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Fate, accumulation and impact of metallic nanomaterials in the terrestrial environment

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Chapter 6

General Discussion

The rapid increase in the manufacturing and application of engineered nanoparticles (NPs) is raising concerns on their release into the environment. A large part of the released NPs is expected to accumulate in soil, which results in an increasing concern about their negative impacts in soil ecosystems, especially in the soil-plant system[315,30,34]. Understanding the impacts of NPs on plants is of utmost importance for the ecotoxicity assessment of NPs, since plants can serve as a bridge to connect the underground components (e.g. soil bacteria) and higher-level consumers. Within this PhD I aimed to investigate the uptake, translocation and impacts of metallic NPs in plants and potentially in terrestrial food chains under different exposure scenarios. Within these studies there was a specific focus on distinguishing the relative contribution of the nanoparticulate versus the released ionic form from metallic NPs to the overall toxicity in plants. Importantly, the majority of studies on the NPs and plants are short term experiments. We conducted long(er) term exposures in order to partially fill up the associated knowledge gap on adverse effects after longer term exposure. Within these experiments we incorporated the exposure routes, exposure dynamics and physicochemical properties of NPs to study their fate, accumulation and phytotoxicity in plants. Finally, we investigated the long-term impacts of NPs on the rhizosphere soil bacterial community and their potential transfer and biomagnification into a terrestrial food chain.

In this final chapter I will first answer the research questions formulated in chapter 1, which have been addressed in Chapters 2-5:

1. How does the exposure pathway affect the uptake, translocation, and phytotoxicity of AgNPs in plants? (Chapter 2 and 4)

2. How do the shape, size and coating of NPs affect the fate, accumulation and phytotoxicity of AgNPs? (Chapter 2 and 3)

3. What is the relative contribution of the nanoparticulate and the released ionic form to the overall toxicity of suspensions of NPs and on metal accumulation in plants? (Chapter 2 and 3)

4. How and to what magnitude does the dynamic dissolution of AgNPs in soil affect their bioavailability to plants? (Chapter 4)

5. How does the soil rhizosphere bacterial community respond to exposure to AgNPs, and does this response change over time? (Chapter 4)

6. How does a mixture of AgNPs and TiO_2NPs affect the transfer of the individual NPs along a terrestrial food chain of lettuce-snails and the associated impacts on the consumer? (Chapter 5)

I will first briefly highlight the main findings of my thesis, and subsequently provide implications for environmental risk assessment and the agricultural application of NPs. I will also give an outlook and recommendations for future research here.

6.1 Answers to the research questions

6.1.1 How does the exposure pathway affect the uptake, translocation, and phytotoxicity of AgNPs in plants? (Chapter 2 and 4)

A higher reduction of the biomass of plants and stronger oxidative stress and alterations of the activities of enzymatic antioxidants in lettuce were observed following root exposure as compared to foliar exposure. This indicates that root exposure induced more phytotoxicity than foliar exposure at equal exposure concentrations. Additionally, exposure pathway-specific uptake and translocation of AgNPs was observed as well. The Ag uptake in the exposed tissue of plants for root exposure to AgNPs is higher than in the case of foliar exposure to AgNPs, whereas the translocation of Ag inside the plants from the exposed part to the unexposed part is more efficient following foliar exposure rather than following root exposure. Furthermore, soil exposure of AgNPs to plants was much less toxic compared to hydroponic exposure due to the lower bioavailability of AgNPs in soil.

6.1.2 How do the shape, size and coating of NPs affect the fate, accumulation and phytotoxicity of AgNPs? (Chapter 2 and 3)

The dissolution of AgNPs in Hoagland solution was found to be shape and coating–dependent but size-independent. The dissolution extent of silver nanospheres was higher than for the silver nanowires, and dissolution rates of uncoated silver nanowires were higher than dissolution rates of coated Ag nanowires. Additionally, the phytotoxicity and accumulation of AgNPs in plants were also shape-dependent.

