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Nano Impact Statement

Site specific risk assessment of engineered nanoparticles (ENPs) requires spatially resolved fate models. Validation of such models is difficult, due to present limitations in detecting ENPs in the environment. Here we report on progress towards validation of the spatially resolved hydrological ENP fate model NanoDUFLOW, by comparing measured and modeled concentrations of < 450 nm metal-based particles in a river. Concentrations measured with Asymmetric Flow-Field-Flow Fractionation (AF4) coupled to ICP-MS, clearly reflected the hydrodynamics of the river and showed satisfactory to good agreement with modeled concentration profiles. Together with the general applicability of the model framework, this legitimizes an optimistic view on the potential to validate such models, with important implications for the risk assessment of ENPs.

Towards validation of the NanoDUFLOW nanoparticle fate model for the river Dommel, The Netherlands

Jeroen J.M. de Klein[1], Joris T.K. Quik[1,2], Patrick S. Bäuerlein[3], Albert A. Koelmans[1,4,*]

[1] Aquatic Ecology and Water Quality Management Group, Department of Environmental Sciences, Wageningen University, P.O. Box 47, 6700 AA Wageningen, The Netherlands.

[2] National Institute for Public Health and the Environment, RIVM, Centre for Sustainability, Environment and Health, DMG, P.O. Box 1, 3720 BA, Bilthoven, the Netherlands.

[3] KWR Watercycle Research Institute, Groningenhaven 7, 3433 PE Nieuwegein, The Netherlands.

[4] IMARES – Institute for Marine Resources & Ecosystem Studies, Wageningen UR, P.O. Box 68, 1970 AB IJmuiden, The Netherlands.

* corresponding author bart.koelmans@wur.nl

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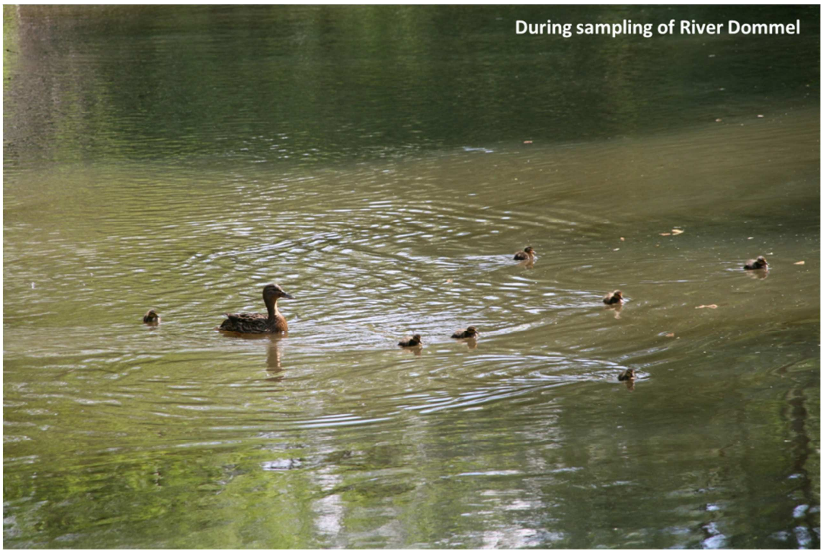

Abstract

It is generally acknowledged that fate models for engineered nanoparticles (ENPs) hardly can be validated, given present limitations in analytical methods available for ENPs. Here we report on progress towards validation of the spatially resolved hydrological ENP fate model NanoDUFLOW, by comparing measured and modeled concentrations of < 450 nm Ce, Al, Ti and Zr -based particles for river Dommel (NL), as measured by Asymmetric Flow-Field-Flow Fractionation (AF4) coupled to ICP-MS. NanoDUFLOW simulates advection, aggregation-sedimentation, resuspension, dissolution and burial for singular ENPs, 5 classes of ENP homoaggregates and 25 classes of heteroaggregates, dynamically in space and time, and uses actual hydrological data of the river, 5 tributaries and a waste water treatment plant effluent. Validation for Ce particles was very good, whereas for Al, Ti and Zr particles, reasonable results were obtained. Model output was relatively insensitive to the attachment efficiency parameter, due to fast heteroaggregation. We argue that although the results cannot be taken as formal validation of singular <100 nm ENP behavior, they probably validate the reflection of that behavior on the level of natural and ENP-inclusive aggregate transport in the modeled system.

Introduction

During the past decade, nanotechnology and use of engineered nanoparticles (ENP) have developed enormously. This calls for an assessment of the risks of these materials to man and the environment, which therefore has become an important area of scientific research. Recent reviews emphasize the importance of being able to accurately measure concentrations of ENP in environmental matrices, as well as being able to mechanistically model the fate of ENPs, in order to establish a balanced exposure assessment.[1,2,3,4,5] However, ENP concentrations in the environment are very low, and the limitations of analytical methodologies to detect and identify ENPs are substantial.[6] Consequently, exposure assessments based on measured concentrations are not yet possible and exposure assessment therefore has to rely on modeling. The present models probably are valid in terms of their agreement to first principles and accordance with design criteria, yet they are hardly validated against measured data. Gottschalk et al.[1] reviewed studies providing model-based predictions of environmental concentrations (PECs) for various environmental compartments and compared the resulting concentration ranges to ranges of *measured* environmental concentrations (MECs) in similar compartments. They concluded that measurements and model outcomes were in agreement roughly, however the comparisons still were limited and the MECs mostly related to total elemental concentrations and not necessarily to the nano-form of the element. Furthermore, the PEC/MEC comparisons related to average background concentrations like they are calculated by the mass flow models considered. Recently, spatially explicit fate models for ENPs have become available[7,8,9] that are more realistic with respect to particle behavior and actual system properties, which however are not yet validated. As for validation, we follow the definition of that term as provided by Rykiel[10]; ‘Validation is establishing the truth of a model in the sense of (a) consistancy with data, (b) accordance with current knowledge, (c) conformancy with design criteria’.

