



Universiteit  
Leiden  
The Netherlands

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

Wu, J.

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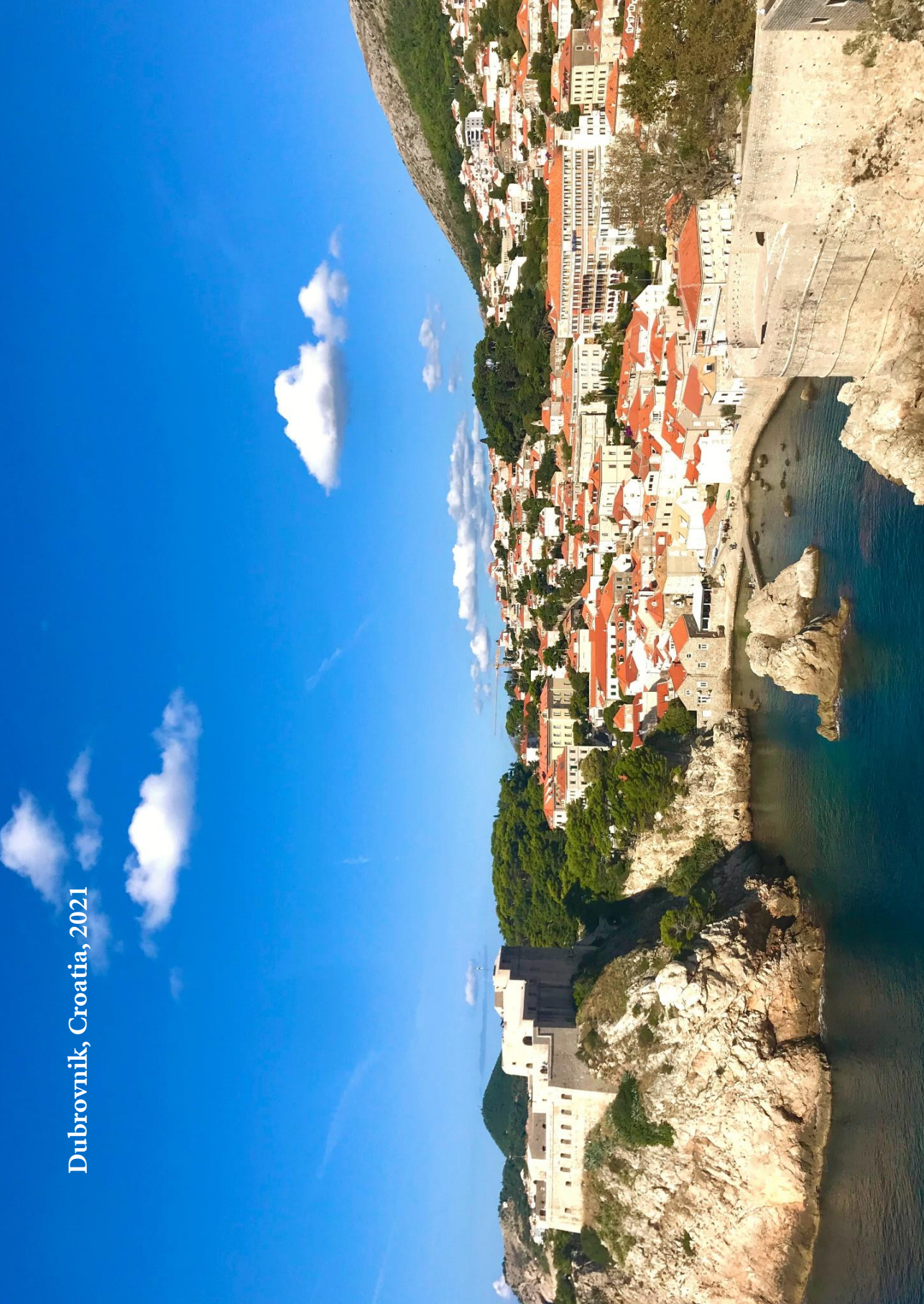
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## Summary