Specifically, exposure to Ag nanospheres resulted in higher phytotoxicity in plants as compared to exposure to Ag nanowires. Further, the phytotoxicity and Ag accumulation in plants of the tested Ag nanowires was diameter (size) dependent, but coating independent. Exposure to the smaller sized silver nanowires induced more phytotoxicity and higher Ag accumulation in plants. This could be caused by the fact that AgNPs with smaller diameters might easier pass through the pores in/between cell walls due to the size exclusion limit of cell walls and/or apoplast, and hence induce higher toxicity[68].

6.1.3 What is the relative contribution of the nanoparticulate and the released ionic form to the overall toxicity of suspensions of NPs and on metal accumulation in plants? (Chapter 2 and 3)

According to the response addition model, we observed that nanoparticulate Ag ($NPs_{(particle)}$) was the predominant driver/descriptor of the overall toxicity and Ag accumulation in the plants rather than the released ionic Ag ($NPs_{(ion)}$) forms, as $NPs_{(particle)}$ accounted for more than 65% of the overall toxicity in all exposure scenarios. However, the relative contribution of $NPs_{(particle)}$ versus $NPs_{(ion)}$ to the overall effects was influenced by the exposure concentration and the extent of dissolution of the Ag nanowires. The contributions of dissolved ions to the overall toxicity of AgNPs suspensions showed an increasing tendency upon increasing exposure concentration. In addition, the contribution of $NPs_{(ion)}$ to the overall effects in AgNPs with a high dissolution ability was higher than in the cases of AgNWs with a low dissolution ability.

6.1.4 How and to what magnitude does the dynamic dissolution of metallic NPs in soil affect their bioavailability to plants? (Chapter 4)

Our results revealed that the extractable Ag from AgNPs amended soil increased with the increasing exposure concentration and changed over time as a result of the continuous dissolution and uptake of AgNPs by the plants. The pattern of Ag concentration in plant roots changing over time was similar to the change of the extractable Ag in the rhizosphere soil over time. Furthermore, the Spearman correlation demonstrated that the amount of Ag accumulated in the plant root and

the shoots were correlated positively with DTPA-extracted Ag in the soil. These results show the important role of the dissolution of AgNPs in soil in influencing their bioavailability.

6.1.5 How does the soil rhizosphere bacterial community respond to exposure to AgNPs, and does this response change over time? (Chapter 4)

We found that the alterations in the structure and composition of the rhizosphere soil bacterial community varied over time. For the short-term exposure (7d), we did not observe any significant impact of AgNPs on the rhizosphere bacterial community regardless of exposure concentration. However, after long-term exposure (63d) to 50 mg/kg AgNPs, the decrease of the Shannon index, the separation of the bacterial community from the control and a total of 16 significantly changed featured taxa were observed. The alterations in the rhizosphere soil bacterial community were potentially associated with the abundance changes in the bacterial groups related to element (e.g., N and S) cycling and stress tolerance.

6.1.6 How does a mixture of AgNPs and TiO_2NPs affect the NPs transfer of the individual NPs along a terrestrial food chain of lettuce-snails and the associated impacts on the consumer? (Chapter 5)

We found that both Ag and Ti could be transferred from lettuce leaves to snails with trophic transfer factors (TTFs) of 0.2 to 1.1 for Ag and 4.7 to 49 for Ti when lettuce was exposed to either AgNPs or TiO_2NPs via the root. Moreover, the majority of Ag captured by snails in the AgNPs-containing treatments was excreted via the feces, whereas more than 70 % of Ti was distributed in the digestive gland of snails in the TiO_2NPs-containing treatments. In addition, treatment of snails with TiO_2NPs contaminated leaves strongly affected their feces excretion whereas AgNPs strongly affected their activity (expressed as the average BSS). Furthermore, the concurrent application of AgNPs and TiO_2NPs induced more severe inhibition of the growth and activity of snails but did not affect the biomagnification and distribution patterns of Ag and Ti in snails as compared to the application of AgNPs or TiO_2NPs alone.