Validation of mechanistic ENP fate models with respect to consistency with data is desirable, yet problematic for several reasons.[11] In the environment, ENPs and natural nanoparticles (NPs) are subject to numerous transformations.[2,5] Furthermore, they exist in mixtures of different particles, originating from different sources whereas the composition of the mixtures changes over space and time.[2,12,13] It is presently impossible to unambiguously identify the sources of ENPs and to distinguish between the natural NPs and anthropogenic ENPs, based on environmental measurements.[6] The causal links between properties of emitted ENPs and those of eventually transformed ENPs and how such links change over space and time are fundamentally indeterminate.[2,4,8,13,15] For modeling the fate of metals and organic contaminants similar problems exist, which however have been solved by (a) lumping and averaging process parameters to conditional parameters that are relevant at the actual scale of environmental systems, and (b) incorporating only that level of detail needed for the actual application the model scenario is designed to address. A similar engineering approach can be adopted for nanoparticles, which can be classified in terms of the main process parameters determining fate; like those for aggregation, particle attachment, settling and transport[14,15], whereas the variability of such parameters among nanoparticles has been shown to converge when nanoparticle fate is considered at the system scale.[16] Consequently, we argue that fate models for ENPs can be evaluated against data on operationally defined classes of generalized nanoparticles or (nano-)particle aggregates, rather than on *a priori* defined specific types of (pristine) ENPs. Another problem relates to the fact that near-nano or > 100 nm submicron particles (i.e. 100-1000 nm) may contribute to measured particle concentrations, which then would be erroneously attributed to the measured NP fraction.[1,6]

We propose that this problem can be pragmatically circumvented by refraining from model validation against measured ‘free < 100nm ENPs or NPs’. Instead, *modelled* total particulate elemental concentrations that are calculated from the dynamically (Smoluchowski-)modeled aggregate size distribution, can be evaluated against *measured* total particulate elemental concentrations, which - after all - reflect the sum of the elemental concentrations of all primary (nano-)particles and aggregates present in the actual size distribution. We realize that taking this sum of (nano-)particles and aggregates (hereafter '∑(N)P') as the endpoint for validation is formally not a validation of the < 100 nm nanoparticles size class. However, given the present limitations in ENP analysis this is the best available option and the dynamic behavior of ∑(N)P in an environmental system still is highly dependent on the behavior of the initial 'free NP' concentration, which thus comes down to an indirect validation of that behavior.

The aim of the present work was to evaluate the level of agreement between modeled ∑(N)P concentrations and measured concentrations of <450 nm particles taken as a proxy for Σ(N)P), in a river system in The Netherlands. As explained above, this concerned modeling of ∑(N)Ps in general, without the aim or necessity of uniquely identifying the free ENP component in the mixture. The hydrological and water quality model NanoDUFLOW was used, which was fed with actual hydrological data for the main river and tributaries in the catchment. NanoDUFLOW[9] keeps track of 35 particle classes (homo-, hetero-aggregates, natural colloids) according to a simplified Smoluchowsky-Stokes algorithm, in which flow shear calculated from the hydrological module feeds back into the calculation of spatially heterogeneous collision frequencies. Elements possibly related to ENPs; i.e. Ti, Ce, Ag, Au, Al,and Zr, were measured in water samples using ICP-MS and Asymmetric Flow-Field-Flow Fractionation (AF4). The simulations used actual flow rate data to acquire a most realistic simulation of dependence of flow in time, accounting for flow dependent factors and processes like water and particle transport, shear, resuspension-sedimentation and aggregation collision frequency.

Materials and methods

Chemicals

Ultrapure water (H_2O) with a resistivity of >18 MΩ cm was obtained from a Milli-Q Plus system (Millipore, Amsterdam, The Netherlands). Sodium hydrogen carbonate ($NaHCO_3$), BioXtra 99.5–100.5%, was purchased from Sigma-Aldrich (Zwijndrecht, The Netherlands) and nitric acid (HNO_3), 65%, suprapur, was purchased from Merck (Darmstadt, Germany). Calibration standard solutions for the concentration determination were made of element stock solutions from Inorganic Ventures (Christiansburg, USA).

