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## FINGERPRINTING OF GAS CONTAMINATING GROUNDWATER AND SOIL IN A PETROLIFEROUS REGION, ALBERTA, CANADA

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### 1 INTRODUCTION

The impact on groundwater quality by petroleum development is increasingly becoming a societal concern. Recently, Osborn et al.<sup>1</sup> received significant press coverage with their report of methane contamination of drinking water from drilling and hydraulic fracturing associated with shale-gas extraction in the states of Pennsylvania and New York in the USA. They suggested two possible sources for increased methane concentrations observed in groundwater near gas wells: (1) methane moving laterally and vertically through the fracture system at hundreds of meters underground to leaky well casings; or (2), upward migration of methane above the target shale formation through a fracture system with increased connectivity that was generated by the process of hydraulic fracturing. They found isotopic values of dissolved methane in shallow groundwater and ratios of methane to higher chain hydrocarbons that were consistent with deeper thermogenic methane sources but they did not attempt to pinpoint the specific source depth of the gas. They concluded that “long-term coordinated sampling and monitoring of industry and private homeowners is needed”<sup>1</sup>.

In the Western Canada Sedimentary Basin (WCSB), sixty years of petroleum development has resulted in over 500,000 petroleum wells being drilled, many in agricultural areas that rely on groundwater as a source of drinking water. Relatively new CBM development (Figure 1) overlies intensive exploitation of the deeper conventional oil and gas fields. The news media has carried many water quality complaints by landowners, including incidents where tap water can be ignited. As of May 2006, the government of Alberta requires testing of every domestic water well within 600m of a proposed shallow CBM well, for both water quality and gas content. In addition, water gas from at least one well per location that contains free methane must be submitted to the laboratory for isotopic analysis.

Methane in an aquifer can come from microbial sources such as reduction of CO<sub>2</sub> or by fermentation, but can also be thermogenic gas which has migrated from oil, gas or CBM wells. Microbial methane is very low in <sup>13</sup>C ( $\delta^{13}\text{C}$  more negative than -55 per mil) and associated CO<sub>2</sub> may be high in <sup>13</sup>C. Microbes do not add ethane, propane and butane to aquifers. Thermogenic gas in aquifers has the isotope fingerprint of its source, perhaps modified by oxidation. Unless very mature or highly biodegraded, thermogenic gas will have measurable quantities of methane, and also ethane, propane and butane. Gas in an aquifer may be a mixture of local microbial gas and a migrating gas from a

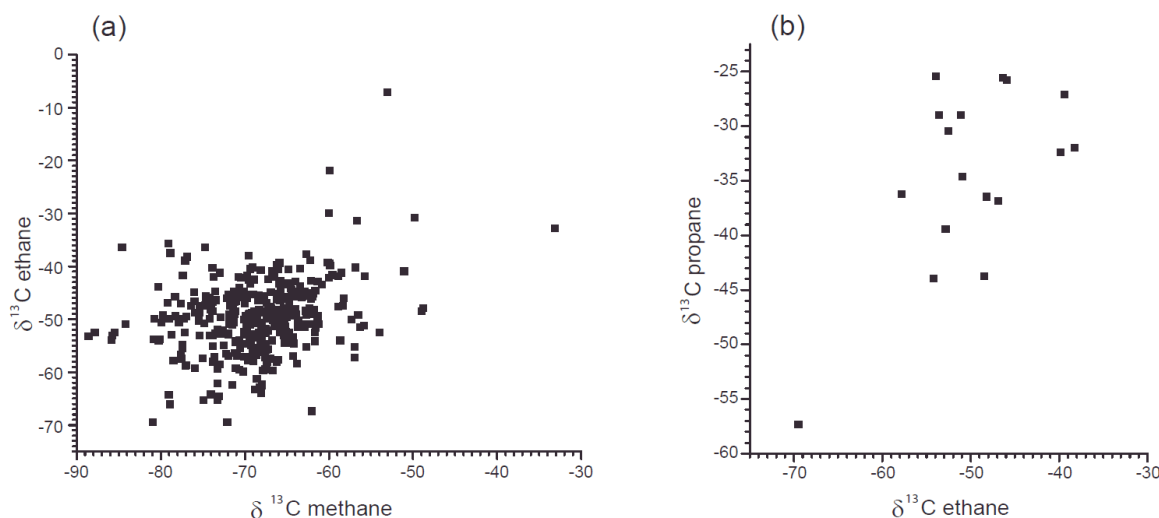


**Figure 1** Map of Alberta showing the locations of the Wildmere heavy oil field and the locations of the other three case studies presented here (white dots). The light grey shading indicates the distribution of coal zones with CBM potential<sup>2</sup> and the darker grey shading shows the locations of Alberta oil sands/heavy oil deposits.

