ACS Sustainable Chemistry & Engineering

Research Article

pubs.acs.org/journal/ascecg

Estimating Potential Life Cycle Releases of Engineered Nanomaterials from Wastewater Treatment Plants

Anastasiya Lazareva* and Arturo A. Keller

UC Center on the Environmental Implications of Nanotechnology and Bren School of Environmental Science and Management, University of California, Santa Barbara, 2400 Bren Hall, Santa Barbara, California 93106-5131, United States

Supporting Information

ABSTRACT: In the absence of experimental data, a life cycle modeling approach can be used to predict engineered nanomaterial (ENM) concentrations in environmental media. Several such models have been created with various geographic scopes. This study presents an environmental release model that accounts for local differences in product consumption, wastewater treatment levels, waste incineration, and biosolids management and provides estimates of ENM release from wastewater treatment facilities in New York City, London, and Shanghai. The results illustrate how these local variations in model parameters contribute to differences in predicted ENM concentration in wastewater effluent and biosolids on a local level. Our analysis also takes a first step toward conducting a local-level risk assessment by providing the approximate locations and quantities of ENM discharge into aquatic systems. We find that there is significant uncertainty in model parameters that leads to a wide range of concentration estimates, yet we find that local variations in model parameters predict ENM concentration estimates that are within the same order of magnitude.

KEYWORDS: *Nanomaterial exposure, Aquatic risk, Life cycle, Regional exposure, Emerging contaminants*

INTRODUCTION

Engineered nanomaterials (ENMs) are incorporated into a growing variety of products ranging from common household items to novel medical technologies. Research is underway to determine the risks associated with the potential release of engineered nanomaterials to the environment in order to ensure that the proliferation of nanotechnology does not lead to unintended environmental consequences.[1] These efforts involve the study of ENMs fate and behavior in natural systems as well as their toxic effects on aquatic and terrestrial organisms. Such studies require an understanding of the likely quantities of environmental ENM release and the resulting environmental concentrations.

The ability to conduct experiments using environmentally relevant ENM concentrations has been hindered by the difficulty of detecting ENMs in environmental media using currently available technology. Consequently, there is a heightened need for predictive exposure models to determine the likely concentrations of ENMs in the environment. Several approaches have been developed to model environmental releases of ENMs from a life cycle perspective for a variety of ENMs and geographic locations. These studies take into account the possibility of ENM release during manufacturing, product use, and disposal. Boxall et al. assessed the likely environmental concentrations for a variety of ENMs in the United Kingdom and identified potential release pathways for ENMs from a life cycle perspective.[2] Muller and Nowack created a deterministic life cycle material flow model to generate estimates of the environmental concentrations of TiO_2, Ag, and CNT in Switzerland.[3] Gottschalk et al. developed a probabilistic model of life cycle ENM releases in order to account for the uncertainty in input parameters.[3] The model was used by Gottschalk et al. to predict environmental concentrations of TiO_2, ZnO, Ag, CNT, and fullerenes for Europe, United States, and Switzerland[4] and by Sun et al. in order to generate new estimates using updated production and release assumptions.[6] Money et al. used Bayesian networks to estimate the likely exposure and risk of nanomaterials entering the environment.[7] Keller et al. produced a global life cycle release assessment for 10 major nanomaterials[8] and developed a framework for using a top-down approach in order to generate release estimate on a regional and local level.[9]

Life cycle ENM release studies have identified wastewater treatment facilities (WWTPs) as a significant exposure pathway to aquatic and terrestrial ecosystems.[10−12] Recognizing the need to better understand ENM transport though these systems, several studies used laboratory-scale WWTPs to investigate the behavior of ENM during wastewater treatment and determine ENM partitioning between effluent and biosolids.[13−17] Predictive models, using a probabilistic life cycle release approach, have developed a screening tool to determine likely concentrations of nano-Ag in wastewater

Special Issue: Sustainable Nanotechnology 2013

Received: February 21, 2014
Revised: April 29, 2014
Published: May 21, 2014

effluent and sludge.[13] Additionally, sampling has been conducted at full-scale WWTP facilities to determine nano-TiO_2concentrations in wastewater effluent and biosolids[18−20] and to measure change in TiO_2 concentrations after primary, secondary, and tertiary treatment.[21]

Previous studies have identified the need to account for the regional difference in ENM production and use within specific applications when conducting a multi-regional ENM release analysis.[5] This study presents an environmental release model that accounts for these differences by incorporating market data as well as available economic indicators to estimate regional ENM production and use. We demonstrate this approach by modeling nanomaterial releases from WWTPs in New York City, London, and Shanghai. The model is executed using global ENM production estimates based on a market study as well as newly available European regulatory review of nanomaterials. The results illustrate how local variations in product consumption, wastewater treatment availability, and wastewater treatment levels contribute to differences in predicted ENM concentration in wastewater effluent and biosolids in a local level. Our analysis also takes a first step toward conducting a local-level risk assessment by providing the approximate locations and quantities of ENM discharge into aquatic systems.

METHODS

A life cycle material flow model was developed using a mass balance approach to account for environmental ENM releases during the entire product life cycle, as described previously,[9] by adjusting model parameters specific for each of the three studied locations. Several new studies and data sources were considered in this enhancement of the previous methods and are discussed below. We consider ENM release during production, use, wastewater treatment, management of biosolids, product disposal, and waste incineration. Therefore, release variables and transfer coefficients were collected for each location (New York City, London, and Shanghai) included in the study. These parameters were obtained from scientific literature, market information, and assumptions based on quantitative analyses using publically available statistics. Equations used to derive the final environmental distribution of ENMs in the environment are presented in the Supporting Information. The following sections describe the methods used to gather release variables and model inputs.

Production. The model considers global ENM production estimates collected from two sources: a market study[22] and a regulatory review of nanomaterials by the European Commission (EC).[23] There is a significant difference in the reported global ENM production rates between these studies, summarized in Table 1. Note that the market study did not consider carbon black, which is a high-volume ENM according to EC. Therefore, we provide release estimates based on inputs from both sources. Although the EC report provides information about the major uses of each ENM, only the market study[22] provides a quantitative estimate of ENM use within specific applications.

Our model takes into account ENM release during the production process (Table S1, Supporting Information) based on previous life cycle release studies.[10] Currently, information about the exact locations of ENM manufacturing facilities is unavailable for individual nanomaterials. However, the market study[22]provides a general high-level overview of ENM production locations. According to the study, the United States accounts for 50% of global ENM production, China for 12%, and the European Union manufactures 19% of all nanomaterials produced worldwide.

