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Predicted Releases of Engineered Nanomaterials: From Global to Regional to Local

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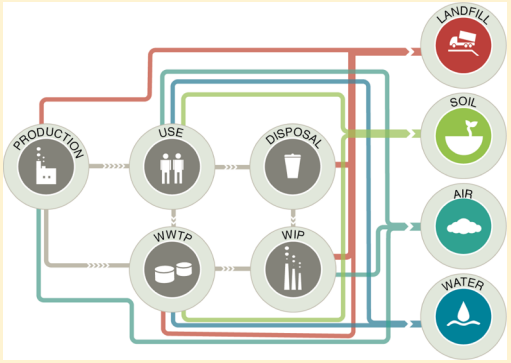
Supporting Information

ABSTRACT: A key question for industry, regulators, toxicologists, and risk assessors working with nanomaterials is what relevant environmental engineered nanomaterial (ENM) concentrations should be considered. Answering this question requires ENM material flow estimates at the local level. Using a life-cycle approach, global ENM production and application data were used to estimate releases at global, regional, national, and local levels. Local level emissions were then used to estimate releases to water (direct and from wastewater treatment effluent), soils (direct and from runoff and biosolids), and air (direct and from incineration of ENM-containing products). Waste management data for dozens of countries were used to estimate the flow of 10 major ENMs through eight world regions. A national and local release example was conducted with data from the United States, providing predicted wastewater effluent concentrations for the San Francisco Bay area, ranging from low nanograms per liter to micrograms per liter depending on the ENM.



INTRODUCTION

The rapidly growing use of engineered nanomaterials[1] (ENMs) requires novel approaches to assess the likelihood of exposure to humans and ecological receptors, based on predicted concentrations over time of exposure (i.e., dose). To predict concentrations at points of release (e.g., wastewater effluent and biosolids applied to land), it is necessary to estimate the magnitude of releases of the ENM to water, soil, and air at the local level. The letter presents the conversion of estimated global ENM production to regional, national, and local release estimates.

Several studies have predicted environmental concentrations of ENMs, as recently summarized.[2] Work by Nowack's group has led the way in developing methods for estimating ENM production and emissions.[3−6] Other studies have been more limited in scope in terms of spatial scale, life cycle, applications, or a range of ENMs.[7−12] Using global production estimates, our recent study provided the first view of the global mass flow of ENMs,[13] but estimates at more refined levels are needed. Our coverage of a wide range of applications and types of ENMs, as well as the country-specific data sets for economic development, handling of wastewater, biosolids and incineration, and the methodology to convert the information to a local level, sets this work apart from previous studies.

METHODS

Global ENM production and distribution through eight world regions (Table S3 of the Supporting Information) were based on a detailed market study.[14] The market study production estimates are higher than previous studies, in some cases by more than an order of magnitude (cf. Table S4 of the Supporting Information for a detailed comparison), which can result in an overly conservative (i.e., too high) estimate of releases. Release estimates were calculated on the basis of the high and low production estimates from the market study. Estimates of ENM release during production to air, water, soil, and landfill were based on previous studies[3,5,6,13,15] and are expected to be a minor fraction (0.1−2%) of overall releases. Thus, 98−99.9% of ENMs produced are expected to flow into applications. For ENM use in 20 applications, we considered the population in each region[16] and development level[17] [based on the United Nations inequality-adjusted human development index (IHDI)] in major countries in each region. A higher IHDI was assumed to correlate with increased consumption of products with ENMs, for example, electronics, automobiles, or cosmetics (Table S6 of the Supporting Information). Although this measure is clearly an imperfect measure of capacity and ability to purchase these products, it is better than assuming that all world inhabitants consume these products, or that they are only consumed in advanced economies. Population-weighted national IHDI values were used to develop regional IHDI values and allocate regional ENM consumption (Table S7 of the Supporting Information). Estimated releases during use in each application (Table S11 of the Supporting Information) were based on available studies. Several estimates are based on studies of the actual release of ENMs from

