

1 **Assessing Connectivity Between an Overlying Aquifer and a Coal Seam Gas Resource Using**
2 **Methane Isotopes, Dissolved Organic Carbon and Tritium.**

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10 **Coal seam gas (CSG) production can have an impact on groundwater quality and**
11 **quantity in adjacent or overlying aquifers. To assess this impact we need to determine**
12 **the background groundwater chemistry and to map geological pathways of hydraulic**
13 **connectivity between aquifers. In south-east Queensland (Qld), Australia, a globally**
14 **important CSG exploration and production province, we mapped hydraulic**
15 **connectivity between the Walloon Coal Measures (WCM, the target formation for gas**
16 **production) and the overlying Condamine River Alluvial Aquifer (CRAA), using**
17 **groundwater methane (CH₄) concentration and isotopic composition ($\delta^{13}\text{C-CH}_4$),**
18 **groundwater tritium (³H) and dissolved organic carbon (DOC) concentration. A**
19 **continuous mobile CH₄ survey adjacent to CSG developments was used to determine**
20 **the source signature of CH₄ derived from the WCM. Trends in groundwater $\delta^{13}\text{C-CH}_4$**
21 **versus CH₄ concentration, in association with DOC concentration and ³H analysis,**
22 **identify locations where CH₄ in the groundwater of the CRAA most likely originates**
23 **from the WCM. The methodology is widely applicable in unconventional gas**
24 **development regions worldwide for providing an early indicator of geological pathways**
25 **of hydraulic connectivity.**

26

27

28 Unconventional gas production, which is increasingly important to the global energy
29 industry, is the focus of major environmental questions. Debates about the impact of gas
30 production can hinge on claims about CH₄ leaks and emission, but methodologies to
31 fingerprint gas sources are as yet weak. The production of unconventional gas typically
32 requires the joint extraction of very large quantities of groundwater per day, which can affect
33 groundwater levels in neighbouring aquifers.^{1,2} Another environmental concern is the impact
34 of gas migration on shallow groundwater resources.¹⁻⁵ Recent studies around shale gas
35 production sites in the USA report elevated CH₄ in aquifers up to two kilometres away from
36 the production wells.^{6,7} More recent studies have argued that this may not be a result of shale
37 gas production.^{8,9} Although research is largely associated with shale gas developments in the
38 USA¹⁻⁹ similar issues associated with aquifer hydraulic connectivity also accompany CSG
39 developments worldwide. It is clear that a methodology to quantify potential impacts of
40 unconventional gas production needs to be developed, as well as an understanding of existing
41 pathways of hydraulic connectivity, prior to significant gas production.

42 This research tests the hypothesis that CH₄ can be used to map zones and identify
43 pathways of hydraulic connectivity between a gas production site and an adjacent freshwater
44 aquifer. Natural pathways of connectivity may be via faults, fracture networks and permeable
45 sedimentary formations.¹⁰ There are also potential pathways of hydraulic connectivity via
46 abandoned exploration wells and faulty well casings.^{11,12}

47 Previous studies in the USA near shale gas production have made use of stable
48 isotopes to identify sources of CH₄ in shallow groundwater.^{13,14} This study, for the first time,
49 tests the suitability of jointly using $\delta^{13}\text{C-CH}_4$, DOC concentration [DOC] and ³H activity in
50 the groundwater to assess hydraulic connectivity. These three measurements provide
51 considerable insights into pathways of groundwater and gas movement because:

52 - ³H activities provide information on groundwater residence times and recharge pathways,

53 - [DOC] provides a measure of the carbon inputs, either from the river recharge or the
54 upward migration of CH₄ from a coal bed, and

55 - δ¹³C-CH₄ can be used to characterize the potential sources of the CH₄ within an aquifer.

56 The suitability of using ³H, [DOC] and δ¹³C-CH₄ as key parameters for identifying
57 locations where there is hydraulic connectivity between a freshwater aquifer and an
58 underlying unconventional gas reservoir is described in detail below. The methodology is
59 applied to a hydraulic connectivity investigation between the target WCM (on an
60 international scale, a large unconventional gas development) and the overlying CRAA,
61 which supplies water for irrigated agricultural regions, producing a billion dollars worth of
62 commodities. The methodologies presented here are applicable to the many large and
63 geologically similar CSG resources worldwide, including those from the USA, India, China
64 and South Africa,¹⁵ because we measure geochemical parameters that are common to all
65 sedimentary systems.

66

67 **Study Area.**

68 In Australia, CSG exploration and production have expanded rapidly throughout south-east
69 Qld over the last decade (Figure 1).¹⁵ This has generated considerable public concern about
70 the impact on adjacent aquifers used to support irrigated agriculture, stock and domestic
71 water supplies. The proximity of gas extraction to aquifers used for irrigation or domestic
72 water supply is common to many CSG production sites globally. In this study we investigate
73 groundwater from the unconfined CRAA, which has historically supplied 81.4 GL/year of
74 water for irrigated agriculture.¹⁶ This aquifer is located immediately east of the expanding
75 Daandine and Kogan North CSG developments, which began producing in 2006.¹⁷ Currently,
76 in the 50 km from the western boundary of the CRAA, there are around 500 producing wells

77 (Figure 1). The target gas resource for production wells (WCM) starts at approximately 300
78 m below the ground surface.¹⁸

79 There are insufficient baseline CH₄ data of near-surface ambient air and dissolved gas
80 in groundwater within the Condamine Catchment,¹⁹⁻²¹ and our understanding of the extent of
81 hydraulic connectivity between the WCM and the CRAA is limited. Owen *et al.*²⁰ used
82 principal component analysis (PCA) to investigate connectivity using historical geochemical
83 major ion data from 879 wells within the CRAA and adjacent Surat Basin. They concluded
84 “in general, no relationships were observed between CSG groundwater in the WCM and the
85 alluvial groundwater.”²⁰ Major ions migrate between aquifers via advection and there would
86 need to be significant movement of water between formations for geochemical mixing to be
87 apparent. They did not examine [DOC], CH₄ concentration [CH₄] or isotopic composition
88 ($\delta^{13}\text{C-CH}_4$) within the groundwater. Another study in the region, using ³H, dissolved
89 inorganic carbon isotopes ($\delta^{13}\text{C-DIC}$) and Sr isotopes (⁸⁷Sr/⁸⁶Sr) found that there were
90 limitations in using conventional tracers to assess aquifer connectivity.²² The authors
91 concluded that “other innovative tracers need to be tested in order to confirm inter-aquifer
92 interactions in CSG environments”.²²

