Detection of Fe-DOM and As-DOM complexes using Fluorescence Spectroscopy and ^{1}H NMR

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Complexation of arsenic (As) with dissolved organic matter (DOM) in reducing aquifers is one of the mechanisms that controls the As concentration in aqueous solution. It has been shown that in the presence of iron (Fe), DOM may either compete with As for adsorption sites and/or bind to form ternary complexes (As-Fe-DOM) or binary complexes (As-DOM). The use of fluorescence spectroscopy (FS) with excitation-emission matrix (EEM) has been proven to be an effective tool for characterization of DOM and its properties. FS has been used to determine conditional stability constants for DOM-metal complexes. Recent advances in solution nuclear magnetic resonance (NMR) spectroscopy have also improved the characterization of DOM in environmental samples. This work applied fluorescence and ^{1}H NMR spectroscopy to detect binary and ternary complex formation of As, Fe and Suwanee River Fulvic Acid (SRFA) as the DOM source. Experiments were designed using a natural range of Fe, SRFA, and As concentrations and under oxic and anoxic (under N_2) conditions, as titrations of Fe (1ppm – 50 ppm) with SRFA (6ppm and 12 ppm) solution, As (1ppb – 100 ppm) with SRFA solution and As with SRFA+Fe solution. The results of fluorescence quenching experiments provided clear evidence for the formation of Fe-DOM complexes under all conditions. By contrast, As-DOM or Fe-As-DOM complexes did not show any fluorescence quenching. Either the As-DOM complex was not formed or not detected using FS. To further confirm whether As-DOM complexes really did not form, samples were analyzed using ^{1}H NMR spectroscopy. Different molar ratios of As:SRFA were used based on natural concentrations in relevent study areas (Bengal basin). Results indicated that the change in chemical shifts and intensity after addition of As occurred mostly in non-aromatic region protons and was negligible in the aromatic region. Given that fluorescence tyically results from double bonds, particularly those in araomatic carbon rings, this result may explain why As-DOM complexes were not detected using FS. The detection of As-DOM binary complex formation using ^{1}H NMR is relevant for studies of arsenic mobility in reducing groundwater in that such complexes could maintain high As concentrations in groundwater.