NERC Open Research Archive
sharing our research

Centre for Ecology & Hydrology
NATURAL ENVIRONMENT RESEARCH COUNCIL

Article (refereed) - postprint

Williams, Richard J.; Harrison, Samuel; Keller, Virginie; Kuenen, Jeroen; Lofts, Stephen; Praetorius, Antonia; Svendsen, Claus; Vermeulen, Lucie C.; van Wijnen, Jikke. 2019. **Models for assessing engineered nanomaterial fate and behaviour in the aquatic environment**.

© 2018 Elsevier Ltd.
This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/
(cc) BY-NC-ND

This version available http://nora.nerc.ac.uk/521731/

NERC has developed NORA to enable users to access research outputs wholly or partially funded by NERC. Copyright and other rights for material on this site are retained by the rights owners. Users should read the terms and conditions of use of this material at http://nora.nerc.ac.uk/policies.html#access

NOTICE: this is the author's version of a work that was accepted for publication in *Current Opinion in Environmental Sustainability*. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in ***Current Opinion in Environmental Sustainability*** **(2019), 36. 105-115. https://doi.org/10.1016/j.cosust.2018.11.002**

www.elsevier.com/

Contact CEH NORA team at
noraceh@ceh.ac.uk

The NERC and CEH trademarks and logos ('the Trademarks') are registered trademarks of NERC in the UK and other countries, and may not be used without the prior written consent of the Trademark owner.

Models for assessing engineered nanomaterial fate and behaviour in the aquatic environment

Richard J. Williams*[1], Samuel Harrison[2], Virginie Keller[1], Jeroen Kuenen[3], Stephen Lofts[2], Antonia Praetorius[4,5] , Claus Svendsen[1], Lucie C. Vermeulen[6,7], Jikke van Wijnen[8]

[1.] Centre for Ecology and Hydrology, Wallingford, Oxfordshire, OX10 8BB, UK
[2.] Centre for Ecology and Hydrology, Lancaster Environment Centre, Library Avenue, Bailrigg, Lancaster, LA1 4AP, UK
[3.] TNO, Department of Climate, Air and Sustainability, PO Box 80015, 3584 TA Utrecht, The Netherlands
[4.] Department of Environmental Geosciences and Environmental Science Research Network, University of Vienna, Althanstr. 14, UZA II, 1090 Vienna, AT
[5]Research Platform Nano-Norms-Nature, University of Vienna, Althanstr. 14, UZA II, 1090 Vienna, AT
[6.] Environmental Systems Analysis Group, Wageningen University, PO Box 47, 6700 AA Wageningen, the Netherlands
[7.] Zoonoses and Environmental Microbiology, Centre for Infectious Diseases Control, National Institute for Public Health and the Environment (RIVM), Bilthoven, the Netherlands
[8.] Department of Science, Faculty of Management, Science & Technology, Open University, Heerlen, the Netherlands

*corresponding author: rjw@ceh.ac.uk

Abstract

Engineered nanomaterials (ENMs, material containing particles with at least one dimension less than 100 nm) are present in a range of consumer products and could be released into the environment from these products during their production, use or end-of-life. The high surface to volume ratio of nanomaterials imparts a high reactivity, which is of interest for novel applications but may raise concern for the environment. In the absence of measurement methods, there is a need for modelling to assess likely concentrations and fate arising from current and future releases. To assess the capability that exists to do such modelling, progress in modelling ENM fate and since 2011 is reviewed. ENM-specific processes represented in models are mainly limited to aggregation and, in some instances, dissolution. Transformation processes (e.g. sulphidation), the role of the manufactured coatings, particle size distribution and particle form and state are still usually excluded. Progress is also being made in modelling ENMs at larger scales. Currently models can give a reasonable assessment of the fate of ENMs in the environment, but a full understanding will likely require fuller inclusion of these ENM specific processes.

Keywords: modelling, Engineered Nanomaterials, aggregation, transformation, aquatic environment

Highlights

- Models of nanomaterial release are needed to drive nanomaterial fate models
- Nanomaterial-specific processes are now being included in fate models
- The form and state in which particles are released needs to be considered
- There is progress towards process based modelling at large scales

1. Introduction

Engineered nanomaterials (ENMs) are increasingly being used in a range of consumer products and are likely to be released into the environment from these products during their production, use or end-of-life phases. Nanomaterials are defined by their size (e.g. according to the EU recommendation for the definition of a nanomaterial as a material containing particles with one or more dimensions in the size range 1- 100 nm [1] see Box 1) rather than their chemical composition. The high surface to volume ratio of nanomaterials imparts a high reactivity which is of interest for novel applications but raises concern for human and environmental health. In both these areas the general concern is whether the size of the particles will mean that they have behaviours and effects that might not be predictable from knowledge of the behaviour of the “conventional” form of the material.

Box 1

Engineered nanomaterials are challenging to identify and quantify in the environment [2-6], although recent progress has been made for graphene based ENMs [7] and various inorganic ENMs [8-10]. It is therefore difficult to get a real sense of the extent of the distribution, concentrations and therefore impacts that ENMs are likely to have in the environment. In the absence of widespread observational data, modelling provides a means of estimating likely concentrations in the environment from materials that are already in use or from new-to-market products. The outputs of such appropriately constructed models could predict concentrations in environmental compartments and likely hotspots of exposure. As with “conventional” chemicals, such data can be used to assess the extent of exposure of organisms in the environment which is one part of the risk assessment processes. It is very likely that policy makers, manufacturers, environmental agencies and citizens will want to know how ENMs move through the environment; whether, for example, they accumulate in sediments in lakes and rivers or are taken up by animals and plants. A major route for ENMs into the environment is through sewage treatment plant (STP) discharges [11,12] and therefore modelling their fate and behaviour in aquatic systems (rivers and lakes) is an important area of study.

A key aspect of ENMs both from the regulatory and scientific point of view is their definition, specifically that a material is classed as a “nanomaterial” as a result of its physical characteristics rather than its chemical properties. This means that ENMs can in principle and reality be highly diverse in their chemistries. Examples of ENMs in current commercial use include metal–based materials such as cerium, titanium and zinc oxide, copper and copper oxide, metal sulphides, selenides and tellurides, and carbon–based materials including single and multiwalled carbon nanotubes. Further potential developments include nanosized micelle–based structures for targeted drug delivery [13] and nanocarrier–type materials as nanopesticides [14]. The challenge for simulation of aquatic (and indeed environmental) fate of ENMs is thus in part a challenge of simulating the potentially diverse behaviours of these materials. We will show that previous modelling efforts, at least those for distributed (spatial) simulation of ENM fate, have tended to have a relatively narrow focus, while what is needed is an approach to generalise the principles of ENM behaviour as far as possible while allowing for new behaviours to be incorporated.

