Water Research 91 (2016) 214–224

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Modelling the transport of engineered metallic nanoparticles in the river Rhine

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ARTICLE INFO

Article history:
Received 15 September 2015
Received in revised form
4 December 2015
Accepted 4 January 2016
Available online 9 January 2016

Keywords:
Nanoparticles
Modelling
Risk-assessment
Aquatic environment
Suspended particulate matter

ABSTRACT

As engineered nanoparticles of zinc oxide, titanium dioxide and silver, are increasingly used in consumer products, they will most probably enter the natural environment via wastewater, atmospheric deposition and other routes. The aim of this study is to predict the concentrations of these nanoparticles via wastewater emissions in a typical river system by means of a numerical model. The calculations rely on estimates of the use of nanomaterials in consumer products and the removal efficiency in wastewater treatment plants as well as model calculations of the fate and transport of nanoparticles in a riverine system. The river Rhine was chosen for this work as it is one of the major and best studied rivers in Europe. The study gives insight in the concentrations that can be expected and, by comparing the model results with measurements of the total metal concentrations, of the relative contribution of these emerging contaminants.

Six scenarios were examined. Two scenarios concerned the total emission: in the first it was assumed that nanoparticles are only released via wastewater (treated or untreated) and in the second it was assumed that in addition nanoparticles can enter the river system via runoff from the application of sludge as a fertilizer. In both cases the assumption was that the nanoparticles enter the river system as free, unattached particles. Four additional scenarios, based on the total emissions from the second scenario, were examined to highlight the consequences of the assumption of free nanoparticles and the uncertainties about the aggregation processes.

If all nanoparticles enter as free particles, roughly a third would end up attached to suspended particulate matter due to the aggregation processes nanoparticles are subject to. For the other scenarios the contribution varies from 20 to 45%. Since the Rhine is a fast flowing river, sedimentation is unlikely to occur, except at the floodplains and the lakes in the downstream regions, as in fact shown by the sediment mass balance. Nanoparticles will therefore be transported along the whole river until they enter the North Sea.

For the first scenario, the concentrations predicted for zinc oxide and titanium dioxide nanoparticles are in the order of 0.5 μg/l, for silver nanoparticles in the order of 5 ng/l. For zinc and titanium compounds this amounts to 5–10% of the measured total metal concentrations, for silver to 2%. For the other scenarios, the predicted nanoparticle concentrations are two to three times higher.

While there are still considerable uncertainties in the inputs and consequently the model results, this study predicts that nanoparticles are capable of being transported over long distances, in much the same way as suspended particulate matter.

1. Introduction

Engineered nanoparticles are used in many consumer and industrial products, in particular metal and metal oxide nanoparticles, such as titanium dioxide, zinc oxide and silver, It is therefore inevitable that they enter the natural environment such

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http://dx.doi.org/10.1016/j.watres.2016.01.003
0043-1354/

as rivers or lakes and finally coastal and marine environments (Wagner et al., 2014). When entering the environment, they will be transported along with the water but they will also interact with the suspended particulate matter (SPM) that is present (Quik et al., 2014; Van Koetsem et al., 2015). For a proper risk assessment of these substances an important step is to gain insight in expected concentrations, transport and fate of nanoparticles in water bodies. This requires insight in the sources of engineered nanoparticles as well as the pathways by which they enter the environment. Furthermore, their interactions with the environment itself need to be understood.

This article provides a prediction of the influences of transport, aggregation and sedimentation processes on the environmental fate of metallic nanoparticles in river systems, elaborating on work published by us and by numerous other groups. To this end a water quality model was adapted to incorporate these processes of specific importance to nanoparticles, while the transport component of this model was based on an existing hydrodynamic and water quality modelling system (Stelling and Duinmeijer, 2003; Postma et al., 2003; Smits and van Beek, 2013; Markus et al., 2015).

The modelling approach taken here differs from that of multimedia models, such as the SimpleBox4Nano model by Meesters et al. (2014) or the compartmental dynamic model by Liu and Cohen (2014), in that such modelling approaches usually focus on global aspects of the distribution of contaminants in a generic environment. The multimedia approach makes it possible to study this distribution in various environmental compartments simultaneously, but it does not easily allow for including complicated interactions between substances and the environment. The generic character of the multimedia approach also makes it difficult to include specific regional details or to compare the results to field measurements.