6.2 Implications for risk assessment

6.2.1 Implications for environmental risk assessment

In the public consultation "Towards a Strategic Nanotechnology Action Plan (SNAP) 2010-2015", the European Commission highlighted four priority thematic areas of nanosafety research in the near future: 1) material identification and classification; 2) exposure and transformation; 3) hazard mechanisms including both human toxicology and ecotoxicology; and 4) risk prediction tools including databases and ontologies[316]. The observations in this thesis improve the understanding of the second and third issues described above by 1) investigating the fate, accumulation and impacts of metallic NPs in soil-plant systems and food chain, and 2) differentiating the main driver of toxicity of the particulate and the dissolved ionic forms. Also, our results can partly contribute to set up the ecotoxicological database of NPs, which is associated with the fourth issue of risk prediction tools including databases and ontologies as proposed by SNAP.

Our findings advance the understanding of exposure and transformation of NPs by providing novel data on the interactions between metallic NPs and terrestrial biota. **First**, we found that root exposure of AgNPs induced higher toxicity and different biodistribution patterns of Ag in plants compared to foliar exposure. The results regarding the effects of exposure pathway on plants improve the risk evaluation of metallic NPs exposure related to intentionally added applications in agriculture as well as unintentionally exposures from air-born emissions and soil emissions.

Secondly, we incorporated the dynamic exposure processes including the time-dependent dissolution and sedimentation profiles of NPs in the exposure medium into the risk assessment of metallic NPs. The dissolution and sedimentation of NPs were found to largely and dynamically affect their effective exposure concentrations and hence affect their biological impacts. As a result we showed that the EC_{25} and EC_{50} values of AgNPs to lettuce based on the time-weighted exposure concentration (incorporating the dynamic exposure conditions) were lower than the EC_{25} and EC_{50} values based on the initial exposure concentration (considering exposure as being static and hence ignoring dissolution and sedimentation). Therefore, this highlights

the importance of incorporating dynamic processes when evaluating the impacts of NPs on organisms to gain a more accurate and realistic assessment of NPs toxicity.

Thirdly, we distinguished the main driver for the impacts of NPs and the mode of actions of the nanoparticulate form and the released ionic form. The results demonstrate that the toxic effects of AgNPs are dramatically underestimated if there is only a focus on the impacts of dissolved ionic forms from metallic NPs alone. Also, the findings facilitate the mechanistic understanding of interactions between NPs and biological systems.

Fourthly, we quantified the toxicokinetic parameters of dissolved versus particulate forms of Ag nanowires associated with different physicochemical properties. This information is valuable for facilitating the establishment of toxicokinetic models to predict the accumulation and toxicity of NPs in higher plants. Moreover, we demonstrated that it is key to assess the actual time-related process of particles and ions in their uptake and toxicity to organisms.

Finally, we carried out the chronic exposure of NPs under more realistic exposure scenarios, such as assessing the transfer and toxicity of NPs in a microcosm consisting of the soil-lettuce-rhizosphere bacterial community as well as in a simulated terrestrial food chain of lettuce to snails. Our results clearly showed an upwards transfer of NPs in the terrestrial ecosystem from soil to plants and to snails, and a downward impact on the soil rhizosphere bacterial community. This highlights the potential risks of NPs in the terrestrial ecosystem. Importantly, we did not observe any significant impact of AgNPs on the rhizosphere bacterial community in short-term exposure, but long-term exposure to a high concentration of AgNPs indeed altered the structure and composition of the rhizosphere bacterial community. This indicates the importance of taking the long-term application of nanoparticles into account to better understand the ecological risks of nanoparticles in terrestrial ecosystems. The confirmed trophic transfer of NPs along the food chain emphasizes the importance of considering trophic transfer as a potential pathway for exposure of terrestrial herbivores to nanoparticles, especially given the increasing likelihood of application of nanoparticles in agriculture and soil remediation.

Overall, the findings of this thesis highlight the importance of 1) taking the intrinsic

properties and exposure modes of the NPs into consideration for accurate assessment of their ecotoxicological impacts, 2) considering the long term time-resolved dynamics of organisms in response to nanoparticle exposure, and 3) investigating the accumulation and translocation of NPs in organisms for environmental risk assessment of NPs.