Table 1. Global ENM Production as of 2010

ENM	Future Markets[22] (metric tons/year)	European Commission[23] (metric tons/year)
Ag	360−450	22
Al_2O_3	18,500- 35,000	200,000
carbon black		9,600,000
CeO_2	7500−10,000	10,000
CNT	2916−3200	500
Cu and CuO_x	22−200	
Fe and FeO_x	33,000−42,000	100
nanoclays	9200−10,400	
SiO_2	82,500−95,000	1,500,000
TiO_2	83,500−88,000	10,000
ZnO	31,500−34,000	8000

To estimate ENM production in the United Kingdom, additional assumptions were made using publically available statistics. High technology export data[24] and information about the relative investment in research and development (R&D)[25] for each European country were used as a proxy for nanomaterial production. It was assumed that countries with established high technology industries and high investments in research and development are responsible for the majority of European ENM production. We assume that countries that fall into the top 30% in both R&D and high technology exports are responsible for 80% of European ENM production. Among European countries, the U.K. is in the 80th percentile for high technology exports and in the 70th percentile for R&D investments. Therefore, we assumed that the U.K. belongs to the group of high-producing countries responsible for 80% of European ENM production. European production was allocated evenly between 10 countries that fell into the "high production" category. As a result, the U.K. was assumed to account for roughly 8% of Europe's ENM production.

A similar analysis was performed to determine ENM production levels for each state in the United States. State-level data on the prevalence of high technology business establishments[26] and investments in R&D[27] was used as a proxy for ENM production within each state. New York State was ranked the 30th percentile in R&D expenditures and in the 40th percentile in the abundance of high technology industries. As a result, New York State was assumed to account for roughly 0.5% of the U.S. ENM production. Country and state production estimates were further adjusted for each city based on reported population residing in each city.

Use. We assume that the level of development in each country is correlated with its residents' capacity to consume ENM-containing products. The Inequality-Adjusted Human Development Index (IHDI) was used to determine the relative development levels of all countries.[28] The fraction of people using nanomaterials in each country was based on the country's IDHI decile score (Table S2, Supporting Information). For example, the United States' and United Kingdom's IDHI are in the 80th percentile; as a result, 27−40% of the population is assumed to use ENM-containing products. China's IHDI falls into the 50th percentile, and thus, we assume that only 18−25% of China's population use products containing ENMs.

To improve our previous estimates,[9] for applications where market information was available, it was used to better estimate regional consumption of ENM-containing products. The use of ENMs contained in personal care products was based on a cosmetics industry market study.[29] The use of nanomaterials in the automotive sector was based on a global automotive sales report.[30] Estimates for the electronic, optics, and sensors applications were based on an electronics industry market report.[31] The regional shares of ENM use in medical applications was based on a government analysis.[32] Reports on several applications only provide consumption data on a regional level, aggregating consumption for European, Asian, and North American countries. Regional consumption for these applications is summarized in Table S4 of the Supporting Information.

In order to determine the local level of consumption within these ENM applications, consumption data for each country was estimated by adjusting regional data based on the IHDI-based regional consumption fractions calculated for each country. According to the analysis, China consumes 47% of Asia's ENM-containing products, the U.K. accounts for 9% of Europe's ENM use, and the United States accounts for 74% of North American use of ENMs. Table 2 shows the resulting use fraction assumptions for each application included in this analysis.

Table 2. Percent of Global ENM Use by Application

application	China (%)	United Kingdom (%)	United States (%)	ref
automotive	18	2	18	30
catalysts	23	2	8	22
coatings, paints, and pigments	23	2	8	22
cosmetics	12	3	15	29
composites	23	2	8	22
electronics and optics	17	3	18	31
energy and environment	23	2	8	22
medical	6	2	53	32
plastics	23	2	8	22
sensors	17	3	18	31
textiles	23	2	8	22
tires	18	2	18	30

A similar analysis was performed for each U.S. state based on per capita GDP.[33] Tables S3 and S4 of the Supporting Information summarize the assumptions made for the United States state-level use of ENMs. New York State's per-capita GDP falls into the 90th percentile; therefore, 39% of its population is assumed to consume ENM-containing products, accounting for 7% of ENMs consumed in the United States.

Release during Use. Release during use was based on data collected from experimental and life cycle modeling studies of ENM release from multiple applications including coatings,[34] paints,[35−37] textiles,[38−40] composites,[41] and plastics.[42] Release from personal care products was based on a consumer survey.[43] Release of ENMs from tires was based on a recent Swiss study.[44] Use release assumptions are presented in Table S7 of the Supporting Information.

Some applications, such as personal care products, coatings, paints, and pigments, lead to significant ENM release to wastewater during use. Not all ENMs that are released to wastewater will eventually end up in wastewater treatment facilities. A fraction of wastewater will be treated in independent treatment systems such as septic tanks, and a fraction will remain untreated and be released directly into surface water. In order to account for these factors, we used available information (Table S6, Supporting Information) on the level of wastewater treatment and the fraction of wastewater that undergoes independent treatment for each country included in our study. It was assumed that untreated wastewater will be released directly into surface water bodies and that 5% of ENM's released from septic tanks will eventually end up in surface water while 95% will remain in the soil. In addition to direct release to wastewater treatment during use, we assume that a fraction (15−25%) of ENMs that are released directly to air and soil during use will enter wastewater facilities via surface runoff. This is an assumption, given that the fraction depends on uncertain estimates of atmospheric removal, attachment, and detachment from solid surfaces and stormwater capture by sewer systems; all of these processes depend on myriad factors. The net effect of this assumption is that we estimate a larger amount of the final ENM mass passes through the WWTP than if we assume 0%; it is unlikely that there is high transfer efficiency in all of the processes.

Release from Wastewater Treatment. Several studies suggest that a higher fraction of ENMs is removed in facilities that employ secondary or tertiary treatment technologies. Studies that focused on EMN removal during primary wastewater treatment found lower ENM removal rates[15,21] than those measured in experiments featuring higher levels of treatment technology.[14,17] It is important to note that ENM release from WWTPs can depend on intermediate transformation processes such as ENM dissolution (Zn0 and Ag), sorption to organic matter (all ENMs), sulfidation (metal ENMs), and biodegradation (CNT). These factors were not incorporated into our model. However, we assume that these transformations were captured in the release rates measured in previous experimental studies that are used as inputs into our model.

According to the OECD, 99% of U.K. wastewater undergoes secondary or higher treatment and 91% of U.S. wastewater undergoes secondary or higher treatment.[45] The reported secondary treatment rate for Shanghai is only 19.8%.[46] We assume that 3−25% of ENMs that enter WWPTs will be released from facilities that employ secondary or higher levels of treatment[3] and 20−60% will be released from facilities that offer only primary treatment based on the available experimental results. The resulting release variables for each location are summarized in Table S6 of the Supporting Information.

Biosolids Management. Our model considers three methods of biosolids management: application to agricultural soils, incineration, and landfilling. Information on the management of biosolids in China and the United States was gathered from[47] and is summarized in Table S7 of the Supporting Information. The application of biosolids in the United Kingdom was based on the average reported numbers for EU15. Within the United States, state-specific information on the management of biosolids was used.[48]

Waste Incineration. The percent of municipal solid waste that is incinerated in the U.K. (11%) and China (12.9%) was provided by a UN report.[49] The incineration fraction in New York State is assumed to be 21.7%.[50] Releases from Waste Incineration Plants (WIP) to the air are assumed to vary based on the emission control technology employed at the facilities.

