

Considering the forms of released engineered nanomaterials in probabilistic material flow analysis

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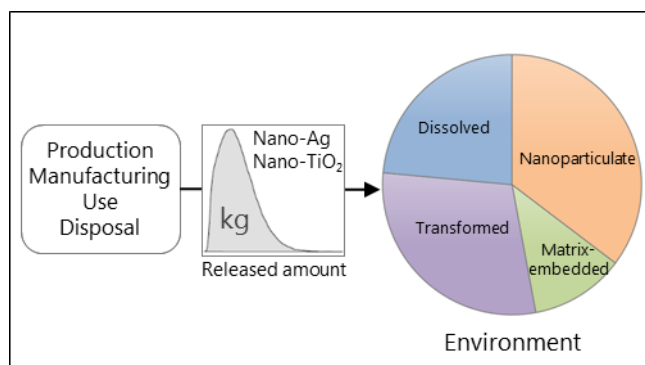
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Abstract

Most existing models for assessing the releases of engineered nanomaterials (ENMs) into the environment are based on the assumption that ENMs remain in their pristine forms during their whole life cycle. It is known, however, that this is not always the case as ENMs are often embedded into solid matrices during manufacturing and can undergo physical or chemical transformations during their life cycle, e.g. upon release to wastewater. In this work, we present a method for systematically assessing the forms in which nano-Ag and nano-TiO₂ flow through their life cycle (i.e. production, manufacturing, use and disposal) to their points of release to air, soil and surface water. Input data on the forms of released ENMs were probability distributions based on peer-reviewed literature. Release data were incorporated into a probabilistic material flow analysis model to quantify the proportions of ENMs in product-embedded, matrix-embedded, pristine, transformed and dissolved forms in all technical and environmental compartments into which they flow, at the European scale. Releases of nano-Ag to surface water and soil were modelled to occur primarily in transformed forms (Q25 and Q75 of 35-58% and 75-85%, respectively, with means of 46% and 79%), while releases to air were mostly in pristine and matrix-embedded forms (38-46% and 36-44%, respectively, with means of 42% and 40%). In contrast, nano-TiO₂ releases to air, soil and water were estimated to be predominantly in pristine form (75-85%, 90-95%, 96-98%, respectively, with means of 80%, 91% and 97%). The distributions of ENM releases between forms developed here will improve the representativeness and appropriateness of input data for environmental fate modelling and risk assessment of ENMs.

Graphical abstract



HIGHLIGHTS

- Probabilistic material flow analysis was used to model two ENMs forms of release.
- Most releases of nano-Ag to soil and water were modelled as transformed.
- Releases of nano-Ag to air were mostly found in pristine form.
- Releases of nano-TiO₂ to air, water and soil were mostly in pristine form.
- These results will improve current fate and exposure modelling.

KEYWORDS

Probabilistic material flow analysis, nano-TiO₂, nano-Ag, environmental release

INTRODUCTION

As the market for ENMs continues to expand (European Commission, 2013; Future Markets, 2014), there are concerns about the potential risk they may pose to human and environmental health (Scott-Fordsmand *et al.*, 2016; Selck *et al.*, 2016). Potential releases of ENMs to the environment during their complete life cycle (i.e. from their production and the manufacturing, use and disposal of the nanoproducts in which they are contained) have been assessed in several material flow analysis (MFA) studies (Baalousha *et al.*, 2016; Hendren *et al.*, 2013; Nowack, 2017). One of the earliest nano-MFA models was developed by Gottschalk *et al.* (2009). The model inputs include production volumes, allocation among product categories and releases from different products. In the last decade, this model was improved in a variety of ways, e.g. to model the flows of more ENMs, in various geographic

regions and with different levels of detail with respect to specific model compartments. Sun *et al.*'s work (2014) includes most recent data on four ENMs: nano-TiO₂, nano-Ag, nano-ZnO and CNT. A significant addition to the original model has been the addition of a temporal dimension, which has enabled the assessment of release variability over time (Sun *et al.*, 2016, 2017). Other MFA modelling approaches have been used elsewhere, e.g. by Keller and co-workers. They worked at U.S. and global scales and also included release dynamics (Keller *et al.*, 2014, 2013; Lazareva and Keller, 2014; Song *et al.*, 2017).

Since the forms in which ENMs are released to the environment affect both their fate and toxicity, the potential transformations of pristine nanoparticles (NPs) during their life cycle need to be considered (Lowry *et al.*, 2012; Mitrano *et al.*, 2015). If NPs are released in a solid matrix (e.g. paints), their fate is governed by the matrix properties and their bioavailability depends on the degradation of the matrix (Wohlleben and Neubauer, 2016). ENMs can also form aggregates upon release, in which case they undergo different fate compared to free nanoparticles (Meesters *et al.*, 2014; Praetorius *et al.*, 2012). If they are transformed (e.g. through sulfidation), they present different toxicities from the pristine material (Levard *et al.*, 2012). Finally, when they are dissolved in water, they completely lose their nano-specific properties.

The function of MFA models for ENMs is to track the flows of ENMs through the technosphere and into the environment. However, the majority of existing models do not consider the different forms of the released ENMs. Sun *et al.* (2016, 2014) partially account for ENM transformations along their life cycle by considering the elimination of nano-Ag and nano-ZnO through dissolution and sulfidation during use and wastewater treatment. Yet, a systematic assessment of whether the ENMs are released as pristine or transformed nanoparticles, dissolved or matrix-embedded is still absent from the literature. A first step in this direction has been made with the GuideNano tool (www.guidenano.eu), where users (industry) can specify the forms of the materials potentially released to the environment in the aim of evaluating the potential risks associated with their nanoproducts.

The number of published experimental studies into the release of materials from nanoproducts has increased in recent years (Caballero-Guzman and Nowack, 2016; Froggett *et al.*, 2014; Koivisto *et al.*, 2017). The characterization approach of the released form of the materials differs from one study to another: Whilst some studies assess the forms (composition and sizes) of the released particulate fraction, most of them are limited to an assessment of the dissolved versus the particulate fraction that is released. Hence, the data available for the characterisation of the forms of release is incomplete and heterogeneous (Caballero-Guzman and Nowack, 2016). This highlights the need for a probabilistic modelling, by which we are able to consider uncertainties in the outcome.

The aim of this work is to use the data available on the forms of nanomaterial release to improve the accuracy of the existing MFA model of Sun *et al.* (2014). Specifically, we focus on the potential transformations that nano-Ag and nano-TiO₂ undergo during their life cycle and assess the forms in which they are released to the environment. Nano-Ag and nano-TiO₂ were chosen because a high number of published studies on releases from nanoproducts could be found on these ENMs (Caballero-Guzman and Nowack, 2016; Froggett *et al.*, 2014). Moreover, they behave differently in the environment: nano-Ag is expected to undergo major transformations and dissolution, while nano-TiO₂ is more stable. The present evaluation of the forms of release is mainly based on critical evaluation of experimental data provided in the literature. Following this, the proportions of pristine, dissolved, transformed and matrix-embedded ENMs released to the environment are quantified. Their further transformations in environmental compartments are beyond the scope of this work.