93

94 **Hydrogeological Setting.** The entire study area sits within the Surat Basin, which is part of
95 the Great Artesian Basin (GAB) in south-east Qld (Figure 1). The units of the GAB,
96 including the WCM, vary locally between semi-confined and confined²³ and the WCM in
97 places immediately underlie the CRAA (Figure 2).²⁴

98 The environment of deposition for the Surat Basin was mainly fluvio-lacustrine
99 during the late Triassic-Jurassic and shallow marine and coastal in the Cretaceous, similar to
100 associated GAB units.²⁵ The middle Jurassic WCM are a low-rank CSG resource in the Surat
101 Basin.²⁵ They consist of very fine- to medium-grained sandstone, siltstone, mudstone and

102 coal, with minor calcareous sandstone, impure limestone and ironstone.²⁶ The coal consists of
103 numerous discontinuous thin lenses separated by sediments of low permeability.²⁷ The WCM
104 are up to 700 m thick, however the thickness of the coal makes up less than 10% of the total
105 thickness of the unit. The WCM dip gently ($\sim 4^\circ$) to the west, consistent with the general trend
106 of the Surat Basin in this region. In the region of study, the WCM is thicker (150 m to 350 m)
107 along the western margin of the CRAA, and thins to approximately 50 m in the east, where it
108 outcrops.²⁶ Also, along the eastern margin of the valley, the CRAA is bounded by the Main
109 Range Volcanics.²⁴ The WCM overly the Eurombah Formation (a conglomeratic sandstone
110 with minor siltstones and mudstone beds) and underlies the Kumbarilla beds (predominantly
111 sandstone, with lesser mudstone, siltstones and conglomerates).²⁶ The unconfined CRAA fills
112 a palaeovalley that was carved through the GAB formations. These reworked eolian and
113 alluvial sediments were deposited throughout the mid-Miocene to the present.^{23,28} The valley-
114 filling sediments, which have a maximum thickness of 134 m near Dalby,^{23,24} consist of
115 gravels and fine- to coarse-grained channel sands interbedded with floodplain clays and, on
116 the margins, colluvial deposits.

117

118 **Sources of Methane.**

119 Within the Condamine Catchment there are many potential sources of CH₄ that could
120 contribute to the measured [CH₄] and $\delta^{13}\text{C-CH}_4$ in the groundwater and air. These include
121 CH₄ from:

- 122 - the upward migration of gas from the WCM,
- 123 - biological activity in the saturated zone beneath rivers and wetlands,
- 124 - biological activity in the saturated zone of the CRAA,
- 125 - biological activity in the vadose zone (CH₄ sink),
- 126 - biological activity within the borehole, and

127 - anthropogenic inputs into the atmosphere.

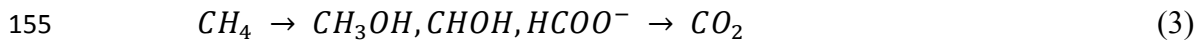
128 Each of the above CH₄ sources potentially has a unique δ¹³C-CH₄ signature.²⁹ Coal
129 commonly has a portion of the CH₄ derived from thermogenic origins and therefore contains
130 more ¹³C, resulting in a less negative δ¹³C-CH₄ signature. In contrast, all the listed biological
131 sources of CH₄ will be depleted in ¹³C relative to thermogenic sources and atmospheric
132 background, resulting in a more negative δ¹³C-CH₄ signature.^{11,30} However, there can be
133 complications in interpreting the isotopes, as various processes can alter the concentration or
134 isotopic composition of the gas. Oxidation of CH₄ in the vadose zone and atmosphere,³¹
135 groundwater flow fractionation within boreholes,³² and the mixing of various sources of
136 CH₄³³ can alter the isotopic signature. Therefore, improved knowledge of the sources of CH₄
137 is required if we are to attribute measured changes in concentration in the groundwater and
138 air to the appropriate sources.

139 Biological activity in saturated zones produces CH₄ as a result of methanogenesis.
140 This can occur via either acetate fermentation or reduction of carbon dioxide (CO₂) (equation
141 (1) and (2) respectively):³¹



144 Anaerobic oxidation of CH₄ (AOM), via reduction of sulphate (SO₄²⁻) or denitrification of
145 nitrate (NO₃⁻) may also occur in the saturated zone.³⁴⁻³⁶ One of the conditions required for
146 AOM is elevated concentrations of SO₄²⁻ or NO₃⁻ in the groundwater. Therefore, testing the
147 groundwater for SO₄²⁻ or NO₃⁻ can give an indication as to the potential for AOM to occur.
148 Microbes in the deep aquifer are also responsible for AOM.³⁷ However, no member of the
149 methanotrophic Euryarchaeota group responsible for anaerobic oxidation has been cultured
150 yet and the various pathways by which AOM occurs are still largely unknown.³⁷

151 Biological activity within the vadose zone yields a net consumption (oxidation) of
152 CH₄. Oxidation of CH₄ results in an enrichment of ¹³C, as the methanotrophs preferentially
153 consume ¹²C.³¹ This process can go through different reaction intermediates before
154 producing CO₂ (equation (3)):³¹



156 Methanotrophic processes can mask the full extent of the upward migration of CH₄ because
157 they deplete the concentration of CH₄ in the subsurface. Oxidation processes in the near
158 surface can also alter the source isotopic signature via fractionation. This allows us to detect
159 methanotrophic activity in a ¹²C rich environment, such as the vadose zone, because the
160 isotopic signature of CH₄ will be depleted in ¹²C. This is evident in the results presented
161 below.

162 Within the WCM most of the CH₄ is adsorbed to the coal, however a small portion
163 can exist in a free state.¹⁵ Methane in its free state is buoyant, and over time may migrate
164 upwards. Since the 1960s groundwater levels within the CRAA have declined²⁴ by 25 m and
165 this may have enhanced the upwards migration of CH₄. The reduction in weight immediately
166 overlying the WCM has the potential to unload the coal interval, releasing a portion of the
167 free state CH₄. This CH₄ will have an isotopic signature that is different from near-surface
168 microbiologically produced CH₄.

169

170 **Using Isotopes of Carbon and Hydrogen to Attribute the Source of Methane.**

171 To assess the potential of CH₄ as a marker for hydraulic connectivity, we measured [CH₄]
172 and δ¹³C-CH₄ in both the groundwater and air of the Condamine Catchment. The [DOC] was
173 measured in each irrigation borehole to investigate pathways of groundwater flow. Tritium
174 activity was measured in the groundwater to provide insights about groundwater residence
175 times, recharge processes and potential groundwater mixing. Anions (SO₄²⁻ and NO₃⁻) were

176 also measured to provide insights into anaerobic processes deep in the aquifer and $\delta^{13}\text{C}$ of
177 dissolved inorganic carbon ($\delta^{13}\text{C}\text{-DIC}$) was measured to give insights into the source of the
178 inorganic carbon in the groundwater.