This review considers how the state of modelling has developed since 2011, to show the progress that has been made in developing ENM-specific fate models. A number of previous workers have reviewed aquatic ENM fate modelling efforts within this fast–developing field [15,16]. In this paper, we will assess past and current modelling efforts in the context of (i) the most up to date knowledge of nanomaterial speciation, particularly speciation at entry points into the environment, and (ii) the specificity of current models for particular types of nanomaterials, and how models may be made more generic in order to anticipate new types of nanomaterials.

Modelling water quality can take place at a range of scales from the catchment through to regions, whole continents and even more recently at the global scale [17]. For pollutants global models exist for nutrients [18], plastics [19], pathogens [20,21], pharmaceuticals[22] and in a simple way (see Section 4), ENMs [23] among others (see this issue for more details of these types of model [24,25]) . Such models are useful for scenario analysis of climate, socio-economic change, policy assessment [26], estimating concentrations where observed data are not available[27] or giving a global picture for a particular water quality indicator of concern[28]. This review therefore concludes by looking forward to the prospects for modelling ENMs in a physically realistic way at large scales.

2. Nanomaterial Behaviour in the Environment

The key behaviours of ENMs in aquatic environments are reasonably well established and have been incorporated into a number of models previously. Models of chemical fate need to consider mass flows among different environmental compartments [29,30]. In the aquatic systems considered here, that means advection with flowing water and exchange with the suspended matter and bed sediments. ENMs may attach to each other (homoaggregation) or to particulate matter in the water column (heteroaggregation). These processes are irreversible, or, at least, the reversible process is so slow as to be negligible, and so equilibrium–based methods to compute distributions of chemicals between particle–associated and dissolved forms, such as the partition coefficient, are not applicable to nanomaterials [31]. Aggregates so formed, might then be deposited to the river (or lake) bed sediments [32,33]. Here they might be removed from the system by burial to depth or be re-suspended back into the water column as flow conditions change. There could also be loss of ENMs to the bed sediment by direct interaction or deposition, for example in rivers that lose flow to groundwater or have a very active hyporheic zone. ENMs in the water column can also undergo dissolution into an ionic form (e.g. nano-ZnO) [29,34]. The presence of metal–complexing ligands, particularly NOM, in solution, and the aggregation state of the particles, may change solubility rates [35-37] or sorb to the particle surfaces and influence their stability against agglomeration [38]. Other surface reactions include sulphidation (e.g. Ag nanoparticles to Ag_2S [39]) or oxidation, for example, photooxidation of Ag nanomaterial surfaces to Ag_2O [40] and oxidation of Cu to CuO in the presence of organic ligands[41] have been demonstrated. Furthermore, a loss or transformation of the manufactured coating on the nanomaterial surface can lead to a change of its properties [42].

ENMs may thus be present in the environment in numerous forms and states [29,34,43] as illustrated in Figure 1. It is useful to separately consider the structure and composition of nanomaterials at the level of the individual particles and in terms of overall physical state. We use the term form to describe the structure and composition at the level of the individual particle. This encompasses, such considerations as whether the particle retains a manufactured coating, an environmental corona of adsorbed material such as NOM, or a shell (outer layer) of differing physicochemical properties to that of the core (inner layer) wherein by design or as a result of chemical transformation during the particle lifecycle. We use the term state for the physical state of particle populations in the environment, such as, the degree to which they are present as free particles, homoaggregates or heteroaggregates or attached to the solid matrix in a soil. The form and state of nanomaterials is key to their fate, through their influence on properties such as aggregation behaviour, solubility and particle density. By way of illustration: (i) particles heteroaggregated to suspended sediments in waters are subject to transfer to the bed sediments if the suspended sediment is deposited out of the water column; (ii) particles having an environmental corona may have modified surface properties that reduce their tendency to heteroaggregate to particulate matter. Not all types of nanomaterials may adopt all the possible forms and states – for instance, not all particles are manufactured with a surface coating.

Figure 1

3. Modelling nanomaterials in the Aquatic Environment.

The current status of models to predict environmental concentrations of engineered nanomaterials (ENMs) for the purpose of assessing risk was reviewed as recently as 2012 [15]. At that time the authors identified a number of existing nano-specific models (i.e. those specifically designed to account for the processes that determine fate and behaviour for ENMs); six for surface waters, six for sub-surface transport and another six multimedia models. A number of other modelling systems that are currently used for regulatory assessment of non-nano chemical forms were also assessed to make reasonable assessment of ENMs with some modifications. Subsequently, four further reviews were published. Gottschalk et al. [44] traced the evolution of ENM specific models to 2012 and provided an assessment of a dozen different models. Dale et al. [45] reviewed models for aquatic systems and made an assessment of their strengths and weaknesses. Nowack [46] looked specifically at modelling ENMs from a regulatory context, while Baalousha et al. [16] took a more general view of modelling ENM fate, but with a specific emphasis on aquatic systems.

ENM models that have been published since 2012 are summarised in terms of some of their key features (Table 1); it is from this point that efforts in ENM-specific modelling started to accelerate. There is still a range in complexity in the models in terms of the representation of ENM fate, from only considering advection [47], through to multiple processes representing heteroaggregation, dissolution, sediment deposition and resuspension, sediment burial, soil runoff and biotic uptake (e.g. MendNano [48,49]). However, in ENM specific terms, most models only take heteroaggregation and dissolution into account. Notable exceptions are the NanoDUFLOW modelling study of nano-TiO_2 [50,51] in the River Dommel, (the Netherlands) and the modelling of nano-TiO2, nano-ZnO and nano-Ag in the River Rhine [52,53]. The former adds homoaggregation to the other two processes mentioned, while the latter further considers transformation (removal of ENM coating) and mineralisation (although these mechanisms were not implemented in the actual model application to the River Rhine). The most recently published ENM model currently available is NanoFATE [54], which is a dynamic multimedia fate and transport model accounting for aggregation, dissolution, sorption to suspended particles and subsequent sedimentation. It is designed to be able to account for other ENM-specific processes such as oxidation, sulfidation and loss of the original coating when these processes are sufficiently well understood to be incorporated into a model. However, it has only limited spatial resolution in the estimates of ENM concentrations.

Despite progress to date, there is still scope for improving ENM models through collaboration between modellers and experimentalists [45]. The review of Dale et al. looks specifically at this point and identified eight key areas for collaboration including; better descriptions of heteroaggregation, and reactive ENM chemistry, model spatial resolution of models, sensitivity analysis and model testing.