MATERIAL AND METHODS

Scope of the study and general methodology

The material flow analysis (MFA) of nano-Ag and nano-TiO₂ within Europe presented by Sun *et al.* (2014) was taken as the basis of our model. The forms in which the ENMs occur are assessed over their complete life cycles, from production to end-of-life management, in Europe in 2012. The model

includes ten technical compartments and three environmental compartments (Figure S1, Supporting Information). As the focus of this work is on the forms of *releases* of ENM to the environment, consideration of transformations that occur *in* the environment (i.e. within each environmental compartment) was deemed beyond the scope of this work. Following the approach of Sun *et al.* (2014), the landfill and recycling processes were considered as sinks, meaning that no releases are modelled from these compartments. Hence, potential transformations occurring within these sinks were not assessed.

Five different forms of ENM release were considered:

- Dissolved: Any dissolved species released from an ENM. All nano-properties are lost after dissolution. Consequently, the assessment of the risks incurred by the resulting ions should be performed following conventional metal fate or risk assessment.
- Transformed: ENMs which have been subject to chemical reactions, for example sulfidation. Due to almost complete lack of data, we only considered transformations of the core material, not those of the potential coatings of the ENMs.
- Matrix-embedded: The released ENM is embedded in a solid matrix, e.g. a piece of polymer nanocomposite, paint or cement.
- Pristine: Non-transformed released nanoparticles, as they were inserted in the product. They are not embedded in a solid matrix or product. This category includes single, aggregated and agglomerated pristine nanoparticles. We could not distinguish in the model between the different states of aggregation because of lack of data: Even though some studies do provide estimations of the proportions of single and aggregated particles, most of them do not. To be able to combine all input data in a consistent way, we had to leave this consideration out of the scope of our model.
- Product-embedded: ENMs that are still contained within a complete nano-product. This only applies to flows from manufacturing and use phases and to the fraction of ENM that is disposed as solid waste and which enters waste management processes as a part of a whole

product. The potential transformations of product-embedded ENMs to any other form included in this assessment occur during waste management. Releases occurring during use of liquid or gel nanoproducts (e.g. sunscreens) to wastewater were not considered as being product-embedded, as the liquid product would disperse in water.

The approach for assessing the distributions of ENMs between release forms from each stage of their life cycle followed a stepwise procedure (Figure 1). Firstly, the fractions of dissolved and particulate releases were assessed. Secondly, the distinction was made between transformed and unchanged particulate material. It is worth highlighting that the transformed form was considered permanent, i.e. we assumed that the ENM would not subsequently revert to its pristine form following transformation. Finally, the unchanged fraction was further divided between pristine and matrix-embedded releases.

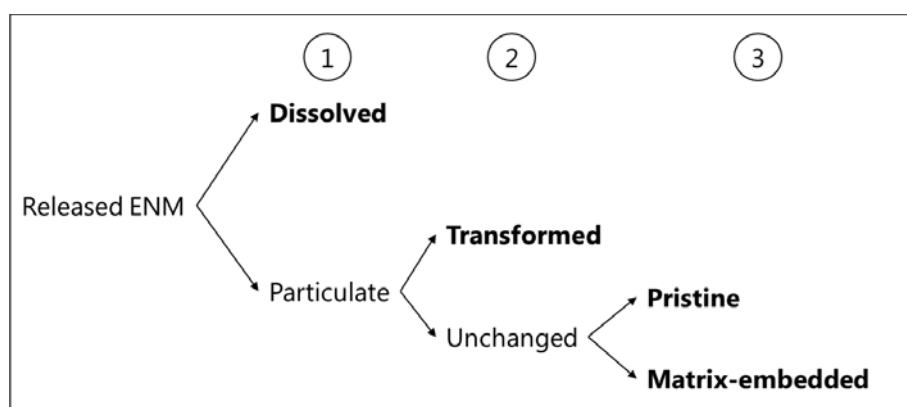


Figure 1: Assessment scheme used for assessing the distributions of released forms

Inclusion of data uncertainty in the model

Each mass flow that was previously determined by Sun *et al.* (2014) was divided into the five forms of ENMs described above. Probability distributions were defined to describe the forms in which the ENMs flow. This assessment was based on experimental data, which was available to different extents depending on the stage of the ENM life cycle and, regarding the use stage, on the product category from which the ENM is released. Where multiple data were available, triangular distributions were determined to characterize the distribution of the mass flow between the forms in which the ENM flows. The modes of these distributions are the outputs (Tables 1 and 2) of the calculations described

in the following section and in Tables S1-S7, while the minima and maxima of the probability distributions correspond to those found in the literature. For those life-cycle stages and product categories for which information on ENM releases were not available, data for the most similar scenario were used to produce uniform probability distributions. The width of these probability distributions then included the uncertainty caused by the use of this approximation. It is important to highlight that very few studies provide information on all five forms of release defined in this work. Despite this limitation, we combined all available data in as consistent and systematic a way as possible, as described in the specific sections of the method and supplementary information.

The following sections provide details of the approach used to define the forms of released ENMs during each life cycle stage, for each product category and from each compartment. The flows considered are those defined in Sun *et al.* (2014).

Determination of ENM transformations in each compartment

Transformations during production and manufacturing

ENMs are only integrated into products during the manufacturing stage. Hence, all releases during the production stage are in pristine form. During manufacturing, nano-Ag and nano-TiO₂, typically held in suspensions, are incorporated into products so most of them flow to further stages of the life cycle as product-embedded. Embedment in a matrix (and subsequently in a product) occurs only during the final stages of processing. Therefore, ENM releases to wastewater and the environment were assumed to be mostly in a pristine form. This resulted in two uniform distributions for each ENM, from 0 to 5% of releases to wastewater and air as matrix-embedded releases and the remainder as pristine.

Transformations during use

Release to waste water - Electronics: Ag and TiO₂ ENMs occur in the coatings of electronics and, for nano-Ag, in printed circuit boards. No release can be expected from printed circuit boards during use, so all ENMs flowing from the use of this product category were product-embedded, as electronic waste. However, coatings can be altered by contact with skin. Since no study has been performed on this subject, we do not know the proportions in which the different forms of ENMs will be released. For nano-TiO₂, uniform distributions from 0 to 100% were attributed to pristine and to matrix-embedded releases. No dissolution of nano-TiO₂ was considered, as it is considered insoluble under environmental conditions (Schmidt and Vogelsberger, 2009). Regarding nano-Ag, the same uniform distributions (0-100%) were attributed to pristine, matrix-embedded, dissolved and transformed forms of release.

Release to waste water - Textiles: The dissolved fraction was calculated as the mean of the data reported in the literature (see Table S1). There is high variability in the reported data on the fraction of nano-Ag that is transformed, which depends on the type of ENM and nano-textile tested and the experimental setup. Here, we assumed that 50% of the non-dissolved fraction was transformed and 50% remained metallic (both matrix-embedded and pristine). Based on results from Geranio *et al.* (2009), Lorenz *et al.* (2012) and Mitrano *et al.* (2014), 85% of this non-dissolved, non-transformed fraction was assumed to be matrix-embedded, 15% staying pristine. The filter pore size threshold of 450 nm was used to distinguish both fractions: material larger than 450 nm was assumed to be embedded in textile fibres (Hernandez *et al.*, 2017) while smaller material was assumed pristine. The final triangular probability distributions have modes of 22%, 39%, 6% and 33%, respectively, for the dissolved, transformed, pristine and matrix-embedded forms. The minima and maxima of the distribution describing the flows in the dissolved were 0 and 100%; the width of the other distributions depend on this one: the minima are all 0% (when the dissolved fraction is 1), the maxima are 50%, 42.5% and 7.5%, respectively, for the transformed, matrix-embedded and pristine forms (when the dissolved fraction is null).

