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Measuring Aqueous CH_4 Concentration Profiles in Shales and Tills to Define Source, Transport, and Fate of Organic Gases

M.J. Hendry[a,1], A.L. Bangsund[a], E.E. Schmeling[a], S.L. Barbour[b]

aUniversity of Saskatchewan, Geology, 114 Science Place, Saskatoon, SK, Canada, S7N 5E2
bUniversity of Saskatchewn Department of Civil and Geological Engineering, 57 Campus Dr., Saskatoon SK, Canada, S7N 5A9

Abstract

The rapid development of unconventional shale resource plays has generated public concern with respect to potential contamination of potable groundwaters and surface waters by fugitive natural gases dominated by methane (CH_4). Continuous core samples collected at six drill sites to a maximum depth of 240 m below ground were used to define the vertical distribution of dissolved CH_4 and conservative Cl^- through Cretaceous shales and overlying glacial tills in the Williston Basin, Canada. The interpretation of potentially reactive CH_4 depth profiles in conjunction with conservative profiles provide insights into the source, transport, and fate of CH_4 in aquitards-aquifer sequences and present baseline gas concentrations for use in fugitive gas migration investigations.

Keywords: Baseline characterization; methane; groundwater; shale; glacial till

1. Introduction

Natural gas extraction from unconventional shale resource plays has transformed the energy outlook globally. The rapid development of this resource has, however, generated public concern with respect to potential contamination of potable groundwaters and surface waters by fugitive natural gases dominated by methane (CH_4). Aging conventional oil wells can also create conduits for fugitive gas release to shallow groundwater. A key limitation to defining the impact of fugitive gases on groundwater resources is the lack of knowledge of non-impacted baseline concentrations. Collecting porewater samples representative of *in situ* dissolved gas concentrations in aquifers using groundwater wells can be challenging[1]. Characterizing background dissolved gas

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* Corresponding author.
  E-mail address: jim.hendry@usask.ca

concentrations through aquitards (*e.g*. shale and glacial tills) that separate aquifers from shale-gas or conventional oil production zones can provide insights into the source, origin, fate and transport of CH_4 in the shallow subsurface. However; slow groundwater recharge rates confound sampling of water from wells installed in aquitards because they prohibit purging the standing water from these wells and can result in a mixed sample of altered and unaltered formation porewater[2]. This limitation combined with the high costs of groundwater and observation well installations (or other groundwater sampling instrumentation) warrant the investigation of alternate methods to collect and analyze gas concentrations in shales. The objectives of this study were to define the distribution of dissolved CH_4 through Cretaceous shales and overlying glacial tills using core samples and provide examples of how these data, when used in conjunction with a conservative tracer, Cl^-, can be used to define the source, transport, and fate of CH_4 in aquitards-aquifer sequences.

2. Methods

Mud rotary drilling, geologic logging, and coring were performed at two study areas in the Williston Basin, Saskatchewan, Canada: the Weyburn and Birsay study areas (Fig. 1a). Five boreholes were drilled (named sites 1-5) to between 150 (Site 2) and 200 m (Site 5) below ground surface (BG) at Weyburn (Fig. 1b) and one borehole was drilled to 240 m BG at Birsay. Continuous core samples (75 mm ID × 3.05 m long) were collected in duplicate at 1-3 m depth intervals at all sites. Upon retrieval, the outer 2-5 mm of the core samples were immediately trimmed to minimize contamination by drill mud (confirmed with stable isotopes of water data, not presented). Additional continuous coring was conducted at Sites 2-4 to depths of 20 m BG using auger drilling methods. Cores were collected at 1-3 m depth intervals using a split spoon core barrel.
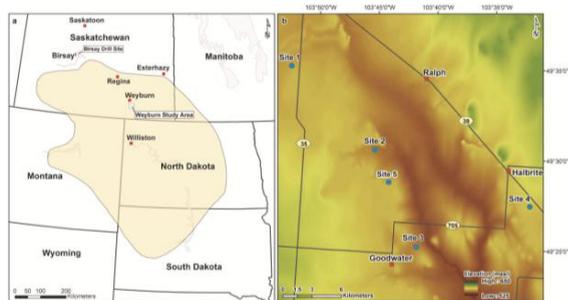

Fig. 1. Location of the (a) Williston Basin and the Weyburn and Birsay Study Areas and (b) topography and drill sites at the Weyburn study area.

One set of trimmed core samples were placed in Isojars (~660 cm^3, hereafter termed jars), flushed with an inert gas (nitrogen or argon) for ~20 s, sealed, and stored in the laboratory at standard temperature and pressure (STP). Based on testing by[3], the samples were stored for > 90 d (Weyburn for 101 d and Birsay for 90 d) prior to CH_4 analyses. In all cases, about 10 cm^3 of gas headspace were collected from each jar using a 60 cm^3 syringe and injected into the septa port of an Agilent 7890 GC equipped with a flame ionization detector. The accuracy of the analytical method was ±5% with a 1.1 ppm limit of quantification. Concentrations of CH_4 measured in the headspace of the core and cutting jar samples (ppmV) were converted to dissolved gas concentrations (mg/L) at *in situ* pressure (sum of atmospheric pressure + gauge pressure) and temperature (from thermistors installed in each core hole or down hole measurements in monitoring wells; data not presented) using the method outlined in[4] and total porosity (n_T) values (based on gravimetric water contents and density measured on each core sample; data not presented). Several authors[3,5] assessed the core-jar technique with respect to physical and biologic activity and concluded that the method can be used to determine dissolved concentrations of CH_4.

