Fundamental aspects of interaction between metals and humics in the environment

W.H. VAN RIEMSDIJK[1] AND L.P. WENG[2]

[1]Dreienplein 10 Department Soil Quality, Wageningen University, The Netherlands (willem.vanriemsdijk@wur.nl)
[2]Dreienplein 10 Department Soil Quality, Wageningen University, The Netherlands (liping.weng@wur.nl)

Metal ion interaction with humic substances is pH dependent, and the pH dependence has to obey the thermodynmamic consistency principle. One of the simplest models in this respect is the pH dependent Freundlich model. Such models have their limitation, because they can not easily be extended to include metal-metal competition and moreover the basic proton buffering behavior of humics is not icluded in the simplified models. The NICA-Donnan model and model V/VI do link the basic charging behavior of the humics with competitive metal ion binding. The NICA-Donnan model has been applied to model metal ion binding and mobility in soils with quite some succes. Especially the possibility to measure the free metal ion at very low concentration with the recently improved DMT technique is very helpful to test the quality of the models. The mobility of metal ions will be affected by the binding to DOC and by the binding to the immobile phase. The DOC concentration can be influenced by the binding of the DOC to the immobile mineral phase. Metal ions may also interact with humics that are in close association with mineral particles. The DOC-mineral-metal interaction process is in our opinion the next frontier for a better understanding of the mobility of metal ions in the environment. Minerals have a rather complex surface chemistry, and to combine this type of chemistry with the also rather complex chemistry of humics is an enormous challenge. A first attempt in this direction has been the development of the LCD model, which combines the NICA-Donnan model for humics with the CD-MUSIC model for metal(hydr)oxides. This model has been applied to fulvic acid binding to goethite. Extension of this model to humic acid binding has so far been an unresolved challenge. We will show a new theoretical approach that will probably allow to solve this challenging problem.

Influence of SOM on aluminium mobility in a forested brown acidic soil: A view from soil solutions held at different matrix potentials

F. GÉRARD[1], J. JAFFRAIN[1], J.-P. BOUDOT[2] AND J. RANGER[1]

[1]INRA Nancy, BEF, 54280 Champenoux, France
[2]CNRS Nancy, LIMOS, 54501 Vandoeuvre, France

We studied a number of soil water samples held at different matrix potential from the surface horizons of a brown acidic forested soil. The matrix potential can be converted into an equivalent pore diameter. Solutions have been analysed for total chemistry in major elements, pH and total inorganic monomeric Al. We used the WHAM VI speciation model to calculate Al speciation, by fitting results to the mesured pools of inorganic monomeric species.

Results are shown in the figure below. Black symbols represent solutions collected beneath the litter layer (0 cm), white symbols stand for solutions collected at 15 and 30 cm depth by mean of tension lysimeters (matrix potential; $|\psi| < 600$ hPa), and grey symbols are for solutions held by centrifugation (1800 hPa $< |\psi| <$ 16000 hPa) at the 0-15 cm and 15-30 cm depth intervals.
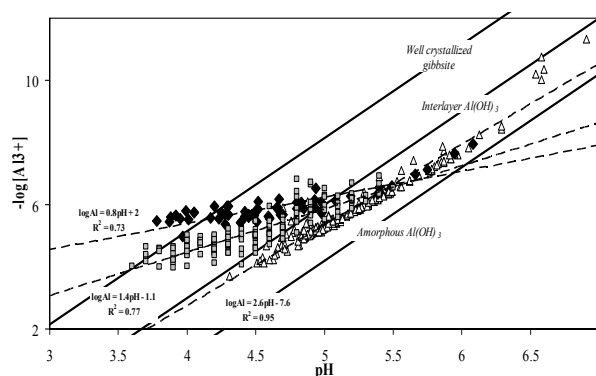
We found that Al mobility in solutions collected in the larger soil pores (tension lysimeters) are controlled by the neoformation of poorly crystallized Al-hydroxides, likely to be interlayer Al. In smaller pores (centrifugation) and especially those from the top soils, which contain more acidic water, a control by Al^{3+}-H^+ exchange reactions with SOM is found. The maximum control by SOM is consistently found beneath the litter layer.