Only one published study was identified concerning the assessment of nano-TiO₂ releases from textiles to wastewater. Windler *et al.* (2012) found that around 50% of the released material containing TiO₂ was above 450 nm and 50% was below 450 nm. Therefore, here we attributed 50% of releases to the pristine form and 50% to the matrix-embedded form, with an uncertainty of 50%. This resulted in triangular probability distributions with minima of 25%, modes of 50% and maxima of 75% for both forms of release.

Release to waste water - Cosmetics: Nano-Ag may undergo transformation whilst in contact with the skin. The likelihood of these potential transformations was based on several studies into releases of Ag NPs from nano-Ag textiles to human sweat (Ding *et al.*, 2016; Kim *et al.*, 2017; Quadros *et al.*, 2013; von Goetz *et al.*, 2013; Wagener *et al.*, 2016; Yan *et al.*, 2012). These studies show that dissolution and subsequent transformation rates are high. Hence, we here considered that all particulate silver was transformed (Table S2). Neither transformation nor dissolution of nano-TiO₂ can reasonably be expected in water, so releases from cosmetics were considered to be 100% in pristine form. We stress the fact that the only transformations considered in this work are those of the core material. Despite the fact that transformations of nanoparticles coatings in sunscreens were shown (Botta *et al.*, 2011), this is the only application for which information is available, so we could not include changes to the coatings in our systematic assessment.

Release to waste water - Paints and coatings: As only one study into the release of nano-Ag from paints was identified (Kaegi *et al.*, 2010), another one relevant to the more general category “coatings” was also used to define the forms of nano-Ag release from these product categories (Künniger *et al.*, 2014). Both studies show contrasting results (Table S3). Kaegi *et al.* (2010) show that nano-Ag released from outdoor façades are, for the vast majority, embedded in chunks of paints. Transformed and pristine nanoparticles were also found in the runoff water sampled after weathering. In the opposite, Künniger *et al.* (2014) found that all nano-Ag released in surface water after runoff on wood coatings were dissolved. Thus, we had to assume uniform probability distributions to account for every possible case:

dissolved and matrix-embedded forms were assumed to have probability distributions from 0 to 100%, while transformed and pristine forms were given uniform distributions with a range of 0 to 10%.

Three studies were found that could be used for the assessment of nano-TiO₂ releases from paints and coatings to wastewater (Table S4). Al-Kattan *et al.* (2013) measured a small quantity of nano-TiO₂ released from paints exposed to sunlight and rain. No transformation nor dissolution was observed in the other relevant studies (Kaegi *et al.*, 2008; Shandilya *et al.*, 2015). Therefore, the means of the pristine and matrix-embedded amounts found in each study were calculated to obtain the distribution of nano-TiO₂ in both these forms of release. This resulted in triangular probability distributions, with modes of 30% for the pristine form (minimum: 10%; maximum: 50%) and 70% for the matrix-embedded form (minimum: 50%; maximum: 90%).

Other releases to waste water: The rationale used to assess the nano-Ag and nano-TiO₂ forms released during use of minor product categories to waste water are described in Section 2 of the SI.

Release to environmental compartments - Air. Releases of nano-Ag to air occur during the use phase of textiles, paints and filters. No experimental study was found that has assessed these types of release. As they occur through abrasion, no dissolution or chemical transformation was expected during release. Moreover, releases of ENMs during the use phase mostly depend on the matrix in which they are embedded (Mitrano *et al.*, 2015). Nano-Ag was assumed to always be incorporated in the coatings of textiles and filters. Therefore, we used data obtained from experiments on nano-TiO₂ releases from coatings for both nano-Ag and nano-TiO₂. Conflicting data were collected on the releases of nano-TiO₂ from coatings to air: Bressot *et al.* (2017) found that most of the nano-TiO₂ contained in a tile coating was released as matrix-embedded, while Shandilya *et al.* (2015) observed a high quantity of free TiO₂ NPs in samples obtained after seven months of coating abrasion. Based on this, we assumed that 0-100% of the release would be matrix-embedded and 0-100% would be pristine, using uniform distributions. This assumption was also made for filters, sporting goods and textiles, where nano-TiO₂ is present in coatings. An exception was made for nano-Ag-containing textiles, for which transformations were found to occur prior to washing: only 50% of the Ag NPs contained in these

textiles are metallic; 50% being AgCl or Ag₂S (Lombi *et al.*, 2014). Therefore, we attributed 50% of the pristine release to the transformed form, resulting in an overall distribution between release forms of 50% matrix-embedded, 25% pristine and 25% transformed. Each of these percentages were taken as the modes of the triangular distributions, applying a +/- 50% variation to find the minima and maxima and these distributions. So for example, the distribution of releases to air in a solid matrix takes 50% as the mode, 25% as the minimum and 75% as the maximum. Releases to air from sprays were modelled as being in a pristine form.

Releases to environmental compartments – Surface water and soil: TiO₂ and Ag ENMs are released to surface water from cosmetics during bathing. Releases to surface and wastewater were considered to be in the same form. They are described in the section above, relative to wastewater. Ag ENMs are also used for soil remediation. In this case, all Ag ENMs were considered to be released in pristine form, as the product is directly poured in the soil. Regarding paints and coatings, releases occur to soil through runoff on outdoor surfaces. The forms of ENMs released are the same, whether this runoff goes directly to soil (in rural environments) or to wastewater (in urban environments). They are described in the section above relative to wastewater.

Transformations during end-of-life

Sewage system and wastewater treatment plants (WWTPs): Transformations of ENMs in wastewater were considered in three steps: (1) transformation upon release from the use phase to wastewater (see section above), (2) transformation in the sewer system, and (3) transformations in WWTPs.

In the sewer system, dissolved, transformed and matrix-embedded ENMs were assumed to remain as such, i.e. they would not undergo further changes in their form. However, the Ag pristine fraction released in sewage can be subject to further transformation. The triangular distribution representing this percentage of transformed Ag ENMs was taken from the only study available on the matter, where

several measurements were performed (Kaegi *et al.*, 2015) (Table S7). It has a minimum of 0%, a mode of 10% and a maximum of 29%. The rest of the flow is pristine.

During wastewater treatment, no dissolved Ag was considered to form because the fraction of dissolved nano-Ag entering WWTPs transforms through sulfidation (Ma *et al.*, 2014). Consequently, if any dissolution would take place, the ions would immediately be further transformed. Kaegi *et al.* (2013) showed that the percentage of nano-Ag sulfidation in WWTPs depends on the size of the nanoparticles: After 24 h in activated sludge, more than 90% of 100 nm particles remained metallic, while more than 95% of 10 nm particles were sulfidised. Both these numbers were used to build uniform probability distributions describing the fractions of nano-Ag (of all sizes) transformed (10-95%) and pristine (5-90%). Matrix-embedded ENMs were assumed to remain as such. In sludge, no dissolved fraction was considered. The residence time of nano-Ag is long enough in the sludge to be completely sulfidised (Kaegi *et al.*, 2011; Ma *et al.*, 2014). It was considered that the core material of TiO₂ ENMs does not undergo any transformation in wastewater, the sewer system, the WWTP or sludge.

