Short- and long-term approaches to determine the fate of silver nanoparticles in soil

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1. Introduction

The increasing use of engineered nanoparticles (ENP) leads to their release into the environment.[1] There is a special focus on silver nanoparticles (Ag ENP) because of their toxic effects to microorganisms. The Ag ENP used in consumer products enter into sewers and wastewater treatment plants with a high predicted removal into the sludge.[2] If the sludge is applied to agricultural soils, decompostation might result in resuspension of the ENP.[3] In general, soils were stated as a large sink for ENP.[4] However, the fate and impact of Ag ENP in soils is still not clarified and there is a lack of knowledge about their long-term fate. Here, we summarize the results about the fate of Ag ENP (AgNM-300k, OECD Sponsorship Programme) in soils from the two research projects “UMSICHT” and “DENANA”. The unique feature of the investigations is that experimental designs of increasing complexity were choosen to test the same soils and Ag ENP on different timescales.

2. Materials and methods

All experiments were performed with sterically stabilized Ag ENP and the Refesol 01A (slightly loamy Cambisol, OECD standard). The column experiments were also conducted with a medium clayey silt (Luvisol).

2.1. Test systems

The column remobilization experiments were performed according to DIN 19528, and adapted to the physico-chemical properties of Ag ENP.[5] The AgNM-300k (50 mg l^{-1}) was spiked to air-dried Luvisol and Cambisol. Afterwards, the soils were incubated for 3 and 92 days in the dark at 20°C. After incubation, the soils were filled into columns and eluated with artificial rainwater. Filtration (0.45 µm) and nitric acid (HNO_3) digestion was applied to the eluates. The soils were digested with aqua regia after the experiments.

Undisturbed soil columns (l = 16 cm, diameter = 10 cm) were sampled from farmland soils in Germany (Cambisol, Luvisol). The AgNM-300k dispersion (8 mg l^{-1}) was percolated through the soil columns under saturated and unsaturated conditions. The percolates were fractionated and digested with HNO_3, the soil columns were cut into eight slices and digested with aqua regia.

The AgNM-300k was spiked to the sewage sludge of a public wastewater treatment plant. After the addition of a flocculant, the sludge was mixed to the soil, and subsequently applied to the field lysimeters. The set concentrations of AgNM-300k in the upper 20 cm of the three lysimeters were 0; 1.7; 7 mg kg^{-1}. The percolate water was sampled monthly for three years, fractionated (0.45 µm filtration, ultracentrifugation), and afterwards acidified or digested. The crops and soils were sampled anually, and digested by HNO_3 or aqua regia. To regard more details about the ecotoxicologial experiments please refer to Schlich et al.[6]

2.2. Analytics

The total Ag concentrations (Ag_{total}) of all digested AgNM-300k dispersions, eluates, percolates as well as the digested plant materials and soils were measured by ICP-OES (Ciros Vison, Spectro, Kleve, Germany) or ICP-MS (7500 Series, Agilent, Santa Clara, USA). For the characterization of the AgNM-300k dispersion and the filtered column percolates a NanoZS (Malvern Instruments, Malvern, UK) was used.

3. Results and discussion

3.1. Remobilization experiments with disturbed soil columns

The remobilization of Ag_{total} was on a very low level in all percolation steps in both soils. The first percolation step after three days of the Cambisol incubation showed the highest remobilization of Ag which was below

1 % of the Ag_{total} concentrations in the soil columns. The correlation between remobilized Ag_{total} and Al_{total} concentrations suggests that the remobilized amount of Ag was associated to soil colloids.

3.2. Saturated and unsaturated percolation experiments with undisturbed soil columns

The breakthrough of AgNM-300k was high but incomplete in the Cambisol and the Luvisol. Particularly, columns with preferential flow pathways showed low AgNM-300k retention. In the unsaturated experiments the matrix flow dominated the water transport which results in higher residence time and retention. Furthermore, in unsaturated soil columns the attachment to the air-water interface was identified as a key process for Ag ENP retention.[7] However, a nearly complete retention was solely found for the silty Luvisol with a clearly smaller pore size structure than the sandy Cambisol. The Cambisol showed a reduced but measureable AgNM-300k breakthrough in the unsaturated experiments.

3.3. Long-term field lysimeter experiments

The horizontal displacement of Ag_{total} was low and very likely related to soil tillage as well as bioturbation. A low but significant Ag_{total} release (t = 480 d, control = 24 ng l^{-1}, Lysimeter (7 mg kg^{-1}) = 56 ng l^{-1}, measurement according to DIN 38402-11) was obtained for the highest AgNM-300k application. This lysimeter induced a steady inhibition of the soil microflora that was not detected in the lysimeter with the lower AgNM-300k concentration.[6] The roots of wheat, canola, and barley showed an uptake of Ag_{total}. However, a root-shoot barrier clearly reduced the Ag_{total} concentrations in the aerial parts of the plants.

3.4. Implications regarding the environmental fate and impact of Ag ENP

The results from different experimental setups could lead to different implications about the fate of Ag ENP in soils. The breakthrough of AgNM-300k through undisturbed soil columns of the Cambisol indicates a risk for groundwater contamination, though the breakthrough decreases with a increasing complexity of the experimental design. On the contrary, the long-term lysimeter experiments as well as the short-term column remobilization experiments indicate a rather low risk for groundwater contamination. Even if there is a translocation in soils, the Ag ENP are presumably attached to soil colloids. In general, all experimental approaches have their eligibility and should be taken into account for holistic risk assessment. Despite the different implications, all column experiments identified a clearly higher Ag dynamic for the sandy Cambisol. Hence, the Cambisol might be considered as a worst case soil regarding the mobility of Ag ENP.

4. Conclusion

All approaches showed a more or less high retention and demobilization of Ag ENP in soils why soils are a sink for Ag ENP. The demobilization in the lysimeter was high but incomplete because of root uptake and inhibition of the soil microflora. Thus, the impact of a repeated sludge application to the soil microorganism and the root uptake (e.g. beet) needs further long-term investigations. In addition, method development is needed to determine the unclear speciation (particulate or dissolved) of the low Ag concentrations in the roots.

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5. References

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