6.2.2 Implications for agriculture

The loss of global crop production induced by pests and diseases and the growing food requirements as a result of the burgeoning global population are the major challenges faced by the agricultural sector, especially in developing countries[2,15]. This encourages the application of nanotechnology in agriculture to increase crop production and prevent the loss of global crop production induced by pest and diseases. To date, several metallic NPs have been applied in agriculture as nano-fertilizer (e.g Cu-based nano-agrochemicals), nano-pesticide (e.g AgNPs) or nano-carrier for delivery of agrochemicals to improve the use efficiency and to enhance crop productivity[15,317]. However, the application of NPs in agriculture not only brings benefits (including increased crop production and decreased application dose of pesticides), but potentially also presents adverse effects on the function and stability of the terrestrial ecosystem. As revealed by our findings, the impacts of NPs on plants depend on the application conditions such as the application dose, exposure duration and application method, as well as on the physicochemical properties of NPs. For example, we have shown that nanowires and larger sized AgNPs are less toxic compared to nanospheres and smaller sized AgNPs. These findings exemplify the potential of enabling the industry to optimize the desired properties of AgNPs with the aim of reducing unwanted side effects within the environment whilst preserving their basic functionalities. This is an important step to achieve "green and clean" claims that are a common requirement for novel materials nowadays. In addition, the exposure pathway determines how and to what extent the NPs can enter and translocate inside plants due to the size limitations of the xylem and the phloem. Future design of environmentally friendly nano-agrochemicals should also include this information. Moreover, we observed the slow but continuing dissolution of AgNPs in soil over a period of 63 days. This information can provide sustained antimicrobial effects against plant pathogens. This implies that repeated applications

of AgNP are not needed, which likely diminishes the total Ag load applied. However, we observed a relatively high amount of Ag in plant roots and the long-term disruptions of the composition of the rhizosphere bacterial community by Ag. Further, we confirmed the trophic transfer of NPs from lettuce to snails and associated negative impacts on snails. The findings highlights the potential risk of NPs being transferred to humans through the supply of crops treated with nano-agrochemicals. All these negative findings call for more attention that should be paid to balance between the potential negative effects of nano-agrochemicals and their implications in agriculture before their field application. Collaborative research among ecotoxicologists, agriculturists, physicists, chemists, material scientists and biologists is needed, as well as between the scientific community and industry to develop environmentally-friendly, efficient, mass-produced and cost-effective nano-agrochemicals that can actually get the label "green and clean".

6.3 Future research in nanoecotoxicology

Based on my research I want to provide advice on key research areas which need to be addressed in future studies to move this research field forward. Three of these area relate to the development of better analytical techniques, and another three focus on improved and more realistic toxicity testing.

6.3.1 Development in analytical techniques

The adequate detection and characterization of NPs in environment and biota are important for the accurate and comprehensive risk assessment of NPs, this section therefore addresses current challenges in the analytical techniques of NPs and the necessity of developing advanced analytical techniques.

1) Knowing the actual NPs concentrations in environmental compartments is a key prerequisite for the effective environmental risk assessment of NPs. Unfortunately, the current methods for the accurate detection, identification and quantification of NPs in environmental samples are still not optimal. ICP-MS based techniques, such as single-particle ICP-MS are being developed for quantifying the concentration of non-soluble metal-based nanospheres (e.g., AuNPs and CeO_2NPs). The dynamic nature of nanomaterials in the environment makes the effective extraction from

environmental compartments (such as soil and sewage sludge) however a challenge. Moreover, many of the current extraction methods have the potential to modify NPs. Although the concentrations of some NPs in the environmental compartments were predicted with the help of mathematic modeling, these results need to be further validated with appropriate analytical techniques. Therefore, future research is needed to improve the methods for sample preparation and to extend more techniques to make them suited for the detection of NPs in the environment.