Waste incineration plants (WIP): After sludge incineration, Meier *et al.* (2016) found that Ag₂S was absent from the ash. Rather, metallic Ag was identified as the main Ag component in these ashes. This shows that oxidized Ag is reduced back to metallic Ag during incineration. Moreover, electron microscopy pictures show that these particles stay at the nanoscale after incineration (Meier *et al.*, 2016). Based on this, we assumed that all metallic nano-Ag occurring in pristine, matrix-embedded or product-embedded form in the inflow to WIP would occur in pristine form in the outflow: All matrices are consumed and no chemical transformation of nano-Ag occurs during incineration. However, even if transformed nano-Ag was shown to be reduced back to metallic Ag, these could not be considered pristine Ag NPs, so the transformed fraction was considered to remain as such after incineration.

Massari *et al.* (2014) showed that after incineration of nano-TiO₂ paint debris, most of the NPs are transformed into calcium titanate. However, in their study of releases during the incineration of polymers containing nano-TiO₂, Singh *et al.* (2016) observed pure TiO₂ nanoparticles in the ash. The

difference in the results is most probably due to the different matrices tested: In contrast to the case of polymers, calcium is available in large quantities in paints, enabling the formation of calcium titanate. As these are the only two papers we could use to assess the forms of nano-TiO₂ after incineration of nanoproducts, we had to use uniform distributions and assume that 0-100% could stay pristine and the balance (i.e. 100% - pristine) would be transformed.

Integration of data into the model

After all distributions of ENM forms were defined (Tables 1 and 2), they were integrated into a probabilistic MFA model, based on the work of Sun *et al.* (2014). Three types of input data were taken from the base model (Sun *et al.*, 2014): (1) the mass of ENM produced, (2) the allocation of this mass to product categories, (3) the transfer coefficients describing the fractions of ENM flowing from product categories to technical and environmental compartments. One change was made from the base model: The transfer coefficient describing "matrix-embedded" ENM flows from WWTP to sludge was based on data from microplastic studies, as this removal efficiency mostly depends on the size of the particles studied, and many of the matrix-embedded ENMs can be considered similar to those of microplastics (see Table S8), especially because polymers constitute an important fraction of the used matrices (Scott-Fordsmand *et al.*, 2017).

The last type of data needed for the model are the transfer coefficients describing the transformations occurring in each compartment, i.e. the mass of ENM in a given form which "flows to" another form within the same compartment. This dataset comprises the results of the assessment described above, which is the division of the mass flows into five forms.

All input data was finally combined in a code written in R, which enabled the visualisation of the aggregated masses of ENMs flowing in dissolved, transformed, matrix-embedded and pristine forms along their life cycles, for the year 2012. Matrix algebra was used in this code, which solves Equation 1:

325 $A \cdot X = I$ (1)

326 Where I is the input vector: it contains all initial inputs to each compartment. In our case, the only
327 compartment to receive input is Production. A is a matrix of size $(n \times n)$, with n the number of
328 compartments in the system. This matrix contains all transfer coefficients between compartments. In
329 our case, each compartment is a combination of processes (e.g. Production, WWTP, Surface Water)
330 and forms. Consequently, they are of type Production_Pristine, or WWTP_Transformed. X is the
331 output vector of the model, containing the masses of ENMs flowing to each compartment. Since
332 probabilistic MFA is used, a second dimension is added to vectors I and X and a third to matrix A ,
333 representing the number of simulation runs: The final result given by the model is a matrix containing
334 the probability distributions associated with the masses of the ENMs forms flowing between the
335 compartments.

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338 Table 1: Forms of nano-Ag released during use. Product categories and shares of production are taken from Sun *et al.* (2014) The minima and maxima of the uniform distributions
339 (blue) and the modes of the triangular distributions (green) are reported. The full descriptions of the triangular distributions are available in the text. P: Pristine; M: Matrix-
340 embedded; D: Dissolved; T: Transformed.

| Product category | Share of ENM production (%) | Release to (%) | | | | | | | | | | | | | | | |
|--------------------------|-----------------------------|-----------------|-----------------|-------|-----------------|-------|-------|----|------|-------|-------|------|---------------|---|----|----|---|
| | | Waste water | | | | Air | | | Soil | | | | Surface water | | | | |
| | | P | M | D | T | P | M | T | P | M | D | T | P | M | D | T | |
| Electronics & Appliances | 38 | 0-100 | 0-100 | 0 | 0-100 | - | - | - | - | - | - | - | - | - | - | - | - |
| Textiles | 25 | (100-D)*50*15 | (100-D)*50*85 | 22 | (100-D)*50 | 50 | 25 | 25 | - | - | - | - | - | - | - | - | - |
| Cosmetics | 10 | 0 | 0 | 67 | 33 | - | - | - | - | - | - | - | 0 | 0 | 67 | 33 | |
| Food | 7 | 25-75 | 0 | 0 | 25-75 | - | - | - | - | - | - | - | - | - | - | - | - |
| Cleaning agents | 6 | 100 | 0 | 0 | 0 | - | - | - | - | - | - | - | - | - | - | - | - |
| MedTech | 4 | 0-100 | 0 | 0-100 | 0-100 | - | - | - | - | - | - | - | - | - | - | - | - |
| Plastics | 3 | (100-D)*(0-100) | 0 | 88 | (100-D)*(0-100) | - | - | - | - | - | - | - | - | - | - | - | - |
| Paints | 3 | 1-10 | 0-100 | 0-100 | 1-10 | 0-100 | 0-100 | 0 | 1-10 | 0-100 | 0-100 | 1-10 | - | - | - | - | - |
| Metals | 2 | 1-10 | 0-100 | 0-100 | 1-10 | - | - | - | - | - | - | - | - | - | - | - | - |
| Glass & Ceramics | <1 | 1-10 | 0-100 | 0-100 | 1-10 | - | - | - | - | - | - | - | - | - | - | - | - |
| Soil remediation | <1 | - | - | - | - | - | - | - | 100 | 0 | 0 | 0 | - | - | - | - | - |
| Filters | <1 | (100-D)*(0-100) | (100-D)*(0-100) | 95 | 0 | 0-100 | 0-100 | 0 | - | - | - | - | - | - | - | - | - |
| Sanitary products | <1 | 0 | 0 | 67 | 33 | - | - | - | - | - | - | - | - | - | - | - | - |

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343 Table 2: Forms of nano-TiO₂ released during use. Product categories and shares of production are taken from Sun *et al.* (2014) The minima and maxima of the uniform distributions
344 (blue) and the modes of the triangular distributions (green) are reported. The full descriptions of the triangular distributions are available in the text. P: Pristine; M: Matrix-
345 embedded; D: Dissolved; T: Transformed.

| Product category | Share of ENM production (%) | Release to (%) | | | | | | | |
|--------------------------|-----------------------------|----------------|--------|-------|-------|------|----|---------------|---|
| | | Waste water | | Air | | Soil | | Surface water | |
| | | P | M | P | M | P | M | P | M |
| Cosmetics | 59 | 100 | 0 | - | - | - | - | 100 | 0 |
| Paints | 9 | 30 | 70 | 0-100 | 0-100 | 30 | 70 | - | - |
| Electronics & Appliances | 7 | 0-100 | 0-100 | - | - | - | - | - | - |
| Cleaning agents | 6 | 100 | 0 | - | - | - | - | - | - |
| Filters | 6 | 30 | 70 | 0-100 | 0-100 | - | - | - | - |
| Plastics | 4 | 30 | 70 | - | - | - | - | - | - |
| Coatings | 4 | 30 | 70 | 0-100 | 0-100 | 30 | 70 | - | - |
| Glass & Ceramics | 2 | 30 | 70 | - | - | - | - | - | - |
| Sporting goods | 2 | 0-100 | 0-100 | 0-100 | 0-100 | - | - | - | - |
| WWTP | <1 | 100 | 0 | - | - | - | - | - | - |
| Food | <1 | 100 | 0 | - | - | - | - | - | - |
| Textiles | <1 | 50 | 50 | 0-100 | 0-100 | - | - | - | - |
| Spray | <1 | 100 | 0 | 100 | 0 | - | - | - | - |
| Metals | <1 | 30 | 70 | - | - | - | - | - | - |
| Cement | <1 | 0-1 | 99-100 | - | - | - | - | - | - |