The rapidly increasing commercial application of metallic nanoparticles (NPs) within products will inevitably enhance the amount of NPs being released into environment. A large part of the released NPs is expected to accumulate in soil, which results in an increasing concern about their negative impacts on soil ecosystems. Knowledge on the fate, accumulation and impacts of NPs on plants is critical for understanding the environmental risk of NPs in soil ecosystems. The majority of studies aiming to assess potential effects of NPs were performed at early growth stages under root exposure with a short exposure time, which does not capture the long-term responses of plants to NPs. Very limited studies were carried out to examine the impact of engineered nanomaterials on plants upon foliar exposure, even though most nano-enabled agrochemicals are recommended to be applied by foliar spraying, relying on the so-called leaf-contact application. It is known that the behavior of NPs during the exposure period is determined by dynamic processes such as aggregation, sedimentation and/or dissolution, which results in the effective exposure dose changing over time. Nonetheless, the majority of published research, reports on experimental knowledge obtained making use of static initial exposure concentrations to quantify the dose of NPs without considering the impacts of these dynamic processes on their effective dose. Moreover, the dissolution of metallic NPs leads to the co-presence of nanoparticulate and ionic forms of metals. Subsequently, the overall effects of NPs to biota may be induced by the nanoparticulates and/or the released ions. Despite numerous studies on investigating the impacts of metallic NPs on plants, it is still unknown if their toxicity originates from the nanoparticles themselves or is caused by the released ions. Furthermore, one of the big quests is related to whether NPs have the potential to transfer to higher-level consumers via food chains. In this thesis, we integrated the exposure routes and exposure dynamics of NPs to investigate the uptake, translocation and impacts of metallic NPs in plants upon long-term exposure. We furthermore investigated the long-term impacts of NPs on the rhizosphere soil bacterial community and the potential transfer and biomagnification within a food chain.

In chapter 2, we quantified the uptake, translocation, biodistribution of Ag and various phytotoxic endpoints in lettuce by exposing lettuce to AgNPs (nanosphere, NSs) suspensions following either foliar or root pathway for 15 days. We found that the exposure pathway significantly affects the uptake, translocation and phytotoxicity of AgNSs in lettuce. Root exposure to AgNPs induced more phytotoxicity than foliar exposure at the same exposure level as revealed by the enlarged biomass reduction of plants, higher oxidative stress, and alterations of the activities of enzymatic antioxidants in plants after root exposure. Also, the plants accumulated more Ag following root exposure to AgNPs as compared to foliar exposure to AgNPs at the same exposure level. Interestingly, the translocation of Ag inside the plants from the exposed part to the unexposed part is more efficient following foliar exposure than in case of root exposure, as revealed by the higher translocation factors for the foliar exposure scenarios. The differences observed for root exposure and foliar exposure are likely due to their different mechanisms associated with the uptake and translocation of NPs. NPs can be taken up through stomatal openings and/or across waxy cuticles and then transported to other parts of the plants through phloem loading mechanisms. For root uptake and translocation, NPs need to traverse across the cell walls and the epidermal layers and are further transported upwards via xylem loading mechanisms.

In chapter 3, we determined the impacts of size, length and coating of Ag nanowires (AgNWs) on the fate, accumulation and phytotoxicity of AgNPs in lettuces upon root exposure. Firstly, we found that the dissolution of AgNPs in the growth medium (Hoagland solution) was coating-dependent. The dissolution extent and dissolution rate constant of the uncoated AgNWs (HAR-AgNW: 39 nm diameter $\times$ 8.4  $\mu$ m length) were both higher compared to the PVP coated AgNWs (LAR-AgNW: 43 nm diameter $\times$ 1.8  $\mu$ m length, and MAR-AgNW: 65 nm diameter $\times$ 4.4  $\mu$ m length). Additionally, the phytotoxicity, uptake rate constants and bioaccumulation factors of the PVP-coated AgNWs (43 nm diameter $\times$ 1.8  $\mu$ m length) and the uncoated AgNWs (39 nm diameter $\times$ 8.4  $\mu$ m length) were similar, but both parameters were higher than those of the PVP-coated AgNWs with the larger



diameter (65 nm diameter $\times$ 4.4  $\mu$ m length). These findings imply that the diameter rather than the length and coating of the AgNWs predominantly determines their toxicity and Ag accumulation in plants. Further, taking together the results of chapters 2 and 3, we also found that the dissolution, accumulation and phytotoxicity of AgNPs in plants was shape-dependent. The AgNSs resulted in higher dissolution ability and phytotoxicity but in less Ag uptake by the root of plants as compared to exposure to AgNWs. Our results highlight that the intrinsic characteristics of NPs need to be taken into consideration in investigating the interactions between metallic NPs and plants.