The testing of ENM model predictions against observed data is challenging, because ENMs are present in low concentrations and non-nano material (e.g. ionic metal) could be associated with nano-sized particles that occur naturally in the environment. Therefore, concentrations of material measured in appropriate size fractions might not originate from an ENM source. In order to test the

NanoDUFLOW model [50] when applied to the River Dommel in the Netherlands, observed concentrations of colloidal (2- 450 nm) Ce, Al, Ti and Zr based particles were compared to concentrations of those materials in the < 450nm size class predicted by the model. Very good simulations were achieved for Ce and acceptable simulations for the other materials. The authors suggested that this goes some way to validating the simulation of aggregated ENMs (a likely form in the environment depending on ENM size and particulate concentration [55,56]) in their model, if not a formal validation of ENM modelling *per se*. Generally speaking, even if a formal validation of ENM models may not be achievable in the near future, basic model assumptions may be validated by small scale micro-/mesocosm set-ups or controlled laboratory studies [57].

Table 1

Three of the previous model reviews make the very useful distinction between materials flow analysis (MFA) models and environmental fate models (EFM) [44-46]. MFA models estimate the release into the environment of ENMs from products during their use, recycling and final disposal, while EFM describe the fate and behaviour of ENMs in one or more environmental compartments (EFMs are summarised in Table 1). Most MFA models typically do not include mechanistic nano-specific process descriptions, but rather average transfer coefficients between different, mostly technical, compartments [45]. While the main goal of MFA models is to provide estimates of ENM release, most then use this information to make broad estimates of environmental concentrations. Such an approach was used to calculate the possible release of TiO_2 from sunscreen by means of a simple dilution model to estimate concentrations in rivers across two regions of the UK [47]. Another more sophisticated approach used probabilistic estimates of release from products across the European Union in general and for the specific country cases of Switzerland and Denmark to make estimates of accumulations of a number of different ENMs in soils and concentrations of ENMs in river waters averaged across these geographical areas [11,58-61]. This approach has subsequently been developed to provide country specific estimates for all the European Union member states

[62]. The reader is directed to Nowack [46] for a more complete review of these models. The importance of quantifying the forms and states in which ENMs are released into the environment was discussed above. Recently a first estimation of the quantities in which nano-Ag and nano-TiO_2 are released as different forms and states into the environment at the European scale has been made [63]. In that publication, five different releases were considered; dissolved, transformed (ENM subjected to chemical reaction), matrix embedded (in a solid material e.g. in cement), pristine (non-transformed released ENM), and product-embedded (ENM still contained within the complete product).

Modelling concentrations of ENM in the environment relies heavily on information regarding their release rates. While for small-scale models this may be available through local measurements, for large-scale models a different approach is required (described above). However, these inventories so far lack the spatial and temporal disaggregation needed for use in large-scale fate models. A clear next step on this aspect is to make the releases spatially and temporally more explicit by distributing the annual releases for the modelled area (e.g. European Union) to a grid and distributing them temporally over the year. A major issue with the release data is the large uncertainties that exist around the production of ENMs as independent estimates may vary by more than one order of magnitude [65]. Attempts to better quantify the amount of releases are hampered by the fact that this information is often considered confidential, and therefore estimates are usually based on expert judgement.

4. Modelling ENMs at large scales

Several of the available ENM models are spatially explicit [23,33,45,50-52,54], i.e. they make predictions that vary over the geographical domain of the simulation. Primarily, these simulations are along rivers and estuaries systems, with the river catchment being the geographical unit of choice (Table 1). The GWAVA model [23] is the only one that makes estimates over very large areas – in this case continental Europe – with spatial discrimination (approximately 6km by 9km grid cells).

The model takes estimates of the material flows of nano-Ag and nano-ZnO for the modelled area [11], which are then assumed to be discharged through sewage treatment works into the European river system. The spatial variation comes from the location and size of the sewage treatment works discharges and the local dilution in receiving waters. There are no nano-specific processes modelled, but there is scope for a removal in sewage treatment and sedimentation of ENMs as they move downstream. Despite this simple approach, the authors were able to investigate the sensitivity of the model to different parameter assumptions through a series of scenarios; best case, worst case and expected case. Predicted no-effect concentrations (PNECs) were available for both of the ENM models, and maps could be produced that indicated where these PNECs might be exceeded and under what model assumptions. In addition, looking at this larger scale allowed an assessment of the total river lengths that might be affected by higher than desirable concentrations of nano-Ag and nano-ZnO.

5. Discussion

Models for the fate of ENMs in aquatic systems have been developed at a range of levels of complexity and with a range of approaches to describing the processes of nanomaterial transformation. Focusing on the models in Table 1, some general strengths and weaknesses can be identified:

- Modelling of aggregation features in the majority of models, reflecting the perceived importance of attachment to other particles and suspended sediments as an intermediate fate process. Current models do not however generally account for whether rates of attachment are a function of water chemistry variables;
- Dissolution processes are generally recognised as important for those metal/metal–based nanomaterials for which dissolution is considered thermodynamically possible. However a relatively small number of models explicitly consider dissolution. This is in part because

some modelling studies have focused on 'insoluble' ENMs such as TiO_2 and CeO_2, but also in part due to perceived challenges in robustly modelling dissolution (e.g. [52]);

- Transformation processes such as particle sulphidation are generally not included, again partly because the particles modelled do not undergo such transformations;
- The potential roles of manufactured coatings and formation of an environmental corona (adsorbed monolayer of molecules) in influencing fate are not currently modelled;
- The importance of particle size distribution is generally acknowledged, but not necessarily modelled explicitly;
- The importance of form and state on entry to the aquatic environment are sometimes acknowledged, but not explicitly set in modelling, with the exception of Dale and co–workers [30] and the recent MFA modelling of Adams and co-workers [63];

The implications of form and state on entry to the aquatic environment is of particular note. Specific examples of where this may be important may be readily found; for example, the sulphidation of nano–Ag particles within wastewater treatment systems prior to discharge reduces the solubility of Ag considerably, with potential implications for its tendency to remain in particle form within the environment as opposed to dissolving. Particles associated with material such as biosolids, applied to land, may enter surface waters following soil erosion, already attached to soil particles that become part of the river sediment load. Generally, these examples suggest that modelling ENM fate within aquatic systems needs to be seen in the context of transformations through the whole ENM lifecycle. This implies a need for a generalised approach to ENM transformation modelling, for example based around the concepts of form and state which we have presented (Figure 1), and transformations of these both prior to and following ENM entry to the aquatic environment. If implemented well, such an approach ought to be sufficiently flexible to allow for a range of complexity in approaches to transformation modelling within the same model framework. The approach also has the advantage of being potentially more applicable to new types of nanomaterial not the subject of past and current modelling (for example functionalized carbon nanotubes developed for drug delivery [66]).