nearby oil or gas well. The isotopic composition of the contaminated aquifer gas will depend on the proportions of mixing, as well as both the chemical and isotopic compositions of the two end-members. Such mixing can be modelled by mass balance.<sup>3</sup>

Figures 2a and 2b are isotope cross plots of  $\delta^{13}\text{C}_1$  versus  $\delta^{13}\text{C}_2$  and  $\delta^{13}\text{C}_2$  versus  $\delta^{13}\text{C}_3$  for gas from domestic water wells, sampled as part of the CBM Alberta government mandated testing program. The majority of methane falls within the range for biogenic gas or shallow thermogenic gas, but there are a few samples where  $\delta^{13}\text{C}$  methane is heavier than -55 per mil suggesting contamination from a deeper thermogenic gas. Gases plotted in Figure 2b all contain ethane and propane, which suggests that these gases are not purely of biogenic origin. The range in isotope ratios for the 'baseline' water gases illustrates that there may be multiple gas sources and processes that affect the isotope ratios of the free gas in aquifers, and this is even before the drilling of the CBM wells in the immediate vicinity of the aquifer.

We have found that, when appropriate background data is available, we can do more than conclude that the origin of the problem gas is biogenic or thermogenic. In the best case scenario, where a mudgas isotope depth profile is available, we can determine the probable source depth of contaminating gases. Here, we present four case studies (located in Figure 1) where landowners complained that their domestic water wells were impacted by oil and gas field activities. As each case study varies in the type and amount of



**Figure 2** Isotope cross plots of (a)  $\delta^{13}C_1$  versus  $\delta^{13}C_2$  and (b)  $\delta^{13}C_2$  versus  $\delta^{13}C_3$  for gas from domestic water wells sampled as part of the CBM Alberta government mandated testing program.

background data available, so do the conclusiveness of the results.