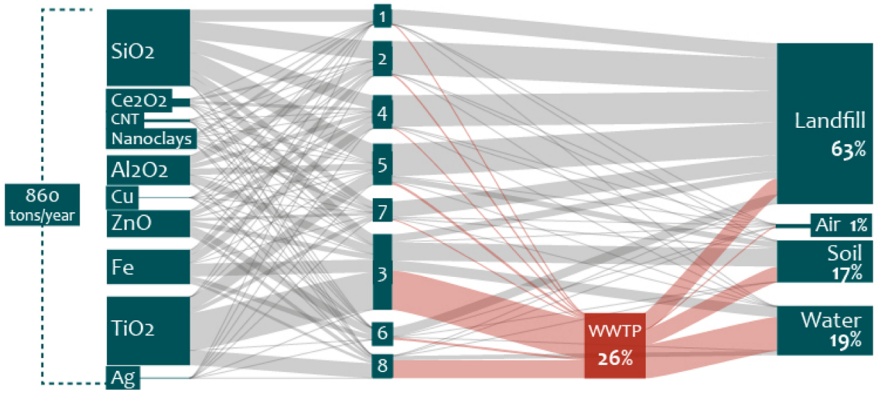


Figure 1. Shanghai life cycle ENM flows based on high release scenario and market study production estimates. (1) Automotive, (2) Catalysts, (3) Coatings, paints, and pigments, (4) Electronics and optics, (5) Energy and environment, (6) Medical, (7) Other, and (8) Personal care products.

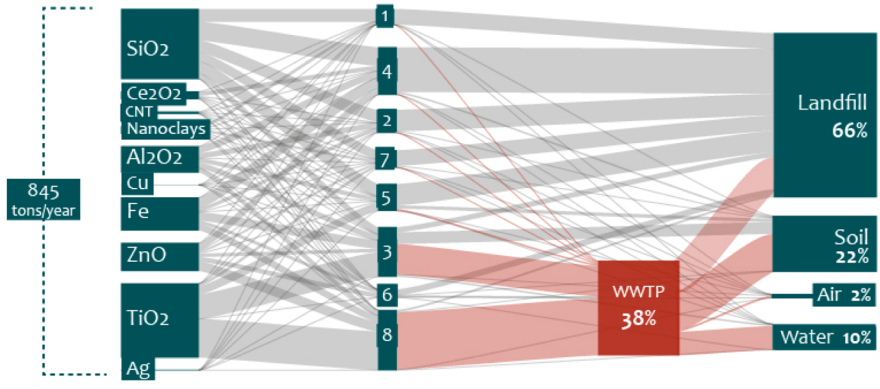


Figure 2. London life cycle ENM flows based on high release scenario and market study production estimates. (1) Automotive, (2) Catalysts, (3) Coatings, paints, and pigments, (4) Electronics and optics, (5) Energy and environment, (6) Medical, (7) Other, and (8) Personal care products.

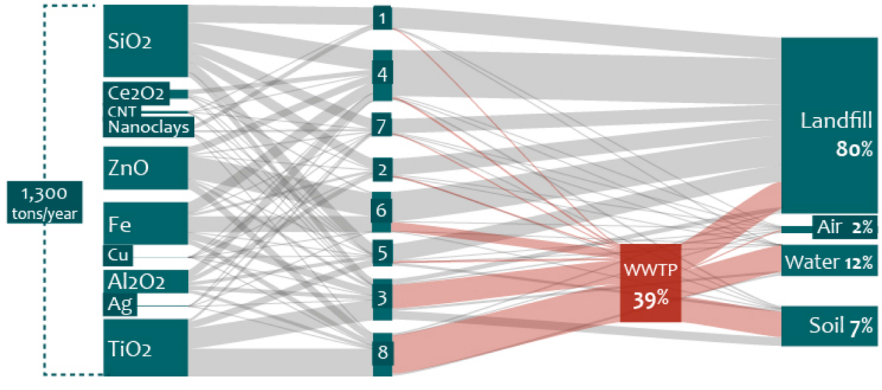


Figure 3. New York City ENM life cycle ENM flows based on high release scenario and market study production estimates. (1) Automotive, (2) Catalysts, (3) Coatings, paints, and pigments, (4) Electronics and optics, (5) Energy and environment, (6) Medical, (7) Other, and (8) Personal care products.

There is a lack of information about WIP emissions control technology used within each country and the effectiveness of different technologies on removing ENMs. Therefore, we assume that the level of development in each country is correlated with the level of WIP emissions control with a minimum and maximum level.[3] Countries with the lowest IHDI will have no air emission technology, resulting in the release of all ENMs that would have otherwise been captured by filters; countries with the highest IHDI will have the maximum emissions control reported.[3] Table S8 of the Supporting Information lists the WIP assumptions that were incorporated into our model.

Wastewater Treatment Facilities. The mass of ENMs consumed within each metropolitan area was assumed to be proportional to the areas' population. The population of Shanghai (~18.8 million) accounts for less than 1% of China's total population,[46] London's population makes up roughly 13% of U.K.'s population,[51] and New York City represents 43% of New York State's population.[52]

The locations and daily flow data for New York City wastewater treatment facilities were gathered from USEPA

data.[53] The locations of London's WWTP facilities and data on the production of effluent and biosolids were collected from an European Environmental Agency (EEA) database.[54] Shanghai's WWTPs were located based on a recent study,[46] as well as an Internet search to collect WWTP location and daily flow data.

On the basis of the WWTP information, the WWTP effluent discharge was estimated to be 1.49 billion m^3/yr in London, 1.23 billion m^3/yr in New York City, and 1.84 billion m^3/yr in Shanghai. Additional information on effluent discharge calculations can be found in the Supporting Information.

RESULTS

The life cycle ENM material flows and final environmental distribution in Shanghai, London, and New York City are shown in Figures 1−3, considering the market study 2010 production and high emissions to the environment estimates. ENM transfer through WWTP and final distributions in landfill, air, soil, and water are presented as a percentage (displayed in the boxes) of the total ENM release within each city. On the basis of the differences in applications and waste handling, a higher fraction of ENMs are expected to end in landfills in New York City (80%) than in London (66%) and Shanghai (63%). Conversely, 38% of ENMs are predicted to pass through WWTPs in London and 39% in New York City, while only 26% of ENMs transport though WWTPs in Shanghai. Given the higher level of wastewater treatment, only 10% of ENMs (and their dissolution or transformed residuals) would be emitted via the effluent in New York City or London, while 19% would be released to water bodies in Shanghai. Air emissions are 1−2% for the three metropolitan areas. Although we expect ENM release from WWTPs effluent and direct release to water, air, and soil during use to be localized, ENMs contained in biosolids or contained in discarded products may be transported outside city limits.

