**3.11.7 Rigorous physicochemical framework for metal ion binding by nanoparticulate humic substances: implications for speciation codes and biovailability models**    R.M. Town, Systemic Physiological and Ecotoxicological Research (SPHERE), University of Antwerp / Department of Biology (SPHERE Research Group); H.P. van Leeuwen, Wageningen University and Research / Physical Chemistry and Soft Matter; J.F. Duval, CNRS / Laboratoire interdisciplinaire des environnements continentaux LIEC CNRS UMR.  Humic substances (HS) are natural soft nanoparticulate complexants which play an important role in buffering free metal ion concentrations in aquatic ecosystems. It is widely assumed that the equilibrium concentration of the free metal ion is the relevant parameter for predictions of bioavailability. In this context, there is widespread use of equilibrium speciation codes, notably NICA-Donnan (incorporated in Visual MINTEQ) and WHAM, to compute free metal ion concentrations, which are subsequently used in ecotoxicological risk assessment models, e.g. BIO-MET and PNEC-PRO. The risk predicted by such bioavailability-based models is thus dependent on the parameters used by the speciation codes to compute the extent of metal ion binding by HS. In recent years a rigorous generic theoretical framework has been developed to describe the electrostatic and chemical contributions to metal ion binding by nanoparticulate complexants. The theory describes the way in which the reactivity of charged nanoparticles towards metal ions depends on particle size and particle type (i.e. reactive sites distributed within the particle body or confined to the surface), as well as the ionic strength of the aqueous medium, and the nature of the metal ion. HS dispersed in aquatic systems generally carry a net negative charge; the particle electric field has the potential to electrostatically impact on the chemical speciation dynamics. For the example case of soft environmental particles such as HS, we have delineated practical strategies for determining intraparticulate metal ion speciation, and for evaluating intrinsic chemical binding affinities. The heterogeneity of the chemical binding derived from our nanoparticulate treatment of HS is in good agreement with that independently determined by electrochemical measurements. In contrast, the outcomes of the NICA-Donnan and WHAM models lead to heterogeneity parameters that are not supported by independent experimental data. The presentation will discuss the findings in terms of a physicochemical analysis of the discrepancies generated by these equilibrium speciation codes, thereby revealing the a priori hypotheses adopted therein and the inappropriateness of some of their key parameters. It follows that attempts to correlate metal speciation computed by these codes to dynamic features such as lability, bioavailability, and/or toxicity are bound to suffer from physicochemically poor outcomes.