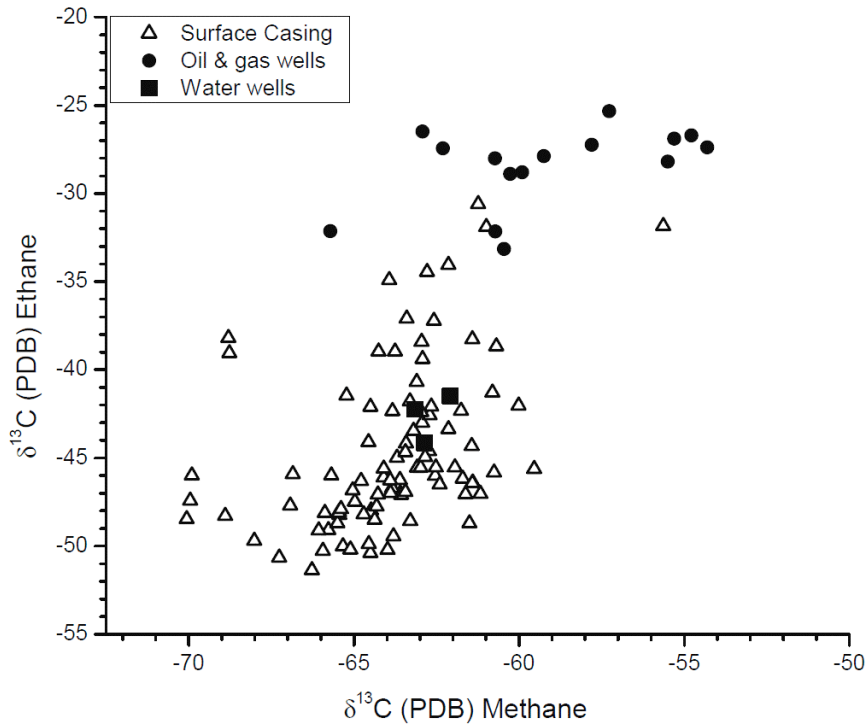
## 2 CASE STUDIES

### 2.1 Free Gas in Groundwaters in the Wildmere Heavy Oil Field

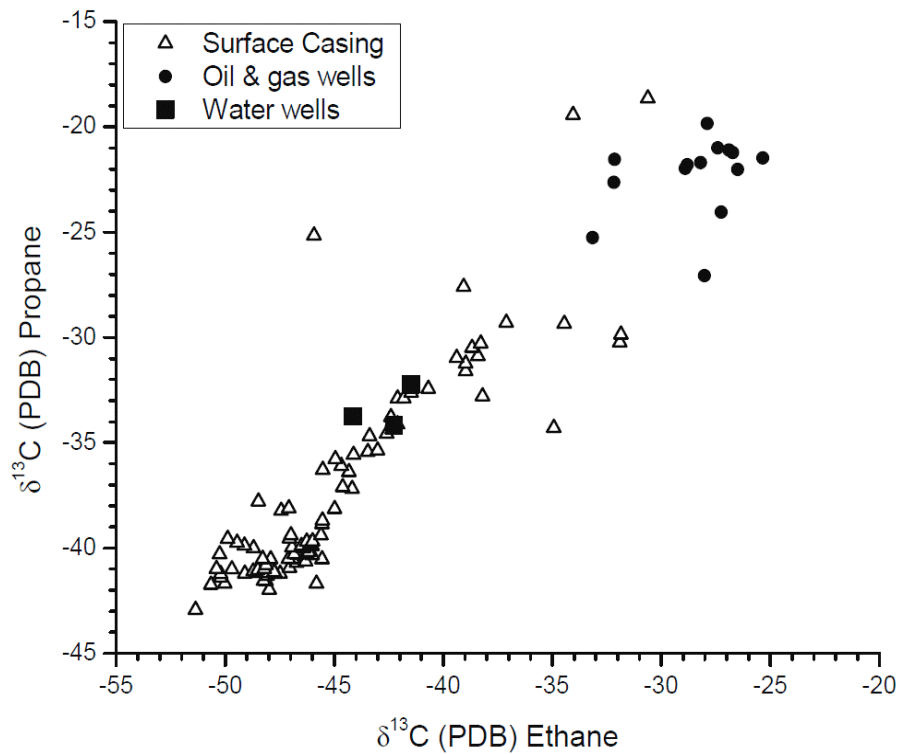
The Wildmere heavy oil field in east-central Alberta (Figure 1) is a densely drilled area (about 24 oil wells per square mile) where heavy oil has been produced since the mid 1970's. Figures 3, 4 and 5 show isotope cross plots for problem gases from three domestic water wells in the Wildmere heavy oil field along with analyses for surface casing vent flow (SCV) gases and production gases. The abundance of SCV gases from this area indicates that there has been a history of leaking gases, the majority of which were found to be sourced from above the production horizons. Comparison of the isotope ratios of the SCV gases with those of the production gases (Figures 3, 4 and 5) confirms that the majority of the leaky SCV gases are not from the production zones<sup>4</sup>. As the water gases fall within the isotopic range of the SCVs, without additional background data, we could conclude that the water gas is also not sourced in the production horizons. Of note, the presence of ethane, propane and butane in the problem water gases indicates that the gases are not of purely biogenic origin.

The forensic study of problem gases in water wells in the Wildmere area is fortunate in that a gas isotope depth profile is available for a well only 2.5 km away from the water wells in question. The isotope ratios of the water gases can be compared to this isotope depth profile (Figure 6). The profile shows the isotope ratios for methane, ethane and propane in drilling mud gases plotted against depth.<sup>4,5</sup> The isotope depth profile represents gas samples at average depth intervals of about 10 meters, but ranging from depth intervals of 2 to 20 meters. The water gas isotope data can be plotted on the horizontal axis and then moved upwards until the  $\delta^{13}C_1$ ,  $\delta^{13}C_2$ , and  $\delta^{13}C_3$  best visually match the profile. The depth of the best visual match is the source depth of the problem gas<sup>4</sup>. The three gases from water wells 'match' the profile at depths of 480-510m, i.e. above the production

