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Release, Transport and Fate of Engineered Nanoparticles in the Aquatic Environment

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Summary

Nanoparticles are particles with a size of 100 nm or less in at least one dimension. They can be of natural origin (for example the ultrafine particles found in volcanic dust) or man-made, either deliberately or accidentally (as a consequence of abrasive processes for instance). Deliberately produced nanoparticles are commonly known as engineered nanoparticles and these are the main subject of this thesis.

A consequence of the small size of these particles is that their relative surface area is very large. One gram of particles of 100 nm has a total surface area which is ten times larger than a gram of particles of 1 µm. Since most chemical reactions occur at the surface, this makes these particles more reactive just because of their size. Another aspect is that at these dimensions quantum effects begin to play a role – gold nanoparticles have a colour that depends on their size and they are chemically active, instead of being inert as gold particles of larger size are.

While they consist of well-known substances like silver, zinc oxide or even clay, nanoparticles have properties that set them apart from the bulk material. One such property concerns zinc oxide and titanium dioxide. If the particles are of "classical" size, then they are white, scattering visible and ultraviolet light in all directions. This scattering of UV light makes them useful as sunscreen, for instance. However, once the size is in the order of 100 nm or smaller, they become transparent to visible light and lose their colour. Sunscreens that use such small particles are therefore also transparent. This is just one application of the special properties of nanoparticles. Other applications are: targeted drug delivery, transistors and other elements in electronic devices, biosensors to detect enzymes and other biochemical substances. Not only inorganic substances are used, also organic materials, such as liposomes and micelles, which are used for drug delivery as well as nanofertilizers and nanopesticides. Fullerenes and carbon nanotubes form another class of nanoparticles based on carbon.

Titanium dioxide and zinc oxide nanoparticles also display photoreactivity, that is, under the influence of visible or UV light, they generate reactive oxygen species. This is a property that is not desirable for sunscreens, so in such products the nanoparticles are coated to reduce this activity. Coatings may also be used for other purposes, such as giving the nanoparticles the desired functionality instead of merely suppressing unwanted properties. Once released into the environment via waste streams, the nanoparticles may lose this protective coating and become reactive. Thus, while nanoparticles are potentially very useful for a wide variety of products, they may possibly also form an environmental hazard.

The goals of the research described in the present thesis were to gain insight in the distribution of engineered nanoparticles in the aquatic environment, that is, the release of nanoparticles into surface waters via wastewater and runoff from arable land and urban areas, their transport, and their eventual fate in water and sediment. In previous work direct measurement of the concentration and even the detection of nanoparticles have turned out to be very difficult, given the complexity of the water matrix and the low concentrations of nanoparticles that need to be dealt with. The main method used in this thesis is therefore mathematical modelling:

- The first step has been to estimate, on the basis of available data for the use of personal care products and other consumer products, the amount of nanoparticles that may be released into the environment. For this three types of nanoparticles were selected: titanium dioxide, zinc oxide and silver, since for these types most information was available, even if that information proved to be scarce.

  For the three metals also long-term concentration measurements were available for the rivers Rhine and Meuse, the two largest rivers flowing through the Netherlands. This enabled a comparison between the inflow of these metals and the emission of nanoparticles from Dutch households and industry. According to the calculations the contribution within the Dutch parts of the river basins of nanoparticles in terms of the total metal concentrations is in the order of 2 to 5% for the Rhine and 20% for the Meuse for zinc, silver and titanium.

  These figures do not take into account that wastewater treatment plants may retain a significant fraction of these nanoparticles in the sewage sludge. When this is accounted for, the percentages drop to 0.5 to 2% for the Rhine and about 6% for the Meuse.

- The second step was to examine the processes as reported in the literature, namely aggregation of nanoparticles to clusters, adsorption to suspended solids and subsequent sedimentation of these larger particles, and to develop a mathematical model that describes and accounts for these processes. The model is shown to be capable of describing the development of the concentration of nanoparticles as observed in laboratory experiments. In the model the nanoparticles are distributed over three different fractions: unbound or free nanoparticles, nanoparticles clustered into larger but homogeneous aggregates and nanoparticles adsorbed to suspended solids. Several processes are distinguished to describe the conversion of one fraction into another by aggregation or adsorption.

  Analysis of the model thus developed indicates that in natural water systems the most important process is the adsorption of nanoparticles to suspended solids. The concentrations of nanoparticles that have been predicted for these water systems are so low that homoaggregation of nanoparticles to larger clusters is a negligible process.