A further consideration not covered in modelling approaches to date is the potential for fate behaviour, e.g. rate of ENM attachment to sediments, to be dependent upon the physicochemical properties of the immediate environment such as pH and sediment composition.

Taking a life cycle approach implies modelling of aquatic ENM fate in the wider context of environmental fate, i.e. a multimedia approach. A number of ENM fate models already take a multimedia approach [49,52], but this has not yet been combined with spatiotemporal modelling. This is in part due to concerns regarding the robustness of spatiotemporal estimation of nanomaterial releases (Section 4).

Despite these concerns, there is current research into joining up temporally and spatially distributed MFA models with similarly distributed multi-media fate models for ENMs (e.g. in the novel framework for urban environments proposed by Domercq et al. [67]). A further example is the European Commission H2020 funded project, NanoFASE [68]. This project is moving towards the general requirement for a framework for regional or catchment scale modelling of ENMs based on a multimedia modelling and life cycle analysis approach [43]. Such a framework would allow investigations of environmental fate under a range of putative scenarios.

6. Conclusions

There has been considerable scientific effort over the past decade to understanding ENM fate in the environment. This review has shown that this knowledge is being translated into mathematical models of ENM fate which account for specific ENM processes in the aquatic environment. Presently however, this is currently limited in the main part to aggregation processes and (less often) dissolution. Transformation processes (e.g. sulphidation), the role of the manufactured coatings, particle size distribution and particle form and state are still usually excluded. As with all conventional modelling there is the need to drive these models with reliable data on ENM releases. Such data are not currently available and so a number of other related modelling approaches have been put in place to generate the required inputs. Despite this, these models are moving in the right direction to provide realistic estimates of the fate of ENMs in the environment and likely concentrations. However, there is still progress to be made and research is needed on methods to generate observed ENM concentrations to test both the models of environmental fate and ENM releases against observed data. This is the main route to raise confidence in the models and the predictions they make, as well as the policy decisions based on those predictions.

7. Acknowledgements

This paper evolved from a workshop titled "Water Quality: a new challenge for global scale modelling" held at Wageningen University 18-21 September 2017. Funding for this workshop came from the OECD-CRP, the support of which is gratefully acknowledged. Part of this research was supported by the NanoFASE project (Grant Agreement No. 646002) within the framework of the EU Horizon 2020 research and innovation programme.

The authors declare no conflict of interest

8. References

1. European Commission: **2011/696/EU Commission Recommendation of 18 October 2011 on the definition of nanomaterial** *Official Journal of the European Union* 2011, **L275, 54**:38.
2. Laborda F, Bolea E, Cepria G, Gomez MT, Jimenez MS, Perez-Arantegui J, Castillo JR: **Detection, characterization and quantification of inorganic engineered nanomaterials: A review of techniques and methodological approaches for the analysis of complex samples**. *Analytica Chimica Acta* 2016, **904**:10-32.
3. Majedi SM, Lee HK: **Recent advances in the separation and quantification of metallic nanoparticles and ions in the environment**. *Trac-Trends in Analytical Chemistry* 2016, **75**:183-196.
4. Petersen EJ, Flores-Cervantes DX, Bucheli TD, Elliott LCC, Fagan JA, Gogos A, Hanna S, Kagi R, Mansfield E, Bustos ARM, et al.: **Quantification of Carbon Nanotubes in Environmental Matrices: Current Capabilities, Case Studies, and Future Prospects**. *Environmental Science & Technology* 2016, **50**:4587-4605.
5. Rodrigues SM, Trindade T, Duarte AC, Pereira E, Koopmans GF, Romkens P: **A framework to measure the availability of engineered nanoparticles in soils: Trends in soil tests and analytical tools**. *Trac-Trends in Analytical Chemistry* 2016, **75**:129-140.

6. von der Kammer F, Ferguson PL, Holden PA, Masion A, Rogers KR, Klaine SJ, Koelmans AA, Horne N, Unrine JM: **Analysis of engineered nanomaterials in complex matrices (environment and biota): General considerations and conceptual case studies**. *Environmental Toxicology and Chemistry* 2012, **31**:32-49.

7. Goodwin DG, Adeleye AS, Sung L, Ho KT, Burgess RM, Petersen EJ: **Detection and Quantification of Graphene-Family Nanomaterials in the Environment**. *Environmental Science & Technology* 2018, **52**:4491-4513.

8. Mitrano DM, Ranville JF, Bednar A, Kazor K, Hering AS, Higgins CP: **Tracking dissolution of silver nanoparticles at environmentally relevant concentrations in laboratory, natural, and processed waters using single particle ICP-MS (spICP-MS)**. *Environmental Science: Nano* 2014, **1**:248-259.

9. Praetorius A, Gundlach-Graham A, Goldberg E, Fabienke W, Navratilova J, Gondikas A, Kaegi R, Gunther D, Hofmann T, von der Kammer F: **Single-particle multi-element fingerprinting (spMEF) using inductively-coupled plasma time-of-flight mass spectrometry (ICP-TOFMS) to identify engineered nanoparticles against the elevated natural background in soils**. *Environmental Science: Nano* 2017, **4**:307-314.

10. Reed RB, Martin DP, Bednar AJ, Montano MD, Westerhoff P, Ranville JF: **Multi-day diurnal measurements of Ti-containing nanoparticle and organic sunscreen chemical release during recreational use of a natural surface water**. *Environmental Science: Nano* 2017, **4**:69-77.

* 11. Sun TY, Gottschalk F, Hungerbühler K, Nowack B: **Comprehensive probabilistic modelling of environmental emissions of engineered nanomaterials**. *Environmental Pollution* 2014, **185**:69-76.

12. Johnson AC, Jürgens MD, Lawlor AJ, Cisowska I, Williams RJ: **Particulate and colloidal silver in sewage effluent and sludge discharged from British wastewater treatment plants**. *Chemosphere* 2014, **112**:49-55.

13. Hubbell JA, Chilkoti A: **Nanomaterials for Drug Delivery**. *Science* 2012, **337**:303-305.

14. Cătălin Balaure P, Gudovan D, Gudovan I: **4 - Nanopesticides: a new paradigm in crop protection**. In *New Pesticides and Soil Sensors*. Edited by Grumezescu AM: Academic Press; 2017:129-192.