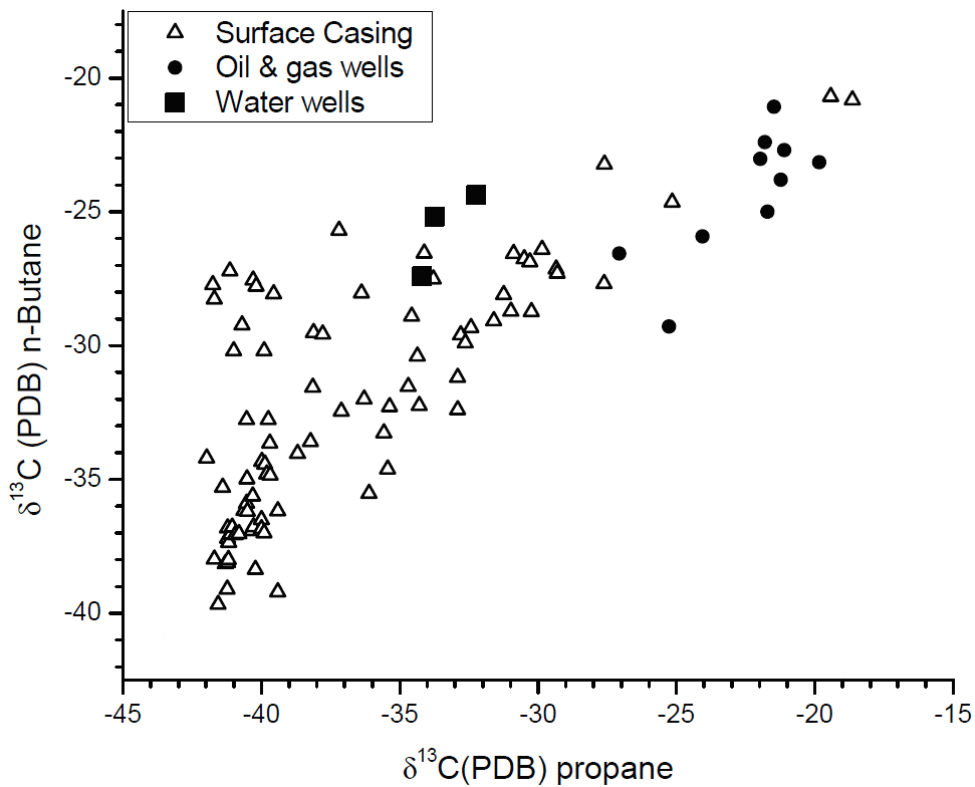
horizons. The implication is that gases have somehow migrated from this depth to the water wells,



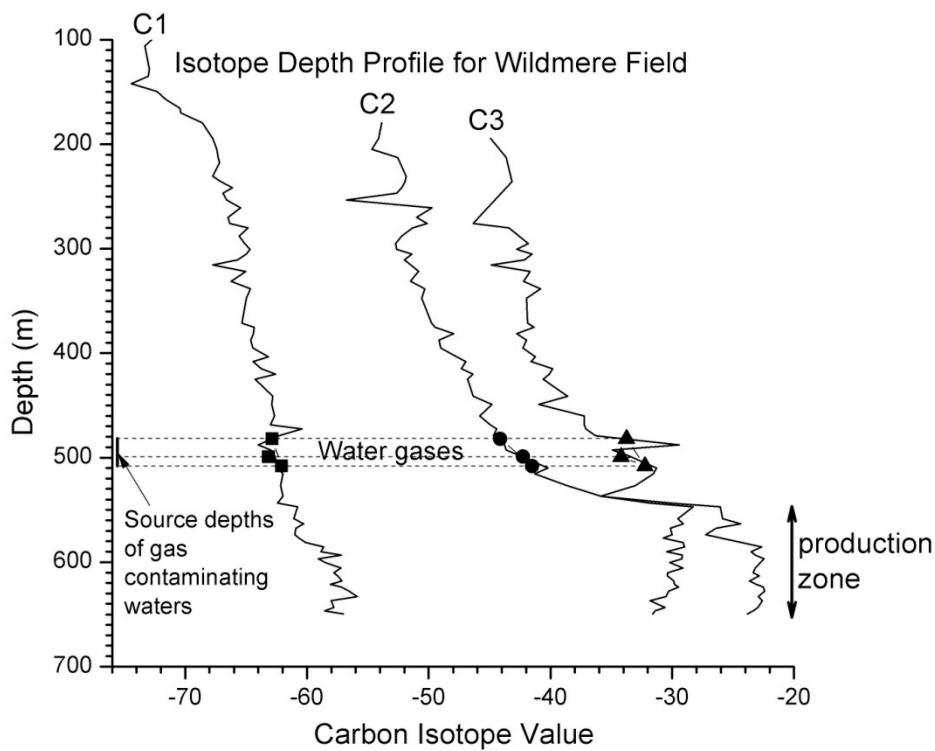
**Figure 3**  $\delta^{13}\text{C}$  of methane and ethane in gases from problem water wells, surface casing vent flows, and oil and gas wells in the Wildmere heavy oil field, east central Alberta.



**Figure 4**  $\delta^{13}\text{C}$  of ethane and propane in gases from problem water wells, surface casing vent flows, and oil and gas wells in the Wildmere heavy oil field, east central Alberta.