- The mathematical model described above formed the basis for further model development that would allow predicting the transport and fate of nanoparticles in the river Rhine. To this end an existing one-dimensional hydrodynamic model for the Rhine was used that extends from Maxau (near Karlsruhe) in Germany to well downstream of the Dutch/German border. The hydrodynamic model includes the main tributaries such as the Mosel, the Main and the Neckar in its schematisation. The model was used to simulate the flow in the river system for the period 2007--2009, as this was the period for which detailed inflow data for the upstream area and the tributaries were available. To estimate the release of nanoparticles into the river from households in the river basin, a database on the wastewater treatment plants in the whole Rhine basin was used. This way a detailed simulation for this period was possible.

In total six scenarios were studied. Two different emission scenarios were formulated, in the first the only source considered was the emission from the wastewater treatments. The second scenario included a diffuse source of nanoparticles along the river, representing potential runoff from the application of sludge as a fertilizer. In these two scenarios the nanoparticles were considered to be released as free particles that are then subject to aggregation, adsorption and sedimentation, conform the mathematical model that was developed using laboratory experiments. Not only the concentration of the various fractions of nanoparticles was modelled but also the concentration of suspended solids, as these are involved in the adsorption process.

In four additional scenarios, all based on the second emission scenario, the initial distribution as well as the rate coefficients of the processes were varied to examine the effects on the distribution over the fractions.

To gain confidence in the model set-up additionally the concentration of suspended particulate matter and the total concentration of zinc were modelled, using the available total zinc concentration measurements for the upstream boundary and the tributaries. The comparison of the model results for total zinc and suspended solids with the measurements for the simulation period shows that the model is indeed capable of predicting the concentration in the whole river for these two water quality parameters.

As there are no measurements available to date for nanoparticles in the Rhine river, the results for the concentration of nanoparticles cannot be compared with actual data. Furthermore, the model relies on estimates of the emissions, as described above. According to this emission scenario, nanoparticles may contribute 5 to 10% to the total concentration of zinc and titanium. In the second emission scenario the increase in the amount of nanoparticles released into the river leads to higher concentrations. The contribution relative to the observed total concentrations is still in the order of 10%.

From the modelling results it is also clear that nanoparticles may be transported over a large distance in much the same way as suspended particulate matter, as the nanoparticles are mostly adsorbed to these larger particles.

Very few if any publications exist regarding direct measurements of the concentrations of nanoparticles in natural water systems, but it is possible to use indirect techniques. In a second phase of this research, water samples were collected at 11 locations in a small, easily accessible river in the Netherlands, the Dommel, together with samples of the influent, effluent and sewage sludge of the large wastewater treatment plant that discharges on this river. The samples were analysed for seven metals (zinc, titanium, zirconium, gold, silver, cerium and lanthanum) using ICP-MS, ultrafiltration and scanning electron microscopy. The total concentration determined from the samples was used to identify the influence of possible sources, such as the wastewater treatment plant and surface runoff. This influence turned out to be minimal, as for some metals the background concentration was found to be higher than that of, for instance, the effluent.

The concentrations of cerium and lanthanum were found to have a constant ratio, indicating that there is no anthropogenic release of either element into the river Dommel. The ratio is in agreement with natural abundance ratios reported in the literature.

Filters of various mesh sizes were used to determine the size distribution of the particles in which the metals occur. It turned out that most metal is filtered out (up 80 to 90%) when using the coarsest ultrafilter used with a mesh size of 450 nm. This indicates that nanoparticles present in the river water are almost all attached to suspended matter or alternatively are present as aggregates of at least several hunderd nanometers. Using scanning electron microscopy nanoparticles of titanium dioxide and gold were shown to be present in the sewage sludge and the wastewater influent, as well as nanoparticles consisting of both cerium and lanthanum. The individual particle sizes are in the order of 20 nm, but especially the titanium dioxide particles were almost exclusively present as aggregates. The concentrations as calculated from these observations were an order of magnitude lower than expected on the basis of the estimates from the first part of this study.

The overall conclusion is that while nanoparticles of various types are present in everyday products and consequently appear in the wastewater, their contribution to the total concentration in such rivers as the Rhine and Meuse, but also the Dommel is limited. From the estimates based on the scarce data that are available, it would seem that at most 5 to 10% of the mass concentration can be attributed to nanoparticles. The river Dommel measurements have shown that, at least for this river and at the time of the sample collection, the contribution of nanoparticles may actually be much lower.