Scientists*; McGraw-Hill: New York, 1997.
(65) US EPA. Time Lag and Composition of Durable Goods U.S. Environmental Protection Agency Office of Resource Conservation and Recovery. April 2014.
(66) Nanocoatings Market http://www.futuremarketsinc.com/the-global-market-for-nanocoatings/ (accessed July 19, 2017).
(67) Future Markets Inc. Future_Markets (2012) *The global market for nanomaterials* 2002−2006: production volumes, revenues and end use markets. http://www.futuremarketsinc.com/index.php?option=com_content&view=article&id=176&Itemid=73.
(68) Robichaud, C. O.; Uyar, A. E.; Darby, M. R.; Zucker, L. G.; Wiesner, M. R. Estimates of Upper Bounds and Trends in Nano-TiO2 Production As a Basis for Exposure Assessment. *Environ. Sci. Technol.* **2009**, *43* (12), 4227−4233.
(69) Hendren, C. O.; Mesnard, X.; Dröge, J.; Wiesner, M. R. Estimating Production Data for Five Engineered Nanomaterials As a Basis for Exposure Assessment. *Environ. Sci. Technol.* **2011**, *45* (7), 2562−2569.
(70) 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.
(71) Sprow, F. B. Evaluation of research expenditures using triangular distribution functions and Monte Carlo Methods. *Ind. Eng. Chem.* **1967**, *59* (7), 35−38.
(72) Qin, Y.; Suh, S. What distribution function do life cycle inventories follow? *Int. J. Life Cycle Assess.* **2017**, *22* (7), 1138−1145.
(73) Jacoboni, C.; Lugli, P. *The Monte Carlo Method for Semiconductor Device Simulation*; Springer Science & Business Media, 2012.
(74) Binder, K. *Applications of the Monte Carlo Method in Statistical Physics*; Springer Science & Business Media, 2013.
(75) Eberle, L. G.; Sugiyama, H.; Schmidt, R. Improving lead time of pharmaceutical production processes using Monte Carlo simulation. *Comput. Chem. Eng.* **2014**, *68*, 255−263.
(76) Hendren, C. O.; Badireddy, A. R.; Casman, E.; Wiesner, M. R. Modeling nanomaterial fate in wastewater treatment: Monte Carlo simulation of silver nanoparticles (nano-Ag). *Sci. Total Environ.* **2013**, *449*, 418−425.
(77) Vinodh, Sekar; Rathod, Gopinath Application of life cycle assessment and Monte Carlo simulation for enabling sustainable product design. *J. Eng. Des. Technol.* **2014**, *12* (3), 307−315.
(78) Suh, S.; Qin, Y. Pre-calculated LCIs with uncertainties revisited. *Int. J. Life Cycle Assess.* **2017**, *22* (5), 827−831.

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