* 15. Hendren CO, Lowry M, Grieger KD, Money ES, Johnston JM, Wiesner MR, Beaulieu SM: **Modeling Approaches for Characterizing and Evaluating Environmental Exposure to Engineered Nanomaterials in Support of Risk-Based Decision Making**. *Environmental Science & Technology* 2013, **47**:1190-1205.

** 16. Baalousha M, Cornelis G, Kuhlbusch TAJ, Lynch I, Nickel C, Peijnenburg W, van den Brink NW: **Modeling nanomaterial fate and uptake in the environment: current knowledge and future trends**. *Environmental Science-Nano* 2016, **3**:323-345.

17. Kroeze C, Gabbert S, Hofstra N, Koelmans AA, Li A, Löhr A, Ludwig F, Strokal M, Verburg C, Vermeulen L, et al.: **Global modelling of surface water quality: a multi-pollutant approach**. *Current Opinion in Environmental Sustainability* 2016, **23**:35-45.

18. Beusen AHW, Bouwman, A. F., Van Beek, L. P. H., Mogollón, J. M., and Middelburg, J. J.: **Global riverine N and P transport to ocean increased during the 20th century despite increased retention along the aquatic continuum**. *Biogeosciences* 2016, **13**:2441-2451.

19. Siegfried M, Koelmans AA, Besseling E, Kroeze C: **Export of microplastics from land to sea. A modelling approach**. *Water Research* 2017, **127**:249-257.

20. Hofstra N, Bouwman AF, Beusen AHW, Medema GJ: **Exploring global Cryptosporidium emissions to surface water**. *Science of The Total Environment* 2013, **442**:10-19.

21. Vermeulen LC: **Cryptosporidium in rivers of the world – the GloWPa-Crypto model**. In *Environmental Systems Analysis Group*. Edited by. Wageningen, the Netherlands: Wageningen University; 2018. vol PhD.]

22. Pistocchi A, Marinov D, Pontes S, Gawlik BM: **Continental scale inverse modeling of common organic water contaminants in European rivers**. *Environmental Pollution* 2012, **162**:159-167.

* 23. Dumont E, Johnson AC, Keller VDJ, Williams RJ: **Nano silver and nano zinc-oxide in surface waters – Exposure estimation for Europe at high spatial and temporal resolution**. *Environmental Pollution* 2015, **196**:341-349.

24. Strokal M, Spanier JM, C. K, Koelmans AA, Flörke M, W. F, Hofstra N, Langan S, Tang T, van Vliet MTH, et al.: **Global multi-pollutant modelling of water quality: scientific challenges and future directions** *Current Opinion in Environmental Sustainability* in Press.

25. van Vliet MTH, Flörke M, Harrison J, Hofstra N, Keller VDJ, Ludwig F, Kroeze C, Spanier JE, Strokal M, Wada Y, et al.: **Model inter-comparison design for large-scale water quality models**. *Current Opinion in Environmental Sustainability* in Press.

26. Reder K, Bärlund I, Voss A, Kynast E, Williams RJ, Malve O, Flörke M: **European Scenario Studies on Future In-Stream Nutrient Concentrations** *Transactions of the ASABE* 2013, **56**:1407-1417.

27. Johnson AC, Dumont E, Williams RJ, Oldenkamp R, Cisowska I, Sumpter JP: **Do Concentrations of Ethinylestradiol, Estradiol, and Diclofenac in European Rivers Exceed Proposed EU Environmental Quality Standards?** *Environmental Science & Technology* 2013, **47**:12297-12304.

28. van Vliet MTH, Franssen WHP, Yearsley JR, Ludwig F, Haddeland I, Lettenmaier DP, Kabat P: **Global river discharge and water temperature under climate change**. *Global Environmental Change* 2013, **23**:450-464.

* 29. Peijnenburg WJGM, Baalousha M, Chen J, Chaudry Q, Von der kammer F, Kuhlbusch TAJ, Lead J, Nickel C, Quik JTK, Renker M, et al.: **A Review of the Properties and Processes Determining the Fate of Engineered Nanomaterials in the Aquatic Environment**. *Critical Reviews in Environmental Science and Technology* 2015, **45**:2084-2134.

** 30. Dale AL, Lowry GV, Casman EA: **Stream Dynamics and Chemical Transformations Control the Environmental Fate of Silver and Zinc Oxide Nanoparticles in a Watershed-Scale Model**. *Environmental Science & Technology* 2015, **49**:7285-7293.

31. Praetorius A, Tufenkji N, Goss K-U, Scheringer M, von der Kammer F, Elimelech M: **The road to nowhere: equilibrium partition coefficients for nanoparticles**. *Environmental Science: Nano* 2014, **1**:317-323.

** 32. Nowack B, Ranville JF, Diamond S, Gallego-Urrea JA, Metcalfe C, Rose J, Horne N, Koelmans AA, Klaine SJ: **Potential scenarios for nanomaterial release and subsequent alteration in the environment**. *Environmental Toxicology and Chemistry* 2012, **31**:50-59.

33. Praetorius A, Scheringer M, Hungerbühler K: **Development of Environmental Fate Models for Engineered Nanoparticles—A Case Study of TiO2 Nanoparticles in the Rhine River**. *Environmental Science & Technology* 2012, **46**:6705-6713.

34. Nowack B, Bucheli TD: **Occurrence, behavior and effects of nanoparticles in the environment**. *Environmental Pollution* 2007, **150**:5-22.

35. Liu J, Hurt RH: **Ion Release Kinetics and Particle Persistence in Aqueous Nano-Silver Colloids**. *Environmental Science & Technology* 2010, **44**:2169-2175.

36. Bian S-W, Mudunkotuwa IA, Rupasinghe T, Grassian VH: **Aggregation and Dissolution of 4 nm ZnO Nanoparticles in Aqueous Environments: Influence of pH, Ionic Strength, Size, and Adsorption of Humic Acid**. *Langmuir* 2011, **27**:6059-6068.

37. Jiang C, Aiken GR, Hsu-Kim H: **Effects of Natural Organic Matter Properties on the Dissolution Kinetics of Zinc Oxide Nanoparticles**. *Environmental Science & Technology* 2015, **49**:11476-11484.

38. Chinnapongse SL, MacCuspie RI, Hackley VA: **Persistence of singly dispersed silver nanoparticles in natural freshwaters, synthetic seawater, and simulated estuarine waters**. *Science of The Total Environment* 2011, **409**:2443-2450.

39. Thalmann B, Voegelin A, Sinnet B, Morgenroth E, Kaegi R: **Sulfidation Kinetics of Silver Nanoparticles Reacted with Metal Sulfides**. *Environmental Science & Technology* 2014, **48**:4885-4892.