179 Atmospheric background concentrations of CH_4 change with latitude due to changing
180 sources and sinks.³⁸ The background concentration of CH_4 at the Cape Grim Baseline Air
181 Pollution Station in Tasmania, Australia (40.683°S), was 1.754 ± 0.002 ppm in 2013.³⁹
182 Continuous measurements from the Commonwealth Scientific and Industrial Research
183 Organisation (CSIRO) and Geoscience Australia station at Arcturus, central Queensland
184 (24.027°S) currently range between 1.750 ppm and 1.770 ppm.⁴⁰ The isotopic signature value
185 ($\delta^{13}\text{C}\text{-CH}_4$) commonly reported for ambient background air is -47‰.⁴¹

186 Accepted threshold values and isotopic ranges allow us to attribute a source from the
187 measured $\delta^{13}\text{C}\text{-CH}_4$ obtained for each source of CH_4 encountered throughout the region.⁴¹
188 Australian CSG has a $\delta^{13}\text{C}\text{-CH}_4$ value of less than -60‰ for biologically sourced gas
189 (biogenic CH_4) and greater than -50‰ for gas sourced from coal at depth (thermogenic
190 CH_4).⁴² The intermediate zone is classified as being of mixed source. Previous studies have
191 measured the CH_4 from the WCM using core samples from gas wells. The $\delta^{13}\text{C}\text{-CH}_4$ readings
192 for these cored samples ranged from -58.5‰ to -45.3‰,^{25, 43, 44} which indicates that the gas
193 within the WCM is secondary biogenic in origin, with a minor thermogenic component.²⁵

194

195 **Results and Discussion**

196 **Background ambient air.** We established the background [CH_4] and isotopic signature of air
197 in rural New South Wales (NSW) and Qld by collecting 8 ambient air samples in areas of
198 native vegetation and dryland farming between Narrabri (NSW) and Dalby (Qld). The
199 average background [CH_4] was 1.774 ± 0.002 ppm and the isotopic signature was $-47.0 \pm$
200 0.05 ‰ (n = 8; Supplementary Table S3 online). These values are slightly higher than those

201 reported for the Cape Grim Baseline Air Pollution Station in Tasmania, and at Arcturus in
202 central Qld.^{39,40}

203

204 **Co-produced water storage reservoir.** We were unable to measure [CH₄] directly from
205 CSG well-heads; however, at each production well large quantities of water are co-produced.
206 This water is stripped of most of the CH₄ and then stored in large holding reservoirs. We
207 were able to indirectly measure the gas from the WCM by analysing the emissions from one
208 such reservoir with dimensions 800 m by 500 m. To determine the signature of the gas being
209 produced from the WCM we surveyed immediately adjacent to and downwind (east) of the
210 reservoir (Figure 3a). At the closest point the measurements were within 50 m of the
211 reservoir. We detected an area of elevated [CH₄] that had a peak of 2.107 ppm and a width of
212 2.3 km.

213 The [CH₄] measured during the near-reservoir traverses are plotted in Figure 3b. Each
214 coloured curtain represents a single survey run in the vehicle. For each run, there are slight
215 differences in the recorded [CH₄] at the same location. We attribute this to the varied mixing
216 processes associated with the fluctuating winds (both direction and speed).

217 The isotopic composition of a mixed air sample, which consists of a point source
218 ($\delta^{13}\text{C-CH}_4$ (s); [CH₄ (s)]) added to background air ($\delta^{13}\text{C-CH}_4$ (b); [CH₄ (b)]), is determined
219 from:⁴⁵⁻⁴⁷

220

$$221 \quad \delta^{13}\text{C}_{\text{CH}_4(a)} = [\text{CH}_4(b)](\delta^{13}\text{C}_{\text{CH}_4(b)} - \delta^{13}\text{C}_{\text{CH}_4(s)}) \left(\frac{1}{[\text{CH}_4(a)]} \right) + \delta^{13}\text{C}_{\text{CH}_4(s)}, \quad (4)$$

222

223 where $\delta^{13}\text{C-CH}_4$ (a) and [CH₄ (a)] are the isotopic value and concentration measured in the
224 ambient air sample, respectively.

225 For $\delta^{13}\text{C-CH}_4(\text{b})$ and $[\text{CH}_4(\text{b})]$ we used the average of the air samples collected in areas
226 of natural vegetation for the background values ($\delta^{13}\text{C-CH}_4(\text{b}) = -47.0\text{‰}$; $[\text{CH}_4(\text{b})] = 1.774$
227 ppm). The isotopic signature of the off-gassing co-produced water reservoir was then
228 determined by fitting equation (4) to the data using the nonlinear model fitting function in
229 Mathematica⁴⁸ (Figure 4; Supplementary Table S6 online). To determine the source $\delta^{13}\text{C-}$
230 CH_4 value for the WCM three air samples collected along line A-B (Figure 3), when the wind
231 was blowing from the west directly across the reservoir, were combined with two other
232 samples downwind of the CSG region. Figure 4 shows the mixing model (equation (4)) line
233 of best fit for the combined samples. This yielded a value of -50.8‰ (90% CI, -55.7‰ to -
234 45.8‰) for $\delta^{13}\text{C-CH}_4(\text{s})$. The isotopic signature of the CH_4 off-gassing from the reservoir
235 indicates that the gas has mixed thermogenic/biogenic origin. The broad confidence interval
236 (-55.7‰ to -45.8‰) is due to a combination of the sample size and measurement error. These
237 90% confidence interval bounds sit within the $\delta^{13}\text{C-CH}_4$ range reported for the WCM.⁴³ We
238 therefore use the isotopic signature of -50.8‰ as our reference value for the WCM. In the
239 discussion below we use this isotopic signature for the WCM as part of attributing the source
240 of CH_4 within the aquifers.

241

242 **The irrigation district.** The irrigation district, to the south of Dalby and the east of Cecil
243 Plains, has a zone of CH_4 production along the Condamine River, with $[\text{CH}_4]$ peaks as high
244 as 1.930 ppm. However, most of the region is undergoing methanotrophic processes,
245 resulting in a slight decrease in $[\text{CH}_4]$ in the irrigation district. In and around the irrigation
246 district, the continuous CH_4 survey (Figure 1) recorded low $[\text{CH}_4]$ values, with the lowest
247 concentration measured being 1.764 ppm. The average $[\text{CH}_4]$ recorded in the continuous
248 survey throughout the district was 1.771 ± 0.007 ppm ($n = 8954$), slightly lower than the
249 regional atmospheric background ($\delta^{13}\text{C-CH}_4(\text{b}) = -47.0\text{‰}$; $[\text{CH}_4(\text{b})] = 1.774$ ppm).