Praetorius et al. (2012) present a modelling study somewhat similar to the current study, but they used a schematic representation of the Rhine and assumed that sedimentation would take place along the whole river. As a consequence their model predicts the distance over which nanoparticles are expected to be transported to be fairly limited, depending on the rate of heteroaggregation and sedimentation. They represent the nanoparticles using several size classes and allow for interaction processes such as aggregation.

In a recent publication Quik et al. (2015) also use a representation of the nanoparticles via size classes and similar interaction processes, but they use a detailed hydrological model of a small river in the Netherlands to study the effect of these processes on the transport and fate of nanoparticles. Moreover the emphasis of their study is on the effect of spatial heterogeneity in the process coefficients on the predicted concentrations in water and sediment.

In the present study we focus on a larger river system, namely the Rhine as it passes through Germany, using a different modelling approach. Instead of particle size classes, three fractions of nanoparticles are distinguished, free or unadsorbed nanoparticles, homoaggregates (clusters of nanoparticles) and heteroaggregates (nanoparticles adsorbed to suspended particulate matter). For these fractions interaction via aggregation processes is modelled (for details see the supporting information (SI) and Markus et al. (2015)). Since it is currently not possible to quantify the influence of environmental conditions or of specific properties of the nanoparticles on these processes, the implicit assumption is that the conditions are sufficiently uniform and that aggregation is similar for the considered nanoparticles. Velzeboer et al. (2014) actually found the aggregation behaviour of different types of nanoparticles under different circumstances to be quite similar.

For each of the three fractions the mass concentration of nanoparticles is determined, based on transport, processes and emissions. The focus of the study is on nanoparticles, but the model allows us to simulate the concentration of suspended particulate matter and the total concentration of zinc as well, enabling a comparison with historical measurements of these water quality parameters.

2. Materials and methods

2.1. Area investigated

The area covered by the model is the catchment of the river Rhine from Maxau near Karlsruhe in southern Germany to the eastern parts of the Netherlands (see Fig. 1). The area was chosen for practical reasons:

- The Rhine is one of the most important rivers in Europe and the chosen stretch is more or less self-contained – there are a number of tributaries, such as the Mosel and the Main, but further downstream in the Netherlands the Rhine is joined by the Meuse and splits into parallel branches.
- Both the hydrological and environmental conditions in the Rhine have been studied for many years and this has resulted in extensive datasets of measurements, containing information about numerous substances and the flow rates (BAFG, 2015b; ICPR, 2015; RWS, 2015). Furthermore information about the tributaries and wasteloads is available (ICPR, 2014), allowing the set-up of a comprehensive model.

2.2. Modelling the hydrodynamics and transport of substances

To investigate the transport and fate of nanoparticles in the Rhine river, a numerical model was developed, based on an existing modelling system, namely SOBEK-River for the hydrodynamics and DELWAQ for the water quality (Stelling and Duinmeijer, 2003; Postma et al., 2003; Smits and van Beek, 2013).

The modelling system solves the so-called Saint–Venant equation, which describes the hydrodynamics of a river system (Moussa and Bocquillon, 2000), and the one-dimensional advection–diffusion equation for the water quality in such a river system:

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} + g\frac{\partial h}{\partial x} = g\left(S - S_f\right) \tag{1}$$

$$\frac{\partial A}{\partial t} + \frac{\partial Q}{\partial x} = q \tag{2}$$

$$\frac{\partial AC}{\partial t} + \frac{\partial QC}{\partial x} = D\frac{\partial}{\partial x}\left(A\frac{\partial C}{\partial x}\right) + processes \tag{3}$$

where Eq. (1) is the momentum equation for the flow velocity u averaged over the cross section and the water depth h. In this equation g is the gravitational acceleration, S represents the effect of the bottom slope, and S_f that of bottom friction. The flow rate Q is related to the flow velocity and the width of the main channel of the river.

Eq. (2) represents the continuity equation relating the change in water depth to the gradients in the flow velocity and the lateral inflow q. A is the wet cross-section of the river. Eq. (3) uses the flow field (flow velocity and water depth) and mixing or dispersion processes (as quantified by the coefficient D) to describe the transport of a substance, possibly subjected to specific water quality processes.

The model itself consists of a one-dimensional schematisation of