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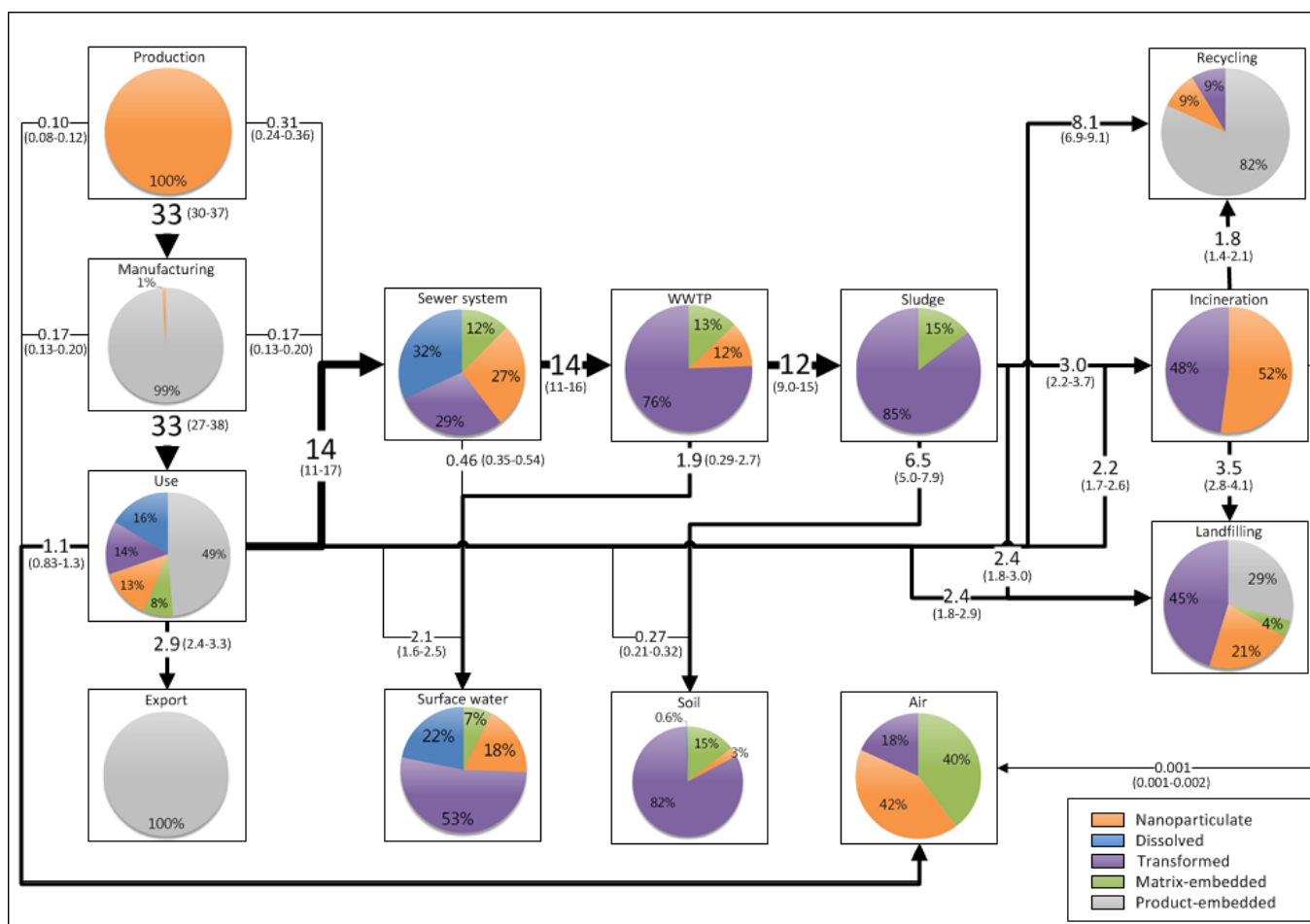
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RESULTS

Flow diagrams

Since probability distributions were associated with input data, results given by the model were probability distributions associated with the masses of ENMs flowing in each form in the system. Figures 2 and 4 show the mean values of probability distributions. The probability distributions associated with mass flows into the environmental compartments are shown on Figures 3 and S2. In the text, ranges indicate 25th and 75th percentiles of the distributions.

Most releases of nano-Ag to the environment were estimated to flow to soil (Figures 2 and 3, Table S9). There, only 2-3% (mean of 3%) of nano-Ag were present in pristine form, while 78-86% (mean = 82%) had been subject to chemical transformations in WWTP and sludge. The remainder was mostly matrix-embedded (11-19%, mean = 15%) with a small fraction of dissolved Ag (0.3-1%, mean = 1%). Most transformations of nano-Ag occurred during wastewater treatment through sulfidation. Four forms of nano-Ag were present in surface water: transformed (34-58%, mean of 53%), pristine (16-22%, mean of 18%), dissolved (17-34%, mean of 22%) and matrix-embedded (5-12%, mean of 7%). A high proportion of the nano-Ag released to air was found to be in pristine form (38-46%, mean of 42%), coming from production, manufacturing and use. The matrix-embedded releases to air mainly came from abrasion during use. The fraction released in transformed forms to air (15-21%, mean of 18%) only came from abrasion of textiles during use.



366

367 Figure 2: Flows of nano-Ag and distributions among the forms released during its life cycle. All flows are described in tons/year in the European Union with the means of the
 368 probability distributions. Numbers in brackets are the 25th and 75th percentiles of the probability distributions. Pie charts represent the means of the forms in which the ENMs flow
 369 out of the compartments, except for the environmental compartments (sinks) where they represent the final released form. The statistical description of the probability distributions
 370 obtained for all nano-Ag flows is described in Table S9. The probability distributions of the forms of nano-Ag flowing to air, surface water and soil are reported in Figure 3.