Study area

The study area has been described before[9], a brief summary is provided here. The Dommel is a relatively small river in The Netherlands, flowing through The Netherlands over a distance of 80 kilometers, of which 40 km are covered in the model. In the present implementation based on water discharges provided by the Dommel water board, the flow velocity ranged between 0.0036 and 0.54 m s^{-1} with a river stretch averaged flow velocity of 0.32 m s^{-1}. The river contains a sediment settling area and several weirs and receives inflows of 5 tributaries and effluent from a wastewater treatment plant (WWTP) in the city of Eindhoven. Approximately fifty combined sewer overflows are situated at the Dommel River, discharging untreated domestic and industrial wastewater during heavy rainfall, which contains a complex cocktail of contaminants.[17]

Sampling

Thirteen samples were taken from the water column; before and after sediment traps, before and after the WWTP discharge location and in WWTP influent and effluent. As for the tributaries, two samples were available both in the Tongelreep. Samples were taken by means of a Ruttner water sampler and immediately stored in 250 mL PE bottles. The bottles were stored with ice-packs in a cool box during transport and stored at 4 °C in the lab. A map of the Dommel river and sampling locations is provided in the Supporting Information (Figure S1).

Analysis

Samples were filtered using a 0.45 µm regenerated cellulose (RC) filter (Whatman, Dassel, Germany. Water samples were used for analysis of *total* i.e. dissolved plus particulate metal concentrations, and for analysis of metal particle concentrations. Total concentrations of Ti, Ce, Ag, Au, Al and Zr were measured using an inductively coupled plasma mass spectrometer (ICP-MS) type XSeries II (Thermo Fisher Scientific, Breda, The Netherlands). Aliquots of each of the samples were digested by adding nitric acid to the sample and subsequently using a Multiwave ECO microwave (Anton Paar, The Netherlands) to dissolve the sample. The internal standard was a 10 µg/L Rh-solution (2% HNO_3). Detection limits ranged from 0.005 µg/L (Ce) to 0.5 µg/L (Al), and relative standard deviations ranged from 2.35 (Ce) to 4.60 (Ti), on average (Table S5). Determination of the metal concentration of particles in the sample (size between 2 - 450 nm) was achieved using a Postnova AF2000 system (Postnova Analytics GmbH, Landsberg, Germany) consisting of an Asymmetric Flow-Field-Flow Fractionation (AF4) module connected to the ICP-MS. The membrane was a 350 µm regenerated cellulose membrane with a cut-off of 10 kDa. A solution of 0.01% $NaHCO_3$ served as eluent. The manual injection volume was 500 µL. Internal standard for the ICP-MS was a 10 µg/L Rh solution (2% HNO_3).

Modeling

The NanoDUFLOW model implementation for the river Dommel has been described before[9] and is summarized here briefly. NanoDUFLOW is the combination of DUFLOW Modelling Studio (v3.8.7), a software package for simulating one-dimensional unsteady flow in open-channels,[18,19] and the defined set of equations describing the fate of nanoparticles. Water levels and flow rates are determined by solving the St. Venant equations of continuity and momentum for 471 a priori defined sections of the river network, using the incoming flow and downstream water level as boundary conditions (Table S1). In addition to the previous model[9] incoming discharges from 5 tributaries and effluent of the WWTP are set as boundary conditions as well (Table S2). Discharges from tributaries were set at the mean values of May 2013, as the water sampling was done at the end of this month. NanoDUFLOW calculates discharge, water level and mean velocity for each section and for each time step. Chemical transport is modelled by solving the advection-diffusion equation simultaneously with the hydrology for all network sections.

For ENPs, concentrations of 35 particle classes are calculated in water and sediment following different transformation processes. The transformation processes: homo- and hetero-aggregation, dissolution and degradation are modeled, coupled with the transport processes: advection, sedimentation, resuspension and burial to deeper sediment layers. Calculation of aggregation and sedimentation is based on the Von Smoluchowski-Stokes theory. Following Quik et al.[9], hetero-aggregation is modeled for five ENP size classes interacting with five suspended solid size classes leading to 25 hetero-aggregates modeled in place and time. Homo-aggregation is modeled using five size classes of ENPs that homoaggregate from one class to the next, a simplification that has been shown to cause negligible error for the scenarios studied.[9] In the calculation of the orthokinetic aggregation a shear rate is required, which is calculated from the flow rate provided by the DUFLOW hydrology model, thus providing a direct feedback between river hydrodynamics and aggregation behavior. The dissolution of ENPs in the water column, and degradation and burial in the sediment layer are approximated as first-order processes.[9,20] Resuspension is modeled following Partheniades, using a critical shear stress below which resuspension does not occur.[21] When the critical shear stress is exceeded, a resuspension flux is calculated based on the ratio between the actual and the critical shear stress and a resuspension rate constant. A detailed model description from our previous paper[9] is updated for the present work and provided as Supporting Information.