**Figure 5**  $\delta^{13}\text{C}$  of propane and butane in gases from problem water wells, surface casing vent flows, and oil and gas wells in the Wildmere heavy oil field, east central Alberta.

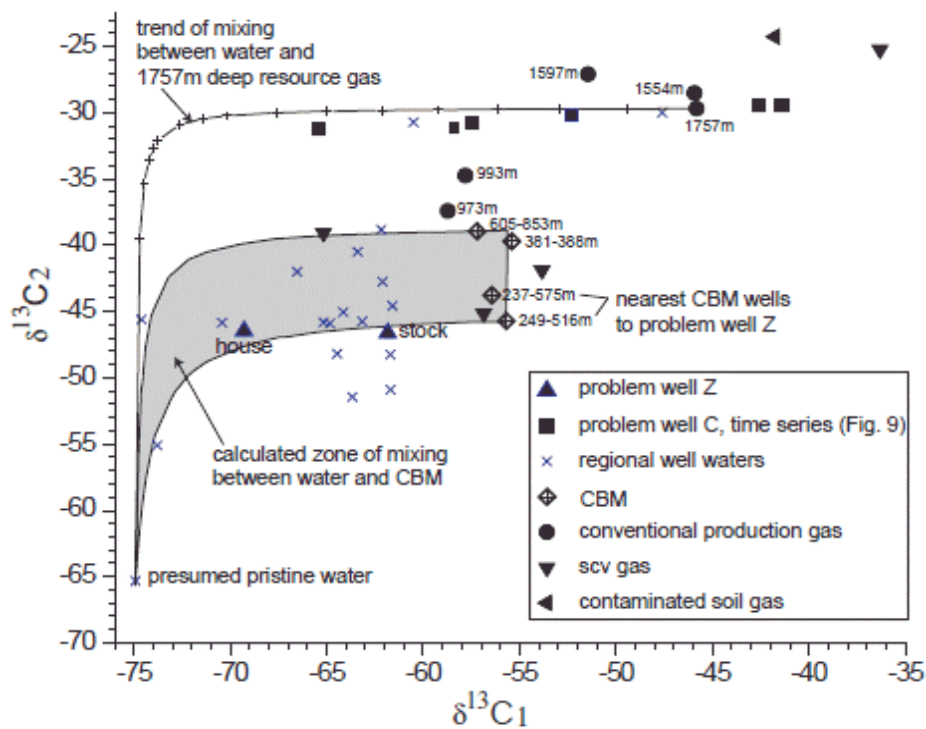


**Figure 6** Isotope depth profile for a well in the Wildmere heavy oil field (solid curves) showing the isotope ratios of gases from 3 water wells and the depths from which the contaminating gas most likely originated.

a migration caused by well casing and/or cementing failure. In this case, the issue between the landowner and the operator was resolved amicably.

## 2.2 Case Studies 2 and 3. Problem Wells C and Z

Problem water wells for our second and third case study are located within 25 kilometers of each other and so share much of the same background isotope data. Unfortunately, no isotope depth profiles were available for this area, so background data was limited to baseline water data, SCVs, soil gases and production gases (Figure 7). As the problem water gases do not match isotopically with any known production gases, we assumed that biogenic gas mixed with migrating production gas and calculated mixing curves based on mixing of these two end members using the mass balance equations of Jenden et al.<sup>2</sup> We also assumed for the calculations that the most isotopically negative gas from water in the area was the pristine water not impacted by petroleum development.



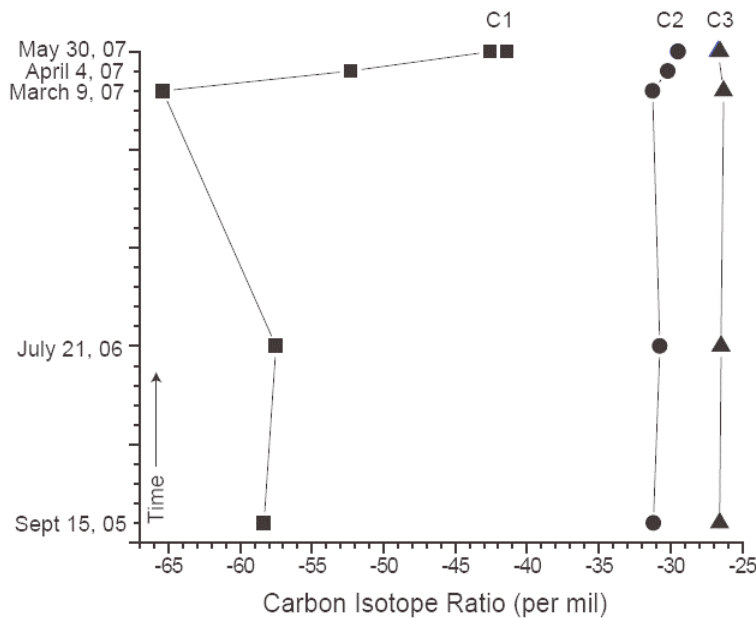
**Figure 7** Methane versus ethane carbon isotope plot for gases from problem water wells Z and C, compared to gases from water wells, CBM, resource wells, and SCV flows in the surrounding area. Mixing curves were calculated using the mass balance approach of Jenden et al.<sup>2</sup>