40. Grillet N, Manchon D, Cottancin E, Bertorelle F, Bonnet C, Broyer M, Lermé J, Pellarin M: **Photo-Oxidation of Individual Silver Nanoparticles: A Real-Time Tracking of Optical and Morphological Changes**. *The Journal of Physical Chemistry C* 2013, **117**:2274-2282.

41. Mudunkotuwa IA, Pettibone JM, Grassian VH: **Environmental Implications of Nanoparticle Aging in the Processing and Fate of Copper-Based Nanomaterials**. *Environmental Science & Technology* 2012, **46**:7001-7010.

42. Labille J, Feng J, Botta C, Borschneck D, Sammut M, Cabie M, Auffan M, Rose J, Bottero J-Y: **Aging of TiO2 nanocomposites used in sunscreen. Dispersion and fate of the degradation products in aqueous environment**. *Environmental Pollution* 2010, **158**:3482-3489.

* 43. Lofts S, Dumont E, Keller V, Williams R, Praetorius A, von der Krammer F, Cornelis G, Loureiro S, Van den Brink N: **A Multimedia Model For Nanoparticle Fate And Biotic Update In The Environment** In *Interdisciplinary Approaches to Health and the Environment, 26th Annual ISES Meeting 9-13th October 2016*; *Utrecht, NL*: 2016.

* 44. Gottschalk F, Sun T, Nowack B: **Environmental concentrations of engineered nanomaterials: Review of modeling and analytical studies**. *Environmental Pollution* 2013, **181**:287-300.

45. Dale AL, Casman EA, Lowry GV, Lead JR, Viparelli E, Baalousha M: **Modeling Nanomaterial Environmental Fate in Aquatic Systems**. *Environmental Science & Technology* 2015, **49**:2587-2593.

46. Nowack B: **Evaluation of environmental exposure models for engineered nanomaterials in a regulatory context**. *NanoImpact* 2017, **8**:38-47.

47. Johnson AC, Bowes MJ, Crossley A, Jarvie HP, Jurkschat K, Jürgens MD, Lawlor AJ, Park B, Rowland P, Spurgeon D, et al.: **An assessment of the fate, behaviour and environmental risk associated with sunscreen TiO2 nanoparticles in UK field scenarios**. *Science of the Total Environment* 2011, **409**:2503-2510.

48. Meesters JAJ, Quik JTK, Koelmans AA, Hendriks AJ, van de Meent D: **Multimedia environmental fate and speciation of engineered nanoparticles: a probabilistic modeling approach**. *Environmental Science: Nano* 2016, **3**:715-727.

49. Meesters JAJ, Koelmans AA, Quik JTK, Hendriks AJ, van de Meent D: **Multimedia Modeling of Engineered Nanoparticles with SimpleBox4nano: Model Definition and Evaluation**. *Environmental Science & Technology* 2014, **48**:5726-5736.

50. Klein JJMd, Quik JTK, Bauerlein PS, Koelmans AA: **Towards validation of the NanoDUFLOW nanoparticle fate model for the river Dommel, The Netherlands**. *Environmental Science: Nano* 2016, **3**:434-441.

51. Quik JTK, de Klein JJM, Koelmans AA: **Spatially explicit fate modelling of nanomaterials in natural waters**. *Water Research* 2015, **80**:200-208.

52. Markus AA, Parsons JR, Roex EWM, de Voogt P, Laane RWPM: **Modelling the transport of engineered metallic nanoparticles in the river Rhine**. *Water Research* 2016, **91**:214-224.

53. Markus AA, Parsons JR, Roex EWM, Kenter GCM, Laane RWPM: **Predicting the contribution of nanoparticles (Zn, Ti, Ag) to the annual metal load in the Dutch reaches of the Rhine and Meuse**. *Science of The Total Environment* 2013, **456–457**:154-160.

54. Garner KL, Suh S, Keller AA: **Assessing the Risk of Engineered Nanomaterials in the Environment: Development and Application of the nanoFate Model**. *Environmental Science & Technology* 2017, **51**:5541-5551.

55. Quik JTK, Stuart MC, Wouterse M, Peijnenburg W, Hendriks AJ, van de Meent D: **Natural colloids are the dominant factor in the sedimentation of nanoparticles**. *Environmental Toxicology and Chemistry* 2012, **31**:1019-1022.

56. Therezien M, Thill A, Wiesner MR: **Importance of heterogeneous aggregation for NP fate in natural and engineered systems**. *Science of The Total Environment* 2014, **485**:309-318.

* 57. Nowack B, Baalousha M, Bornhoft N, Chaudhry Q, Cornelis G, Cotterill J, Gondikas A, Hassellov M, Lead J, Mitrano DM, et al.: **Progress towards the validation of modeled environmental concentrations of engineered nanomaterials by analytical measurements**. *Environmental Science: Nano* 2015, **2**:421-428.

58. Gottschalk F, Lassen C, Kjoelholt J, Christensen F, Nowack B: **Modeling Flows and Concentrations of Nine Engineered Nanomaterials in the Danish Environment**. *International Journal of Environmental Research and Public Health* 2015, **12**:5581.

59. Gottschalk F, Kost E, Nowack B: **Engineered nanomaterials in water and soils: A risk quantification based on probabilistic exposure and effect modeling**. *Environmental Toxicology and Chemistry* 2013, **32**:1278-1287.

60. Gottschalk F, Ort C, Scholz RW, Nowack B: **Engineered nanomaterials in rivers – Exposure scenarios for Switzerland at high spatial and temporal resolution**. *Environmental Pollution* 2011, **159**:3439-3445.

61. Gottschalk F, Scholz RW, Nowack B: **Probabilistic material flow modeling for assessing the environmental exposure to compounds: Methodology and an application to engineered nano-TiO2 particles**. *Environmental Modelling & Software* 2010, **25**:320-332.

* 62. Adam V, Nowack B: **European country-specific probabilistic assessment of nanomaterial flows towards landfilling, incineration and recycling**. *Environmental Science: Nano* 2017, **4**:1961-1973.

** 63. Adam V, Caballero-Guzman A, Nowack B: **Considering the forms of released engineered nanomaterials in probabilistic material flow analysis**. *Environmental Pollution* 2018, **243**:17-27.

64. Gottschalk F, Nowack B: **The release of engineered nanomaterials to the environment**. *Journal of Environmental Monitoring* 2011, **13**:1145-1155.

65. Piccinno F, Gottschalk F, Seeger S, Nowack B: **Industrial production quantities and uses of ten engineered nanomaterials in Europe and the world**. *Journal of Nanoparticle Research* 2012, **14**:1109.