Model parameterization, boundary conditions and evaluation against data

The input parameters of the model are the characteristics of the natural colloid particles and the ENPs, which are used for the calculation of aggregation and sedimentation rates. ENP specific characteristics are initial particle size distribution and particle density. Initial distributions < 450 nm were assumed to be realistic, that is, in accordance with measured distributions resulting in distributions that spanned from <100 nm to several hundreds of nanometers. Particle densities for the most commonly found metal oxides or hydroxides were used (Table S3). It has been shown before, that heteroaggregates with natural colloids dominate transport of ENPs, which implies that transport is insensitive to differences in initial size distribution of ENPs.[7,9,16] Following earlier reasoning, we used a freshwater literature value for the attachment efficiency (α_{het}).[9] For one of the metals (Ce), the sensitivity of the model output to variability in this parameter was assessed. The other parameters are as in Quik et al[9] and are provided as Supporting Information. None of the parameters was optimized. Measured concentrations at start of the Dommel, in the tributaries and in the WWTP effluent were used as boundary conditions to model the 40 km downstream concentration profile (Table S2). Literature search provided no a priori information on point sources of ENPs or natural metal-based NPs other than the one WWTP (Figure S1). Therefore, diffuse sources were assumed to dominate and the concentrations assessed for one tributary in the catchment were assigned to all tributaries. The model was run with fixed boundaries and a calculation time step of 1 minute to simulate a period of 5 days, to assure that a steady-state condition was reached. The modeled NP size fraction concentrations were summed after which the $\sum$(N)P size fractions were evaluated against the < 450 nm elemental particulate concentrations measured. An overview of the model setup and further motivation of the parameters is provided as Supporting Information (Table S6).

Results and discussion

Colloids and nanoparticles in the Dommel catchment

Ag was not detected in any of the samples. Gold concentrations varied between 0.02 and 0.7 µg/L. However, only in six samples gold was observed and therefore gold was – just like silver – not used for the evaluation of the model. AF4 measurements confirmed the occurrence of the elements Ce and Al in the <450 nm sized particles in all water samples (Table S5). Based on the well-established geochemistry of these elements, they were assumed to occur as CeO_2 and $Al(OH)_3$ respectively.[22] AF4 did not confirm the presence of particles for any of the other metals measured. However, Ti and Zr were detected in the <450 nm filtrates, metals that are known to be insoluble and therefore can be assumed to be in particulate form as well, i.e. as TiO_2 (rutile) and ZrO_2 (baddeleyite) respectively. [22,23,24,25] The densities of these four minerals were used in the modeling (Table S3). In terms of detection limit and relative standard deviation among replicate measurements, Ce was the most accurately measured metal (Table S5). The Ce elemental ∑(N)P concentration ranged 0.04 – 0.27 µg/L (Table S5), which agrees very well to concentration ranges assessed in < 450 nm filtrates from the Dommel between 2005 and 2007 of 0.034 – 0.39 µg/L[26], and in the nearby Rhine-Meuse estuary for the year 2000 of 0.021 – 0.122 µg/L.[27] The lower ends of these measured ranges come close to the higher ends of a modeled range for nano-sized CeO_2 found for Irish surface water, i.e. 4.4–51.4 ng/L.[28] The Al elemental ∑(N)P concentration ranged 2.2 – 5.9 µg/L, which is somewhat lower than the 'dissolved' value provided for world rivers[23], probably due to the smaller size fraction in the present study. The Ti concentration ranged from 0.63 to 1.15 µg/L, which agrees to the typical range for rivers of 0.02 - 2.3

µg/L.[29] Zr ∑(N)P concentrations ranged 0.074 – 0.23 µg/L, which also agrees well with a reported general background range for surface waters of 0.03–0.98 µg/L.[29] Overall, the particulate elemental concentrations in <450 nm filtrates in the Dommel agree well to previously reported background concentrations for these elements.

Assessing the 100 nm and smaller fraction of ∑(N)P particulates was not an aim of the present study, but the general likeliness of the presence of nanomaterials and/or the anthropogenic origin of particles in the Dommel catchment can be assessed in several ways. Recently, Markus et al. applied <450 nm filtration and < 100 nm nanofiltration to Dommel samples and found that for Ti 63 – 74% and for Ce 18 – 64% of <450 nm elemental concentrations were smaller than 100 nm.[30] Furthermore, for many inert geogenic materials characteristic elemental ratios exist that define origin or type of the material. Therefore, such ratios can be used to correct for grain size effects or to distinguish anthropogenic sources.[23,24,31] It has been argued that Ti/Al ratios are approximately 20−50 for manufactured UV-filter nanoparticles and 0.1 for natural soils, and therefore Ti/Al in suspended matter could serve as an indicator of anthropogenic input of Ti to surface waters.[24] Based on EDS and SEM imaging, Gondikas et al. detected TiO_2 particles from sunscreens in an Austrian lake, together with Ti/Al ratios of ~ 0.05. The present Ti/Al elemental ratios detected in our <450 nm filtrates ranged 0.11 – 0.51, that is, up to an order of magnitude higher, with one extreme outlying value of 109. Following Gondikas et al, this may suggest an anthropogenic source for titanium in the Dommel. This does not necessarily imply however, that these particles were manufactured nanoparticles. After all, the increase might also be influenced by natural variations at the sampling locations. Furthermore, the SEM data by Gondikas et al showed a size of natural Ti NPs of about 500 nm, and UV-filter particles of about 1000 nm[24], sizes that both would not comply with the definition of a nanomaterial, but that nevertheless are consistent with the assumptions on particle and aggregate size in the NanoDUFLOW model (Table S6).