250 We were able to further examine the processes occurring in the unsaturated and
251 saturated zones of the aquifer by analysing the [CH₄] and isotopic signatures within irrigation
252 boreholes in the region.

253

254 **Irrigation boreholes.** The second data set focused on the groundwater and gas within private
255 irrigation boreholes, details of which are provided in Supplementary Table S4 online.

256 Our $\delta^{13}\text{C-DIC}$ and $\delta^{13}\text{C-CH}_4$ measurements from all irrigation boreholes display no
257 correlation ($R^2 = 0.04$), with the values falling outside of the methanogenesis or sulfate
258 reduction zones⁷ (Figure 5; Supplementary Table S5 online). The DIC in this groundwater is
259 in part from the dissolution of regolith carbonates formed in the vertosols. These calcareous
260 soils are often distributed close to areas with Ca-rich bedrock, such as limestone and basalts,
261 such as the Main Range Volcanics in the study area.⁴⁹ Therefore the lack of a correlation
262 between $\delta^{13}\text{C-DIC}$ and $\delta^{13}\text{C-CH}_4$ implies that the CH₄ is from a different source. In other
263 studies microbial CH₄ from shallow depths has a strong positive correlation between $\delta^{13}\text{C-}$
264 DIC and $\delta^{13}\text{C-CH}_4$.⁷ Results obtained for $\delta^{13}\text{C-DIC}$ are 18‰ to 22‰ lighter (more negative)
265 than values expected for DIC sourced from microbial CH₄ in shallow groundwater.

266 In this study we use the absence of ³H and [DOC] above the detection limit to provide
267 insights into hydraulic connectivity because this combination implies that, in the old
268 groundwater (> 70 years), there is another source of [DOC]. Recorded ³H activities in the
269 groundwater from irrigation boreholes were generally higher in the Condamine River
270 corridor, and lower compared to modern rainfall values in the central portion and east of the
271 catchment.

272 To interpret the CH₄ measurements from the boreholes we plotted $\delta^{13}\text{C-CH}_4$ versus $1/[\text{CH}_4]$
273 [Figure 6; Supplementary Table S5 online (Figure 6b highlights the cluster of irrigation
274 borehole samples around 0.55 ppm⁻¹ in Figure 6a.)). Two distinct distributions of points are

275 shown in Figure 6. These relate to the measured activity of ^3H , $[\text{DOC}] > 0.1 \text{ mg/L}$, $[\text{CH}_4]$ and
276 $\delta^{13}\text{C-CH}_4$. We assigned samples to subsets for fitting equation (4) to the data (allowing the
277 background values to float) based on the presence or absence of ^3H activity and $[\text{DOC}]$. Only
278 samples 9, 16, 17 and 19 have ^3H activity below the quantification limit and $[\text{DOC}]$ above the
279 detection limit, and these samples were assigned to subset A. The remaining samples have a
280 mixture of ^3H activities and detectable $[\text{DOC}]$ values, and were assigned to subset B.

281 Under the assumption that there are only two end members, an estimate of their
282 isotopic signatures can be obtained from a least squares regression fit of equation (4). Subset
283 A has a y -axis intercept for the regression line of -55.9‰ (90% CI, -58.3‰ to -53.4‰). This
284 is the source signature of the CH_4 in these boreholes. The isotopic value falls within the range
285 reported for gas from the WCM and is also similar to our recorded value for the WCM from
286 the co-produced water reservoir. The other end member indicated from the line of best fit has
287 a value of -40.7‰ (90% CI, -40.75‰ to -40.74‰), which is consistent with mixing from an
288 oxidised source (for example the vadose zone). The absence of ^3H activity in the subset A
289 samples indicates that recharge from the river corridor takes > 70 years to reach these
290 locations. The elevated $[\text{DOC}]$ in subset A cannot be attributed to recharge. This is because in
291 the time that it takes for the recharge to reach these boreholes (> 70 years), it is reasonable to
292 assume that biological processes would have already consumed the available DOC. Therefore
293 another source is supplying the detected DOC. Upwards migration of CH_4 from the WCM
294 would be the most likely source.

295 Subset A boreholes all had elevated concentrations of DO; including the highest three
296 values recorded in our study (Supplementary Table S5 online). Microbial activity would
297 consume this oxygen.⁵⁰ We therefore infer that there is minimal biological activity occurring
298 at depth within the aquifer at these locations. In addition, the SO_4^{2-} and NO_3^- concentrations
299 in the groundwater across the irrigation boreholes were too low to support AOM

300 (Supplementary Table S5 online). Anaerobic oxidation requires one of these pathways to
301 occur and therefore it is reasonable to assume that oxidation deep within the aquifer is
302 minimal.

303 In summary for subset A, the absence of ^3H activity in irrigation boreholes with
304 detectable [DOC], in association with the isotopic value of the regression line within the
305 range of the WCM, suggests local connectivity between the CRAA and the WCM in these
306 areas. The detected CH_4 is attributed to the upward migration of gas from the WCM.

307 Subset B has a y -axis intercept for the regression line of -69.1‰ (90% CI, -73.2‰ to $-$
308 65.0‰), which indicates a biological source. The regression line indicates a second end
309 member with an isotopic signature of -29.3‰ (90% CI, -29.33‰ to -29.32‰), which
310 represents mixing with a highly oxidised background (the vadose zone). All samples located
311 in a cluster at 0.55 ppm^{-1} have [DOC] below the detection limit, with the exception of
312 irrigation borehole 8, despite many of these irrigation boreholes being near the river.
313 However, the ^3H activity indicates that samples 3, 5, 8, and 18 are all sourcing water less than
314 70 years old, which indicates that these irrigation boreholes are extracting water influenced
315 by near surface processes. Samples 1, 2, 4, 6, 7, 10, 11, 12, and 14 have no recorded ^3H
316 activity and the [DOC] is below the detection threshold. This indicates that these samples are
317 accessing water > 70 years old and the DOC has already been utilised by biological
318 processes.