Table 3 shows the estimated range of per capita ENM mass entering WWTP facilities by ENM type, while Table 4 shows the estimated per capita mass discharged in WWTP effluent after treatment. Carbon black is expected to be the predominant ENM in wastewater effluent across all three locations, followed by TiO_2, ZnO, Fe, and Fe Oxides. Per capita effluent release of ENMs is estimated at 1−138 g/year in New York City, 1−65 g/year in London, and 3−61 g/year in Shanghai. Although per capita release in Shanghai is expected to be lower, the city's high population makes Shanghai's total quantity of ENM release comparable to total release in London.

Table 3. Predicted ENM Mass (low-to-high) Entering WWTPs, Based on Market Study Production Estimates, Except Carbon Black Which Is Based on the EC Report

ENM	New York (g/person-year)	Shanghai (g/person-year)	London (g/person-year)
Ag	0.03−0.13	0.00−0.03	0.03−0.08
Al_2O_3	0.82−3.69	0.15−1.18	0.83−3.48
carbon black	54−348	15−108	31−219
CeO_2	0.06−0.60	0.01−0.18	0.03−0.37
CNT	0.01−0.10	0.00−0.04	0.01−0.08
Cu + CuO_x	0.00−0.02	0.00−0.01	0.00−0.01
Fe + FeO_x	2.16−7.54	0.34−1.73	1.89−5.50
nanoclays	0.34−0.75	0.05−0.19	0.34−0.71
SiO_2	0.26−2.99	0.12−1.29	0.23−2.44
TiO_2	12.02−22.70	1.95−5.88	12.19−22.23
ZnO	3.38−8.19	0.45−1.23	2.96−5.57
total	73−395	18−119	50−260

Table 4. ENM Mass (low-to-high) Discharged via WWTP Effluent, Based on Market Study Production Estimates, Except Carbon Black Which Is Based on the EC Report

ENM	New York (g/person-year)	Shanghai (g/person-year)	London (g/person-year)
Ag	0.00−0.05	0.00−0.01	0.00−0.02
Al_2O_3	0.02−1.29	0.02−0.60	0.02−0.87
carbon black	1.07−121.85	2.31−55.15	0.63−54.79
CeO_2	0.00−0.21	0.00−0.09	0.00−0.09
CNT	0.00−0.03	0.00−0.02	0.00−0.02
Cu + CuO_x	0.00−0.01	0.00−0.00	0.00−0.00
Fe + FeO_x	0.04−2.64	0.05−0.88	0.04−1.38
nanoclays	0.01−0.26	0.01−0.10	0.01−0.18
SiO_2	0.01−1.04	0.02−0.66	0.00−0.61
TiO_2	0.24−7.95	0.31−3.01	0.24−5.56
ZnO	0.07−2.87	0.07−0.63	0.06−1.39
total	1−138	3−61	1−65

Tables 5 and 6 show the average predicted concentrations in effluent and biosolids considering the market study. Results based on the EC review are presented in Tables S9 and S10 of the Supporting Information to illustrate the range of WWTP effluent and biosolids concentration estimates using these production estimates. TiO_2 concentrations are expected to

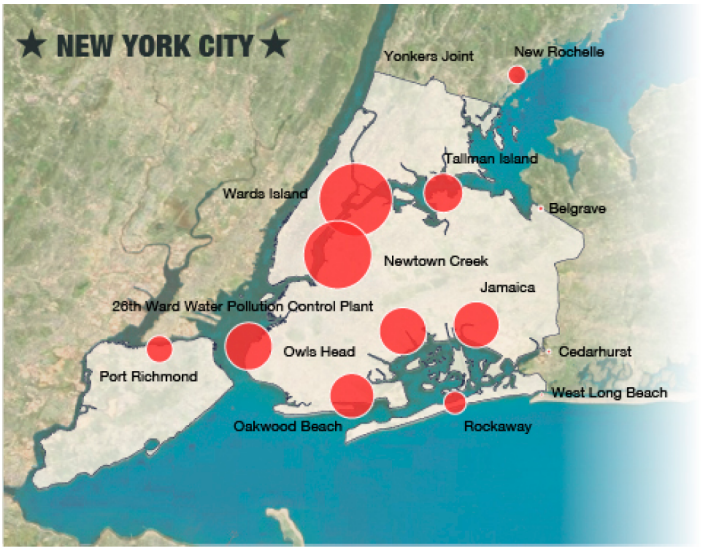
Table 5. Concentrations in Effluent Using Market Study Production Estimates, Except Carbon Black Which Is Based on the EC Report

ENM	New York (μg/L)	Shanghai (μg/L)	London (μg/L)
Ag	0.004−0.26	0.008−0.13	0.003−0.11
Al_2O_3	0.09−7.13	0.25−6.17	0.09−4.56
carbon black	5.912−672.91	23.582−563.06	3.281−287.46
CeO_2	0.007−1.17	0.024−0.93	0.003−0.49
CNT	0.001−0.19	0.006−0.23	0.001−0.11
Cu + CuO_x	>0.001−0.03	>0.001−0.03	>0.001−0.02
Fe + FeO_x	0.24−14.56	0.54−9.02	0.20−7.22
nanoclays	0.04−1.45	0.09−1.00	0.04−0.93
SiO_2	0.03−5.77	0.20−6.74	0.02−3.20
TiO_2	1.33−43.88	3.13−30.73	1.28−29.18
ZnO	0.37−15.84	0.72−6.43	0.31−7.32

Table 6. Concentrations in Biosolids Using Market Study Production Estimates, Except Carbon Black Which Is Based on the EC Report

ENM	New York (mg/kg)	Shanghai (mg/kg)	London (mg/kg)
Ag	0.78−2.01	0.18−0.54	0.58−1.37
Al_2O_3	19−56	6−25	18−57
carbon black	1220−5240	530−2250	675−3620
CeO_2	1.39−9.10	0.53−3.74	0.70−6.16
CNT	0.18−1.49	0.14−0.92	0.15−1.34
Cu + CuO_x	0.01−0.24	>0.01−0.12	0.01−0.21
Fe + FeO_x	49−114	12−36	41−91
nanoclays	8−11	2−4	7−12
SiO_2	6−45	4−27	5−40
TiO_2	273−342	70−123	263−367
ZnO	77−124	16−26	64−92

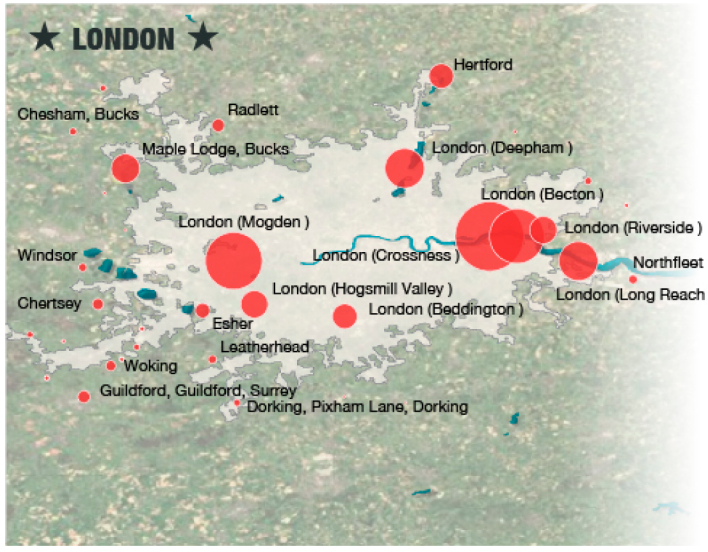
dx.doi.org/10.1021/sc500121w | ACS Sustainable Chem. Eng. 2014, 2, 1656−1665



ENM Mass Loading (kg/year)

	TiO_2	Ag	CeO_2	CNT
·	10	0.06	0.3	0.05
•	100	0.6	2.7	0.45
●	1,000	6	27	4.5
●	10,000	60	270	45
Concentrations				
Effluent (μg/L)	45	0.26	1.2	0.2
Biosolids (mg/kg)	342	2	9.1	1.5

Figure 4. Predicted effluent ENM mass loading (kg/year) from WWTPs in New York City. High release estimate based on market study 2010 production data.