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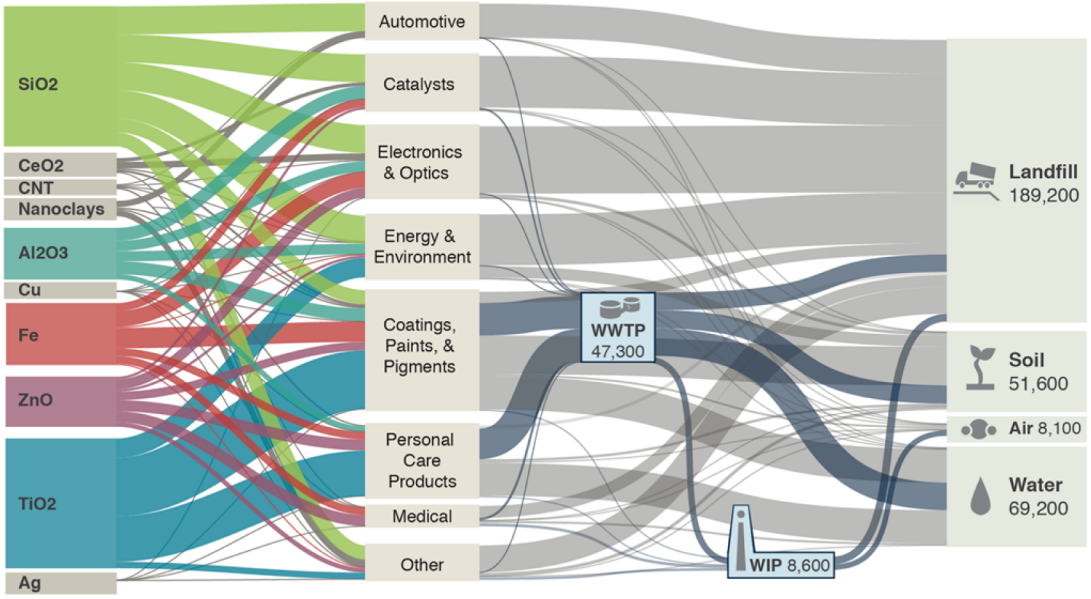

Figure 1. Estimated global mass flow of ENMs (in metric tons per year) from production to disposal or release, considering high production and release estimates as of 2010. Production data are from ref 14, without modification.