319 We attribute the source signature of these samples to biological activity within and
320 near the irrigation boreholes. The low [DOC] and DO measurements in the presence of
321 biologically produced CH_4 is possibly due to microbiological activity after recharge
322 consuming both the DOC and DO. This biological activity would have produced CH_4 as a by-
323 product, and this source of CH_4 dominates the isotopic signature measured in the
324 groundwater at these locations.⁵⁰

325 Measuring $\delta^{13}\text{C}-\text{CH}_4$ and $[\text{CH}_4]$ is not enough to assign source, there is also a need to
326 measure both the ^3H activity and DOC, which is highlighted by samples 5 and 17. Samples 5
327 and 17 both had $[\text{DOC}]$ above the detection limit, however sample 17 had no recorded ^3H
328 activity, whereas sample 5 did. Sample 13 had no detectable $[\text{DOC}]$ and no ^3H activity
329 measured in the groundwater. We propose that biological processes have consumed the DOC.
330 Sample 5 groundwater has been affected by near surface biological activity, whilst sample 17
331 shows evidence of upward migration of CH_4 from the WCM. The difference in these three
332 samples despite their isotopic similarities highlights the need for this combination of
333 measurements in attributing source. The combined method presented here is more robust than
334 the individual measurements because $\delta^{13}\text{C}-\text{CH}_4$ is difficult to interpret individually in
335 environments where both thermogenic and biogenic methanogenesis is occurring along with
336 methanotrophy.

337 **Evidence for aquifer connectivity.** At our case study site in the Condamine Catchment, the
338 isotopic value of -55.9‰ from the irrigation boreholes with detectable $[\text{DOC}]$ is not as ^{13}C
339 enriched in CH_4 as expected from a classical thermogenic source, due to biological processes
340 occurring *in situ*. However, it falls within the range of the isotopic signature from the WCM
341 and is significantly more enriched in ^{13}C than the samples from irrigation boreholes with
342 $[\text{DOC}]$ below the detection limit. Irrigation borehole samples with no ^3H activity and
343 detectable $[\text{DOC}]$ all sat on the isotopic regression line that fell within the range of values
344 reported for the WCM (-58.5‰ to -45.3‰).^{25, 43, 44} The value of this regression had a 5.1‰
345 difference from our own isotopic signature from the co-produced water reservoir. Thus the
346 isotopic signature from off-gassing air samples collected from irrigation boreholes 9, 16, 17
347 and 19 (refer Figure 6), the plume from the co-produced water reservoir, and the literature
348 reported values for gas extracted from coal core samples all sit within the mixed

349 thermogenic/biologic range. This is a strong indicator that the CH₄ sampled from irrigation
350 boreholes 9, 16, 17 and 19 is from the underlying WCM.

351 This research has demonstrated that three conditions need to be present to infer that
352 pathways of geological hydraulic connectivity exist in areas of CSG development. The δ¹³C-
353 CH₄ versus inverse [CH₄] data must plot on a mixing plot regression line with a y-axis
354 intercept value indicative of thermogenic to mixed thermogenic/biogenic gas. However, at
355 high concentrations (low 1/[CH₄]) it is difficult to assign samples to a specific source-
356 determining regression line. Detectable [DOC] can indicate either river corridor recharge or
357 gas migration upwards from depth. Further information about the probable origin of the CH₄
358 and DOC is provided by the ³H activity. Detectable [DOC] along with ³H activity above the
359 quantification limit indicates relatively young water and near-surface biologically sourced
360 CH₄. Conversely, [DOC] above the detection limit and ³H activity below the quantification
361 limit strongly suggests CH₄ dominated by the upward migration of gas from the WCM. Our
362 results show that measurements of the isotopic composition of CH₄, [DOC] and ³H activity in
363 the groundwater and CH₄ in the air can be used as an initial assessment of pathways of
364 geological hydraulic connectivity where an alluvial aquifer overlies coal measures targeted
365 for CSG production.

366

367 **Methods**

368 From 20 January 2014 to 1 February 2014 we collected CH₄ samples from 19 irrigation boreholes. The
369 irrigation boreholes had a gas outlet, which allowed us to pump the gas directly into 3 L Tedlar bags using an
370 SKC 222-2301 battery-operated air pump. This gas was being stripped from the groundwater within the
371 borehole and is representative of the gas within the groundwater. The groundwater was extracted from 35.4 m to
372 199.9 m within the aquifer. The depth to the water table ranged from 5 to 20 m.⁵¹ No purging of these boreholes
373 was required, as the pumps had been running for 2-3 months.

374 We also sampled groundwater from all 19 irrigation boreholes in the same period. A sampling tube was
375 installed 2 m inside the pump outlet to minimise air/water interactions. Physio-chemical parameters (pH, Eh,

376 temperature, electrical conductivity and dissolved oxygen (DO)) were checked for stability prior to sampling,
377 with all samples fully stable within minutes.

378 Sample collection involved an in-line, 0.45 μm , high-volume filter, which was connected to the pump
379 outlet. Samples for $\delta^{13}\text{C}$ -DIC and [DOC] were further filtered through a 0.22 μm membrane and collected in 12
380 mL glass vials (Exetainers) and 60 mL high-density polyethylene (HDPE) bottles, respectively. Samples for
381 $\delta^{13}\text{C}$ -DIC were refrigerated at 4° C and [DOC] samples were frozen within 12 hours of collection until they were
382 analysed. Samples for ^3H analysis were collected in 2 L HDPE bottles. Samples for the SO_4^{2-} and NO_3^- analyses
383 were collected in 125 mL HDPE bottles with no further treatment.

384 A mobile CH_4 survey was conducted from 12 March 2014 to 18 March 2014 (Figure 1). The route
385 covered the irrigation district and CSG developments around Dalby and Cecil Plains to the south, and the
386 location of the irrigation boreholes sampled in January. We sampled the air through Teflon tubing connected to
387 an inlet mounted on top of the vehicle (2.2 m above ground level). This air was passed directly into a Picarro
388 G2301 Cavity Ring-Down Spectrometer (CRDS) (Picarro, Inc., Santa Clara, CA), which measured the [CH_4]
389 every 5 seconds as we drove along the road at 40 km/h. The precision of the Picarro G2301 is < 0.001 ppm over
390 5 seconds. Simultaneously, GPS location was measured using a Hemisphere GPS (model A21), whilst wind
391 speed and direction data were measured with an S2 Climatronics 2D sonic anemometer, which was also attached
392 to the top of the vehicle. The setup is a modification of methods previously used to determine gas leakage
393 around Boston, USA.⁵²

394 Where we discovered an interval of elevated [CH_4] individual samples of ambient air were pumped
395 into 3 L Tedlar bags using a KNF NMP 830 KNDC B Micro Diaphragm Gas Pump. The vehicle was stationary
396 and the engine switched off when we pumped air into the Tedlar bags for later analysis in the laboratory (see
397 Supplementary Information online).