**2.2.1 Case Study 2. Problem Well C.** The gases sampled from water well C during September 2005 to April 2007 lie along the mixing curve for gas from pristine water and conventional production gas from a depth of 1757 m (Figure 7). A thermogenic gas contribution is also suggested by the unusual presence of propane, butanes and pentanes in the gas samples from water well C (Figure 8)

Problem well C is interesting for two reasons: (1) the evidence described above for contamination of the water by deep conventional gas; and (2) methane isotope values of gas from domestic water well C show a temporal variation (Figure 8) that is not observed in the other case studies. Interestingly, the March 2007 water gas sample has more negative methane  $\delta^{13}\text{C}$  ratios than the 2005 and 2006 samples. The methane isotope values

of the most recent gas samples (April and May, 2007) are more positive, approaching and then exceeding the thermogenic values of the deep resource gases in the area. There was noticeably less free gas present in the water during these last two sample periods.

Our interpretation of the data is that a small amount of gas, originating at the commercial gas production depth of 1757 m, has leaked and mixed with biogenic gas in the shallow aquifer. The abundance of gas in the well water appears to be a function of changes in the surface hydrogeologic regime which may control the abundance and proportion of biogenic gas in the aquifer at the site of the water well. The March 2007 gas may represent a period of high biogenic gas input, whereas the more recent samples represent a period of very low influx of biogenic gas and a predominance of the small amount of deep gas contamination. The overly heavy  $\delta^{13}\text{C}$  ratios for methane in the May 2007 gases may be the result of oxidation of the gas in the aquifer.



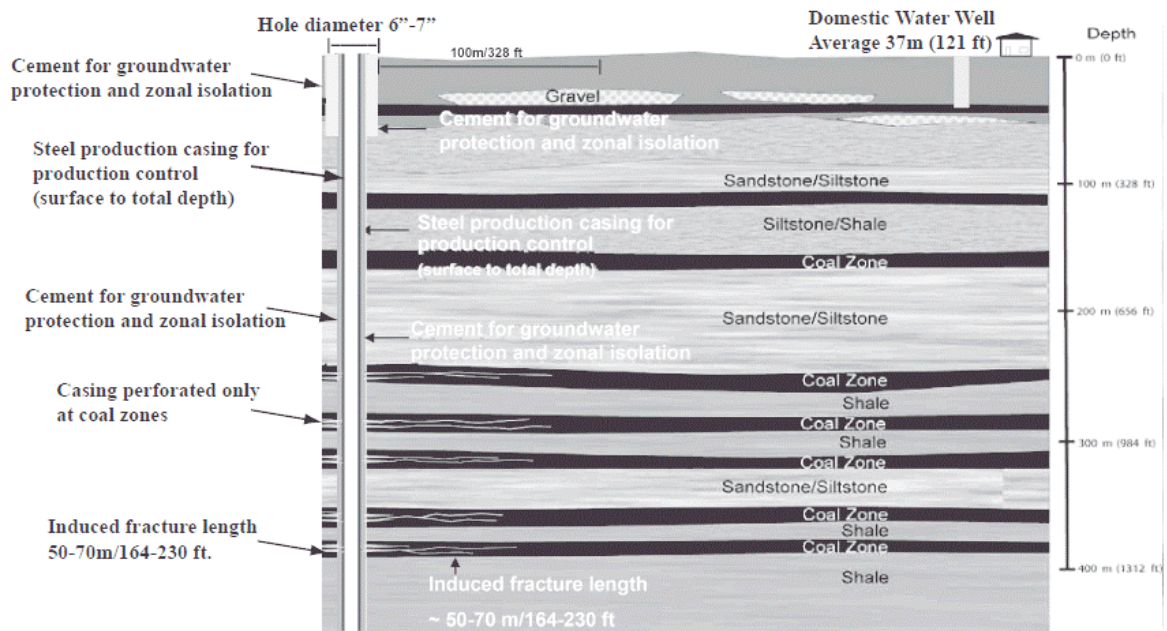
**Figure 8** Temporal trend in carbon isotope ratios of gas from problem water C.