Modeling NPs in the Dommel catchment with NanoDUFLOW

Cerium. Modeled CeO_2 ∑(N)P concentrations showed a remarkably good agreement with the measured data (Figure 1, panel Ce). This implies that the model captures the hydrology of the system well, including the transport and settling of the submicron ∑(N)P particles. Various plateaus and discontinuities in the profile are modeled, which relate to the inflows of the tributaries Keersop, Run, Tongelreep, kleine Dommel and Hooidonkse beek, and the WWTP of the city of Eindhoven (various inflows indicated in Figure 1, panel Ce). All inflows appear to cause a decrease in Ce concentration, which suggests that they cause a dilution of Ce concentrations in the river Dommel. The sharp decrease in Ce concentration at 14.4 km (no arrow) is not associated with an incoming tributary, but relates to the position of the main sedimentation area in the river (de Klotputten).

One of the main uncertainties in fate models for nanoparticles is the parameterization of heteroaggregation.[4,7,8,9,15] Therefore, for Ce, the sensitivity of the model to the selected value for the attachment efficiency for heteroaggregation (α_{het}) was explored. It appears that varying α_{het} between 0.1 and 1 does only marginally affect the modeled concentration profile, whereas only a value of $\alpha_{het} = 0$ leads to a substantial lack of fit (Figure 2). This implies that the default value for α_{het} was adequate for the present modeling, but also that aggregation cannot just be neglected.

Aluminium. Aluminium was the other element confirmed by AF4 to be present as < 450 nm particles. Although the Al data show some more variation than Ce, the model fairly represents the trend in the measured data, including a decrease in the sedimentation area at 14.4 km flow distance (Figure 1, panel Al). At 30 and 40 km flow distance, the measured concentrations are about 30% higher than modeled values. Sewer overflows occurred 4 and

10 days prior to the sampling date and concentrations in WWTP influents were about 4 times higher than in effluents, which potentially renders the overflows as external sources of Al. However, because of multiple possible causes for the higher Al concentrations we have no conclusive explanation for the observed nonalignment.

Titanium. Titanium was not directly detected as particulate material, but was assumed to be present as particulate TiO_2 based on its extremely poor solubility and the <450 nm total concentrations measured. The model again predicts a decrease in concentration at the sedimentation area after 14.4 km flow distance, however this decrease is compensated by inputs from the Tongelreep tributary and from the WWTP (Figure 1, panel Ti). The overall result is a predicted more-or-less constant concentration of Ti, which until 25 km is well represented by the data. Like for Al, in the last 10 km of the Dommel, measured Ti is up to a factor of two higher than the model prediction. Like for Al, this probably relates to an unaccounted source and remains unexplained.

Zirconium. Zirconium was not directly detected as particulate material either, and was assumed to be present as ZrO_2 based on <450 nm total concentrations measured. For this metal, the resolution in the measured concentrations was insufficient to confirm the relatively complex modeled spatiotemporal dynamics of tributary inflows (Figure 1, panel Zr). For Zr, the inflows of the Keersop, Run, Tongelreep and kleine Dommel increase the modeled concentration, whereas sedimentation in the Klotputten and dilution by WWTP effluent decrease the modeled concentration, leading to an overall (roughly) constant concentration pattern (Figure 1, panel Zr). Until about 25 km, the measured data fairly align with the model simulation, after which they are however up to a factor two higher. This again shows that the last 10 km of the Dommel probably has a source of Zr unaccounted for by the model, similar to that for Al and Ti.

NanoDUFLOW as a tool to model the fate of nanoparticles

Our objective was not to present or validate a model that is able to predict ENP environmental concentrations with certainty. We did show however that NanoDUFLOW provided an adequate mechanistic explanation for the concentration profile of < 450 nm Ce, whereas the model also provided a reasonable representation of the measured concentration profiles for Al, Ti and Zr. For the latter three metals, NanoDUFLOW underestimated concentrations at the last 10 km of the river stretch. We emphasize that the measured profiles represent a snapshot in time and that a longer term field campaign with data from different seasons and years, including more variation in weather conditions, variation in stream flow and variation in tributary and WWTP loads, is to be recommended. Nevertheless, we argue that especially for Ce, the presented type of validation probably is as far as validation of ENP fate models presently can get, given the analytical limitations in characterizing the true nature of ENPs as was outlined in the introduction and recent literature. [1,11] The present validation in fact is a validation for <450 nm Ce containing particulates, which approximately will have the same hydrodynamic behavior as analytically identified ‘true’ ENP aggregates. Nowack et al[11] argued that knowing initial size distribution of ENPs is crucial for correct subsequent fate modeling. Several recent papers, including the present one, suggest that whereas this may be true on short time scales, the hydrodynamic behavior of heteroaggregates may rapidly overwhelm that of the singular or homoaggregated ENPs, [1,7,9,16] rendering ENP fate modeling practically equivalent to natural nanoparticle or colloid fate modeling. We feel that seeking validation of truly ENP specific particle level behavior on the scale of environmental systems is extremely complex and might turn out to be a dead end; (a) for the reasons discussed by Nowack et al[11] and Gottschalk et al[1], and (b) because of the fundamentally indeterminate nature of the continuously varying conditions in dynamic environmental systems. Our present results further suggest that hydrodynamic system properties may outweigh the variability in singular ENP nano-specific features, such as surface charge and attachment efficiency. After all, NanoDUFLOW reproduced the concentration profile for Ce submicron particles while accounting for flow, shear and heteroaggregate size and density in a spatiotemporally explicit manner, whereas attachment efficiency was taken as constant during the simulation. This can be explained by heteroaggregation being sufficiently fast, such that the model output is rather insensitive to the exact value for the attachment efficiency parameter (α_{het}). The plausibility of the dominance of system properties has recently been recognized also by Dale et al[32] who used a spatially resolved transport model in which complete heteroaggregation was assumed, i.e. heteroaggregation was not mechanistically modeled. Our previous study introducing the NanoDUFLOW model[9] showed how heteroaggregate size fractions still behave differently in time and space in a river system like the Dommel. Still, heteroaggregates were shown to be formed rapidly, which in that sense supports the assumption of complete heteroaggregation used by Dale et al.[32] Whereas NanoDUFLOW may be considered to be more generally flexible and suitable to test hypotheses on the fate of distinct ENP heteroaggregate species, it also requires more data and is computationally more demanding.