2) As stated in this thesis, the relative contribution of nanoparticulate and dissolved ions to the bioavailability of NPs is important to understanding the toxicity mechanism of NPs. Currently, the quantitative analysis of metallic NPs is usually focused on the metallic mass concentrations as quantified with the help of ICP-MS based techniques. In this thesis, we distinguished the relative contribution of particles and ions with the help of modeling based on the total metal concentration in plants exposed to NPs and on reference experiments with metal salts (referred to as dissolved ions). Directly determining the concentrations of the nanoparticulate form and the dissolved ions released from NPs in organisms is a great difficulty, as faced by environmental and analytical scientists. The sp-ICP-MS and stable isotope-based analytical techniques show great potential in this field. However, these approaches are still in their infancy in this field. Much more effort needs to be paid to optimizing the performance of these techniques and improving their sensitivity to measure NPs. Additionally, to use these two methods NPs need to be extracted first by digestion of the samples, which may modify the properties of the NPs. Similarly, NPs accumulated inside organisms may also undergo a series of dynamic transformations. Therefore, the development of new methods and techniques or the use of a combination of multiple techniques that will enable to quantify the *in-site* and real-time concentration of NPs in organisms is urgently needed.

3) In this thesis, we investigated the uptake and translocation of NP in plants and snails without considering their subcellular location and the potential speciation patterns inside organisms. Such information is very valuable for a better and comprehensive understanding of the internalization of NPs inside biota. Transmission electron microscopy, confocal laser scanning microscopy or

fluorescence microscopy have been used to track the subcellular location of dyed/labeled NPs in organisms. But there are important limitations to these methods, including detachment of dye/labels attached to the NPs, while some techniques are not suitable for undyed/labeled NPs. Microbeam X-ray fluorescence mapping (μ-XRF) and X-ray absorption near edge structure spectroscopy (μ-XANES) can be used to identify the chemical speciation of NPs in organisms. But the lateral resolution of most μ-XRF/μ-XAS beamlines in the world is above 1 μm or a few hundred nm[111]. The development of higher spatial resolution techniques is therefore needed to further advance our understanding of the subcellular fate of NPs in organisms.

6.3.2 NPs exposure

Even though the results presented in this thesis improve the understanding of the interactions of NPs with terrestrial biota to a certain extent and provide implications for risk assessment of NPs, there is still a long way to go to get a fully clear picture of nano-ecotoxicology. Therefore, based on the results of this thesis, I will propose several issues that deserve further investigation:

1) Although we conducted long-term experiments, the results reported in this thesis did not cover the full life cycle of plants and snails. As a result, we may underestimate or overestimate the impacts of NPs on biota. Also, the growth stages of the tested organisms play an important role in affecting the toxicity of NPs. Therefore, full life cycle studies of different plants and snails in response to NPs exposure are needed for future research, as this may give a more realistic evaluation of the real effects of NPs on biota.

2) We investigated the effects of the exposure pathway, the exposure concentration and time, and the physicochemical properties of NPs on their impacts. In addition, environmental conditions such as the pH, the NOM content, the ionic strength are also needed to be considered in assessing the environmental risks of NPs, and these properties are not specifically considered or modified in this thesis. In particular, we found that soil exposure of NPs to plants induced less toxicity compared to hydroponic exposure. The low bioavailability of metallic NPs in soil may be due to reduction of the transport of NPs, as affected by the characteristics of soil including

the pH, soil natural organic matter, the clay and mineral contents in soil, and the activity of soil microbes. To better understand the interactions between NPs and biota, further efforts should be devoted to studying how the environmental conditions influence the toxicity of NPs in plants and how soil components affect the behaviors of NPs in soil.

3) We confirmed the occurrence of mixture toxicity and trophic transfer of NPs along a simple two-trophic level food chain. The design of the experiments was focused on establishing and maintaining controlled conditions. In a natural ecosystem, the exposure conditions are more dynamic and transfer between organisms is likely to be more complex as well as due to the changing exposure conditions the bioavailable fraction of the NPs will change. Further mesocosm studies and even field research including more species and using environmentally relevant concentrations of NPs are therefore needed to properly simulate realistic exposure scenarios.

Sahara, Morocco, 2018
Photo by Yupeng
yupeng

Björkliden, Kiruna, Sweden, 2019

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