66. Vardharajula S, Ali SZ, Tiwari PM, Eroğlu E, Vig K, Dennis VA, Singh SR: **Functionalized carbon nanotubes: biomedical applications**. *International journal of nanomedicine* 2012, **7**:5361-5374.

67. Domercq P, Praetorius A, Boxall ABA: **Emission and fate modelling framework for engineered nanoparticles in urban aquatic systems at high spatial and temporal resolution**. *Environmental Science: Nano* 2018, **5**:533-543.

68. Svendsen C: **Nanomaterial Fate and Speciation in the Environment**. In *Compendium of Projects in the European NanoSafety Cluster*. Edited by Lynch I: European Commission; 2017:62 - 69. vol 2017 Edition.]

69. Williams RJ, Keller VDJ, Johnson AC, Young AR, Holmes MGR, Wells C, Gross-Sorokin M, Benstead R: **A National Risk Assessment for Intersex in Fish Arising from Steroid Estrogens**. *Environmental Toxicology and Chemistry* 2009, **28**:220-230.

70. Money ES, Reckhow KH, Wiesner MR: **The use of Bayesian networks for nanoparticle risk forecasting: Model formulation and baseline evaluation**. *Science of The Total Environment* 2012, **426**:436-445.

71. Sani-Kast N, Scheringer M, Slomberg D, Labille J, Praetorius A, Ollivier P, Hungerbühler K: **Addressing the complexity of water chemistry in environmental fate modeling for engineered nanoparticles**. *Science of The Total Environment* 2015, **535**:150-159.

72. Liu HH, Cohen Y: **Multimedia Environmental Distribution of Engineered Nanomaterials**. *Environmental Science & Technology* 2014, **48**:3281-3292.

73. Liu HH, Bilal M, Lazareva A, Keller A, Cohen Y: **Simulation tool for assessing the release and environmental distribution of nanomaterials**. *Beilstein Journal of Nanotechnology* 2015, **6**:938-951.

74. Jacobs R, Meesters JAJ, ter Braak CJF, van de Meent D, van der Voet H: **Combining exposure and effect modeling into an integrated probabilistic environmental risk assessment for nanoparticles**. *Environmental Toxicology and Chemistry* 2016, **35**:2958-2967.
75. USEPA: **Chesapeake Bay Phase 5.3 Community Watershed Model**. Edited by. Annapolis, MD: US Environmental Protection Agency, Chesapeake Bay Program Office; 2010. vol EPA 903S10002-CBP/TRS-310-10.]
76. Dumont E, Williams R, Keller V, Voß A, Tattari S: **Modelling indicators of water security, water pollution and aquatic biodiversity in Europe**. *Hydrological Sciences Journal* 2012, **57**:1378-1403.
77. Markus AA, Parsons JR, Roex EWM, de Voogt P, Laane RWPM: **Modeling aggregation and sedimentation of nanoparticles in the aquatic environment**. *Science of The Total Environment* 2015, **506–507**:323-329.
78. Wang Y, Kalinina A, Sun T, Nowack B: **Probabilistic modeling of the flows and environmental risks of nano-silica**. *Science of The Total Environment* 2016, **545-546**:67-76.

Figures, Boxes and Tables

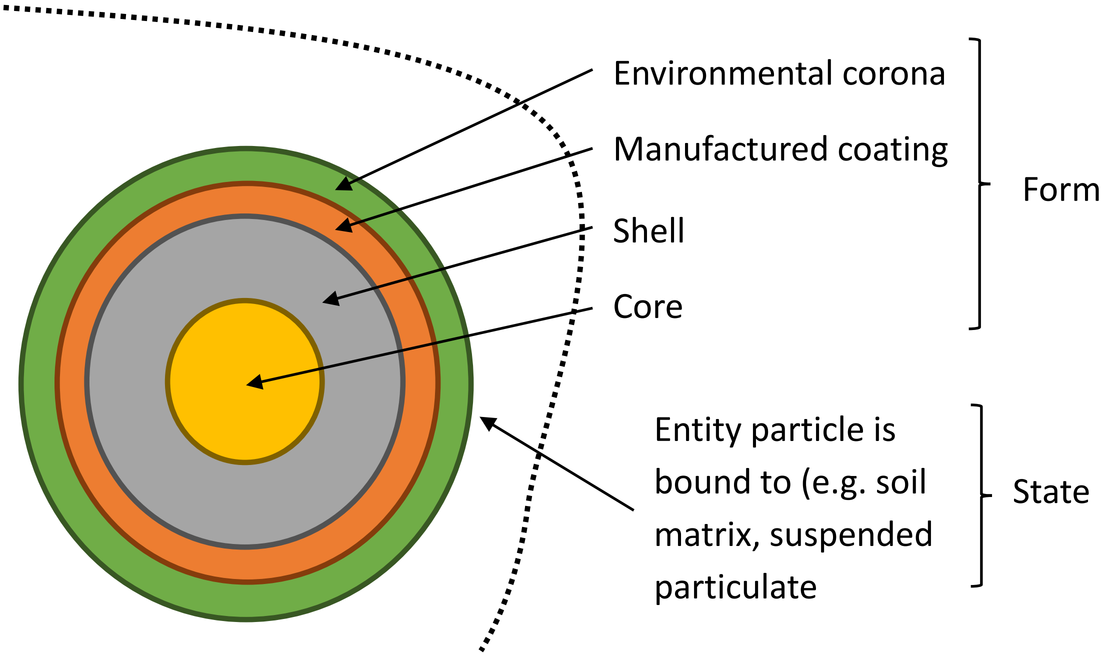

Figure 1. Illustration of the possible forms and states of an engineered nanomaterial in the environment.

Box 1: European Union Recommendation on the Definition of Nanomaterials:

Nanomaterial means a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm–100 nm.In specific cases and where warranted by concerns for the environment, health, safety or competitiveness the number size distribution threshold of 50 % may be replaced by a threshold between 1 and 50 %. By derogation, fullerenes, graphene flakes and single wall carbon nanotubes with one or more external

Table 1 Summary of models for predicting concentrations of Engineered Nano Materials in the environment published since 2011

