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

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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-TiO_2 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 34–58% and 78–86%, respectively, with means of 53% and 82%), 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-TiO_2 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.

1. 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 to 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-TiO_2, nano-Ag, nano-ZnO and CNT. A significant improvement 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

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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 characterisation 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-TiO_2 undergo during their life cycle and assess the forms in which they are released to the environment. Nano-Ag and nano-TiO_2 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-TiO_2 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.

2. Material and methods

2.1. Scope of the study and general methodology

The material flow analysis (MFA) of nano-Ag and nano-TiO_2 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 (Fig. 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.

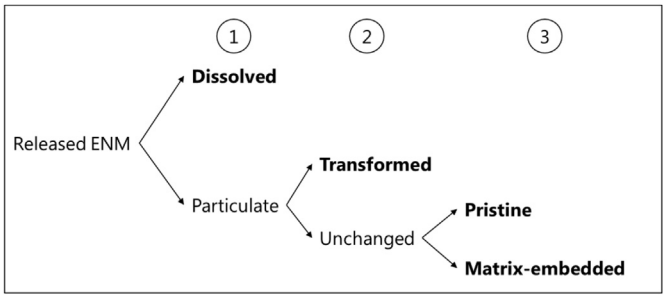

Fig. 1. Assessment scheme used for assessing the distributions of released forms.