

Characterisation of coal seam gas waters in New Zealand

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Abstract

Coal seam gas (CSG) exploration and development requires the abstraction of significant amounts of water. This is so because gas desorption in coal seams takes place only after aquifer pressure has been reduced by prolonged pumping of aquifer water. CSG waters have a specific geochemical signature which is a product of their formation process. These waters have high bicarbonate, high sodium, low calcium, low magnesium, and very low sulphate concentrations. Additionally, chloride concentrations may be high depending on the coal depositional environment. This particular signature is not only useful for exploration purposes, but it also highlights potential environmental issues that can arise as a consequence of CSG water disposal. Since 2002 L&M Coal Seam Gas Ltd and CRL Energy Ltd, have been involved in exploration and development of CSG in New Zealand. Anticipating disposal of CSG waters as a key issue in CSG development, they have been assessing CSG water quality along with exploration work. Coal seam gas water samples from an exploration well in Maramarua closely follow the geochemical signature associated with CSG waters. This has helped to identify CSG potential, while at the same time assessing the chemical characteristics and water generation processes in the aquifer. Neutral pH and high alkalinity suggest that these waters could be easily managed once the sodium and chloride concentrations are reduced to acceptable levels.

Keywords: Coal seam gas, CSG, CSG water, Maramarua groundwater quality, lignites, sodium, TDS, conductivity.

Introduction

Coal seam gas (CSG) is natural gas (mainly methane) which has been generated in underground coal seams either through biogenic or thermogenic processes (or a combination of both). Mining this gas involves installing a well into a coal seam and pumping out coal-aquifer water. This is because the CSG is sorbed into the coal's micropores and it will remain trapped in this structure as long as there is enough aquifer pressure. When aquifer pressure is lowered by pumping water out of the coal formation, CSG is released from the micropores and flow from the well.

This, however, is achieved only after a significant quantity of water has been removed. These CSG waters have a particular chemical signature which is useful for exploration purposes and resource evaluation. The correct identification of CSG waters can be useful for assessing CSG potential, and preventing future environmental issues arising from full scale operations associated with CSG mining activities. For instance, at elevated concentrations, salinity can be toxic to most plants (Soil Improvement Committee, 1995). In addition high sodium accompanied by low calcium-magnesium concentrations has the potential to disperse soils reducing its structure and permeability (Ayers et al., 1985). On the other hand, if CSG water is adequately characterised and managed, it can be used as a resource with many beneficial applications. CSG waters can be used for irrigation, watering stock, cleaning, dust control, and even human consumption if treated. This paper presents water quality from a CSG exploration well in Maramarua, New Zealand. In addition, an interpretation of these data is provided comparing it against the known geochemical signature from CSG basins in the U.S.A.

Geochemistry and origins of CSG waters

Coal seam gas-bearing aquifers have a specific water chemistry that relates to biological, geological, geochemical, and physical processes. Coal seams are interbedded with other geological units (mudstones, shales, clays, or sandstones), and the arrangement and characteristics of these adjoining units define the geochemical processes affecting the chemical composition of CSG waters. In most CSG-producing basins, coal seams act as regional aquifers confined by nearly impermeable units. As recharge water enters the coal seam, it flows very slowly and undergoes chemical and biological transformations over the course of time. In addition, depending on each particular scenario there may be infiltration from other units and some mixing may occur.

Biodegradation of organic matter

CSG is formed through the anaerobic degradation of organic matter. Initially, plant detritus is deposited as peat and then buried by the deposition of sediments of marine or terrestrial origin. The organic matter is first decomposed by microbial aerobic respiration as oxygen is readily available in voids and dissolved in water, which has been in contact with the atmosphere. However, as the burial process continues and oxygen is depleted, these organisms are unable to function aerobically. At this point, the biodegradation process turns from aerobic respiration to anaerobic respiration or fermentation. Anaerobic decomposition is well documented as it normally takes place in anoxic environments such as the digestive tracks of animals, swamps, and landfills to mention a few. In buried coal seams the same processes of anaerobic decomposition occur. Here, facultative anaerobic bacteria break down organic matter in a series of redox chemical reactions (Bartos et al., 2002).

Dissolution of sodium feldspars.

As recharge water flows through the coal aquifer, it dissolves different minerals along its path of flow. One of these minerals is sodium feldspar, which can dissolve with recharge water and increase sodium concentrations (Lee, 1981). When these feldspars are of marine origin (albite for example), chloride concentrations can also increase.