Conclusions

With the present evaluation of NanoDUFLOW against data and the recent model published by Dale et al[32], important progress has been made towards developing spatially resolved mechanistic models for the risk assessment of ENP. These two models complement recent multi-media models[33,34], as well as the earlier category of mass flow analysis models[1], each of which has different design criteria and different domains of application. The main benefit of having access to such a suite of models is that it allows for selecting the appropriate model for the research question to be answered, or for nested model applications, where outputs across different spatial scales are linked.

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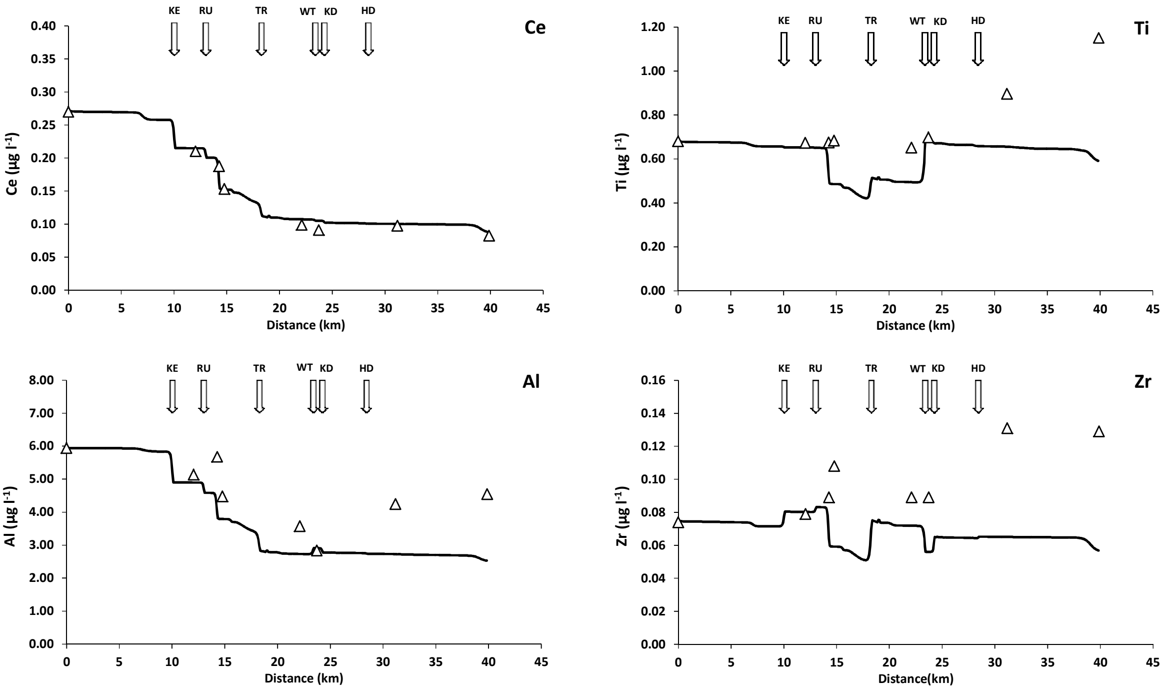

Figure 1. Measured (triangles) and modeled (solid line) concentration profiles for measured < 450 nm Ce, Al, Ti and Zr submicron particles in river Dommel. Arrows indicate inflows of tributaries; KE=Keersop, RU=Run, TR=Tongelreep, WT= WWTP City of Eindhoven, KD=kleine Dommel, HD=Hooidonkse beek.

