

## The Migration and Influence of Thermogenic Hydrocarbons in Shallow Aquifers across the Karoo Basin, South Africa

William Eymold (1), Kelley Swana (2), Myles Moore (1), Colin Whyte (1), Jennifer Harkness (1), Siep Talma (3), Ricky Murray (4), Joachim Moortgat (1), Jodie Miller (2), Avner Vengosh (5), and Thomas Darrah (1)

(1) School of Earth Sciences, The Ohio State University, Columbus, USA (eymold.1@osu.edu; moore.3222@osu.edu; whyte.25@osu.edu; harkness.42@osu.edu, moortgat.1@osu.edu; darrah.24@osu.edu), (2) Department of Earth Sciences, Stellenbosch University, Matieland, South Africa (kelley.swana90@gmail.com; jmiller@sun.ac.za), (3) Natural Resources and the Environment, CSIR, Pretoria, South Africa (sieg.talma@gmail.com), (4) Groundwater Africa, Kommetjie, South Africa (ricky@groundwaterafrica.co.za), (5) Division of Earth and Ocean Sciences, Nicholas School of the Environment, Duke University, Durham, USA (vengosh@duke.edu)

While horizontal drilling and hydraulic fracturing have enhanced global production of unconventional hydrocarbons, these developments have raised environmental concerns regarding water usage and contamination near unconventional energy extraction. We conducted a comprehensive pre-industrial evaluation of the baseline water quality and geochemistry of groundwater in the water-restricted Karoo Basin of South Africa. Our analyses utilized a multi-tracer geochemical approach to evaluate gas and salt chemistry within this sensitive region. Stray gas contamination of groundwater remains a risk for a subset of groundwater wells near shale gas development. Thus, we focus our current efforts on characterization of gas geochemistry of natural hydrocarbon-gas-rich springs and groundwater wells across the Karoo Basin. Twenty-two samples were analyzed for water parameters, dissolved ion chemistry, water isotopes, major gas geochemistry, compound-specific stable isotopes of hydrocarbons, dissolved inorganic carbon and CO<sub>2</sub>, noble gas elemental and isotope geochemistry, and tritium. We find that methane-rich springs targeted for elevated gas contents are associated with Na-Cl-type waters and contain elevated levels of ethane, <sup>4</sup>He and noble gases produced by radioactive decay, and less negative  $\delta^{13}\text{C-CH}_4$  compared to background samples. Gas- and salt-rich samples display evidence of mixing between a low- to mid-thermal maturity thermogenic natural gas that experienced fractionation during migration into shallow aquifers that later mixed with variable amounts of hydrogenotrophic biogenic methane. Gas- and salt-poor samples instead contain more negative  $\delta^{13}\text{C-CH}_4$  and a subset which represents mixing between hydrogenotrophic and acetoclastic methanogenesis. Our approach allows us to identify sources and migration histories for naturally-occurring hydrocarbons in the Karoo Basin.