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545 **Author contributions**

546 Experimental conceptualisation and design was carried out by D.I.C., E.G.N. & B.F.J.K. Fieldwork was
547 conducted by C.P.I., D.I.C., S.I.H., R.E.F., D.L., J.L.F. & B.F.J.K. Geochemical analyses were conducted by
548 D.I.C. & S.I.H. Funding for the work was won by B.F.J.K., D.I.C., A.B. & E.G.N. The manuscript was written
549 by C.P.I. & B.F.J.K with input from all authors.

550 **Competing financial interests**

551 The authors declare no competing financial interests.

552 **List of Figures**

553 **Figure 1.** Site map showing the extent of the region investigated within the Condamine
554 Catchment, south-east Queensland. The shaded polygon delineates the extent of the irrigation
555 district.⁵³ The location of the CSG production and exploration wells are shown as blue⁵⁴
556 circles and the sampled irrigation bores are shown as white circles. The red line highlights the
557 continuous mobile CH₄ survey route around the irrigation district. The black square shows
558 the map area in Figure 3a (Map created in QGIS; data and imagery: MapQuest, Open Street
559 Map and contributors, CC-BY-SA.⁵⁵ Modified with Corel Painter 2015.⁵⁶).

560 **Figure 2.** Geological cross section along A-A' in Figure 1 (adapted from KCB Final
561 Report²⁶).

562 **Figure 3.** (a) A map of CSG developments and co-produced water storage reservoirs. The
563 blue rectangles represent the location of the water storage reservoirs and the red line indicates
564 the route of the mobile survey. The A-B represents the mobile CH₄ measurement traverse
565 lines, where Tedlar bag samples were collected downwind of the co-produced water reservoir
566 to establish the isotopic composition of CH₄ extracted from the WCM (Map created in QGIS;
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568 with Corel Painter 2015.⁵⁶). (b) CH₄ concentration measured along the line A-B in the plume
569 downwind of the co-produced water storage reservoir. The horizontal red line indicates the
570 background CH₄ concentration of 1.774 ppm.

571 **Figure 4.** Co-produced water reservoir downwind plume mixing plot. Background air is
572 shown as a red dot, and the downwind plume samples are the black dots. The blue line is the
573 line of best fit for the mixing model (equation (4)) and the 90% confidence interval bands are
574 shown in orange. Source intercept determined for the mixing model is -50.8‰ (90% CI, -
575 55.7‰ to -45.8‰).

576 **Figure 5.** $\delta^{13}\text{C}$ -DIC against $\delta^{13}\text{C}$ -CH₄ showing no correlation ($R^2 = 0.04$).

577 **Figure 6.** (a) A combined mixing plot for the irrigation bores. The regression lines represent
578 either the bores with detectable [DOC] (intercept: -55.9‰ (90% CI, -58.3‰ to -53.4‰)) or
579 the bores with no detectable [DOC] (intercept: -69.1‰ (90% CI, -73.2‰ to -65.0‰)).
580 Tritium activity is indicated by the marker color. All boreholes with no ³H activity and
581 detectable [DOC] sit on the regression line with intercept of -55.9‰, indicating gas from the
582 WCM. (b) The cluster of bores around 0.55 ppm⁻¹ highlights a mixing of parameters at the
583 intercept of the regression lines. This indicates that the absence of ³H activity can be used to
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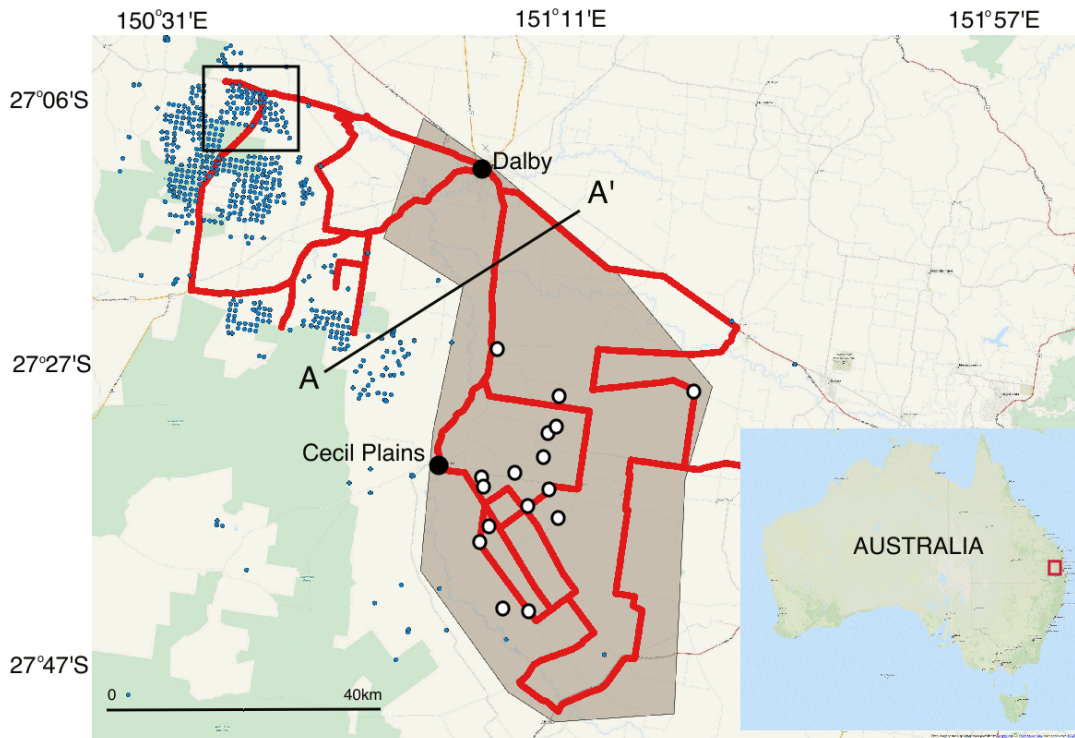


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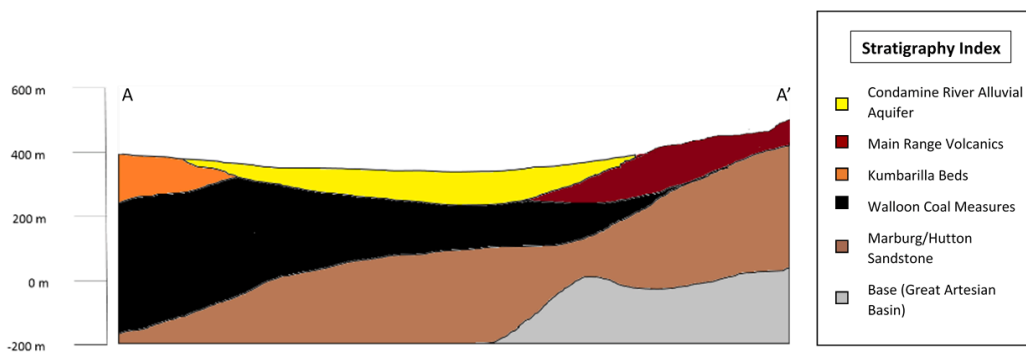