Bicarbonate concentrations.

High bicarbonate (HCO_3^-) content in CSG waters occurs by two aquifer processes: dissolution of carbonate and methanation. When oxygenated recharge waters enter the aquifer these may dissolve carbonate and increase bicarbonate concentrations (Freeze and Cherry, 1979). However, the primary process accounting for high HCO_3^- content in CSG aquifers is methanation, wherein organic matter is transformed into water, hydrogen sulphide, sulphide, and carbon dioxide while at the same time reducing sulphate (SO_4^{2-}) (Decker et al., 1987). Methanation takes place, once sulphate reduction has finalised, through methyl-group fermentation and carbon dioxide reduction (Chapelle, 2001). However, not all the CO_2 is transformed into methane: some of it is

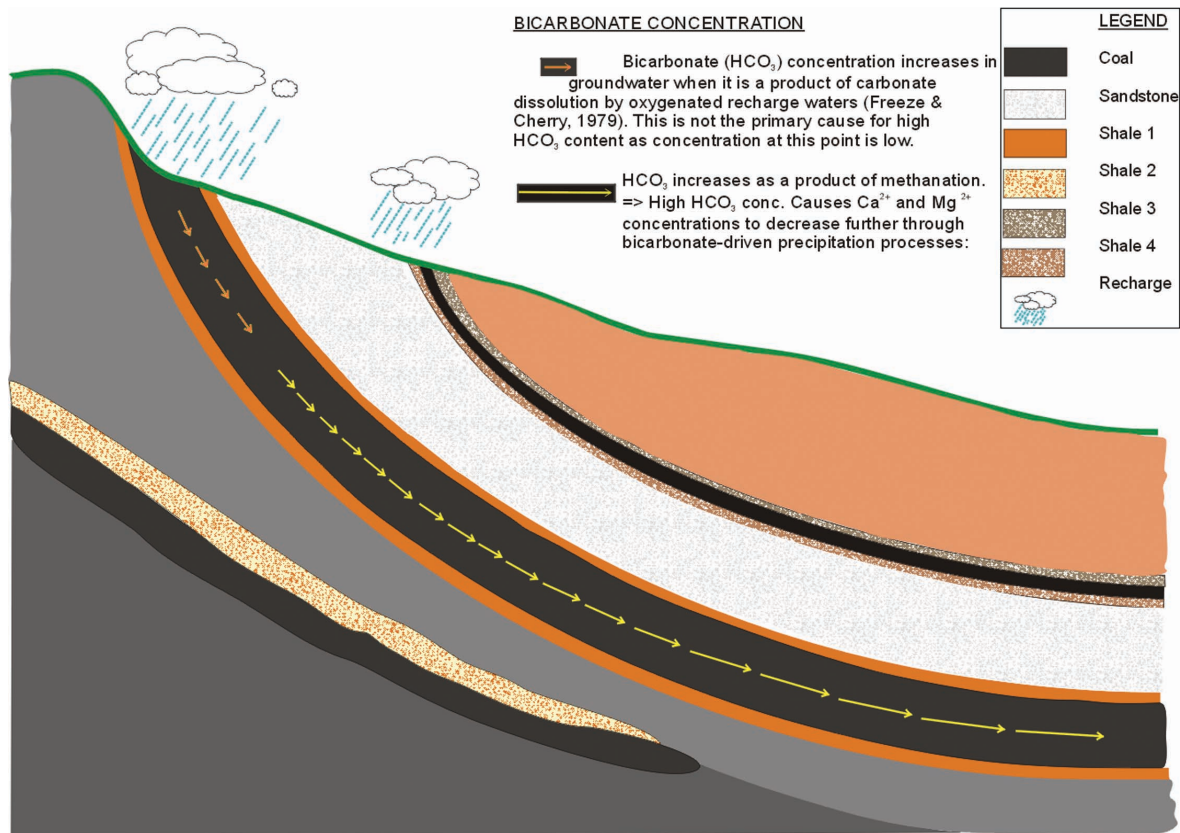


Figure 1. Evolution of bicarbonate concentration in coal seam gas waters.

converted to HCO_3^- , and some of it stays dissolved in the water. Carbonate equilibrium conditions result in the occurrence of HCO_3^- as the dominant species and low $\text{CO}_2(\text{aq})$ concentrations along with alkaline pH values (Decker et al., 1987). Fig. 1 shows the bicarbonate enhancement of recharge waters as these enter and flow through the coal aquifer.