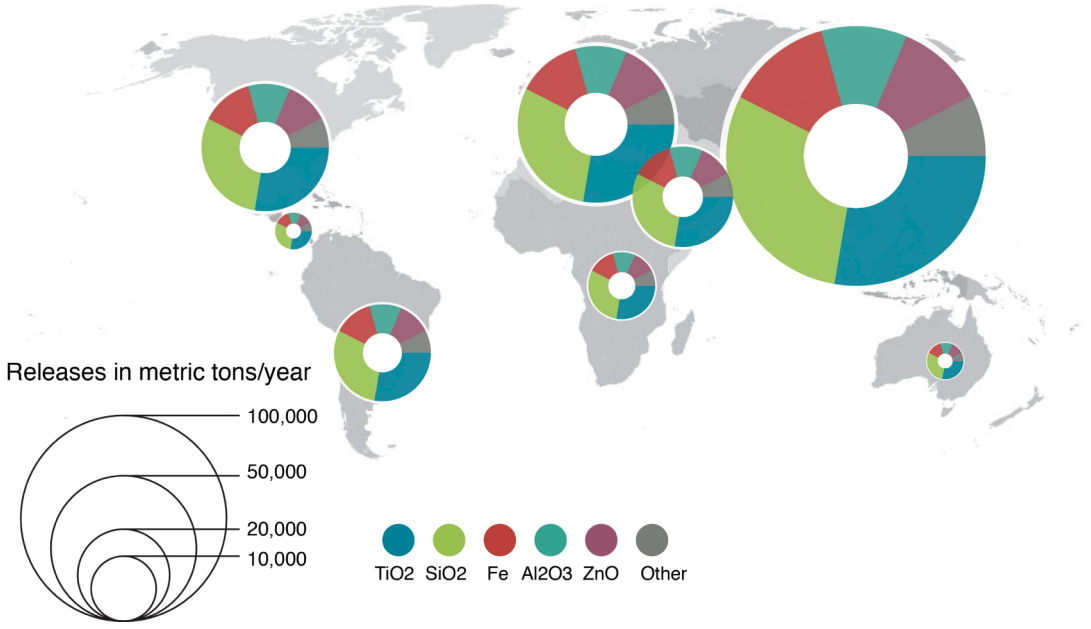

Figure 2. Regional distribution of estimated ENM release to all compartments: air, water, soil, and landfills.

textiles,[18−21] paints,[22,23] coatings,[24] fuel additives,[11] and plastics.[19] Modeling studies[4,15,25] have generated probabilistic estimates for several applications (e.g., plastics, cosmetics, coatings and cleaning agents, batteries and capacitors, paints, consumer electronics, textiles, dietary supplements, and research and development). For some applications with no studies of release estimates, the release factors are our best estimates (e.g., for aerospace and automotive applications, where ENMs used on exposed surfaces are likely to represent a small fraction of total use; release during the use phase is assumed to be 0−1%). To develop a range of release estimates, high- and low-release scenarios were calculated using high and low production volumes and emission factors.

Residence times of ENMs in the use phase can vary widely by application. For example, ENMs used in cosmetics, food additives, or medical applications will have a relatively short residence time compared to those used in electronics, composites, or automotive applications. In our estimates, we used a time-integrated mass balance approach in which the residence time of an ENM in a given application is not explicitly considered, and the variance in residence times was not taken into account.

A sensitivity analysis was conducted on key model parameters to determine the impact of these assumptions on the overall ENM release estimates. We first assessed qualitatively the uncertainty associated with model parameters (Table S25 of the Supporting Information). The low level of uncertainty reflects available data from several studies with error estimates. A medium level of uncertainty indicates data available from one study with uncertainty estimates, or

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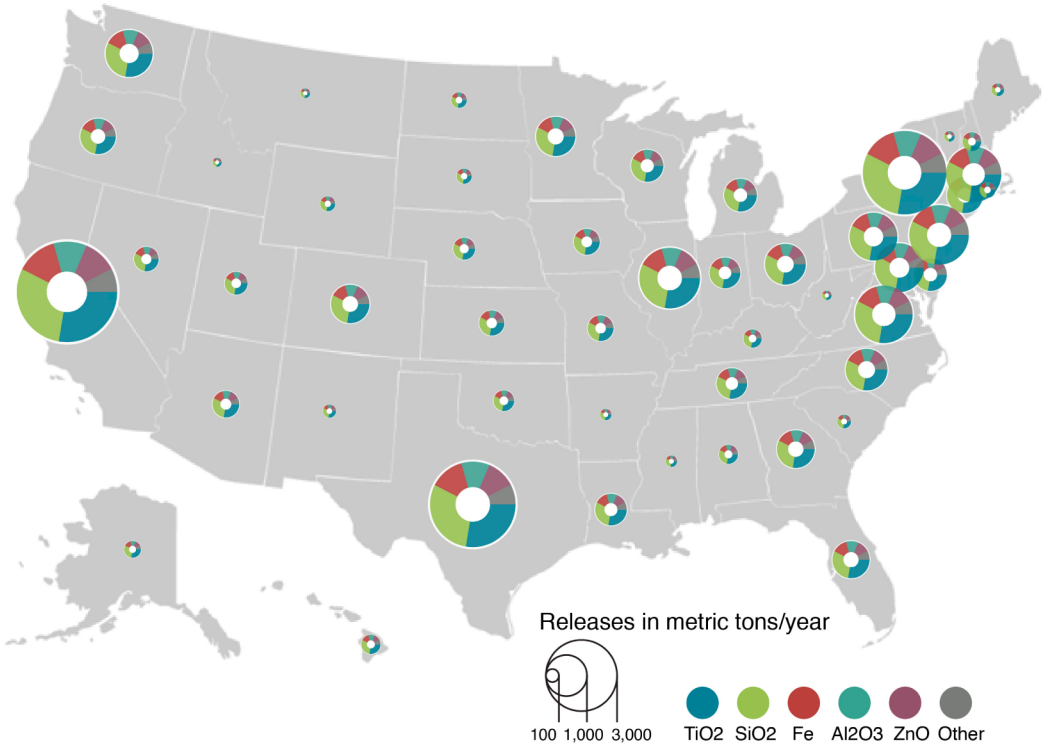