ENM Mass Loading (kg/year)

	TiO_2	Ag	CeO_2	CNT
·	10	0.04	0.17	0.04
•	100	0.4	1.7	0.4
●	1,000	4	17	4
●	10,000	40	170	40
Concentrations				
Effluent (μg/L)	29	0.1	0.5	0.1
Biosolids (mg/kg)	370	1.4	6.2	1.3

Figure 5. Predicted effluent ENM mass loading (kg/year) from WWTPs in London. High release estimate based on market study 2010 production data.

range from 1.3 to 44 μg/L in New York City, 1.9−29 μg/L in London, and 1.3−29 μg/L in Shanghai. The predicted concentrations in biosolids are 273−342 mg/kg in New York City, 263−367 mg/kg in London, and 70−120 mg/kg in Shanghai. For comparison, using production data provided in the European Commission report results in TiO_2 effluent concentrations of 0.16−5 μg/L in New York City, 0.15−3.32 μg/L in London, and 0.37−3.5 μg/L in Shanghai.

Predicted annual mass of ENMs discharged via WWTP effluents are shown in Figures 4−6. The mass loading (kg/year) is based on the high release scenario using market study production estimates. These maps show the range and geographic distribution of ENM releases. Across individual WWTPs, mass loading of TiO_2 ranges from 4 to 12,000 kg/year in New York City, 14 to 11,000 kg/year in London, and 16 to 16,000 kg/year in Shanghai.

DISCUSSION

Differences in predicted local ENM concentrations can be attributed to several factors such as regional differences in product consumption within certain applications, wastewater treatment availability and treatment levels, waste incineration, and biosolids disposal practices. Although the total per capita release of nanomaterials is higher in New York City, the majority of nanomaterials consumed in the United States are used within applications that lead to low release to WWTPs. Applications such as personal care products, and coatings, paints, and pigments lead to high ENM release to wastewater during use. These applications account for roughly 33% of ENMs consumed in the United States, while in the United Kingdom, these applications represent 43% of ENM use. Factors such as slightly lower levels of wastewater treatment, 95% in the U.S. vs 100% in the U.K., and a higher wastewater fraction that undergoes independent treatment further lower

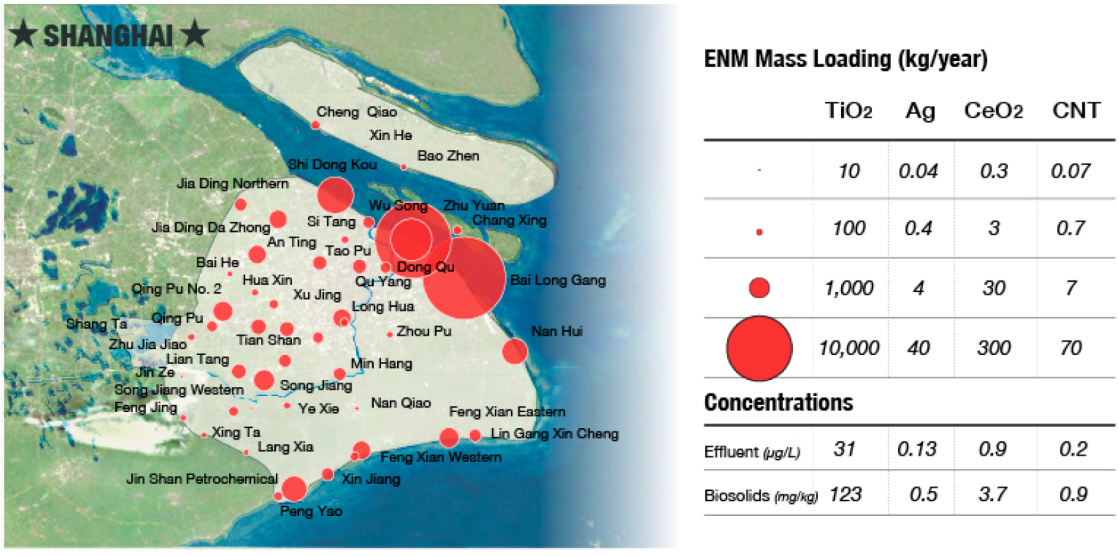


Figure 6. Predicted effluent ENM mass loading (kg/year) from WWTPs in Shanghai. High release estimate based on market study 2010 production data.

Table 7. Predicted ENM Concentrations in Effluent Based on Life Cycle Release Models and Measurements

study (ref)	study type	ENM	location	estimate		range	range details
4	model	TiO_2	Europe	3.47 μg/L	mode	2.5−10.8 μg/L	15−85%
6	model	TiO_2	EU	16 μg/L	mode	13−110 μg/L	15−85%
4	model	TiO_2	Switzerland	4.28 μg/L	mode	3.5−16.3 μg/L	15−85%
6	model	TiO_2	Switzerland	32 μg/L	mode	26−220 μg/L	15−85%
18	measurement	Ti	United Kingdom	3.2 μg/L			
this study	model	TiO_2	London			1.28−29.18 μg/L	low−high
4	model	TiO_2	United States	1.75 μg/L	mode	1.37−6.7 μg/L	15−85%
21	measurement	Ti	United States			<5−15 μg/L	
9	model	TiO_2	San Francisco Bay			3−52 μg/L	low−high
this study	model	TiO_2	New York City			1.33−43.88 μg/L	low−high
4	model	ZnO	Europe	0.432 μg/L	mode	0.34−1.42 μg/L	15−85%
6	model	ZnO	EU	2.3 μg/L	mode	1.7−21 μg/L	15−85%
4	model	ZnO	Switzerland	0.441 μg/L	mode	0.343−1.32 μg/L	15−85%
6	model	ZnO	Switzerland	5.3 μg/L	mode	3.7−45 μg/L	15−85%
this study	model	ZnO	London			0.31- 7.32 μg/L	low−high
4	model	ZnO	United States	0.3 μg/L	mode	0.22−0.74 μg/L	15−85%
9	model	ZnO	San Francisco Bay			0.8−13 μg/L	low−high
this study	model	ZnO	New York City			0.37- 15.84 μg/L	low−high
4	model	Ag	Europe	42.5 ng/L	mode	32.9−111 μg/L	15−85%
6	model	Ag	EU	0.17 ng/L	mode	0/06−16 ng/L	15−85%
4	model	Ag	Switzerland	38.7 ng/L	mode	29.8−127 ng/L	15−85%
6	model	Ag	Switzerland	0.32 ng/L	mode	0.08−23 ng/L	15−85%
this study	model	Ag	London			0.003−0.11 μg/L	low−high
4	model	Ag	United States	21 ng/L	mode	16.4−74.7 ng/L	15−85%
13	model	Ag (bare)	United States	0.02 ug/L	mean	0.001−0.061 μg/L	5−95%
9	model	Ag	San Francisco Bay			0.01−0.2 μg/L	low−high
this study	model	Ag	New York City			0.004−0.26 μg/L	low−high
55	measurement	Ag	United States: Colorado	100 ng/L			
4	model	CNT	Europe	14.8 ng/L	mode	11.4−31.5 ng/L	15−85%
6	model	CNT	EU	4.0 ng/L	mode	3.6−12 ng/L	15−85%
4	model	CNT	Switzerland	11.8 ng/L	mode	7.6−19.1 ng/L	15−85%
6	model	CNT	Switzerland	5.5 ng/L	mode	4.9−16 ng/L	15−85%
this study	model	CNT	London			0.001−0.11 μg/L	low−high
4	model	CNT	United States	8.6 ng/L	mode	6.6−18.4 ng/L	15−85%
9	model	CNT	San Francisco Bay			>0.01−0.3 μg/L	low−high
this study	model	CNT	New York City			0.003−0.20 μg/L	low−high