**2.2.2 Case Study 3. Problem Well Z.** The landowner of well Z complained of gas in both his house and stock water wells following the development of two nearby CBM wells (Figure 7). Figure 7 compares carbon isotope ratios of methane and ethane of the two Z problem wells, regional water wells, resource wells, and associated SCV and contaminated soil gases. The carbon isotope ratio of methane in problem waters of the Z well is not identical to methane in the resource wells, but ethane ratios suggest a small amount of mixing with CBM. The grey shaded zone in Figure 7 represents the zone of mixing between presumed pristine water gas and the various nearby CBM wells. The house and stock well gases are on the mixing curve of pristine water and CBM from the nearest CBM well which produces from depths of 249-515m. A SCV gas also lies on this mixing curve. The greater depth and water production of the stock well water (relative to the house well) may have caused more mixing with CBM gas.

## 2.3 Rosebud Hamlet Possible Water Contamination by CBM

Public attention to possible water well contamination by CBM activity in Alberta originated in the hamlet of Rosebud, Alberta. A very high density of gas wells occurs within the vicinity of this hamlet, up to as many as eleven producing gas wells within one square mile block. The first complaint was submitted in 2004, which was soon followed by complaints from most of the other landowners in the hamlet.

The need for water well testing is evident when the geology is taken into consideration. Figure 9 is a schematic showing the general geology and setting of CBM production wells and domestic water wells in Alberta. Multiple coal seams occur near the surface and the shallowest coal seams are often used as aquifers. The various levels of well casings designed to protect against gas migration are illustrated. However, the numerous surface casing vent flow gases that we have analyzed indicate that the release of hydrocarbon gases to the shallow environment occurs regardless. Gas production is from multiple coal seams that are fractured and the gases from several coal horizons are generally commingled.



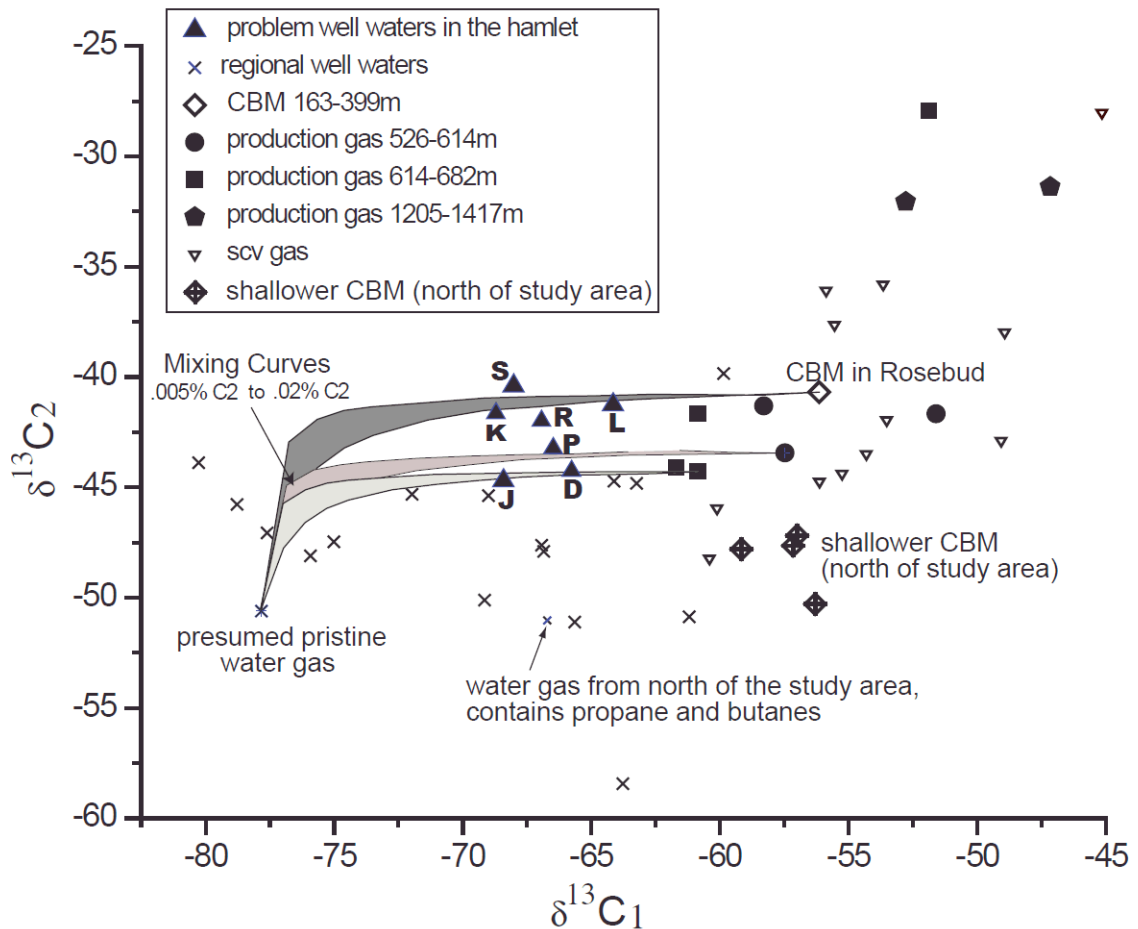
**Figure 9** Schematic showing the general geology and setting of CBM production wells and domestic water wells in Alberta. (Modified from ref. 6)