Figure 3. Estimated overall releases of ENMs to air, water, soil, and landfills in the United States.

sufficient data are available to develop a method for filling data gaps. A high level of uncertainty is considered for major data gaps. For the sensitivity analysis, the model was run with a 10% increase and decrease in one parameter value at a time. Criteria for considering a low, medium, or high level of sensitivity were developed (Table S27 of the Supporting Information).

The next life-cycle stage is disposal, either to a wastewater stream or to municipal solid waste handling. In some countries, the vast majority of wastewater goes to wastewater treatment plants (WWTPs) or septic systems, where it may undergo primary, secondary, or tertiary treatment. In many areas of the world, wastewater is released with no treatment to canals and waterbodies. Wastewater treatment data[26] for a significant number of countries were used to estimate the treatment fraction (Table S10 of the Supporting Information) and level to determine the transfer to effluent or biosolids for each region (Table S14 of the Supporting Information). The ENM mass was tracked regardless of transformation[27−32] to larger particles through aggregation, partial or full dissolution, oxidation, sulfidization, etc. We applied the same transfer factors from influent to effluent and biosolids for all ENMs,[33−40] given very limited information about ENM-specific WWTP transformations. Statistics[26] for countries within each region were used to estimate regional biosolids management practices (land application, incineration, and landfills) (Table S17 of the Supporting Information). Regional fractions of municipal solid waste incinerated or sent to landfills were estimated using United Nations data[41] (Table S19 of the Supporting Information). We estimated the regional fraction of incinerator emissions to air, filter, or slag using regional IHDI values (Table S21 of the Supporting Information).

Detailed calculations and data coverage for the various data sets are given in the Supporting Information. The analysis is applied to the United States, using the same methodology. Model equations are given in the Supporting Information, highlighting U.S.-specific data sets.[42−44] As a local level example, estimates for California were generated on the basis of U.S. and state level data, and then specifically for San Francisco Bay area WWTPs and biosolids management.[45,46]

RESULTS

The flow of 10 major ENMs (production of >100 t/year) through the global economy, their applications, and their end of life are presented in Figure 1, with refined release estimates compared to our previous study, based on the country-specific handling of wastes. Because of the nature of the majority of these applications (e.g., electronics, automotive, and solar panels for energy), 60−86% of ENMs and their transformation products are expected to end up in landfills. Two applications contribute most to soil, water, and air releases: personal care products (including sunscreens and cosmetics) and coatings, paints, and pigments (including food applications). Release of medical applications are smaller, but growing rapidly.