Reference Model name	**Environmental compartments**	**Spatially explicit** (**l**ocale, Grid system)	**Temporally explicit**	**Processes considered** *Nano-specific*	**Materials**	**ENM sizes**	**Comments**
Johnson et al. (2011) [47]	Rivers	Yes Regional concentrations for Anglian and Thames region, UK	Not explicitly Hydrological model predicts annual and monthly flow duration curves from daily–time step runoff	Only advective transport through river, including abstractions	TiO_2	Not explicitly modelled	River water concentrations for sunscreen TiO_2, using LF2000-WQX software [69]
Money et al. (2012) [70] FINE	Surface water Biota	No	Yes As component in Bayesian network	Implicitly included as components in Bayesian network: *Homoaggregation* *Heteroaggregation* Sediment deposition	Ag	Size distribution included as component in Bayesian network	Bayesian network approach to predict aquatic exposure concentrations of Ag
Praetorius et al. (2012) [33]	River Sediment	Yes Rhine river, Germany River split into boxes (520 for 700 km). Length of boxes smallest closest to emission source.	No ENM concentration as function of distance from source is at steady-state	*Heteroaggregation* *Dissolution (not implemented for TiO_2)* Sediment deposition/resuspension Sediment burial Bed transport	TiO_2	Suspended particulate matter and ENMs split into discrete size classes from log-normal distributions	No spatial heterogeneity in water composition and thus single rate constants for entire river Sani-Kast et al. [71] extends to add spatial heterogeneity in water
Liu and Cohen (2014) [72] MendNano	Air Surface water Sediment Soil Biota	No	Yes Time step dynamically selected to reduce numerical errors	*Heteroaggregation* *Dissolution* Sediment deposition/resuspension Sediment burial Atmospheric deposition/resuspension	TiO_2 SiO_2 ZnO CeO_2 Al_2O_3 Ag	Size distribution discretised into size classes	Dynamic multimedia mass balance model with time-independent rate constants RedNano [73] is a web simulation tool that integrates MendNano with a life-cycle

				Soil runoff Biotic and root uptake	Cu Fe Carbon nanotubes Nano-clay		inventory assessment to predict release rates
Meesters et al. (2014) [49] **Meesters et al. (2016) [48]** SimpleBox4Nano	Air Surface water Sediment Soil	No	No	*Heteroaggregation* *Dissolution* Sediment deposition/resuspension Sediment burial Atmospheric deposition Soil runoff Soil leaching	TiO_2 ZnO CeO_2	Size distribution specified as input parameter, e.g., uniform distribution in particle diameters from 1 to 100 nm	Multimedia mass balance model with 1st order rate constants Jacobs et al. [74] implements SimpleBox4Nano in 2D Monte Carlo model
Dale et al. (2015)[30] WSM/WASP7	River Sediment Soil (runoff only)	Yes James River Basin, Virginia River split into 68 segments with mean length of 30 km.	Yes	*Heteroaggregation* *Dissolution* Sediment deposition/resuspension Sediment burial Soil runoff	Ag ZnO	No explicit modelling of size, but implicitly included in dissolution rates, which are averages from data including many sizes/coatings	Coupling of Chesapeake Bay Watershed Model [75] to USEPA water quality modelling suite (https://www.epa.gov/ceam/water-quality-analysis-simulation-program-wasp)
Dumont et al. (2015) [23]	Surface water Sediment	Yes Europe 5’ by 5’ grid (~6 by 9 km)	Yes 31 years, monthly time steps	*Heteroaggregation* *Dissolution* Sediment deposition/resuspension Sediment burial	ZnO Ag	Not explicitly modelled	Uses GWAVA [76] to model ENM concentration from household loading via sewage treatment plants
Gottschalk et al. (2015) [58]	Air Surface water Marine water Sediment (freshwater and sea)	No Constrained by geographical data for Denmark	No	Implicitly included as mass flows: *Dissolution* Sediment deposition/resuspension Atmospheric deposition	TiO_2 Quantum dots (material agnostic)	Not explicitly modelled	Mass flow based on probabilistic material flow, using probabilistic production and use estimates

	Soil Technical compartments (landfill, recycling, incineration, sewage)			Soil runoff	Carbon black $CuCO_3$ ZnO Ag Carbon nanotubes CeO_2		
Quik et al. (2015) [51] de Klein et al. (2016) [50] NanoDUFLOW	River Sediment	Yes Dommel, Netherlands Default scenario: 477 sections with mean length of 88 m.	Yes Scenarios run over a number of days with small time steps (~1 min)	*Heteroaggregation* *Homoaggregation (size classes interact)* *Dissolution/degradation* Sediment deposition/resuspension Sediment burial	TiO_2	Five size classes of ENMs and SPM.	Links ENM-specific processes to spatially explicit hydrological model (DUFLOW – STOWA, 2013)
Markus et al. (2016) [52]	River Sediment	Yes Rhine river, Germany	Yes Model run from 2007-2009	*Homoaggregation* *Heteroaggregation* *Dissolution* *Transformation* *Removal of TiO_2 coating* *Mineralisation* Sediment deposition/resuspension	TiO_2 ZnO Ag	Instead of size classes, ENMs are distinguished as free (unabsorbed) homoaggregates and heteroaggregates	Spatial heterogeneity in water component (unlike, e.g., Praetorius et al [33]) Builds on Markus et al, [77] but excludes dissolution and transformation of coated TiO_2)
Wang et al. (2016) [78]	Air Surface water Sediment Soil Technical compartments (landfill, incineration, cement works, waste water,	No	No	Only mass flows between compartments considered; no explicit processes modelled	Silica	Not explicitly modelled	Material flow analysis of nano-silica in EU and Switzerland

	sewage treatment, recycling)						
Garner et al. (2017) [54] NanoFATE	Air Surface water (fresh and coastal) Sediment Soil	Yes, but limited to a small number of soil and water compartments in which the ENMS are considered homogeneous	Yes	*Heteroaggregation* *Dissolution* Sediment deposition/resuspension Sediment burial Atmospheric deposition Soil runoff Soil leaching splashback from sea water	CeO_2 CuO TiO_2 ZnO	Instead of size classes, ENMs are distinguished as free and small homoaggregates. heteroaggregates and dissolution products	Has been written to be extensible to other ENMs and ENM processes
Adam et al, 2017[62]	Air Surface water Marine water Sediment (freshwater and sea) Soil Technical compartments (landfill, recycling, incineration, sewage)	Yes – for individual country	No	Implicitly included as mass flows: *Dissolution* Sediment deposition/resuspension Atmospheric deposition Soil runoff	Ag TiO_2 ZnO Carbon nanotubes	Not explicitly modelled	Mass flow based on probabilistic material flow, using probabilistic production and use estimates but for individual countries
Adam et al, 2018	Air Surface water Marine water Sediment (freshwater and sea) Soil Technical compartments (landfill, recycling,	No	No	Implicitly included as mass flows: *Dissolution* Sediment deposition/resuspension Atmospheric deposition Soil runoff	Ag TiO_2	Not explicitly modelled, but different forms are estimated – transformed, matrix embedded, pristine and product emmbedded	Mass flow based on probabilistic material flow, using probabilistic production and use estimates

incineration, sewage)