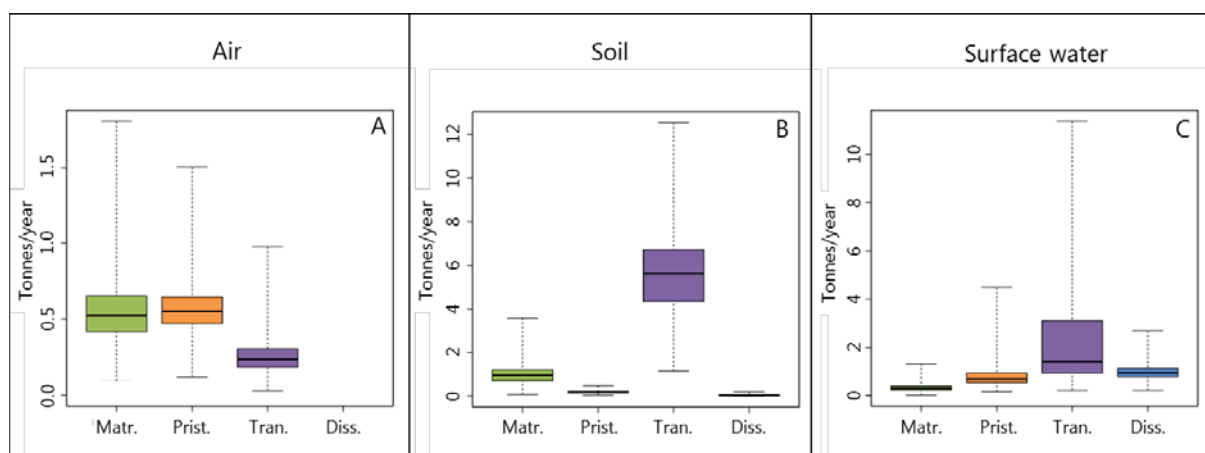
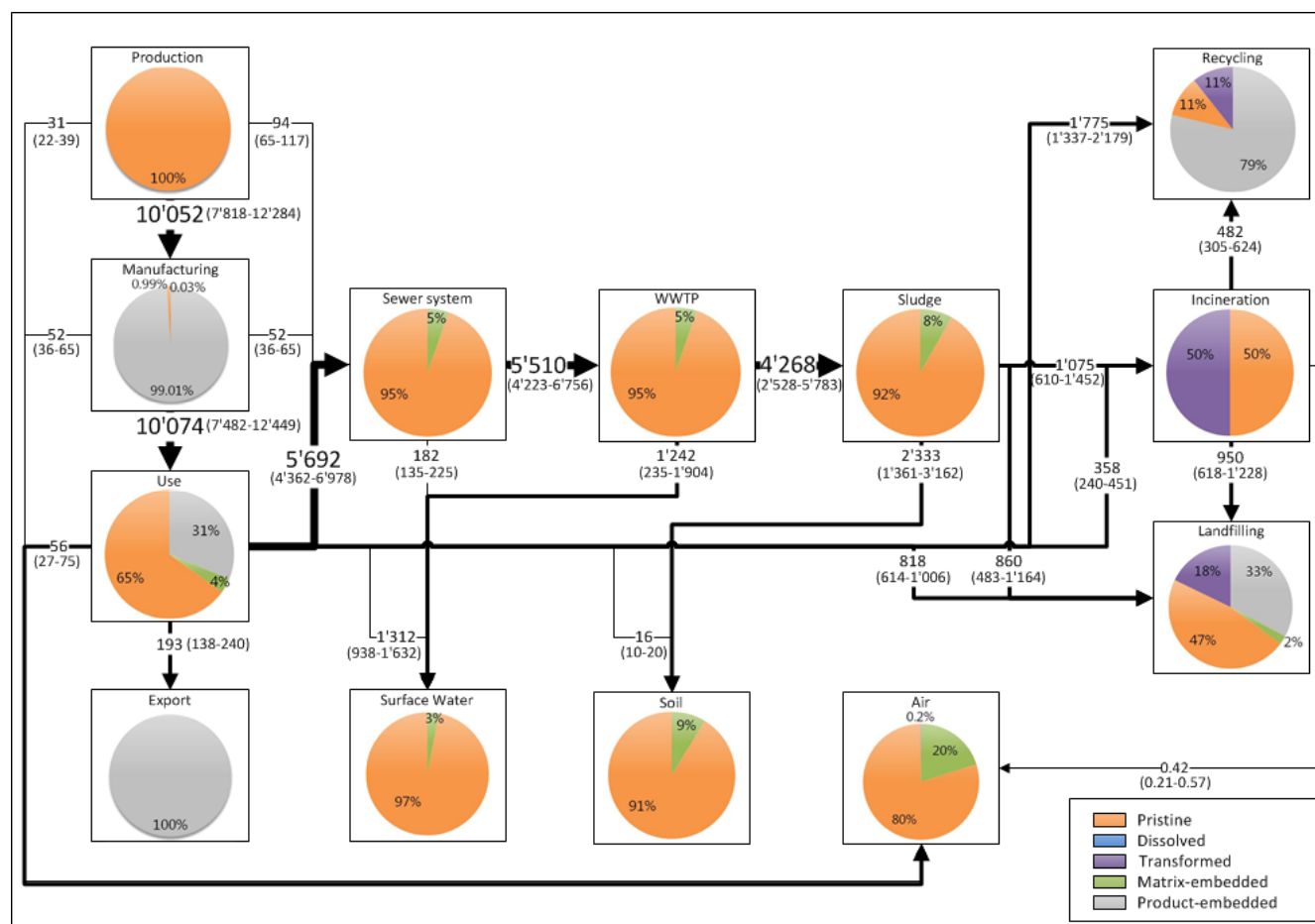


Figure 3: Probability distributions of nano-Ag flows to air (A), soil (B) and surface water (C). For each distribution, boxes contain 50% of the values (25th to 75th percentiles). The line in the box represents the median value. The whiskers extend to the minimum and maximum values of the distributions.

Matr.: Matrix-embedded; Prist.: Pristine; Tran.: Transformed; Diss.: Dissolved.

According to the model, soil and surface water are the environmental compartments receiving most of the nano-TiO₂ (Figures 4 and S2, Table S10). In surface water, the large majority of TiO₂ ENMs were released in pristine form (96-98%, mean of 97%), with only 2-4% (mean of 3%) matrix-embedded (originating from paints, coatings, textiles and cement weathering). 9% (5-10%) of TiO₂ released to soil was matrix-embedded. This fraction was larger than that found in surface water as, in the latter case, most matrix-embedded ENMs collected in the sludge during wastewater treatment, which was subsequently applied to land (resulting in release to soil), rather than being released to surface water in the effluent. 80% (75-85%) of nano-TiO₂ was released to air in pristine form.

The only transformation of nano-TiO₂ reported in the literature takes place during incineration where, depending on the product in which it was embedded, it could transform into calcium titanate. Consequently, transformed TiO₂ ENMs occurred in all three waste management compartments of the system (49-51% (mean = 50%) in waste incineration plants, 16-20% (mean = 18%) in landfills and 8-13% (mean = 11%) in recycling) and in the air (0.09-0.21%, mean of 0.16%).



390

391 Figure 4: Flows of nano-TiO₂ and distributions among the forms released during its life cycle. All flows are described in tons/year in the European Union with the means of the
 392 probability distributions. Numbers in brackets are the 25th and 75th percentiles of the probability distributions. Pie charts represent the means of the forms in which the ENM flows
 393 out of the compartments, except for the sink compartments where they represent the final released form. The statistical description of the probability distributions obtained for all
 394 nano-TiO₂ flows is described in Table S10. The probability distributions of the forms of nano-Ag flowing to air, surface water and soil are reported in Figure S2.

Occurrence of the pristine form in final compartments

Of the five final compartments considered in this model, most pristine Ag flowed to landfill (39-45%, mean of 42%, Figure 5), while 15-23% (mean of 20%) was released to surface water. Recycling received 20-23% (mean of 21%) of the pristine Ag flows. The major flows of pristine TiO₂ were to surface water (22-54%, mean of 37%) and soil (25-46%, mean of 36%). Considerable fractions flowed to soil and landfills, again potentially contaminating surface water through runoff.