According to the response addition model, we quantified the relative contribution of nanoparticulate forms ( $\text{NPs}_{(\text{particle})}$ ) and the released ionic forms ( $\text{NPs}_{(\text{ion})}$ ) to the overall phytotoxicity of AgNPs suspensions and Ag accumulation in plants. As revealed in chapters 2 and 3, particulate Ag was found to be the predominant driver/descriptor of the overall toxicity and Ag accumulation in the plants, accounted for more than 65% for the overall toxicity in all exposure scenarios regardless of the shape, size and coating of AgNPs. The relative contribution of  $\text{NPs}_{(\text{particle})}$  versus  $\text{NPs}_{(\text{ion})}$  to the overall effects was however influenced by the exposure concentration and the extent of dissolution of AgNPs. The contributions of dissolved ions to the overall toxicity of AgNSs and AgNWs showed an increasing tendency upon increasing exposure concentration. The differences in the contributions of the particulate and ionic forms to the overall toxicity may be reflected by their different modes of action as particulate toxicity is shown to originate from the accumulation of Ag in plants by blocking of internal trafficking, while ions toxicity is likely due to the induction of excess ROS production.

In Chapter 4 we further extended the knowledge on the interactions between AgNPs and biota by investigating the dissolution dynamics (the dissolved Ag concentrations determined as the DTPA-extractable Ag concentrations) and accumulation of AgNPs in a microcosm consisting of soil - lettuce - rhizosphere bacterial community. Our results revealed that the extractability of Ag in AgNPs amended soil was concentration-dependent and changed over time as a result of the continuous

dissolution and uptake of AgNPs by the plants. Additionally, the results with use of the Spearman correlation demonstrated that the amount of Ag accumulated in the plant root and the shoots was positively correlated with the DTPA-extracted amount of Ag in the soil. These results highlight the important role of the dissolution of AgNPs in the soil in influencing the overall Ag bioavailability of the NPs. Furthermore, the alterations in the structure and composition of the rhizosphere soil bacterial community were found to be exposure time-dependent. 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 (63 d) to 50 mg/kg AgNPs, the shifts of the bacterial community and a total of 16 significantly changed featured taxa were observed as compared to control. 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.

In chapter 5, we investigated the trophic transfer of single NPs and a mixture of AgNPs and TiO<sub>2</sub>NPs from lettuce to snails and their associated impacts on snails. We found that both Ag and Ti could be transferred from lettuce leaves to snails with trophic transfer factors of 0.2 to 1.1 for Ag and 3.8 to 47 for Ti when lettuce was exposed to either Ag<sup>+</sup>/AgNPs or TiO<sub>2</sub>NPs via the root. Ionic Ag was found to be more readily assimilated and translocated into the other organs of snails than the particulate form. Moreover, the majority of Ag captured by the snails in the AgNPs-containing treatments was excreted via faeces, whereas more than 70% of Ti was distributed in the digestive gland of snails in the TiO<sub>2</sub>NPs-containing treatments. In addition, the behavioral responses of snails to the trophic transfer of AgNPs and TiO<sub>2</sub>NPs were different. Treatment of snails with TiO<sub>2</sub>NPs contaminated leaves strongly affected their faeces excretion whereas AgNPs strongly affected the locomotion activity (expressed as the average BSS) of the snails. Furthermore, concurrent application of AgNPs and TiO<sub>2</sub>NPs did not affect the bioaccumulation and biodistribution patterns of Ag or Ti in snails compared to the trophic transfer following exposure to AgNPs or TiO<sub>2</sub>NPs alone. However, their co-exposure induced

a more severe inhibition of the growth and activity of snails than in the case of applying AgNPs or TiO<sub>2</sub>NPs alone. Our results improve the understanding of the trophic transfer of a mixture of metallic NPs within terrestrial food chains, which is valuable for assessing their possible risks to the environment and to ecosystem health.

To conclude, the newly generated knowledge depicted in this thesis advances the understanding of: 1) the differences in accumulation and phytotoxicity of AgNPs upon foliar exposure and root exposure; 2) the specific characteristics of AgNPs which dominate their fate, bioavailability and phytotoxicity; 3) the Ag forms present in AgNPs suspensions that predominantly drive their impacts on green leafy plants; 4) different mode of actions of particulate and ionic Ag in inducing phytotoxicity; 5) long-term impacts of the dissolution dynamics of AgNPs on Ag accumulation in plants and the rhizosphere soil bacterial community; 6) the possibility of transfer of a mixture of multiple NPs within the food chain, as associated with increased potential risks to higher trophic level organisms. Furthermore, the results highlight that the intrinsic properties of the NPs and the long time-resolved dynamics of NPs exposure should be taken into consideration for accurate assessment of their ecotoxicological impacts in the soil ecosystem. Overall, our results improve the knowledge about the interaction of NPs with different terrestrial biota as well as the hazard evaluation of NPs exposure. Such information assists the development of “Safe by Design” of NPs, which can help to balance between the nanomaterials applications and their implications in the environment and in agriculture.