Ion exchange processes: Ca^{2+} and Mg^{2+} decrease and Na^+ increase

Ion exchange processes between coal aquifer water and adjoining clay units result in a soft groundwater (low calcium and magnesium) with enhanced sodium concentrations (Van Voast, 2003). As water flows through the coal aquifer, calcium and magnesium ions are held more strongly than sodium ions in clays. The outcome of this process is a groundwater with low calcium and magnesium concentrations but high sodium content. This process becomes more pronounced in deeper parts of the basin and away from sources of recharge (Hagmaier, 1971; Hamilton, 1970; Lee, 1981). In addition, high bicarbonate concentrations decrease the solubility of calcium and magnesium ions thus reducing their concentrations in CSG waters (Van Voast, 2003).

Sulphate reduction.

In shallow parts of the coal basin and near recharge areas, sulphate may increase due to the dissolution of gypsum (CaSO_4) and the weathering and oxidation of pyrite and marcasite (FeS_2) (Bartos et al., 2002). In addition, if recharge areas are close to the ocean sulphate in sea spray may find its way into aquifers (Rosen et al., 2001). However, sulphate concentrations in CSG waters are generally very low because of the sulphate reduction process that precedes methanation. In the first stage of anaerobic decomposition, anaerobic bacteria consume the available organic matter thus reducing sulphate concentrations. Once the majority of the sulphate is reduced, the anaerobic process proceeds on to the acidic and methanogenic stages (Rice and Claypool, 1981).

Another path for the production of methane is thermogenesis. As coal seams get deeper within basins, higher temperatures and pressures result in the devolatilisation of organic matter with