The second set of trimmed core samples were placed in medium-sized (1100 mL) Ziploc[TM] polyethylene re-sealable bags with the atmospheric air squeezed out prior to sealing. Each bagged sample was subsequently placed in a large-sized (4600 mL) Ziploc[TM] polyethylene re-sealable bag and the atmospheric air again squeezed out prior to sealing. Porewater samples were squeezed from cores at 5-10 m depth spacing at 50MPa using the method described in[6]. The squeezed porewater samples were analyzed for conservative Cl^- using a Dionex ICS-2100 ion chromatography system (accuracy and precision of ±5% and a method detection limit of 0.5 mg/L).

3. Results & Discussion

The geology at the Weyburn study area consists of a complex series of Quaternary glacial tills (36-77 m thick) containing permeable sand layers overlying thick Cretaceous Pierre Fm shale (590 m thick). The geology encountered during drilling at the Birsay site consists of 80 m of uniform Quaternary glacial till overlying three members of the Cretaceous Bearpaw Fm: Beechy (~40 m thick), Ardkenneth (~42 m thick, an aquifer), and Snakebite (~80 m thick). The top of the Pierre shale at the Birsay Site is at about 320 m BG. The generalized geology at Weyburn Sites 2 and 5 and Birsay site are presented in Fig. 2 and 3.

The naturally occurring conservative Cl^- and CH_4 depth profiles are presented for Weyburn Sites 2 and 5 and Birsay site in Fig. 2 and 3. The Cl^- concentrations at Site 5 exhibit a slight curvilinear (concave down) depth trend from the base of the fractured (higher hydraulic conductivity, K) oxidized zone at the top of the till (4.5 m BG) through the till and underlying Pierre Shale. At Site 2, the Cl^- also exhibit a slight curvilinear (concave down) depth trend that starts near the base of the till (42 m BG), coinciding with the presence of a permeable layer that limits upward diffusion of the Cl^- into the till by flushing it laterally. The Cl^- depth profiles from the other sites exhibit similar increases with depth through the shale.

The source of the Cl^- and shape of its profiles can be attributed to historic, long-term, upward diffusion from deeper basinal sediments[7]. One-dimensional transport modeling of the Cl^--depth profile at Site 2 by[8] confirms that these profiles can be generated by diffusive transport over a time frame of > 1Ma. Low measured K values in the tills and shales at the two study areas are consistent with diffusion-dominated solute transport; the K of unoxidized glacial tills and shales at[9-11] sites are 10^{-12} and $10^{-12\ to}\ 10^{-13}$ m s^{-1}, and 3 x10^{-11} and 10^{-12} m s^{-1}, respectively. A similar near-linear Cl^--depth profile through the Pierre Shale at another site near Esterhazy, Saskatchewan is also attributed to long-term (>1 Ma) near steady-state diffusion[7].

The shape and distribution of the CH_4 depth profiles are very similar to those of Cl^-. These data exhibit a strong linear correlation for both study areas (Weyburn y=0.05x-15.8 R^2=0.90; Birsay y=0.03x-2.8 R^2=0.85; Fig. 4). The strong agreement between the concentrations of conservative Cl^- and the potentially reactive CH_4 suggests the CH_4 acts conservatively throughout much of the till and the shale, a least to the depth of investigation. The source of the CH_4 is from greater depths in the shale, likely the Second White Speckled Shale Formation that underlies the Pierre shale (data not presented). The upper boundary for the CH_4 is not consistent at all sites due to varying hydrogeologic-geochemical conditions. In some cases it is in a permeable zone located at depth in the till (as evidenced by Site 2; Fig. 2) or near the top of the bedrock. In these cases, the strong correlation with the upper boundary for the Cl^- profile suggests groundwater flushing is the dominant control on the upper boundary conditions for the CH_4. In contrast, the upper boundary for the CH_4 profile at Site 5 was 36 m deeper in the till than that for the Cl^- profile (Fig. 2) and 24 m deeper than that for the Cl^- profile near the top of the bedrock at Birsay (Fig. 3). In these cases, the upper boundary was attributed to CH_4 oxidation at greater depths than the upper (lateral flushing) boundary for Cl^-.

