Detection of engineered cerium oxide nanoparticles in soils using single particle ICP-TOF-MS

ANTONIA PRAETORIUS[1], WILLI FABIENKE[1], ALEXANDER GUNDLACH-GRAHAM[2], JANA NAVRATILOVA[1], DETLEF GÜNTHER[2], FRANK VON DER KAMMER[1] AND THILO HOFMANN[1]

[1] University of Vienna, Department of Environmental Geosciences, Althanstr. 14, 1090 Vienna, Austria, antonia.praetorius@univie.ac.at
[2] ETH Zurich, Laboratory of Inorganic Chemistry, Vladimir-Prelog-Weg 1, 8093 Zurich, Switzerland

Engineered cerium oxide nanoparticles (CeO_2 NPs) are expected to be released to the environment during their application as e.g. diesel fuel additives or automotive catalytic converters. There is a clear need to quantify CeO_2 NP in environmental matrices in order to asses their potential risks, but the detection of engineered CeO_2 NPs in complex natural media remains challenging due to a lack of contrast between engineered nanoparticles (ENPs) and natural background particles. Challenges in detecting ENPs in natural samples increase with increasing complexity of the sample matrix. Soil and sediments contain particularly high backgrounds of natural nanoparticles (NNPs) of similar composition as many ENPs. It is therefore necessary, to find strategies to detect contrast between ENPs and NNP to enable the identification of ENPs in the presence of natural background.

We here present a new approach to detect engineered CeO_2 NPs in real soils. In our method we are making use of the relatively constant 2:1 ratio of Ce to Lanthanum (La) in natural soils across Europe which stands in constrast with engineered CeO_2 NPs containig only trace amounts of other rare earth elements. By adding engineered CeO_2 NPs to a natural soil sample the Ce:La ratio should be altered in favor of Ce. However, the natural background concentration of Ce in soils lies in the 10-100 mg/kg range while released CeO_2 NPs to the environment are only expected to reach μg/kg levels. Therefore, bulk approaches, e.g. detecting an increased Ce:La ratio by ICP-MS in soil samples containing CeO_2 NPs, are insufficient for realistic scenarios and an analysis on a single particle level is required to differentiate between ENPs and NNPs. In order to detect contrast between engineered CeO_2 NPs and natural Ce-containing particles we have to go beyond conventional single-particle (sp) ICP-MS towards multi-element methods enabling the simultaneous detection of Ce and La on individual particles in a soil sample. A new instrument, coupling an ICP-MS with a time-of-flight (TOF) mass spectrometer allows the simultaneous measurement of multiple elements at high time resolution [1] and thereby enables us to differentiate Ce-only containing engineered CeO_2 NPs from Ce- and La-containing natural particles.

Our hypothesis was tested with a set of experiments under increasingly more complex (and realistic) conditions. More specifically the following combinations of engineered CeO_2 NPs (Sigma Aldrich, CeO_2 < 50 nm) and natural matrices were studied: (1) A suspension of pristine engineered CeO_2 NPs; (2) A suspension of natural colloids spiked with known amounts of CeO_2 NPs and (3) Colloidal extracts of a natural (uncontaminated) soil which had been spiked with different amounts of CeO_2 NPs. In our study we are able to detect individual engineered CeO_2 NPs using sp-ICP-TOF-MS in all three types of samples described above even at concentrations orders of magnitude below the natural Ce background.

[1] Borovinskaya, O., Gschwind, S., Hattendorf, B., Tanner, M., Günther, D. (2014): Simultaneous Mass Quantification of Nanoparticles of Different Composition in a Mixture by Microdroplet Generator-ICPTOFMS. Analytical Chemistry, 86 (16), 8142-8148.