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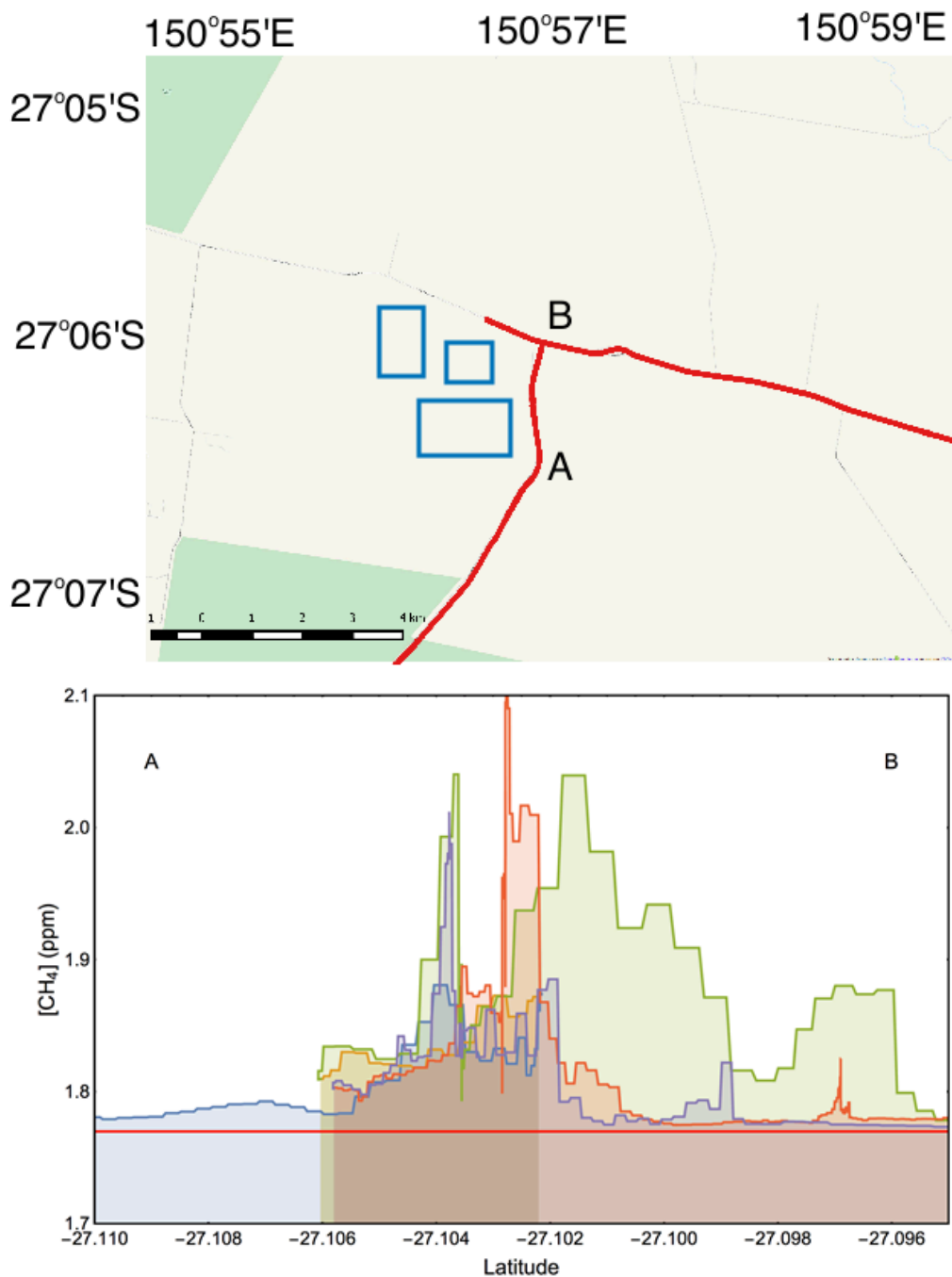


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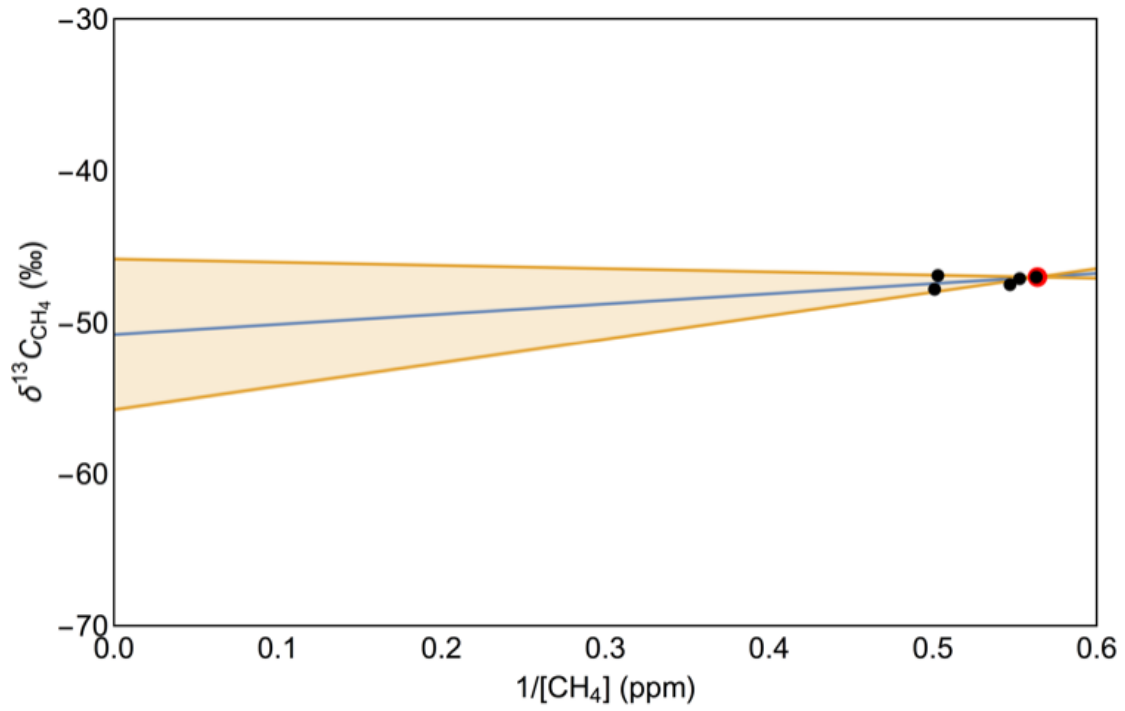


