



## Foreword

## Engineered nanoparticles in soils and waters



Over the last decade, the variety and number of products and techniques based on the use or the addition of engineered nanoparticles has increased dramatically. This includes among others the use of e.g. silver, titanium dioxide, or other nanoparticles in a multitude of personal care products, clothing, colors, and other consumer products (Schaumann et al., 2015-in this issue), and their direct application in the environment, e.g., for site remediation (Fajardo et al., 2015-in this issue; Schöftner et al., 2015-in this issue) or drinking water treatment (Simeonidis et al., 2015-in this issue).

It is widely accepted that such nanoparticles can enter aquatic and terrestrial ecosystems and may impact biotic and abiotic processes in those environments (Schaumann et al., 2015-in this issue). The environmental relevance was recognized longer than a decade ago, and in contrast to the situation for other innovative materials and compounds, the research on potential environmental impacts of engineered nanoparticles has actually started before first negative environmental effects were reported. The pioneer researchers were challenged by limited analytical access to the nanoparticles and demanding experiments arising from the distinctive features of these emerging materials. Not only the chemical composition, but also specific particle characteristics determine their mobility, chemical affinity and biological effects. Even today, it is still highly challenging to detect nanoparticles in environmental matrices and distinguish them from an omnipresent natural colloidal background. The presentations and discussions on the International Workshop *Nanoparticles in Soils and Waters: Fate, Transport and Effects*, held 11th–13th March, 2014 in Landau in der Pfalz, Germany, with 81 participants from 15 countries, 32 oral and 29 poster presentations (Schaumann, 2014), led to a common agreement that it is reasonable and required to summarize and critically discuss current approaches and research activities in a special issue on engineered nanoparticles in soils and waters. This special issue is a collection of 18 publications, part of which is based on presentations during the workshop in Landau. The publications cover a wide spectrum of relevant issues related to engineered nanoparticles in the environment: they (i) stand for the current state of knowledge, (ii) demonstrate actual approaches to experimentally investigate fate and biological effects of six representatives of engineered nanoparticles: Ag, AgCl, TiO<sub>2</sub>, zerovalent iron, magnetite and copper oxide and (iii) present new approaches for characterizing and modeling fate, effects and the life cycle of nanoparticles.

As a large part of engineered nanoparticles enter the environment via wastewater, they will pass waste water treatment systems, which then serve as hotspots for their transformation determining the colloidal speciation and the chemical status of the nanoparticles released from the wastewater treatment plants. This is central for silver (Kaegi et al., 2015-in this issue), but also for other oxidic and metallic nanoparticles (Schaumann et al., 2015-in this issue). Also use activities for products containing

engineered nanoparticles should be considered in exposure assessment. For example, the release of nanomaterials from fabrics into the atmosphere is controlled by the activities performed when wearing these textiles (Wigger et al., 2015-in this issue). When nanoparticles are released to the environment, they will undergo a multitude of additional colloidal and chemical transformation reactions. Aggregation and disaggregation of nanoparticles are only partly or slowly reversible (Metreveli et al., 2015-in this issue). Thus, also the history of the nanoparticles is likely determining their properties and functioning. A general understanding of these coupled mechanisms is required to reliably predict fate and effect of nanoparticles using qualified, process-oriented models yet to be developed.