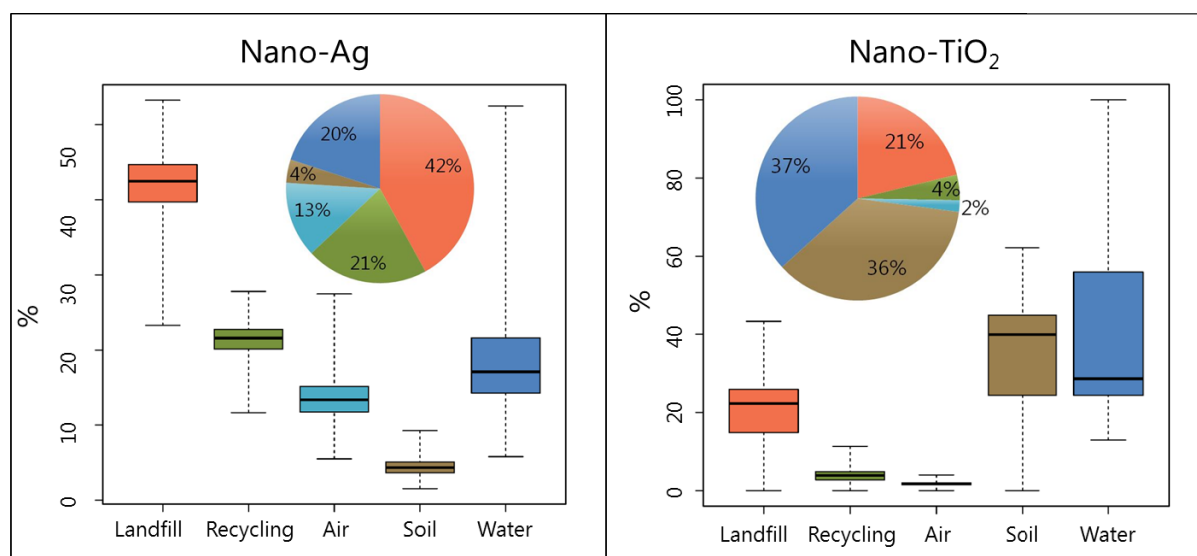


Figure 5: Occurrence of releases of pristine nano-Ag and nano-TiO₂ in final compartments. 100% represent the total of each ENM flows in pristine form to the sink compartments. Mean percentages are reported in the pie charts.

Relative uncertainty

The relative uncertainties of each form flowing between the compartments were calculated by dividing the standard deviations of the probability distributions by their means. Overall, higher uncertainties are associated with nano-TiO₂ than with nano-Ag flows. This reflects the smaller dataset available for the former.

Regarding nano-Ag, the highest relative uncertainty was associated with the mass of transformed ENMs in surface water (83%, Figure 6). Most of this uncertainty came from the removal efficiency of Ag ENMs in WWTPs. The relative uncertainty of *pristine* Ag ENMs released to surface water was lower because of the lower contribution of the flow from WWTPs compared to other flows coming from use and the sewer system, and therefore a lower contribution of the uncertainty associated to the WWTP removal efficiency. Matrix-embedded ENMs were attributed another distribution of removal efficiency, i.e. those of microplastics, for which the probability distribution was narrower. This explains the even lower relative uncertainty associated with this mass flow.

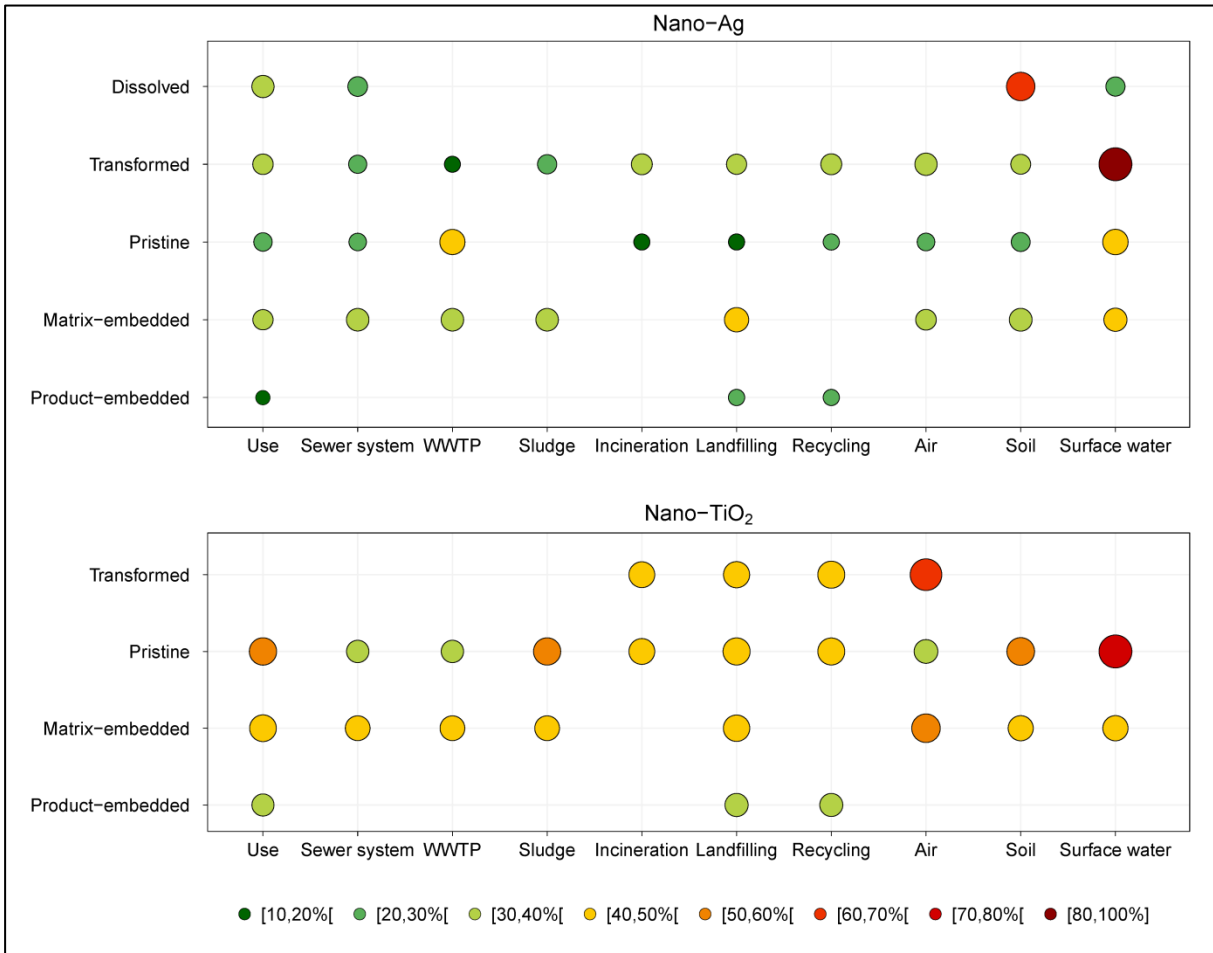


Figure 6: Relative uncertainty (standard deviation/mean) of the flows of nano-Ag and nano-TiO₂ from each compartment. WWTP: Wastewater treatment plant.

The same reason explains the difference between the relative uncertainty associated with pristine and matrix-embedded nano-TiO₂ flowing to surface water. The highest relative uncertainty obtained for nano-TiO₂ is associated with the transformed mass released to air. This is due to the fact that the transformation (or absence of transformation) of the product-embedded, matrix-embedded and pristine TiO₂ ENMs were given a very large uniform probability distribution from 0 (no transformation) to 100% (total transformation) as only two relevant experimental studies were found, illustrating both of these extreme cases.