dx.doi.org/10.1021/sc500121w | ACS Sustainable Chem. Eng. 2014, 2, 1656−1665

Table 8. Predicted ENM Concentrations in Biosolids Based on Life Cycle Release Models and Measurements

study (ref)	study type	ENM	location	estimate		range	range details
4	model	TiO_2	United States	137 mg/kg	mode	107−523 mg/kg	15−85%
21	measurement	Ti	United States			1,000−6,000 mg/kg	
9	model	TiO_2	San Francisco Bay			266−652 mg/kg	low−high
this study	model	TiO_2	New York City			273−342 mg/kg	low−high
4	model	TiO_2	Europe	136 mg/kg	mode	100−433 mg/kg	15−85%
6	model	TiO_2	EU	170 mg/kg	mode	150−540 mg/kg	15−85%
4	model	TiO_2	Switzerland	211 mg/kg	mode	172−802 mg/kg	15−85%
6	model	TiO_2	Switzerland	320 mg/kg	mode	250−950 mg/kg	15−85%
2	model	TiO_2	United Kingdom			701−7,007 mg/kg	low−high
18	measurement	Ti	United Kingdom	305 mg/kg dry weight (DW)			
this study	model	TiO_2	London			263−367 mg/kg	low−high
4	model	ZnO	United States	23.2 mg/kg	mode	17.4−57.7 mg/kg	15−85%
9	model	ZnO	San Francisco Bay			65−164 mg/kg	low−high
this study	model	ZnO	New York City			77−124 mg/kg	low−high
4	model	ZnO	Europe	17.1 mg/kg	mode	13.6−57 mg/kg	15−85%
6	model	ZnO	EU	24 mg/kg	mode	17−110 mg/kg	15−85%
4	model	ZnO	Switzerland	21.4 mg/kg	mode	16.8−64.7 mg/kg	15−85%
6	model	ZnO	Switzerland	45 mg/kg	mode	31−200 mg/kg	15−85%
2	model	ZnO	United Kingdom			2,172- 21,722 mg/kg	low−high
this study	model	ZnO	London			64−92 mg/kg	low−high
4	model	Ag	United States	1.55 mg/kg	mode	1.29−5.86 mg/kg	15−85%
13	model	Ag (bare)	United States	4.5 μg/kg	mean	0.27−13 μg/kg	5−95%
9	model	Ag	San Francisco Bay			1−3 mg/kg	low−high
this study	model	Ag	New York City			0.78−2.01 mg/kg	low−high
4	model	Ag	Europe	1.68 mg/kg	mode	1.31−4.44 mg/kg	15−85%
6	model	Ag	EU	0.02 mg/kg	mode	0.01−0.08 mg/kg	15−85%
4	model	Ag	Switzerland	1.88 mg/kg	mode	1.46−6.24 mg/kg	15−85%
6	model	Ag	Switzerland	0.04 mg/kg	mode	0.02−0.16 mg/kg	15−85%
2	model	Ag	United Kingdom			0.29−2.9 mg/kg	low−high
this study	model	Ag	London			0.58−1.37 mg/kg	low−high
4	model	CNT	United States	0.068 mg/kg	mode	0.053−0.147 mg/kg	15−85%
9	model	CNT	San Francisco Bay			0.3−4 mg/kg	low−high
this study	model	CNT	New York City			0.18−1.49 mg/kg	low−high
4	model	CNT	Europe	0.062 mg/kg	mode	0.047−0.129 mg/kg	15−85%
6	model	CNT	EU	0.15 mg/kg	mode	0.12−0.23 mg/kg	15−85%
this study	model	CNT	London			0.15−1.34 mg/kg	low−high
4	model	CNT	Switzerland	0.069 mg/kg	mode	0.051−0.129 mg/kg	15−85%
6	model	CNT	Switzerland	0.27 mg/kg	mode	0.21−0.40 mg/kg	15−85%
2	model	Al_2O_3	United Kingdom			8.94−894 mg/kg	low−high
9	model	Al_2O_3	San Francisco Bay			19−120 mg/kg	low−high
this study	model	Al_2O_3	London			18−57 mg/kg	low−high
2	model	CeO_2	United Kingdom			8.94−894 mg/kg	low−high
9	model	CeO_2	San Francisco Bay			1−18 mg/kg	low−high
this study	model	CeO_2	London			0.70−6.16 mg/kg	low−high
2	model	SiO_2	United Kingdom			0.02−0.21 mg/kg	low−high
9	model	SiO_2	San Francisco Bay			9−123 mg/kg	low−high
this study	model	SiO_2	London			5−40 mg/kg	low−high

the quantities of ENMs entering public WWTPs in the United States.

In all three cities, carbon black is expected to be present in effluent and biosolids at higher concentrations than other ENMs, followed by TiO_2 and ZnO. Concentrations of carbon black are based on high production estimates provided by the European Commission. According to the report, the majority (73%) of carbon black is used in automotive tires. Although direct release to WWTP is not expected to occur during tire use, 9−17% ENM release to air is expected to occur though abrasion during the use phase of tires.[44] Carbon black releases to WWTPs are expected to occur though subsequent atmospheric deposition and surface runoff.