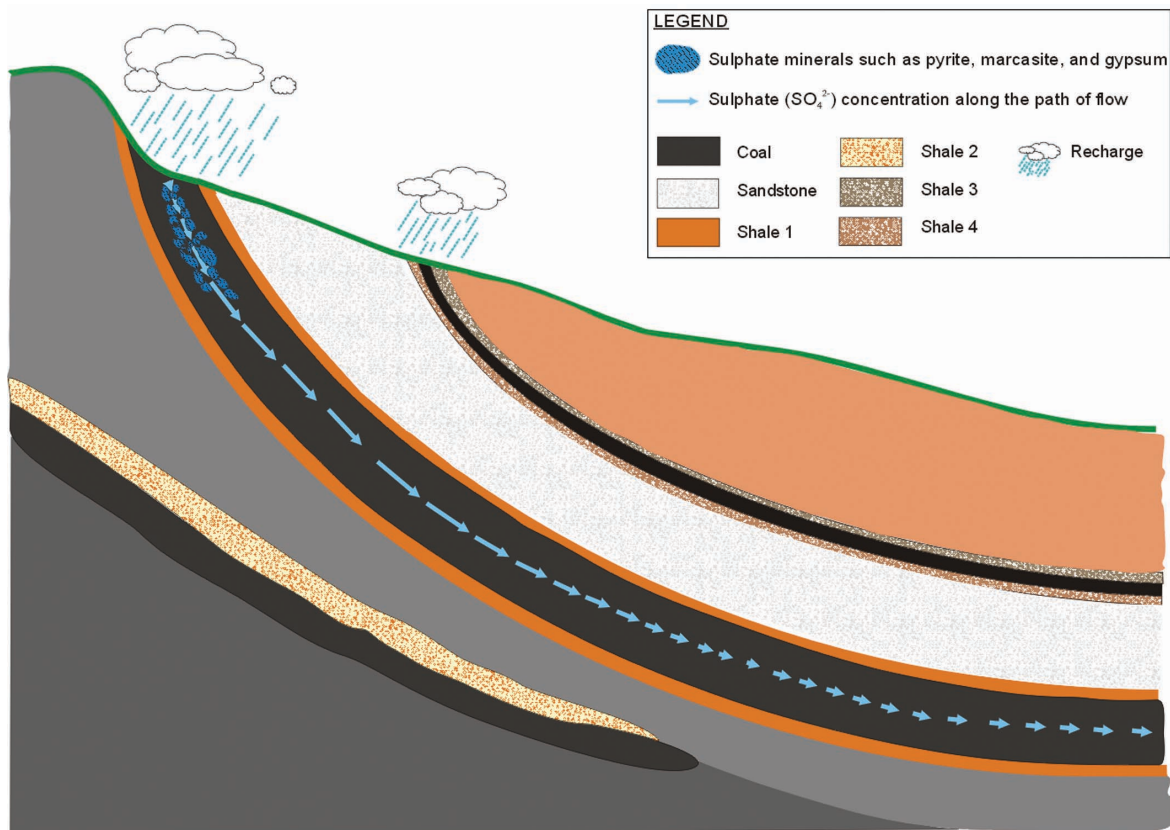


Figure 2. Sulphate reduction in CSG aquifers

the production of water, carbon dioxide, and methane (Stach, 1982). With thermogenesis, sulphate reduction can take place with increasing coalification, because coalification is basically a “metamorphism by pressure and heat of burial” (Van Voast, 2003). Therefore, whether biogenic or thermogenic, CSG waters exhibit very low sulphate concentrations (Fig. 2).

Sulphate concentrations in CSG water can be used as an exploratory tool to assess the potential for methane production in wells. Van Voast (2003) has determined an upper limit of 500 mg/L for sulphate concentrations in CSG water from CSG producing wells in the U.S.A.

Maramarua CSG exploration and water sampling

In 2003, CSG (or CBNG as it is known in the U.S.A.) accounted for about 8% of the total methane production in the U.S.A., and proved reserves for this resource increase at a rate of about 1% per year (Energy Information Administration, 2004). The success of the CSG industry in the United States has inspired many countries (including New Zealand) to explore and develop this technology. Up to the 1990s it was believed that commercial quantities of CSG could only be achieved if this gas originated from thermogenic processes in high-rank coals (Johnson, 2004). However, the Powder River Basin (PRB) success in the 1990s proved that it was possible to extract CSG from low-rank coals in commercial amounts (Johnson, 2004). New Zealand low-rank coals have similar characteristics to those found in the PRB (Moore, 2002). Therefore, New Zealand low-rank coals may hold significant quantities of CSG.

L&M Coal Seam Gas Ltd (L&M) holds a petroleum exploration permit over the Maramarua Coalfield in the Waikato coal region. Coal within the Maramarua coalfield (Fig. 3) is in a single seam, the Kupakupa Seam, and the field has good potential for CSG development due to its rank (sub-bituminous B-C) and low ash content. In addition, significant tonnages of coal are located at depths in excess of 200m. Impermeable mudstones overlying the coal seam and a high hydrostatic head have contributed in preventing CSG desorption (Pope and Trumm, 2004).

In August 2003, borehole C-1 was drilled in the Clifton sector of the Maramarua Coalfield (Fig. 3). The drill hole penetrated through 191.75 m of Tertiary mudstones and sandstones before reaching the 11.55m Kupakupa Seam, which was underlain by thin interbedded mudstone and coal; basement was reached at a depth of 206.00 m. Although the aquifer is artesian, it is not a flowing artesian well. Therefore, the well was sampled using a pump capable of purging the well and collecting a sufficient volume of water for analysis. This was carried out by a subcontractor (D. J. Phelps & Co Ltd) who used a Grundfos MP1 submersible pump to purge the well until pH, temperature, and conductivity became stable. This pump was small enough ($f = 50$ mm) to fit down the borehole ($\gg 100$ mm), and was effective in extracting at least 380 litres of water before collecting the sample on 18/9/2003.

Exploration hole Maramarua C-1 was redrilled in June 2004 for the purpose of conducting gas flow testing. The well was completed with steel casing (100 mm) which effectively isolated the coal seam from overlying geological units, thus preventing the mixing of coal seam waters with waters foreign to the coal formation. A sucker rod pump was installed to reduce the hydrostatic pressure and promote desorption and gas flow by pumping water out of the aquifer. Once

