

## ***Interactive comment on “Redox controls on methane formation, migration and fate in shallow aquifers” by P. Humez et al.***

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Review of Humez et al. for HESS

It was a pleasure reading the manuscript by Humez et al. on coupled aqueous and gas chemistry and isotopes of groundwater in shallow aquifers in Alberta to determine processes of methane formation, removal, and migration. The study uses a multi-tracer approach that can/should be used in other study areas to identify controls on the natural and/or anthropogenic occurrence of methane in groundwater. The paper is well-written, the figures are beautiful, and the conclusions are robust. I have a few minor suggestions on improvement prior to publication, mostly grammatical errors and a few statements that need more explanation.

Specific comments:

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Pg 2, Line 21, my last name is misspelled: “McInstosh et al., 2014” should be “McIntosh”.

Pg 2, Line 28, our companion paper to McIntosh et al. (2014), “Hamilton et al. (2015) Hydrogeology Journal” compared water chemistry to methane concentration in groundwater in Ontario, similar to your study. Please include this reference.

Pg 3, Lines 20-23: Methanogenic systems can also have high d13C-CH4 values from closed system CO2-reduction, where most of the CO2 pool has been depleted, and d13C values of CH4 and CO2 become increasingly more positive (up to -50+ per mil in some cases). This is another way that d13C-CH4 values can seem “artificially” high, but still be methanogenic. See Bates et al. (2011) Chemical Geology. I would add a sentence on this here and point out that d13C-CO2 and/or d13C-DIC values can help distinguish these relatively positive d13C-CH4 values from methanogenic vs. thermogenic gas sources.

Pg 7, Line 28, change “adding” to “summing”.

Pg 9, Line 17, “closed” should be “close” to the LMWL.

Pg 10, section 3.6. Did you measure d13C-C2 values? If so, include. This could help identify microbial oxidation of higher chain hydrocarbons, microbial production of ethane, or mixing with thermogenic gas.

Pg 11, Line 6+, we also found the highest methane values in groundwater in Ontario associated with Na-Cl and Na-HCO3 type waters (see McIntosh et al., 2014; Hamilton et al., 2015).

Figure 5: Plot endmembers on the other plots in Figure 5.

Pg 11, Line 14, Needs further explanation. Does your data (e.g. lack of Br??) differentiate between these two sources of Na-rich waters: brines versus cation exchange? Reader is left wondering which of these processes is important here, which can have implications for fluid migration vs. in-situ water-rock reactions.

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Pg 12, Line 9, your results of finding high CH<sub>4</sub> only when [SO<sub>4</sub>]<sub>2</sub><1 mM is consistent with what has been observed in deeper coalbed methane and organic-rich shale microbial gas systems. I would make this link by adding a sentence and reference to that literature. See Schlegel et al. (2011) or other reference.

Pg 13, Line 2, add “CH<sub>4</sub>” to your list of isotopic compositions investigated.

Pg 13, Section 4.3.1. The question mark for group 3 in Figure 8 needs an explanation – i.e. what does the “question mark” represent?

Pg 14, Line 20+, This part needs clarification because you go on to say, and show in Figure 11, that there are some samples with evidence of methane oxidation, whereas you say here that there is no evidence of oxidation. Be more specific here, or simply remove statement and save for later when you discuss the higher d<sup>13</sup>C-CH<sub>4</sub> values.

Pg 15, Line 27, “has not yet been oxidized” – be more specific: e.g. there is no evidence of methane oxidation because the elevated d<sup>13</sup>C-CH<sub>4</sub> values are not associated with low d<sup>13</sup>C-DIC values, as expected for methane oxidation.

Pg 16, Line 8, change “imparting a d<sup>13</sup>C value” to “imparting a relatively high d<sup>13</sup>C value”.

Pg 16, Line 10, “It is also possible that post-sampling degradation of low-methane samples occurred.” Be more specific. What could have happened (physically) and how might that have changed the isotopic values?

Pg 17, Line 23, change “interpretation of gas composition” to “interpretation of natural gas composition.”

Pg 18, Line 3: add an “and” between “d<sup>13</sup>C, dD”.

Pg 18, Line 7, be more specific about this statement. For example, could add text at the end of the sentence: “such as the introduction of deeply-sourced thermogenic gases into shallow aquifers.”

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Figure 3, part b, It's not clear what the "(C(-4)) becomes stable" label represents. Need to explain in the figure caption and/or text.

Figure 11, part b, there wasn't much (if any?) discussion of the  $\delta^2\text{H-CH}_4$  values in the text - add. BTW - I'm no longer using this plot in my own research because I've found that it is misleading; the  $\delta^2\text{D-CH}_4$  values are low in these western, higher latitude regions not because of a shift in metabolic pathway to "methyl type fermentation", but rather because of isotopic exchange between the  $^2\text{H}$  in the  $\text{CH}_4$  and  $\text{H}_2\text{O}$  (shown in several studies now). Recent microbial studies from several coalbed methane and black shale systems show that both  $\text{CO}_2$  reduction and acetoclastic methanogenesis are typically important/present. I have a paper in review on this topic that will hopefully be published soon. In the meantime, see Bates et al. (2011) Chemical Geology for a reference.

Figure 12, part b, need to subscript " $\text{CH}_4$ " in the y-axis label.

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