

Long term approaches to determine the fate of ceriumdioxid nanomaterial in soil

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1. Introduction

The increasing use of engineered nanomaterials (NM) leads to their release into the environment.¹ There is a special focus on ceriumdioxid nanomaterials (CeO₂ NM) because of their widespread applications (diesel fuel additive, electronic and optical devices, metallurgy, polishing agents for glass and silicon wafers, exterior paints).² Atmospheric deposition and sewage sludge applications have been discussed as source for the environmental release of CeO₂ NM.¹ Sludge amendments will result in a CeO₂ NM input into arable soils, which are supposed to be a sink for NM.³ However, the fate and impact of CeO₂ NM in soils is still uncertain and there is a lack of knowledge about their long-term fate. Here, we summarize the results about the fate and bioavailability of CeO₂ NM from a long term outdoor lysimeter study.

2. Materials and methods

2.1. Application of CeO₂ NM to the lysimeter

The soil (Refesol 01A, slightly loamy Cambisol, OECD standard 216/217) was sampled from the uppermost layer of an arable soil in Lower Saxony (Hagen, Germany). One year before the application of the CeO₂ NM, the soil was filled to five outdoor lysimeters. All experiments were performed with CeO₂ NM (CeO₂ NM-212, OECD Sponsorship Programme) which was applied to the lysimeter by sewage sludge or artificial rainwater. The sludge of a public wastewater treatment plant was spiked with CeO₂ NM. After the addition of a flocculant, the sludge was mixed to the soil, and subsequently applied to the upper 20 cm of three outdoor lysimeters. For the rainwater approach, the lysimeters were watered with artificial rainwater using pure rainwater and a CeO₂ NM containing rainwater. Afterwards, the upper 20 cm of the lysimeters were dug up to receive comparable conditions between the different approaches. The set concentrations of CeO₂ NM after sludge application were 0 mg kg⁻¹ (control), 10 mg kg⁻¹ and 50 mg kg⁻¹ as well as 0 mg kg⁻¹ (control) and 10 mg kg⁻¹ after rainwater application.

2.2. Sampling and analytics of percolating water, soil and plant roots

The percolating water was sampled monthly for two years, fractionated (untreated, 0.45 µm filtration, ultracentrifugation), and afterwards acidified or digested. We conducted four soil sampling campaigns, one after the application of the CeO₂ NM and three each time after harvesting. After sampling, crops (wheat, canola, barley) and soil samples were digested by acid-hydrogen-peroxide. Total Ce concentrations of the percolating water as well as the digested plant materials and the soil samples were measured by ICP-OES (Ciros Vison, Spectro, Kleve, Germany) or ICP-MS (7500 Series, Agilent, Santa Clara, USA). Furthermore, the response of ammonium oxidizing bacteria (AOB) to the CeO₂ NM application was tested applying an ISO guideline.⁴

To retrieve information about the Ce speciation in the lysimeter, two soil samples were investigated with synchrotron based X-ray absorption near edge spectroscopy (XANES). Due to the high detection limits, X-ray absorption spectroscopy (XAS) measurements were only possible in samples of the lysimeter with the highest Ce concentration (50 mg kg⁻¹). The two random soil samples from an outdoor lysimeter cannot represent the population. Nonetheless, information regarding the Ce speciation after CeO₂ NM application to soil are sparse for long term approaches. Hence, we provide these data here though statistical uncertainties are high. The XAS was recorded up to 240 eV above the Ce L₃-edge. Per sample, three spectra were recorded and merged. Data treatment and linear combination fitting (LCF) of reference materials to sample spectra was performed using Athena.⁵

3. Results and discussion

3.1. Cerium concentrations and bioavailability in the lysimeters

For both approaches (sludge and rainwater application), no vertical Ce translocation was detected over two years. However, a relatively high standard deviation of the five replicates per soil layer indicates that the method is not very sensitive. The more sensitive measurements of Ce concentrations in the percolating water showed no differences in Ce release between the CeO₂ NM spiked lysimeters and the unspiked controls. These results imply that the tested soil is a large sink for CeO₂ NM. Compared to the control, there was no enhanced Ce root uptake for wheat. However, the Ce uptake to the plant roots increasing from canola to barely suggests that despite of a large CeO₂ NM retention, the NM are somehow bioavailable in the rhizosphere. These results are in line with another study that found CeO₂ NM uptake to barley roots.⁶

There was no adverse effect on the activity of the AOB due to the CeO₂ NM during the two years of the experiment.

3.2. Speciation of Ce in the lysimeter soil

The digestion method, measuring the total Ce concentrations, provides basic information regarding the fate of the added CeO₂ NM in the lysimeter. However, more detailed information about the speciation of Ce in soil and plant roots are required. The XANES LCF showed that Ce⁴⁺ was partially reduced to Ce³⁺ during the two years of CeO₂ NM aging in the lysimeter soil (50 mg kg⁻¹ approach). In detail, the aging reduced the Ce⁴⁺ species from 85% after CeO₂ NM application to 47% at the end of the experiment. Rico *et al.*⁶ found the same effects but with a faster (60 d) and higher (98%) Ce transformation (Ce⁴⁺ to Ce³⁺) which could be explained by differences in the experimental designs (climate chamber vs. outdoor lysimeter). It was discussed that the transformation of Ce⁴⁺ to Ce³⁺ is needed to facilitate the Ce root uptake.⁶ Hence, the observed Ce transformation might elucidate that the highest Ce uptake was found for the latest crop (barley) planted.

4. Conclusion

All approaches showed a high retention of CeO₂ NM in the Cambisol that is why the soil is supposed to be a large sink for CeO₂ NM. In addition, the results suggest that there exists no risk of groundwater contamination for the tested soil and CeO₂ NM. The demobilization in the lysimeter was high but incomplete because of the Ce root uptake. The Ce root uptake might be related to the transformation of Ce⁴⁺ to Ce³⁺ while aging. However, the underlying mechanism remained unclear because also plant specific characteristics could have caused the enhanced Ce uptake. Thus, the root uptake, localization, and speciation of CeO₂ NM needs further long term investigations under field conditions.

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5. References

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