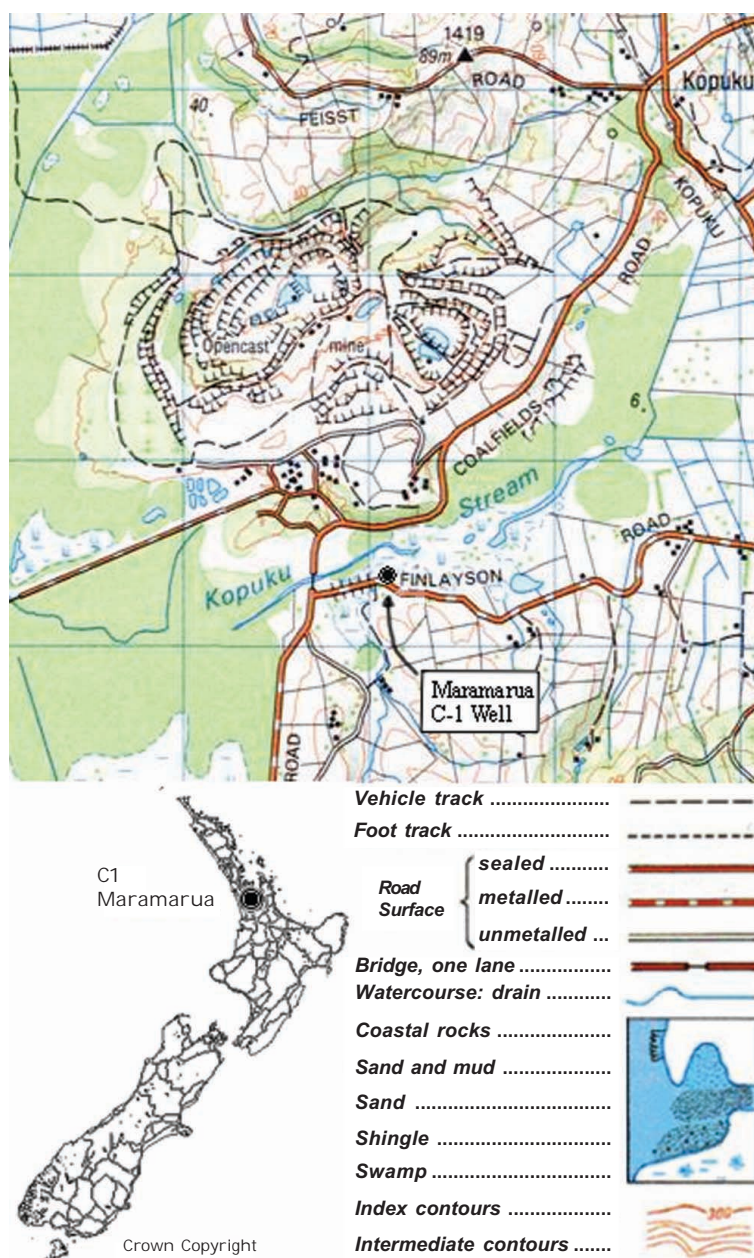


Figure 3. Location of borehole C1

Table 1. Maramarua C1 samples

		Sample date	
		18/09/2003 ^{(1), (3)}	19/08/2004 ^{(2), (4)}
pH	pH units	8.5	7.8
Specific Conductance (T=25°C)	µS/cm	1200 ⁽⁶⁾	1310
TDS	mg/l	756 ⁽⁷⁾	782
Hardness	mg/l as CaCO ₃	76.7 ⁽⁷⁾	18
Alkalinity	mg/l as CaCO ₃	340	360
Bicarbonate (HCO ₃ ⁻)	mg/l	402	435 ⁽⁵⁾
Carbonate (CO ₃ ²⁻)	mg/l	8.8 ⁽⁵⁾	<2
Carbon dioxide (CO _{2(aq)})	mg/l	4.2 ⁽⁵⁾	25
Calcium (Ca ²⁺)	mg/l	20	6 ⁽³⁾
Magnesium (Mg ²⁺)	mg/l	6.5	0.9 ⁽³⁾
Sodium (Na ⁺)	mg/l	184	334 ⁽³⁾
Potassium (K)	mg/l	9.5	3 ⁽³⁾
Chloride (Cl ⁻)	mg/l	49.3	146
Sulphate (SO ₄ ²⁻)	mg/l	27.6	0.7
Fluoride (F ⁻)	mg/l	0.32	0.79 ⁽³⁾
Boron (B)	mg/l	1.95	2.5 ⁽³⁾
Silica (SiO ₂)	mg/l	3.5	10.7 ⁽³⁾
DOC	mg/l	130	11 ⁽³⁾
Total Iron (Fe)	mg/l	55.9	0.4 ⁽³⁾
Manganese (Mn)	mg/l	0.242	<0.01 ⁽³⁾
Arsenic (As)	mg/l	<0.01	<0.02 ⁽³⁾
Barium (Ba ²⁺)	mg/l	0.154	0.024 ⁽³⁾
Chromium (Cr ²⁺)	mg/l	0.031	<0.01 ⁽³⁾
Mercury (Hg)	mg/l	0.0009	<0.002 ⁽³⁾
Selenium (Se)	mg/l	<0.01	<0.02 ⁽³⁾
Zinc (Zn ²⁺)	mg/l	0.17	1.28 ⁽³⁾
Hydrocarbons C7-C9	mg/l	<0.3	<0.03 ⁽³⁾
Hydrocarbons C10-C14	mg/l	117	<0.05 ⁽³⁾
Hydrocarbons C15-C36	mg/l	4	<0.1 ⁽³⁾
Hydrocarbons Total	mg/l	121	<0.2 ⁽³⁾

