

A continental-scale groundwater flow system

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Our understanding of regional scale flow systems is important because they control major geological processes. Modern analogs of regional scale flow systems are rare. The Western Interior Plains aquifer system (WIP) in the mid-continent, U.S.A., has been proposed to be hydraulically continuous from the Colorado Front Range to central Missouri. This study applies geochemical and isotopic variations present in this regional aquifer to ascertain the scale of hydraulic continuity in the WIP. In the study area three distinct groundwater endmembers have been identified in the WIP (1A-1D, 2A-2C, 3A-3C) (Fig. 1).

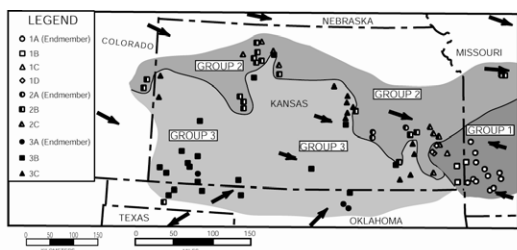


Figure 1: Close up of the study area showing water compositional group locations and their regional extent. Arrows indicate direction of flow [1-3].

Systematic spatial variations of major ion concentrations, stable isotope ratios, and geographic distribution of these three groups on a 1200 km scale were found. Fluid mixing models can account for the regional differences in groundwater composition of these groups. The regional extent of these geochemically and isotopically distinct endmembers suggests that the WIP is a continuous flow system extending over eastern Colorado, Kansas, central Missouri, and northern Oklahoma.

[1] Jorgensen (1989) *Oklahoma Geol. Survey Circular* **90**, 176–193. [2] Jorgensen *et al.* (1986a) *USGS Circular* **1002**, 132–140. [3] Larson (1971) *AAPG Memoir* **15**(2), 1043–1046.

Fe(II)-Fe(III) electron transfer in Fe oxides and clays: Implications for contaminant transformations

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Redox transformations between reduced and oxidized iron (Fe) exert substantial influence on groundwater chemistry. Cycling of Fe between oxidation states, as well as dissolved and mineral phases has been shown to significantly impact nutrient availability, heavy metal cycling, and contaminant remediation. Our group, as well as others, have shown that electron transfer occurs between sorbed Fe (II) and structural Fe (III) in Fe oxides [e.g. 1, 2]. It is unclear, however, whether Fe (II)-Fe (III) electron transfer occurs under the more complex biogeochemical environments found in nature. Here, we use ⁵⁷Fe Mössbauer spectroscopy to investigate whether Fe (II)-Fe (III) electron transfer will occur in clay minerals, as well as cation-substituted and ligand-complexed Fe oxides. Mössbauer spectroscopy results indicate that sorbed Fe (II) reduces structural Fe (III) in clay minerals, as well as aluminum substituted and phosphate coated goethite.

We are also exploring the implications of Fe (II)-Fe (III) electron transfer for contaminant transformations. In batch experiments with nitrobenzene, we have previously shown that magnetite stoichiometry increases after reaction with Fe (II) and results in significantly faster rates of nitrobenzene reduction [3, 4]. We conducted similar experiments with uranium and results from X-ray absorption spectroscopy (XAS) indicate that the extent of uranium reduction is also influenced by magnetite stoichiometry.

[1] Williams & Scherer (2004) *ES&T* **38**, 4782–4790. [2] Silvester *et al.* (2005) *GCA* **69**, 4801–4815. [3] Gorski & Scherer (2009) *ES&T*, **43**, 3675–3680. [4] Gorski *et al.* (2010) *ES&T* **44**, 55–61.