Characterization of aluminum in environmental systems using X-ray absorption and vibrational spectroscopy

-The importance of organic matter

Kristoffer Hagvall

Akademisk avhandling

som med vederbörligt tillstånd av Rektor vid Umeå universitet för avläggande av teknologidoktorsexamen framläggs till offentligt förvar i Lilla hörsalen (KB3A9), KBC, torsdagen den 4 juni, kl. 13:00. Avhandlingen kommer att förvaras på engelska.

Fakultetsopponent: Professor, Dan Berggren Kleja, Institutionen för mark och miljö, biogeokemi, Sveriges Lantbruksuniversitet, Uppsala, Sverige.
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Abstract
The fate and behavior of many metals in the environment are highly dependent on interactions with natural organic matter (NOM), which is abundant in most soils and surface waters. The complexation with NOM can influence the speciation of the metals by affecting their hydrolysis and solubility. This in turn will also have an effect on the mobility and potential toxicity of the metals. For aluminum (Al) these interactions are of high environmental importance since Al have been shown to have negative effects on plant growth, water living organisms, and fish.

This thesis will focus on the interactions between Al(III) and NOM in different environments and under varying geochemical conditions. To study this, infrared (IR) spectroscopy and X-ray absorption spectroscopy (XAS) have primarily been used. Due to the difficulties in analyzing Al using XAS, gallium(III), shown to be a suitable analogue for Al(III), was used as a probe to get complementary information from the Ga(III)-NOM system. The combined results from these studies showed that Ga(III) and Al(III) formed strong chelate complexes with carboxylic groups in NOM and that these complexes were strong enough to suppress the hydrolysis and polymerization of the metals. Furthermore, Al in organic soil and stream water samples was also studied using XAS and the results showed a variation in the speciation from a predominance of organically complexed Al(III) in the stream waters to a mixture of Al(III)-NOM complexes and precipitated Al phases (Al-hydroxides and/or Al-silicates) in the organic soils. To further study mineral-NOM interactions the effects of NOM on the dissolution of gibbsite ($\gamma$-Al(OH)$_3$; a common mineral in the environment) were investigated. The results showed that NOM can promote mineral dissolution and presence of inner-sphere Al(III)-NOM species on the gibbsite surface, detected by IR spectroscopy, could indicate a ligand induced dissolution. To further investigate the structure of the complex formed at the surface of the mineral, an EXAFS study was conducted on the ternary Ga(III)-NOM-gibbsite system. The results indicated either formation of inner-sphere complexes with Ga(III) acting like a bridge between NOM and the gibbsite surface, or the presence of two separate species; Ga(III)-NOM complexes in solution and a precipitated Ga(OH)$_3$ phase.

As a sidetrack to the Al(III)-NOM studies, a new way of characterizing NOM was developed using simultaneous infrared and potentiometric titrations, multivariate data analysis, and chemical equilibrium modeling. An acid/base model for a fulvic acid was constructed, based on spectroscopic information about functional groups and their pK$_a$ values, and indicated that the fulvic acid is to be regarded as a tetra carboxylic acid consisting of at least four fractions of carboxylic acids. This demonstrates new possibilities to study the acid/base and metal complexing properties of NOM, in which the presence of carboxylic acid groups predominate, and to design equilibrium models more reliable than presented before.

Keywords
Aluminum; Organic matter; Soil; Stream water; XAS; IR spectroscopy; Mineral surfaces; Dissolution; Inner-sphere complexation; Chemical equilibrium modeling.