The estimated total release to air, water, soil, and landfills for different regions of the world is presented in Figure 2. Asia dominates use and release (∼50%) of ENMs, based on population (52%) and rising IHDI values for China, India, and countries in Southeast Asia, as well as Japan and South Korea. Europe's high average IHDI (79%) and population (11%) place Europe second in terms of use and releases followed by North America (Canada, United States, and Mexico). Detailed regional release estimates are provided in Table S22 of the Supporting Information, including uncertainty ranges of release estimates. A high release means more emissions to soil, water, and air, and correspondingly less to landfills. The regional differences in wastewater and solid waste handling create the largest differences in emissions to water and soil. For example, we estimate that in Asia around 10−30% of ENM releases will be to water bodies, while this is expected to be only 3−17% in Europe and 4−19% in North America. For reference, the world

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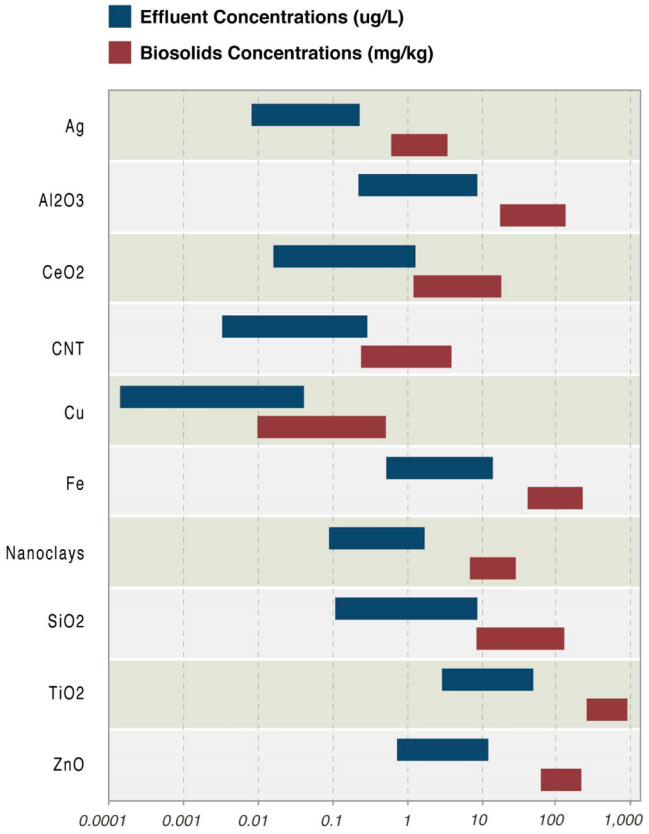

Figure 4. Predicted ENM concentrations in San Francisco Bay WWTP effluent and biosolids.

average release to water is estimated to be 8−22% of ENM mass flows, dominated by TiO_2, Al_2O_3, and iron oxide emissions (Figure S2 of the Supporting Information), given their use in applications (personal care, pigments, and coatings) with high release to water.

Applying the approach to the United States provides estimates of ENM releases (Figure 3) that can serve to estimate local level effluent concentrations. The geographical distribution of ENM releases reflects the population density as well as the level of income by state. The differences in wastewater treatment and biosolids management also result in some differentiation in the fraction of ENMs estimated to be released to air, water, and soil. For example, the fraction of ENMs released to soils in Oregon is estimated to be 14−35%, while for Rhode Island it is 2−23%. The average in the United States is 7−29%.

Predicted ENM concentrations in WWTP effluent and dry biosolids in the San Francisco Bay (SFB) area are presented in Figure 4. The upper bounds of these predicted effluent and biosolids concentrations are in some cases 3−5 times greater than those estimated by others.[2,3,5] The lower bound of our TiO_2 estimates falls within the range observed in wastewater treatment (5−15 μg/L) and biosolids (1−6 g/kg).[33,34] Previous modeling studies[2] have estimated the following ranges of WWTP effluent concentrations (all in micrograms per literL): TiO_2 (1−20), Ag (0.05−0.2), ZnO (0.5−1.5), CNT (0.01−0.05), and CeO_2 (0.5×10^{-4}). For biosolids, the following WWTP effluent concentrations were found (all in milligrams per kilogram): TiO_2 (10−70), Ag (1−8), ZnO (10−80), CNT (0.05−0.1), and CeO_2 (10^{-6}). Consistent with higher production volumes, our estimates range from the high end of these modeling studies to an order of magnitude greater. Figure 5 presents the location and estimated releases of TiO_2 from WWTPs in this area.

