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Biogeochemical constraints on the origin of methane in an alluvial aquifer: evidence for the upward migration of methane from underlying coal measures.

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Geochemical and microbiological indicators of methane (CH_4) production, oxidation and migration processes in groundwater are important to understand when attributing sources of gas. The processes controlling the natural occurrence of CH_4 in groundwater must be characterised, especially when considering the potential impacts of the global expansion of unconventional gas production on groundwater quality and quantity. We use geochemical and microbiological data, along with measurements of CH_4 isotopic composition (δ^{13}C-CH_4), to determine the processes acting upon CH_4 in a freshwater alluvial aquifer that directly overlies coal measures targeted for unconventional gas production in Australia.

A combination of geochemical and microbiological groundwater samples were collected from private irrigation boreholes. The groundwater was analysed for the major ions, water stable isotopes (δ^2H and δ^{18}O), the isotopic composition of dissolved organic carbon ($\delta^{13}C_{DOC}$) and dissolved inorganic carbon ($\delta^{13}C_{DIC}$). Quantitative real-time PCR was used to determine abundances of bacterial and archaeal 16S rRNA gene targets and functional gene targets in the groundwater.

Measurements of CH_4 indicate that there is biogenic CH_4 in the aquifer, however microbial community analysis indicates that there are no methanogenic archaea in the groundwater. In addition, geochemical data, particularly the isotopes of DIC and, as well as the concentration of SO_4^{2-}, indicate limited potential for methanogenesis *in-situ*. Microbial community analysis also showed that aerobic oxidation of CH_4 is occurring in the alluvial aquifer despite the absence of a microbial pathway to produce the CH_4.

The combination of microbiological and geochemical indicators suggests that the most likely source of CH_4, where it was present in the freshwater aquifer, is the upward migration of CH_4 from the underlying coal measures.