It is difficult to verify our estimates of carbon black concentrations in WWTP effluents and biosolids due to a lack of experimental data. However, our predictions of TiO_2 concentrations can be compared to several studies that have been conducted across various WWTP facilities in multiple regions. We predict an annual discharge of 12−23 g/capita of TiO_2 to New York City wastewater treatment facilities and a subsequent release of 0.84−7.5 g/capita in wastewater effluent. These predictions are in line with Ti measurements taken at a United States facility where the Ti mass entering the WWTP

was estimated to be 16−18 g/person-year and releases in effluent to be 1.5 g/person-year.[21] Predicted effluent TiO_2 concentrations range from 4.6 to 42 μg/L in New York City, which are slightly higher than measurements taken at several United States WWTP facilities with concentrations ranging from <5 to 15 μg/L.[21] The predicted concentrations of TiO_2 in London range from 1.9 to 29 μg/L, consistent with measurements of 3.2 μg/L taken at a large WWTP facility in the United Kingdom.[18] Our estimates of TiO_2 concentrations in New York City biosolids (260−352 mg/kg) are lower than the 1000−6000 mg/kg measured during the United States sampling study.[21] A possible explanation for this discrepancy could be bulk (>100 nm) TiO_2 present in the physical samples. In Tables 7 and 8, we present a more detailed comparison of the current study predictions vs previous studies as well as measured values.

The geographic resolution of our analysis allows us to approximate the locations of point source discharges of WWTPs into the aquatic environment. The effluent mass loading predicted by our model can be used to conduct a local-scale risk assessment by modeling the fate and downstream concentrations of ENMs in receiving bodies. For the purpose of such analyses, our model can be further improved by estimating releases at WWTP outfall locations and incorporating WWTP-specific treatment level data in order to produce more accurate predictions of discharge locations and mass loading in effluent and biosolids.

■ ENVIRONMENTAL IMPLICATIONS

In the absence of experimental data, a life cycle modeling approach can be used to predict ENM concentrations in environmental media. The importance of the geographic scope of such models has not been discussed extensively in the literature. It is reasonable to assume that local variability in factors such as product consumption and wastewater treatment levels should lead to differences in ENM concentrations across various geographic locations. However, we find that there are still significant uncertainties in model parameters such as total ENM production and use-phase release though various applications that lead to a wide range of concentration estimates on a local level. An important finding is that although the range of concentrations is specific for each location considered, the range in concentrations are within the same order of magnitude for each ENM. More accurate ENM application and use data will serve to narrow the range of ENM concentrations predicted. These predicted concentrations at the local level can serve to compare against emerging toxicological information, which will determine whether there is a risk to human or ecological health.

■ ASSOCIATED CONTENT

Supporting Information

Detailed release assumptions. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail:: alazareva@bren.ucsb.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This material is based upon work supported by the NSF and USEPA under Agreement DBI-0830117. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of NSF or USEPA. This work has not been subjected to USEPA review, and no official endorsement should be inferred

■ REFERENCES

(1) 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*, 1−15.

(2) Boxall, A.;Chaudhry, Q.; Sinclair, C.; Jones, A.; Aitken, R.; Jefferson, B.; Watts, C. *Current and Future Predicted Environmental Exposure to Engineered Nanoparticles*; Department of the Environment and Rural Affairs, Central Science Laboratory: London, 2007.

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

(4) 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-TiO_2 particles. *Environ. Model. Software* **2010**, *25*, 320−332.

(5) Gottschalk, F.; Sonderer, T.; Scholz, R. W.; Nowack, B. Modeled environmental concentrations of engineered nanomaterials (TiO_2, ZnO, Ag, CNT, fullerenes) for different regions. *Environ. Sci. Technol.* **2009**, *43*, 9216−9222.

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

(7) Money, E. S.; Reckhow, K. H.; Wiesner, M. R. The use of Bayesian networks for nanoparticle risk forecasting: model formulation and baseline evaluation. *Sci. Total Environ.* **2012**, *426*, 436−445.

(8) Keller, A. A.; McFerran, S.; Lazareva, A.; Suh, S. Global life-cycle emissions of engineered nanomaterials. *J. Nanoparticle Res.* **2013**, 1692.

(9) Keller, A. A.; Lazareva, A. Predicted releases of engineered nanomaterials: From global to regional to local. *Environ. Sci. Technol. Lett.* **2014**, *1*, 65−70.

(10) Gottschalk, F.; Nowack, B. The release of engineered nanomaterials to the environment. *J. Environ. Monit.* **2011**, *13*, 1145−1155.

(11) 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*, 1036−1048.

(12) Gottschalk, F.; Sun, T.; Nowack, B. Environmental concentrations of engineered nanomaterials: Review of modeling and analytical studies. *Environ. Pollut.* **2013**, *181*, 287−300.

(13) 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.

(14) Limbach, L. K.; Bereiter, R.; Müller, E.; Krebs, R.; Gälli, R.; Stark, W. J.; Müller, E.; Galli, R. Removal of oxide nanoparticles in a model wastewater treatment plant: Influence of agglomeration and surfactants on clearing efficiency. *Environ. Sci. Technol.* **2008**, *42*, 5828−5833.

(15) Jarvie, H. P.; Al-Obaidi, H.; King, S. M.; Bowes, M. J.; Lawrence, M. J.; Drake, A. F.; Green, M. A; Dobson, P. J. Fate of silica nanoparticles in simulated primary wastewater treatment. *Environ. Sci. Technol.* **2009**, *43*, 8622−8628.

(16) Kaegi, R.; Voegelin, A.; Sinnet, B.; Zuleeg, S.; Hagendorfer, H.; Burkhardt, M.; Siegrist, H. Behavior of metallic silver nanoparticles in a pilot wastewater treatment plant. *Environ. Sci. Technol.* **2011**, *45*, 3902−3908.

