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Kinetics of heavy metal dissociation from natural organic matter

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Natural organic matter (NOM) is probably the most important ligand in the environment that affects the reactivity of heavy metals. The quantitative understanding of the kinetics of heavy metal dissociation from various NOM binding sites is essential for accurately predicting the fate and transport of heavy metals in the environment. In the previous work, we developed a unifying kinetics model for heavy metal dissociation from NOM based on metal reactions with various carboxylic and phenolic binding sites of humic substances [1]. Since the chemcial properties of NOM may vary, how different NOM functional groups with different metal binding properties affect the kinetics of heavy metal dissociation has not been systematically investigated.

In this study, the kinetics of heavy metal dissociation from NOM was studied with a competing ligand exchange method. Three types of organic matter were used in the kinetics experiments, including low-molecular-weight organic acids, model humic substances from IHSS, and organic matter extracted from soil, to investigate the relationship between metal binding constants and dissociation rate constants. There is a significant difference of the metal dissociation rates among different heavy metals and different NOM samples, due to the varying metal binding constants and different functional groups in NOM samples. WHAM 7 and Visual MINTEQ were employed to calculate the equilibrium distribution of heavy metal among different NOM binding sites before the kinetic experiments. We developed a mechanistic-based kinetics model to describe the dissociation of heavy metal ions from various NOM binding sites, based on the relationship between metal binding constants and the dissociation rate constants of NOM binding sites. Our results indicate that the molecular structure of NOM and the binding forms of metal ions (e.g. mono-, bi- or tridentate binding) control the rates of metal dissociation from NOM samples.

[1] Zhenqing Shi, et al. (2016) *Env. Sci. Technol.* **50,** 10476-10484.