Based on a comprehensive analysis of the current knowledge on the fate and effects of two prominent nanoparticles, namely silver and titanium dioxide, it became clear that the mechanism of sorption of natural organic matter to the nanoparticles is central for the dynamics in colloidal states of the nanoparticles, but major controls for these interactions are still largely unknown (Schaumann et al., 2015-in this issue). Recent approaches again underline the relevance of the interaction between organic matter, cations and nanoparticles (Loosli et al., 2015-in this issue). For metallic nanoparticles, chemical transformations further complicate the process understanding. For example, it is consensus that silver nanoparticles undergo dissolution and oxidation with Ag<sub>2</sub>S as a thermodynamically determined endpoint. Also AgCl nanoparticles are transformed into Ag<sub>2</sub>S (Kaegi et al., 2015-in this issue). Although not fully understood, these processes affect the biological impact of nanoparticles (Farkas et al., 2015-in this issue; Pradhan et al., 2015-in this issue) and their colloidal stability and availability in biological test media (Nur et al., 2015-in this issue). In natural systems, these processes will determine which organisms will be exposed to the nanoparticles and which toxicity mechanism applies (Schaumann et al., 2015-in this issue). When used for site remediation, environmental conditions will control the efficiency of the nanoparticles (Fajardo et al., 2015-in this issue). Less is known about the fate and transport of nanoparticles in soils. The study by Klitzke et al. (2015-in this issue) demonstrates that natural organic matter can stabilize silver nanoparticles in soil solution, at high nanoparticle concentration. This is in line with the observation that silver nanoparticles in saturated porous media can be mobile, but at lower flow rates, higher ionic strength and in the presence of divalent cations transport is inhibited (Braun et al., 2015-in this issue). For the transport of nanoparticles in soil under unsaturated transport conditions, the attachment of the nanoparticles to the air–water interface is highly relevant (Kumahor et al., 2015-in this issue). These findings should be considered in future research, as transport in soil often occurs under unsaturated conditions.

A deeper understanding of the transformation mechanisms and the interplay between physicochemical transformation, transport and biological

impact requires the development and improvement of suitable analytical techniques (Schaumann et al., 2015-in this issue). Meanwhile, a wide spectrum of nanoanalytical methods can be applied to investigate the current state of the nanoparticles. Surface enhanced Raman spectroscopy could help to characterize organic coatings of nanoparticles (Kühn et al., 2015-in this issue), and advanced application of light scattering techniques may give further information on the structure and thickness of the organic coating (Tiraferri and Borkovec, 2015-in this issue). Especially the development of single particle analytics using inductively coupled plasma mass spectrometry was a milestone regarding environmental nanoanalytics, but it is still a challenge to characterize and detect the nanoparticles in complex matrices (Schaumann et al., 2015-in this issue).

Ideally, risk assessment should allow prediction of transport, fate and biological effects of engineered nanoparticles on the basis of, first, a well defined and known set of nanoparticle properties and, second, well defined and known characteristics of the environmental system of interest. In their analysis of the suitability of recent fate models for exposure assessment, Koelmans et al. (2015-in this issue) suggest applying a cost-effective multi-step approach from assessment on principles of read-across to higher tier assessments, for example on the basis of controlled model ecosystem field experiments. Fate models not only require knowledge on the fundamental transformation processes controlling the speciation of nanoparticles, but they also need to consider dynamics of environmental conditions and their spatial variability. A first approach for this is described by Sani-Kast et al. (2015-in this issue) on the example of the Rhône River (France) using statistical approaches. The authors showed that the fate of engineered nanoparticles can be best predicted when aggregation is strong near the emission source. This might suggest that the tendency of nanoparticles to aggregate is the dominating property governing their transport and fate, but these two studies also demonstrate how important it is for modeling to understand the colloidal transformation processes and their dependence on the actual environmental conditions and their dynamics and variability.

## Acknowledgment

This special issue was guest-edited by Gabriele E. Schaumann, Thomas Baumann, Friederike Lang, Hans-Jörg Vogel, Ralf Schulz and Werner Manz. The authors thank the editor-in-chief, Prof. Damia Barcelo, for enabling this issue in *Science of the Total Environment*. Thanks also to all editors of the journal and reviewers involved in review processes. The authors further acknowledge financial support by the Deutsche Forschungsgemeinschaft (DFG) within the research unit FOR 1536 INTERNANO and its subprojects, funded by DFG: BA 1592/6, LA1398/9, MA3273/3, SCHA849/16, SCHU2271/5 and VO566/12. The international workshop *Nanoparticles in Soils and Waters: Fate, Transport and Effects* was organized by the team of the research unit INTERNANO ([www.internano.uni-landau.de](http://www.internano.uni-landau.de)), with financial support of the DFG.

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