The higher estimated releases and effluent concentrations predicted here may lead to more societal awareness of the presence of ENMs. This may in turn result in increased monitoring of effluent, biosolids, and environmental concentrations, as methods are developed to more reliably perform

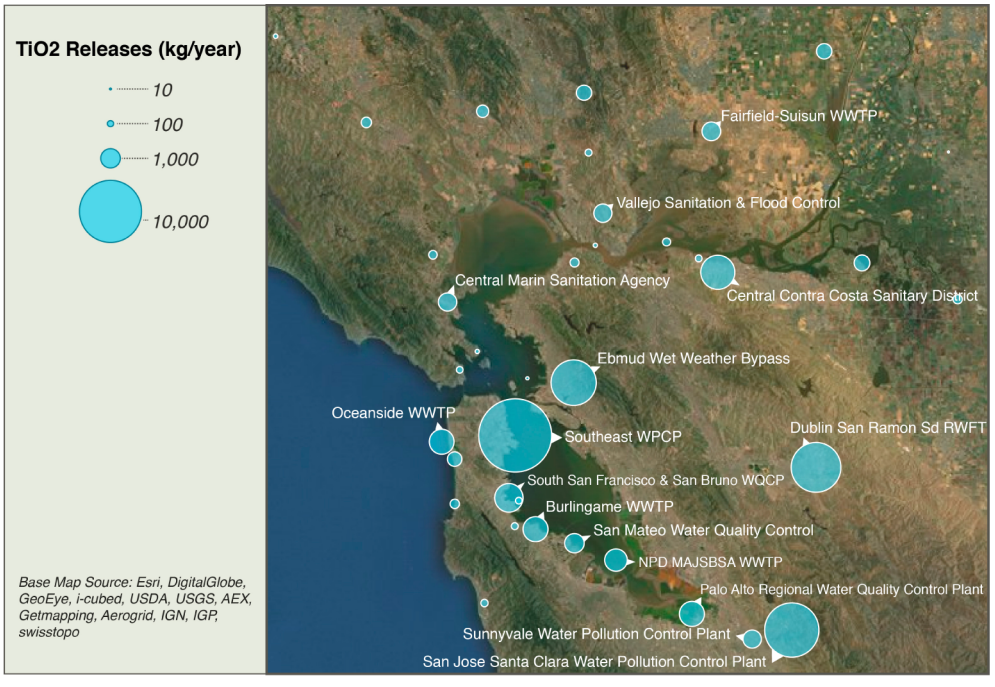

Figure 5. Estimated nano-TiO_2 releases to water bodies in the San Francisco Bay area.

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these assessments. Increasing validation data will serve to improve the release estimates. From an environmental protection perspective, it is better to overestimate production and releases rather than underestimate the risk by considering lower production volumes.

Certain model parameters have a high or medium level of uncertainty (Table S25 of the Supporting Information) because of the sparseness in ENM production rates, application, and release data. The most influential parameters (Table S26 of the Supporting Information) are those associated with production of some ENMs, and the ENM release factors for certain applications [e.g., cosmetics, coatings and paints, and energy (Table S27 of the Supporting Information)]. Therefore, additional information about the probability distribution of the most influential parameters would be needed to conduct a rigorous uncertainty analysis. Additional factors that were not considered in this study could lead to a more accurate estimate of ENM releases. These factors include country-specific ENM applications, ENM-specific transformations during the life-cycle stages, and better estimates of regional, national, and local differences in ENM use.

■ ASSOCIATED CONTENT

Supporting Information

Detailed explanation of data used to estimate regional, U.S., and SFB releases, including 28 tables, and model equations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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