

## ***Interactive comment on “Biogeochemical constraints on the origin of methane in an alluvial aquifer: evidence for the upward migration of methane from a coal seam” by Charlotte P. Iverach et al.***

**M. Currell (Referee)**

matthew.currell@rmit.edu.au

Received and published: 20 September 2016

Iverach et al. present a novel approach to the determination of methane sources in shallow groundwater in the Condamine Alluvium aquifer, Australia. I think the study is of high scientific significance, for two main reasons:

1. The use of combined geochemical and microbiological indicators to study the origins of methane in groundwater is novel. Studies of this kind are relatively rare in the literature, and the microbiological analysis provide insight about the methane sources and degradation processes that couldn't otherwise be gained from the isotopic analyses

C1

alone 2. The topic and research question(s) are of high importance, given the current debate about environmental impacts of coal seam gas (and other unconventional gas), both in this particular area of Australia, and worldwide. There are some minor issues and corrections needed, and some areas where additional information could be included to make the paper more solid. However, overall I think this is a high quality manuscript.

Specific comments: Abstract Line 33-34: Which data? I like to see some actual data values or description of the particular aspects of the data set of greatest significance (and supporting the conclusions described) included in the abstract. If more space is needed in order to do this, I suggest removing the second sentence of the abstract, as this is background information that can be included in the introduction.

Introduction Line 50: I suggest adding the term 'in situ' when discussing biological production of methane in the shallow groundwater. This makes it clear that you are distinguishing two different potential gas sources- one produced in the shallow aquifer itself, and another whereby gas from another unit has migrated to the aquifer. Line 81: 'Therefore' is not really the best word here. It does not follow logically from the preceding discussion that combining geochemistry/microbiology can discriminate the relevant processes; rather you could say that microbiological indicators have the potential to resolve some of the uncertainties just mentioned (e.g. methanogenesis and methane degradation processes), that can't be otherwise determined on the basis of geochemical data alone. Here you could also note the general absence of published studies which have combined geochemical and microbiological indicators to look at methane sources and degradation in an applied setting (an important point to make in your introduction). Line 103: See previous comment; this could be clarified by adding 'in situ methanogenesis' to distinguish from gas migration from another unit. Line 104-108: I think you should expand this paragraph and include some of the actual data, e.g. the observed ranges and mean/median values of  $\delta^{13}\text{CCH}_4$  and  $\delta^{13}\text{CDIC}$  found in the WCM from other published studies. This can be included in the text (e.g. ranges,

C2

mean values etc), as well as in a table. This would help to strengthen your isotopic lines of evidence to support the hypothesised migration mechanism later in the manuscript. Note that Baublys et al 2015 (Int. J. Coal Geol v.147-8, pp85-104) have also reported extensive data on isotopic composition of gases and water in the WCM, which should be included along with other recent published studies.

Study area Line 146-47: Try to avoid repetition (primary/primarily) Line 151: Suggest adding 'including methane concentrations' at the end of this sentence, to highlight the significance of what you are looking at (mostly the methane in groundwater). 2.1 Hydrogeological setting. Could you include a cross section or at least a stratigraphic column to go with your description of the geological units? Line 160: 'The CRAA sits within the Surat Basin, which is a major sub-province of the Great Artesian Basin'. Perhaps refer to one of the Geoscience Australia and/or CSIRO hydrogeology reports on the GAB (e.g. Ransley and Smerdon, 2012). Line 188: The recent studies by the Office of Groundwater Impact Assessment (OGIA) may have more detail about the connectivity between the CRAA and the WCM and the extent of the aquitard(s), e.g. the Surat Underground water impact report (OGIA, 2016). Line 203: Connectivity for gas? water? both?

Method Line 212: Here you should refer to a figure and/or table which includes your sample depths and locations Line 233-34: Were the physico-chemical parameters (EC, pH, DO) monitored during the second round of sampling? If so, you could report these and use as evidence that the water composition between the two sampling events did not change substantially (if this is true). Line 238-239: What about cations? Line 242-243: Can you refer to a published paper where the same method was used? Same for the DIC isotopes (line 245).

Results & Discussion Line 371: Suggest writing 'in situ within the CRAA' instead of 'locally' to be clearer. Line 377: Do you mean the major ion data? Which particular aspects (e.g. sulfate and nitrate concentration data)? Line 396: Suggest changing to: 'major processes resulting in CH<sub>4</sub> in the CRAA' rather than 'producing CH<sub>4</sub> in the

C3

CRAA' (or you could say 'responsible for the presence of CH<sub>4</sub>'). Line 398: Suggest changing 'coming from' to 'derived from'. Line 406-411: This paragraph is a bit confusing and needs re-writing. Is the gas in the WCM really 'typically thermogenic'? All of the isotopic data for <sup>13</sup>CCH<sub>4</sub> I have seen for gases and water in the WCM indicates a bacterial source of methane (e.g. <sup>13</sup>CCH<sub>4</sub> values around -50permil) rather than thermogenic (which should have values higher than -40permil). Is there anything else distinctive about the samples with more depleted <sup>13</sup>CCH<sub>4</sub>, such as a much lower CH<sub>4</sub> concentrations or differences in the major ions that could explain the isotopic difference? Line 431-432: Yes, and further, the evidence about the presence of sulfate and conditions favouring SRB is a further line of evidence that in situ methanogenesis is unlikely to be responsible for the CH<sub>4</sub> in the shallow aquifer Line 434 - 476: The section on methane oxidation is insightful; good use of the microbiological methods to combine with the isotopic data and yield some new insights. Line 478: Use the full name for AOM in the title. Line 499-500: Relative to what? Other water in the CRAA?

General comment I think including a figure showing your isotopic compositions (<sup>13</sup>CCH<sub>4</sub>) and concentrations of methane, (using the data from Iverach 2015) and comparing with other published data on isotopic characteristics of WCM gases would be helpful, to strengthen the evidence for the proposed hypothesis (together with the microbiological indicators).

Conclusions Line 536: You could also note your other lines of evidence here (e.g., that this is supported by the co-existence of CH<sub>4</sub> with sulfate in the groundwater, and the isotopic composition of the methane). Line 547-548: Your study does not really provide information about the precise pathway(s) by which methane migrates from the WCM to the CRAA, only strong evidence that such migration occurs. Hence, the statement about 'through natural faults and fractures' is really just speculation. Unless you can support it with some geological evidence, other mechanisms may also be responsible (such as transport along wells that are not fully sealed, direct leakage of gas between the units where the aquitard is absent). I suggest either talking about all possible path-

C4

ways (including these), or simply leaving out the discussion of the pathway altogether and sticking to what your data shows.

---

Interactive comment on Biogeosciences Discuss., doi:10.5194/bg-2016-359, 2016.