The carbon isotopic composition of gases from water wells (seven from Rosebud itself, 17 from presumed pristine water wells) are compared to oil field gases (production gases from 3 different depth intervals, shallow CBM wells, and surface casing vent flows (SCV)) within a 40 km radius of the hamlet of Rosebud (Figure 10). At first glance the Rosebud water well gases are not identical to the resource gases. However, they may be impacted by mixing. Mixing of presumed pristine well water gas with 3 different resource gases (CBM gas at 163-399m, production gas from 526-614m, and production gas from 614-682m) has been modelled using the mass balance equations of Jenden et al.<sup>3</sup> The range in each of the mixing curves on Figure 10 represents a variation in the estimated proportion of ethane in the pristine water well between 0.02 and 0.005%. The wide range in  $\delta^{13}\text{C}$  values of SCV gas indicates that there is a history of problem gas flow from a wide range of depths in this area.



Comparison of the  $\delta^{13}\text{C}$  values of methane and ethane for gas from the problem water wells in Rosebud with the calculated mixing curves of Figure 10 shows that gases of waters from all seven wells have mixed with either CBM or the deeper production gases. Gases from well waters J and D fall on the mixing curve with the deeper production gas at 614-682m. A deep gas, rather than a shallow CBM, impact on well D is supported by well D's history of gas loading many years before any CBM development began in the area. Water wells K and L fall on the mixing curve for CBM-water gas, with well L apparently the most contaminated. Water well P lies closest to the mixing curve for production gas from 526-614m, whereas water wells S and R lie above and below the CBM-water gas mixing curve. Following the mixing curves, the isotopic differences between waters S, R, K-L and J-D suggest different contaminant sources. These sources cannot be identified unambiguously. They are certainly not from the deepest production zones (1205-1417m), nor the shallowest CBM horizons (<160m). In contrast, contaminated water from just north of the study area (Figure 10) contains propane and butane and has apparently mixed with the shallowest CBM horizons.

We cannot attribute the source of contamination in the Rosebud water wells to specific resource wells because the available isotope data for the CBM gas is from multiple commingled coal-bearing intervals (163-399m, see Figure 9). The source could be any one of individual coal intervals or intermediate depth resource gas (526-682m). If gas isotope analyses of each of the individual coal seams were available then perhaps we could better identify the source.



**Figure 10** *Methane versus ethane carbon isotope plot for gases from water wells and CBM in the hamlet of Rosebud and from water wells, CBM, resource wells and SCV flows in the surrounding area*

### 3 CONCLUSION

In the WCSB, many water wells produce natural gas. Most often, this gas is distinguished by very low methane and ethane carbon isotope values and reflects natural methanogenesis in aquifers. However, years of intensive resource exploitation in agricultural areas have left an impact on some domestic water wells in Alberta. The source of contaminants in groundwater can be best identified by carbon isotope values of ethane which is diagnostic of deeper gas bearing formations beneath the aquifer. Because drilling and completion of resource wells at any given region occurred at multiple depths in different decades, it is often difficult to differentiate between specific putative sources. It is possible to identify specific sources of contaminants in problem water wells if enough isotopic background data is available. One needs not only the pre-development background data on gases from pristine water wells and the production gases themselves, but also a detailed gas isotope stratigraphy of the particular region in question. The isotope profiles are necessary to distinguish between commingled multiple production horizons as well as those that were exploited separately in different production eras. The isotope profiles also can identify gases that migrate into aquifers along well bores from intervening gas rich formations not directly targeted for production.

### References

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