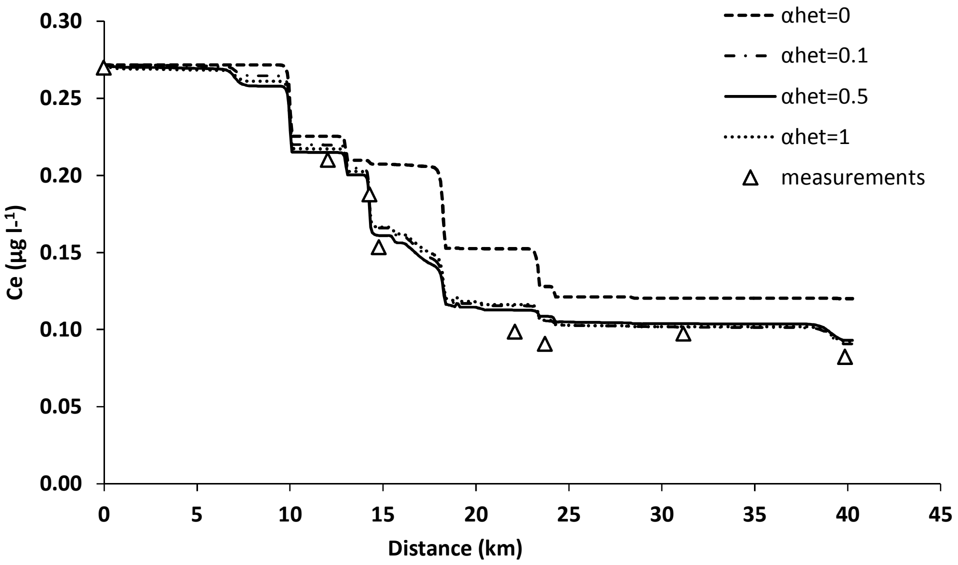

Figure 2. Measured and modeled concentration profiles for < 450 nm Ce submicron particles in river Dommel. The modeled profile was calculated for four values of the attachment efficiency (α_{het}) of 0, 0.1, 0.5 and 1.

References

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[1] F. Gottschalk, T. Sun, and B. Nowack, Environmental concentrations of engineered nanoparticles: Review of modeling and analytical studies, *Environ. Pollution*, 2013, 181, 287-300.

[2] B. Nowack, J. Ranville, S. Diamond, J. Gallego-Urrea, C. Metcalfe, J. Rose, N. Horne, A.A. Koelmans and S.J. Klaine. Potential Scenarios for Nanomaterial Release and Subsequent Alteration in the Environment, *Environ. Toxicol. Chem.*, 2012, 31, 50-59.

[3] C.O. Hendren, M. Lowry, K.D. Grieger, E.S. Money, J.M. Johnston, M.R. Wiesner and S.M. Beaulieu. Modeling approaches for characterizing and evaluating environmental exposure to engineered nanoparticles in support of risk-based decision making, *Environ. Sci. Technol.*, 2013, 47, 1190-1205.

[4] A.A. Koelmans, N.J. Diepens, I. Velzeboer, E. Besseling, J.T.K. Quik and D. van de Meent, D., Guidance for the Prognostic Risk Assessment of Nanoparticles in Aquatic Ecosystems, *Sci. Total Environ.*, 2015, 535, 141–149.

[5] W.J.G.M. Peijnenburg, M. Baalousha, J. Chen, Q. Chaudry, F. von der Kammer, T.A.J. Kuhlbusch, J. Lead, C. Nickel, J.T.K. Quik, M. Renkerg, Z. Wang and A.A. Koelmans, A review of the properties and processes determining the fate of engineered nanomaterials in the aquatic environment, *Critical Rev. Environ. Sci. Technol.*, 2015, 45, 2084-2134.

[6] F. von der Kammer, P.L. Ferguson, P. Holden, A. Masion, K. Roger, S.J. Klaine, A.A. Koelmans, N. Horne and J. Unrine, Analysis of nanoparticles in complex matrices (environment and biota): general considerations and conceptual case studies, *Environ. Toxicol. Chem.*, 2012, 31,32-49.

[7] A. Praetorius, M. Scheringer and K. Hungerbühler, Development of environmental fate models for engineered nanoparticles - a case study of TiO2 nanoparticles in the Rhine River, *Environ. Sci. Technol.*, 2012, 46, 6705–6713.

[8] N. Sani-Kast, M. Scheringer, D. Slomberg, J. Labille and K. Hungerbühler, Addressing the complexity of water chemistry in environmental fate modeling for engineered nanoparticles. *Sci. Total Environ.*, 215, 535, 150–159.

[9] J.T.K. Quik, J.J.M. de Klein and A.A. Koelmans. Spatially explicit fate modelling of nanomaterials in natural waters, *Water Research*, 2015, 80, 200-208.

[10] E.J. Rykiel, Testing ecological models: the meaning of validation, *Ecol. Modelling*, 1996, 90, 229–244.

[11] B. Nowack, M. Baalousha, N. Bornhöft, Q. Chaudhry, G. Cornelis, J. Cotterill, A. Gondikas, M. Hassellöv, J. Lead, D.M. Mitrano, F. von der Kammer and T. Wontner-Smith, Progress towards the validation of modeled environmental concentrations of engineered nanoparticles by analytical measurements. *Environ. Sci.: Nano*, 2015, 2, 421-428

[12] A.A. Koelmans, B. Nowack and M. Wiesner, Comparison of manufactured and black carbon nanoparticle concentrations in aquatic sediments, *Environ. Pollution*, 2009, 157, 1110-1116.

[13] M.R. Wiesner, G.V. Lowry, E. Casman, P.M. Bertsch, C.W. Matson, R.T. Di Giulio, J. Liu, and M.F. Hochella, Meditations on the ubiquity and mutability of nano-sized materials in the environment, *ACS Nano*, 2011, 5, 8466–8470.