4. Conclusions

High-resolution depth profiles of dissolved concentrations of CH_4 can be generated from core samples collected during drilling. These profiles can provide insights into the source, fate and transport of organic gases in aquitard systems. In so doing, these data present baseline conditions for use in fugitive gas migration investigations. The CH_4 profiles can be of greatest value when used in conjunction with a conservative natural tracer such as Cl^- (as shown here), Br^- or stable isotopes of pore water (δ^2H and $\delta^{18}O$)[5,12] or the stable isotopes of CH_4 (δ^2H and $\delta^{13}C$)[8]. The solute data collected from the Ardkenneth aquifer at the Birsay study area suggest this technique should also be applicable to cores collected from aquifers.
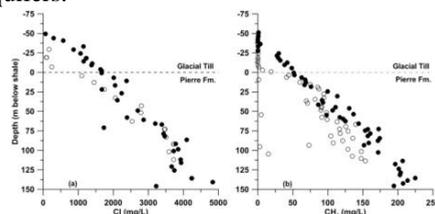

Fig. 2. Geology and dissolved (a) Cl^- and (b) CH_4 concentrations from core samples vs. depth below top of Pierre Shale at Weyburn Sites 2 (open circle) and 5 (closed circle).
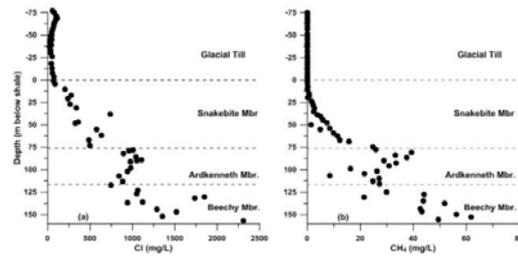
Fig. 3. Geology and dissolved (a) Cl⁻ and (b) CH₄ concentrations from core samples vs. depth below top of Snakebite Shale at the Birsay study area.
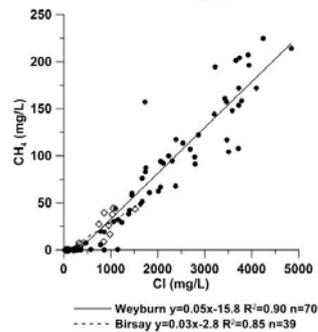

Fig. 4. Cross plot of dissolved Cl⁻ vs. CH₄ from core samples from the Birsay (open diamonds) and Weyburn (solid circles) study areas.

Acknowledgements

References

1. Ryan CM, Roy JW, Deagle DJ. Dissolved gas 'concentration estimates' – A comment on "Origin, distribution and hydrochemical control son methane occurrences in shallow aquifers, southwestern Ontario, Canada" by Jennifer C. McIntosh, Stephen E. Grasby, Stewart m. Hamilton, and Stephen G. Osborn. *Appl. Geochem*. 2015;63:218-221.
2. Wassenaar LI, Hendry MJ. Improved piezometer construction and sampling techniques to determine aquitard porewater Chemistry. *Groundwater* 1999;37(4)564-571.
3. Hendry MJ, Barbour SL, Schmeling EE., Mundle SOC. Measuring Concentrations of Dissolved Methane and Ethane and the ¹³C of Methane in Shale and Till.. *In Submission*.
4. Kampbell DH, Vandegrift SA. Analysis of disolved methane, ethane, and ethylene in ground water by a standard gas chromatographic technique. *J. Chromatogr. Sci*.1998;36(5):253-256.
5. Bangsund A. Characterizing the origin, transport and fate of dissolved gases in glacial till and Cretaceous clay aquitards in West-Central Saskatchewan. Unpublished Master's thesis. University of Saskatchewan, Saskatoon, Canada.
6. Hendry MJ, Barbour SL, Novakowski K, Wassenaar LI. Palaeo-hydrogeology of the Cretaceous sediments of the Williston Basin using stable isotopes of water. *Water Resour. Res*. 2013;49(8):4580-4592, DOI: 10.1002/wrcr.20321
7. Hendry MJ, Harrington G. Comparing vertical profiles of natural tracers in the Williston Basin to estimate the onset of deep aquifer activation. *Water Resour. Res*. 2014;50(8):6496-6506 DOI:10.1002/2014WR015652
8. Hendry MJ, Barbour SL, Schmeling EE, Mundle SOC, Huang M. Fate and Transport of Dissolved Methane and Ethane in Cretaceous Shales of the Williston Basin, Canada. *In Submission*.
9. Smith LA, Barbour SL, Hendry MJ, Novakowski K, van der Kamp G. A Multiscale Approach to Determine Hydraulic Conductivity in Thick Claystone Aquitards Using Field, Laboratory, and Numberical Modeling Methods. *In Submission*
10.Shaw JR, Hendry MJ. Hydrogeology of a thick clay till and Cretaceous clay sequence, Saskatchewan, Canada. *Can. Geotech. J*. 1998;35:1-12.
11. Cey DB, Barbour SL, Hendry MJ. Osmotic flow through a Cretaceous clay in southern Saskatchewan, Canada. *Can. Geotech. J*. 2001;38(5):1025-1033.
12. Hendry MJ, Bangsund A, Schmeling EE, Barbour SL, Mundle SOC, Huang M. Characterizing Origin, Fate and Transport of Methane in Argillaceous Sediments of the Williston Basin, Canada. *In Prep*.