

Effects of natural organic matter properties on the dissolution kinetics of zinc oxide nanoparticles

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Soluble metal-based nanoparticles such as zinc oxide (ZnO) are used in a variety of consumer products and engineered applications and are also known to occur naturally in the environment. The release of metal ions from these nanoparticles (NPs) is a key step controlling metal bioavailability and subsequent toxicity to organisms exposed to the NPs. Likewise, the dissolution rate of soluble NPs is critical for controlling the lifetime of the NPs in environmental systems, and rates depend upon many environmental factors, including the interactions of the NPs with natural organic matter (NOM).

The goal of this research is to study how the characteristics of NOM influence the dissolution rate of ZnO NPs. We utilized anodic stripping voltammetry as a way to directly measure dissolved Zn ions in aqueous solution at a relatively high time resolution (e.g. on the order of 1 min intervals), and examined the effects of 16 different NOM isolates on the dissolution kinetics of ZnO NPs (average primary particle diameter of 20-30 nm) in buffered potassium chloride solution ($I=0.1$ M, $pH = 8.5$) at 25.0 °C. The observed zero-order dissolution rate constant (k_{obs}) and the dissolved zinc concentrations at equilibrium increased linearly with NOM concentration (from 0 to 40 mg-C L⁻¹) for Suwannee River humic and fulvic acids and Pony Lake fulvic acid. When dissolution rates were compared for 16 different NOM isolates at 20 mg-C L⁻¹, values of k_{obs} positively correlated with certain properties of the NOM, including Specific UV Absorbance (SUVA), oxygen/carbon (O/C) ratio, aromatic and carbonyl carbon contents and molecular weight (MW). Dissolution rates were negatively correlated with hydrogen/carbon (H/C) ratio and aliphatic carbon content. The observed correlations indicate that aromatic carbon content is a key factor in determining the rate of NOM-promoted dissolution of ZnO NPs. In addition, a weak negative correlation was observed between k_{obs} and ZnO NP aggregate size in the early stage of dissolution, which in turn is negatively correlated with MW of NOMs. Findings of this study facilitate a better understanding of the fate of ZnO NPs in organic-rich aquatic environments and highlight SUVA as a facile and useful indicator of NP-NOM interactions.