Discussion

By combining an existing material flow model with the knowledge on the forms of nanomaterial releases, we have for the first time been able to estimate ENMs flows segmented into five different categories based on the reactions that ENMs undergo during use and release. Even though the distributions of the ENMs in these forms were assessed in a probabilistic way, the inclusion of this assessment in the model reduces, by itself, the overall uncertainty associated with the results previously obtained (Sun *et al.*, 2014). The model showed that pristine TiO₂ (free, agglomerated and aggregated) represented a high fraction of the overall release of TiO₂ NPs to environmental compartments. Regarding nano-Ag, only small fractions were modelled to be released in a pristine form, with most releases, particularly those to surface water and soil, in a transformed form. While this is what could have been expected based on a general understanding of ENM transformations, our model provided the magnitude of the flows.

The “transformed” category in our model includes all different forms of transformation. Yet, transformations that nano-Ag undergo are of different types (e.g. sulfidation or reaction with chloride) and depend on the release scenario (product category and release medium). During washing of textiles, Ag can form complexes with both Cl and S, forming either AgCl or Ag₂S. Both forms were reported in the literature (Impellitteri *et al.*, 2009; Lorenz *et al.*, 2012; Mitrano *et al.*, 2014). The

proportion of AgCl or Ag₂S formed depends on the nanoparticles integration in the fabric, the detergent used and the occurrence of UV irradiation before washing. Upon release from plastics, Ag was also found in AgCl and AgS forms, although AgCl seemed to dominate (Artiaga *et al.*, 2015; von Goetz *et al.*, 2013). During release from a façade coating, Kaegi *et al.* (2010) reported transformation to Ag₂S, also mentioning the possibility of Ag₂O being present at the edge of the particles. If nano-Ag is in contact with sweat, it can form AgCl (Stefaniak *et al.*, 2014; von Goetz *et al.*, 2013). Nano-Ag then undergoes further sulfidation in the sewer system (Kaegi *et al.*, 2015) and during wastewater treatment. Oxidation of Ag₂S can happen at the end of wastewater treatment if ozone treatment is implemented (Thalmann *et al.*, 2015), but the particles formed at this stage would be different from the pristine ones, so the ENMs stay transformed in the model.

Our study was subject to a number of limitations, mostly due to the occurrence of data gaps. Our assessment of nano-Ag releases was based in principle on experimental data. These data covered 50% of the nano-Ag product categories, which represented 76% of the input mass (Table S11). However, considerably less experimental data were available concerning the forms of nano-TiO₂ releases: 33% of product categories were covered (9% of the nano-TiO₂ mass produced). Consequently, the first limitation of our model is that, in the “pristine” category, no distinction could be made between single, homo-agglomerated and hetero-aggregated particles. This would have been interesting to consider as the extent of ENM aggregation is an important determinant of the surface area and density of the particles, aspects for which an understanding is required for accurate fate assessment. Second, the transformations considered in the model are those of the core materials of the ENM, i.e. metallic Ag or TiO₂. Even though some studies did study the transformations of the ENMs coatings (Botta *et al.*, 2011), there was not enough data in the literature to include them in a systematic way. Third, the size distributions of the released ENMs were mostly not reported in experimental studies. Typically, authors distinguished between particulate fractions that were above and below 450 nm. Optimum input data for environmental fate modelling of ENMs would be the complete size distributions of the released materials. However, in the absence of such data, the separation of a category that includes free and

474 agglomerated particles already represents a significant improvement compared to current standard
475 practice. Finally, regarding system definition, the exclusion of outflows from recycling in this study
476 should be overcome in the future. Yet, recycling processes for different product types vary
477 considerably and few studies exist that assess the fate of ENMs in recycling processes (Caballero-
478 Guzman *et al.*, 2015). Experimental efforts to better understand the flows of ENMs from recycling
479 processes and the forms that ENMs take in such flows take are urgently needed as up to 29%
480 (maximum) of pristine Ag flows to recycling. It is worth noting that despite the fact that the uncertainty
481 rising from grouping all nano-Ag and all nano-TiO₂ together was not assessed, it is in a way included
482 in our assessment, as we did not make any distinction in the data we used to draw probability
483 distributions. All these limitations contribute to uncertainty regarding the model structure. From a
484 more general perspective, the base structure of our model is given by the underlying model of Sun *et*
485 *al.* (2014), in which structural uncertainty might exist such as regarding the allocation of the ENM mass
486 to product categories. Since such data is scarce, a product category might be missing, as well as its
487 associated release scenarios.

488 There are several reasons why the results from the new model are important for the risk assessment of
489 ENMs. From a fate perspective, it matters a lot if the particles are released as free particles or matrix-
490 embedded. When ENMs are released in a solid matrix, they follow the environmental fate of the matrix
491 in which they are embedded, e.g. a polymer matrix or inorganic matrix. Al-Kattan *et al.*, for example,
492 have shown that released TiO₂ embedded in paint matrices have a different colloidal stability than that
493 of pristine nano-TiO₂ (Al-Kattan *et al.*, 2014). In the case of a polymer matrix the particles are actually
494 microplastics and will behave as such (Scott-Fordsmand *et al.*, 2017). In the case of an inorganic matrix,
495 e.g. a concrete chunk, the behaviour will be one of a larger particle. These processes can easily be
496 incorporated into environmental fate models, such as SimpleBox4Nano (Meesters *et al.*, 2014),
497 NanoFate (Garner *et al.*, 2017) or watershed models (Dale *et al.*, 2015). The form-specific flows
498 obtained in this study could in the future also be integrated into more advanced MFA models such as
499 dynamic MFA (Sun *et al.*, 2016) or country-specific assessments (Adam and Nowack, 2017).

Knowledge of the forms in which ENMs flow is also important for hazard assessment. Our estimations showed that the amount of ENM releases in pristine form is likely to be lower than was previously assumed (Sun *et al.*, 2014). Consequently, the concentration of nano-Ag to which organisms are potentially exposed is likely to be much lower: From our model, only a small fraction of the total amount of nano-Ag reaching an environmental compartment was still present in its pristine form. Previous environmental risk assessments have used the total ENM mass flows (all types of release) as basis for the exposure assessment (Coll *et al.*, 2016; Gottschalk *et al.*, 2013). The hazard assessment is based on the pristine form of the ENM. Therefore, if the toxicity of the transformed ENM forms is lower than that of the pristine form (as is the case for, e.g. Ag₂S compared to metallic Ag (Levard *et al.*, 2013)), the risk can be overestimated. For matrix-embedded ENMs, the magnitude of organism exposure to the ENMs depends on the degradability of the matrix. Hence, matrix type is the key determinant of both the fate and bioavailability of the ENM (Scott-Fordsmand *et al.*, 2017). The fate of the dissolved fraction of nano-Ag is entirely different from those of the particulate forms of nano-Ag. All nano-specific properties are lost, hence the mass of dissolved Ag should not be considered in ENM risk assessment, but rather in conventional risk assessment of metals.

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Supporting information

Supporting information includes data and references used for specific calculations of distributions of released forms and of matrix-embedded ENMs removal efficiency during wastewater treatment. It also includes the description of the probability distributions obtained for each flow and boxplots illustrating those of nano-TiO₂ to air, soil and water.

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