

Iron-rich nanoparticle formation and importance for trace metal transport in groundwater and Arctic rivers

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The occurrence, size distribution, aggregation and trace-metal binding of iron-rich nanoparticles in groundwater and river water have been studied using a range of sophisticated nanoanalytical techniques. Atomic force microscopy (AFM) performed under oxygen free conditions showed that sub-oxic groundwater samples from the River Thames flood plain were dominated by discrete semispherical nanoparticles in the 1 nm-20 nm diameter range. Transmission and scanning electron microscopy (TEM and SEM) with energy dispersive X-ray spectroscopy (EDS) detection confirmed that Fe was the major element in the nanoparticles. The field results were validated by AFM-analysis of laboratory mixtures of Fe(II)-sulphate with Suwannee River Humic or Fulvic acid, which yielded nanoparticles with a similar size distributions to those found in the groundwaters. Aeration of both groundwater and synthetic laboratory samples resulted in aggregation of the nanoparticles to form colloids, several hundred nm in diameter. Flow Field-Flow Fractionation coupled on-line to Inductively Coupled Plasma Mass Spectrometry (FIFFF-ICP-MS) showed that a significant proportion (around 40-50 %) of rare earth elements (REEs) in rivers of the Yukon River basin, Alaska, during the spring flood were associated with <8 nm organic/iron-rich nanoparticles, presumably eroded from the upper organic-rich soil horizons. During summer base flow, with higher groundwater inputs to the rivers, REEs were mostly associated to small (<0.5 nm) complexes, but also bound to 0.5-3 nm fulvic acid and 4-40 nm and >40 nm iron-rich nanoparticles and colloids. Nanoparticle, sources, formation and dynamics in the Alaskan rivers will be discussed by comparison with the results from sub-oxic groundwater samples, and their implications for the trace-metal transport by Arctic rivers will be examined.