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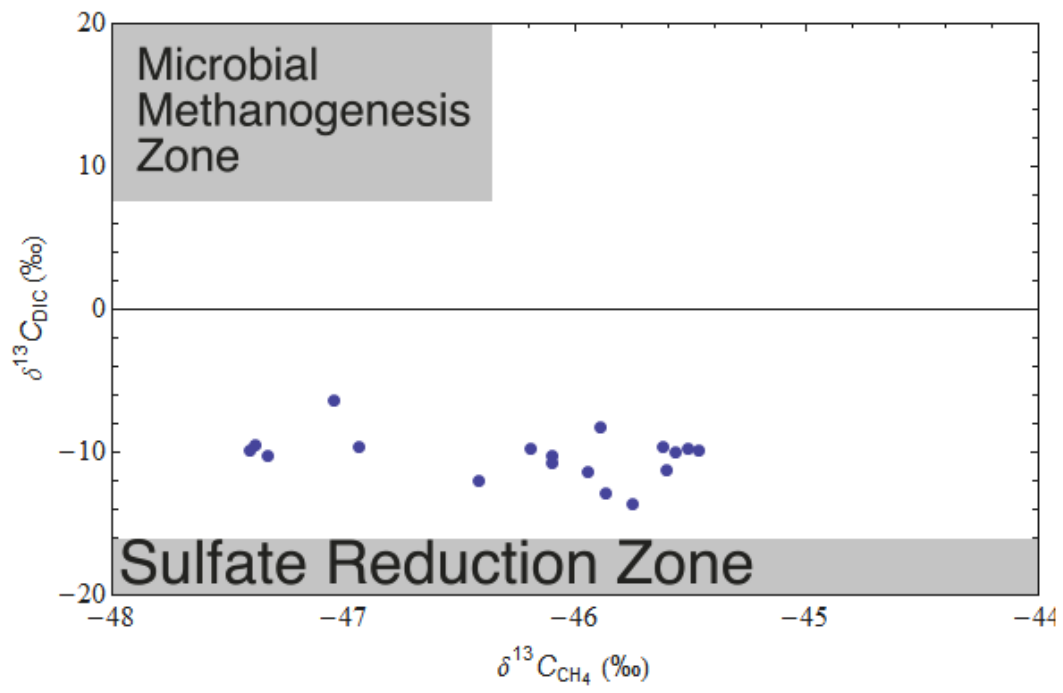


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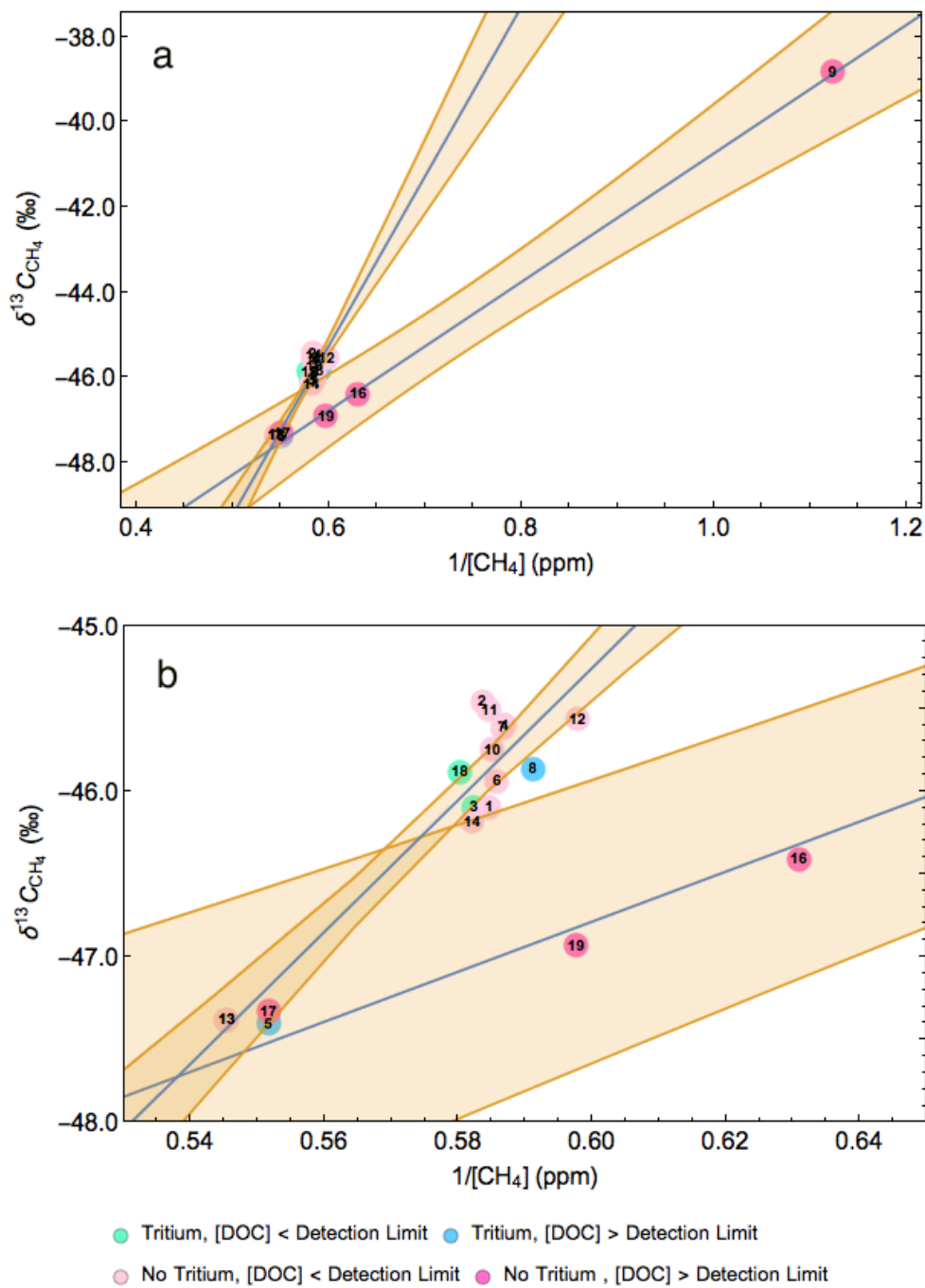


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