(17) Wang, Y.; Westerhoff, P.; Hristovski, K. D. Fate and biological effects of silver, titanium dioxide, and C60 (fullerene) nanomaterials during simulated wastewater treatment processes. *J. Hazard. Mater.* **2012**, *201−202*, 16−22.
(18) Johnson, A. C.; Bowes, M. J.; Crossley, A.; Jarvie, H. P.; Jurkschat, K.; Jürgens, M. D.; Lawlor, A. J.; Park, B.; Rowland, P.; Spurgeon, D.; et al. An assessment of the fate, behaviour and environmental risk associated with sunscreen TiO_2 nanoparticles in UK field scenarios. *Sci. Total Environ.* **2011**, *409*, 2503−2510.
(19) Khosravi, K.; Hoque, M. E.; Dimock, B.; Hintelmann, H.; Metcalfe, C. D. A novel approach for determining total titanium from titanium dioxide nanoparticles suspended in water and biosolids by digestion with ammonium persulfate. *Anal. Chim. Acta* **2012**, *713*, 86−91.
(20) Westerhoff, P.; Song, G.; Hristovski, K.; Kiser, M. A. Occurrence and removal of titanium at full scale wastewater treatment plants: implications for TiO_2 nanomaterials. *J. Environ. Monit.* **2011**, *13*, 1195−1203.
(21) Kiser, M. a; Westerhoff, P.; Benn, T.; Wang, Y.; Pérez-Rivera, J.; Hristovski, K. Titanium nanomaterial removal and release from wastewater treatment plants. *Environ. Sci. Technol.* **2009**, *43*, 6757−6763.
(22) Future Markets, Inc.; The Global Market for Nanomaterials 2002−2016: Production Volumes, Revenues and End Use Markets; 2012; p 371. http://www.futuremarketsinc.com.
(23) European Commission. Commission Staff Working Paper: Types and Uses of Nanomaterials, Including Safety Aspects, 2012. http://ec.europa.eu/nanotechnology/index_en.html.
(24) World Bank. High-Technology Exports (% of Manufactured Exports), 2013. http://data.worldbank.org/indicator/TX.VAL.TECH.MF.ZS.
(25) World Bank. Research and Development Expenditure (% of GDP), 2013. http://data.worldbank.org/indicator/GB.XPD.RSDV.GD.ZS.
(26) National Science Foundation. High-Technology Establishments as a Percentage of All Business Establishments, by State: 2003, 2004, and 2006−2008, 2008. http://www.nsf.gov/statistics/seind12/c8/interactive/table.cfm?table=52.
(27) National Science Foundation. R&D as a Percentage of Gross Domestic Product by State, 2008. http://www.nsf.gov/statistics/seind12/c8/interactive/table.cfm?table=39.
(28) United Nations Development Programme. International Human Development Indicators, 2012. https://data.undp.org/dataset/Table-3-Inequality-adjusted-Human-Development-Inde/9jnv-7hyp.
(29) Lopaciuk, A.; Loboda, M. Global Beauty Indurstry Trends in the 21st Century, 2013; pp 1079−1087. http://www.toknowpress.net/ISBN/978-961-6914-02-4/papers/ML13-365.pdf.
(30) Gomes, C. Global Auto Report, 2013; pp 1−8. http://www.gbm.scotiabank.com/English/bns_econ/bns_auto.pdf.
(31) DECISION. World Electronic Industries, 2009; pp 1−15. http://www.decision.eu/doc/brochures/exec_wei_current.pdf.
(32) United States Government Accountability Office. Nanomanufacturing: Emergence and Implications for U.S. Competitiveness, the Environment, and Human Health, 2014. http://www.gao.gov/products/GAO-14-181SP.
(33) United States Department of Commerce. Real GDP by State 2009−2012, 2012. http://www.bea.gov/newsreleases/regional/gdp_state/gsp_newsrelease.htm.
(34) Hsu, L.-Y.; Chein, H.-M. Evaluation of nanoparticle emissions for TiO_2 nanopowder coating materials. *J. Nanoparticle Res.* **2007**, *9*, 157−163.
(35) Kaegi, R.; Ulrich, A.; Sinnet, B.; Vonbank, R.; Wichser, A.; Zuleeg, S.; Simmler, H.; Brunner, S.; Vonmont, H.; Burkhardt, M.; et al. Synthetic TiO_2 nanoparticle emission from exterior facades into the aquatic environment. *Environ. Pollut.* **2008**, *156*, 233−239.
(36) O'Brien, N.; Cummins, E. Ranking initial environmental and human health risk resulting from environmentally relevant nanomaterials. *J. Environ. Sci. Health, Part A: Environ. Sci. Eng. Toxic Hazard. Subst. Control.* **2010**, *45*, 992−1007.
(37) 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*, 2900−2905.
(38) Benn, T. M.; Westerhoff, P. Nanoparticle silver released into water from commercially available sock fabrics. *Environ. Sci. Technol.* **2008**, *42*, 4133−4139.
(39) Windler, L.; Lorenz, C.; von Goetz, N.; Hungerbühler, K.; Amberg, M.; Heuberger, M.; Nowack, B. Release of titanium dioxide from textiles during washing. *Environ. Sci. Technol.* **2012**, *46*, 8181−8188.
(40) Geranio, L.; Heuberger, M.; Nowack, B. The behavior of silver nanotextiles during washing. *Environ. Sci. Technol.* **2009**, *43*, 8113−8118.
(41) Reijnders, L. The release of TiO_2 and SiO_2 nanoparticles from nanocomposites. *Polym. Degrad. Stab.* **2009**, *94*, 873−876.
(42) 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*, 396−409.
(43) Keller, A.; Vosti, W.; Lazareva, A.; Wang, H. Release of engineered nanomaterials from personal care products throughout their life cycle. *J. Nanoparticle Res.* **2014**, DOI: 10.1007/s11051-014-2489-9.
(44) Wurth, B. Emissions of Engineered and Unintentionally Produced Nanoparticles to the Soil: An Exposure Assessment for Switzerland. Thesis, *ETH Zurich*, 2007.
(45) Organisation for Economic Co-operation and Development. Wastewater Treatment, 2011. http://stats.oecd.org/Index.aspx?DataSetCode=WATER_TREAT.
(46) Jiang, C. A General Investigation of Shanghai Sewerage Treatment System, 2011. http://www.diva-portal.org/smash/record.jsf?pid=diva2:427129.
(47) LeBlanc, R. J., Matthews, P., Richard, R. P., Eds.; *Global Atlas of Excreta, Wastewater Sludge, and Biosolids Management: Moving Forward the Sustainable and Welcome Uses of a Global Resource*; Renouf Publishing Co., Ltd.: Ottawa, Canada, 2008.
(48) Goldstein, N. The state of biosolids in America. *Biocycle* **2000**, *41*, 50−56.
(49) United Nations. Environmental Indicators: Waste, 2011. http://unstats.un.org/unsd/environment/wastetreatment.htm.
(50) Haaren, R. Van; Themelis, N.; Goldstein, N.; Van Haaren, R. The state of garbage in America. *Biocycle* **2010**, *51*, 16−23.
(51) U.K. Office of National Statistics. Mid-1971 to Mid-2010 Population Estimates: United Kingdom; Estimated Resident Population for Constituent Countries and Region, 2010. http://www.ons.gov.uk/ons/rel/pop-estimate/population-estimates-for-uk--england-and-wales--scotland-and-northern-ireland/population-estimates-timeseries-1971-to-current-year/index.html.
(52) United States Census Bureau. Annual Estimates of the Resident Population for Incorporated Places over 50,000, 2012. http://files.hawaii.gov/dbedt/census/popestimate/2012-subcounty-population-hawaii/PEP_2012_PEPANNRSIP.US12A.pdf.
(53) Discharge Monitoring Report (DMR) Pollutant Loading Tool; United States Environmental Protection Agency: Washington, DC, 2013. http://cfpub.epa.gov/dmr/adv_search.cfm.
(54) European Environment Agency. Waterbase - UWWTD: Urban Waste Water Treatment Directive, 2010. http://www.eea.europa.eu/data-and-maps/data/waterbase-uwwtd-urban-waste-water-treatment-directive.
(55) Mitrano, D. M.; Lesher, E. K.; Bednar, A.; Monserud, J.; Higgins, C. P.; Ranville, J. F. Detecting nanoparticulate silver using single-particle inductively coupled plasma-mass spectrometry. *Environ. Toxicol. Chem.* **2012**, *31*, 115−121.