Putting constraints on the life cycle of organic carbon based on ecosystem scale flux measurements

THOMAS KARL

National Center for Atmospheric Research, 3090 Center Green Drive, Boulder, CO, 80301, USA (tomkarl@ucar.edu)

Large quantities of volatile organic compounds (VOC) enter the atmosphere. The annual production of VOC (600 - 2000 TgC/a) likely exceeds that of methane and CO (~500 TgC/a each). Together these gases fuel tropospheric chemistry. Oxidation of VOC leads to the formation of aerosol [1] via complex organic chemistry [2, 3] in the gas and aerosol phase thereby modulating the oxidation capacity of the atmosphere [4]. It is currently believed that a large fraction of VOC originates from biogenic sources (e.g. >80%). The life cycle of organic carbon is ultimately controlled by emission and deposition processes at the surface. Uncertainties in budgets of VOC and potential ramifications for organic aerosol production in the atmosphere will be discussed based on a synthesis of direct VOC flux measurements performed in a range of different ecosystems. These direct flux measurements will be used to address some outstanding questions concerning (1) the amount of reactive biogenic organic aerosol precursors, (2) the magnitude of deposition processes and (3) the lifetime of reactive biogenic organic aerosol precursors in the atmosphere.

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Molecular-level studies of Fe(III) in aquatic systems

T. KARLSSON[1]*, U. SKYLLBERG[2] AND P. PERSSON[1]

[1]Dept. of Chemistry, Umeå Univ., 901 87 Umeå, Sweden (*correspondence: torbjorn.karlsson@chem.umu.se)
[2]Dept. of Forest Ecology & Management, Swedish Univ. of Agri. Sci., 901 83 Umeå, Sweden

The fate and behavior of iron (Fe) in aquatic environments is highly dependent on chemical interactions with natural organic matter (NOM). There is however still limited knowledge about the molecular structure, strength and hydrolysis of the Fe species formed in association with aquatic NOM and few studies that present results obtained by molecular-level probes (e.g. [1, 2]). In this study we have used extended X-ray absorption fine structure (EXAFS) and Fourier transformed infrared (FTIR) spectroscopy in combination with chemical speciation modeling to characterize Fe (III) in different types of aquatic NOM and in dissolved and colloidal material in different size fractions from a boreal stream.

Our results show that Fe in association with NOM and fulvic acid from river water forms two predominant species; mononuclear Fe (III)-NOM complexes and polymeric Fe (III) (hydr)oxides. The distribution of the two species is largely dependent on pH and Fe concentration. The speciation in the boreal stream water is dominated by mononuclear organic Fe (III) complexes irrespective of pH and size fraction. In the organic complexes Fe is coordinated by carboxylic functional groups forming a structure consisting of five-membered chelate rings and these complexes are sufficiently strong to prevent hydrolytic polymerization of Fe even at pH 7.0.

Thus, in oxic aquatic environments, with organic matter present, the fate of Fe will to a large extent be controlled by the properties of the organic Fe (III) complexes. In addition, the stable Fe (III)-NOM complexes formed will have important implications for the biogeochemistry of other elements, such as phosphorus and arsenate, that are known to be strongly associated with Fe (III).

[1] Rose *et al*. (1998) *Colloids & Surf. A* **136**, 11–19. [2] Vilgé-Ritter *et al*. (1999) *Colloids & Surf. A* **147**, 297–308.