Effects of polydispersity on natural organic matter fate and transport

DANIEL MCINNIS, LINDSAY SEDERS DIETRICH, DIOGO BOLSTER, AND PATRICIA MAURICE*

University of Notre Dame, Civil Engineering & Geological Sciences, 156 Fitzpatrick Hall, Notre Dame, IN 46556, USA
dmcinnis@nd.edu, lseders@gmail.com, bolster@nd.edu, pmaurice@nd.edu (* presenting author)

Natural Organic Matter (NOM) is a polydisperse material whose components display a range of adsorption rates and affinities as determined largely by molecular weight (MW). In this study, the mobility of NOM was examined in sand columns at pH 5-8, in 0.001 to 0.1 M $NaClO_4$. Effluent data were modelled using the advection-dispersion equation (ADE). Greater overall mobility of NOM was observed at higher pH and lower ionic strength. High-pressure size exclusion chromatography (HPSEC) was used to monitor the MW distribution of column effluent; results were consistent with fractionation by preferential adsorption of intermediate to high MW components, as previously observed in many batch systems. Transport rates of different components were quantified by dividing the MW distribution into separate 'bins' and examining breakthrough curves for each bin. Heterogeneity in the retardation factor (*R*) led to heavy tailing of breakthrough curves as the experiments progressed. This non-Fickian transport behaviour was described using a continuous time random walk (CTRW) model designed to address variability in geochemical properties controlling sorption-desorption kinetics. Results of this study demonstrate that the effects of NOM compositional heterogeneity on transport can be addressed through a systematic coupling of geochemical and hydrologic approaches.

Origin, distribution and hydrogeochemical controls on methane occurences in shallow aquifers in southwestern Ontario

JENNIFER MCINTOSH[1*], STEPHEN OSBORN[2], STEPHEN GRASBY[3], AND STEWART HAMILTON[4]

[1]Department of Hydrology and Water Resources, University of Arizona, Tuscon, AZ 85721, USA, mcintosh@hwr.arizona.edu
[2]Geological Sciences Department, California State Polytechnic University Pomona, Pomona, CA 91768, sgosborn@csupomona.edu
[3]Geological Survey of Canada, Calgary, Alberta, AB T2L 2A7 Steve.Grasby@NRCan-RNCan.gc.ca
[4]Ontario Geological Survey, Sudbury, Ontario P3E 6B5, stew.hamilton@ontario.ca

Abstract

Fractured organic-rich shales, such as the Marcellus, Antrim, and Utica are major targets for thermogenic and biogenic production in Michigan, New York, Pennsylvania, and Quebec. Age-equivalent shales extend into southwestern Ontario (Findlay Arch region), where there has been no shale gas production to date and little information exists on the origin and distribution of natural gas, despite historical accounts of gas in water supply wells screened in shales. To determine the origin and extent of natural gas, and investigate water quality associated with natural gas occurrences, 912 water supply wells were sampled for gas composition, isotopes, and water chemistry in Paleozoic bedrock and overburden formations throughout southwestern Ontario.

Methane concentrations, measured at the well head, ranged from <5 to 415% in-situ saturation (0 to ~251 ppm) with the highest concentrations in wells screened in the Georgian Bay, Dundee, Marcellus, Hamilton Group, and Kettle Point formations, and overlying glacial drift deposits. Carbon isotopes values of CH_4 (-89.9 to –52.3‰), the correlation of hydrogen isotopes of CH_4 and water, and the lack of higher chain hydrocarbons (C_2+<0.8 mole%), indicates the gas is biogenic in origin. Isotopic signatures of methane in overburden deposits were similar to gas accumulations in underlying bedrock formations, suggesting the gas migrated vertically into shallow aquifers, rather than being generated in-situ. Groundwater associated with methane accumulations are dominantly Na-HCO_3 type, with no dissolved oxygen, low Fe (<0.06 mM), low SO_4 (<0.44 mM), and low H_2S (<0.5 mM). Alkalinity concentrations ranged from 0.2 to 15.0 mM, and there was no correlation with CH_4 concentrations. High CH_4 concentrations were observed in groundwater with variable $\delta^{18}O$ values (-18.6 to –8.3‰), representing microbial methanogenesis associated with both modern and Late Pleistocene recharge. Results from this study provide important baseline data on dissolved gases and water quality in shallow aquifers overlying shales, in the case of future shale gas production, hydraulic fracturing and/or geologic sequestration of carbon dioxide to evaluate potential environmental impacts.