Geophysical Research Abstracts
Vol. 15, EGU2013-11601, 2013
EGU General Assembly 2013


# Isotopic analysis of dissolved organic carbon in produced water brines by wet chemical oxidation and cavity ring-down spectroscopy

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Identification of fluid migration and escape from intentionally altered subsurface geologic systems, such as in hydraulic fracturing, enhanced oil recovery, and carbon sequestration activities, is an important issue for environmental regulators based on the traction that the "fracking" process is gathering across the United States. Given diverse injected fluid compositions and the potential for toxic or regulated compounds to be released, one of the most important steps in the process is accurately identifying evidence of injected fluid escape during and after injection processes. An important tool in identifying differences between the natural groundwater and injected fluid is the isotopic composition of dissolved constituents including inorganic components such as Sr and carbon isotopes of the dissolved organic compounds. Since biological processes in the mesothermal subsurface can rapidly alter the organic composition of a fluid, stable carbon isotopes of the dissolved organic compounds (DOC) are an effective means to identify differences in the origin of two fluids, especially when coupled with inorganic compound analyses. The burgeoning field of cavity ring-down spectroscopy (CRDS) for isotopic analysis presents an opportunity to obtain rapid, reliable and cost-effective isotopic measurements of DOC in potentially affected groundwater for the identification of leakage or the improvement of hydrogeochemical pathway models. Here we adapt the use of the novel hyphenated TOC-CRDS carbon isotope analyzer for the analysis of DOC in produced water by wet oxidation and describe the methods to evaluate performance and obtain useful information at higher salinities. Our methods are applied to a specific field example in a $CO_2$-enhanced EOR field in Cranfield, Mississippi (USA) as a means to demonstrate the ability to distinguish natural and injected DOC using the stable isotopic composition of the dissolved organic carbon when employing the novel TOC-CRDS instrumentation set up.