[14] J.T.K. Quik, D. van de Meent and A.A. Koelmans, Simplifying modelling of nanoparticle aggregation-sedimentation behaviour in environmental systems: A theoretical analysis, *Water Research*, 2014, 62, 193-201.

[15] A.L. Dale, G.V. Lowry and E. Casman, Much ado about α: Reframing the debate over appropriate fate descriptors in nanoparticle environmental risk modeling. *Environ. Sci.: Nano*, 2015, 2, 27-32

---

[16] I. Velzeboer, J.T.K. Quik, D. van de Meent and A.A. Koelmans, Rapid settling of nanoparticles due to heteroaggregation with suspended sediment, *Environ. Toxicol. Chem*. 2014, 33, 1766-1773.

[17] S.J. Dyer, R. Diamond, R. Altenburger, A. Coors, M. Focazio, K. Kidd, A.A. Koelmans, K. Leung, M. Servos, J. Snape, J. Tolls and X. Zhang, Simplifying assessment of mixtures associated with domestic discharge, May 2015, SETAC Annual Meeting, Barcelona, Spain.

[18] R.H. Aalderink, A. Zoeteman and R. Jovin, Effect of input uncertainties upon scenario predictions for the river Vecht, *Water Sci. Technol.*, 1996, 33, 107-118.

[19] A. Clemmens, F.J. Holly and W. Schuurmans, Description and evaluation of program: Duflow. *J. Irrigation Drainage Engin*., 1993, 119, 724–734.

[20] J.T.K. Quik, I. Velzeboer, M. Wouterse, A.A. Koelmans and D. van de Meent, Heteroaggregation and sedimentation rates for nanoparticles in natural waters, *Water Research*, 2014;47:269-279.

[21] G. Blom and R.H. Aalderink. Calibration of three resuspension/sedimentation models. *Water Sci. Technol.*, 1998, 37(3), 41-49.

[22] A. Kabata-Pendias and A.B. Mukherjee, Trace Elements from Soil to Human, 2007, ISBN-10 3-540-32713-4 Springer Berlin Heidelberg New York

[23] J.M. Martin and M. Meybeck, Elemental mass-balance of material carried by major world rivers, *Marine Chemistry*, 1979, 7, 173–206.

[24] A.P. Gondikas, F. von der Kammer, R.B. Reed, S. Wagner, J.F. Ranville and T. Hofmann, Release of TiO2 nanoparticles from sunscreens into surface waters: a one-year survey at the old Danube recreational lake, *Environ. Sci. Technol*., 2014, 48, 5415–5422.

[25] R.L. Linnen, I.M. Samson, A.E. Williams-Jones and A.R. Chakhmouradian, 13.21 – Geochemistry of the Rare-Earth Element, Nb, Ta, Hf, and Zr Deposits. Reference Module in Earth Systems and Environmental Sciences. Treatise on Geochemistry (Second Edition). Volume 13: Geochemistry of Mineral Deposits, 2014, 543–568

[26] E. Petelet-Giraud, G. Klaver and P. Negrel, Natural versus anthropogenic sources in the surface- and groundwater dissolved load of the Dommel river (Meuse basin): Constraints by boron and strontium isotopes and gadolinium anomaly, *J. Hydrology*, 2009, 369, 336–349.

[27] C.T.A. Moermond, J. Tijink, A.P. van Wezel and A.A. Koelmans, Distribution, speciation and bioavailability of Lanthanides in the Rhine-Meuse estuary, The Netherlands. *Environ. Toxicol. Chem.*, 2001, 20, 1916-1926.

[28] N.J. O'Brien and E.J. Cummins, Nano-scale pollutants: fate in Irish surface and drinking water regulatory systems. *Human Ecol. Risk Assess.*, 2010, 16, 847-872.

[29] J. Gaillardet, J. Viers, B. Dupré, Trace elements in river waters. In: Drever JI (ed) Surface and ground water, weathering and soils In: Holland HD, Turekian KK (eds) Treatise on geochemistry. 2003. Elsevier, Oxford 5:225–227

[30] A.A. Markus, P. Krystek, P.C. Tromp, J.R. Parsons, E.W.M. Roex, P. de Voogt, R.W.P.M. Laane. Determination of metal-based nanoparticles in the river Dommel in the Netherlands via ultraltration, ICP-MS and SEM, *Submitted.*

[31] A.A. Koelmans, Geochemistry of suspended and settling solids in two freshwater lakes. *Hydrobiologia*, 1008, 356:15-29

[32] A.L Dale, G.V. Lowry and E.A. Casman, Stream dynamics and chemical transformations control the environmental fate of silver and zinc oxide nanoparticles in a watershed-scale model, *Environ. Sci. Technol*., 2015, 49, 7285–7293.

[33] J. Meesters, A.A. Koelmans, J.T.K. Quik, A.J. Hendriks and D. van de Meent. Multimedia modeling of engineered nanoparticles with SimpleBox 4 Nano: Model definition and evaluation, *Environ. Sci. Technol.*, 2014, 48, 5726−5736.

---

[34] H.H. Liu and Y. Cohen, Multimedia environmental distribution of engineered nanoparticles, *Environ. Sci. Technol*., 2014, 48, 3281−3292.