⁽¹⁾ This sample was collected from the borehole prior to casing installation (to isolate the coal seam from other units).

⁽²⁾ This sample was collected after borehole C-1 had been re-drilled and cased down to coal thus effectively isolating the coal seam.

⁽³⁾ Sample was analysed by Hill Laboratories, Hamilton, and NZ.

⁽⁴⁾ Sample was analysed by the CRL Energy Ltd Laboratory, Wellington, and NZ.

⁽⁵⁾ Calculated from carbonate equilibrium.

⁽⁶⁾ On site measurement

⁽⁷⁾ Calculated from measured ion concentrations

testing started, 22 water samples were collected for analysis between August and October 2004, and sent to CRL Energy Limited (CRL) in Christchurch for analysis of major ion composition and chemistry at the environmental engineering laboratory (EEL), University of Canterbury. In addition, one sample was collected on 19/8/2004 and sent to CRL in Wellington where a detailed analysis, including major and minor ions as well as trace elements, was carried out.

Common standards for sampling wells usually involve purging the well and taking the sample after removing 3-5 well volumes or until pH, specific conductance, and temperature remain

constant (Nielsen, 1990). Therefore, stagnant water is effectively purged from the well prior to taking the sample. In this project, the well was purged continuously, sometimes beyond the volume specified by the standard because the aim of the test was to lower the water level to just above the coal seam rather than just pumping water out of the coal aquifer. Problems with the pump caused a suspension of the programme in November 2004. A Progressive Cavity pump was installed in April 2005, and the test was completed satisfactorily. Eleven more samples were collected which were analysed at the EEL.

Results and discussion

The 2003 water sample was collected when the borehole was uncased, therefore this sample does not exclusively represent coal seam waters. The 2003 sample had high pH, low calcium and magnesium concentrations, and high sodium and bicarbonate concentrations (Table 1). The sulphate concentration is low (27.6 mg/L) and below the concentration for the limit of methane production (500 mg/L) in wells presented by Van Voast (2003). The major ions for this sample are sodium and bicarbonate, therefore this water is classified as of the Na-HCO₃⁻ type. It is also worth noting the relatively high chloride and iron concentrations (49.3 mg/L and 55.9 mg/L, respectively), the high dissolved organic carbon (DOC) (130 mg/L), and the high value for total hydrocarbons (mostly in the C10-C14 range).

Table 1 also includes a complete analysis of the water taken from the same well but with casing installed. This sample was collected on 19/8/2004, and more closely fits the geochemical signature for CSG waters than the 18/09/2003 sample. For example, calcium and magnesium concentrations are lower than in the 2003 sample (70% and 86% less, respectively), and bicarbonate and sodium concentrations are higher (8.2% and 81.5% higher, respectively). Chloride concentrations are higher than before, reaching a value of 146 mg/L (196% higher than the original value). Of significance is the fact that sodium levels have increased by almost 82%. Also, DOC values have decreased to 11 mg/L and iron levels have decreased to 0.4 mg/L. In general, most trace elements decreased in concentration except for zinc which increased moderately in 2004 (from 0.17 to 1.28 mg/L). The total hydrocarbons for this sample are below detection limit and the sulphate concentration is very low (0.7 mg/L which constitutes a 97.4% decrease from the 2003 value). The high chloride content classifies these CSG waters as Na-HCO₃⁻-Cl. The 2003 and 2004 results are markedly different because when the well was sampled in 2004, casing installed to the top of the coal seam prevented mixing of coal seam water with water from other units (sandstones, siltstones and mudstones).

The 33 samples analysed at EEL provide an invaluable insight into the variability of the Maramarua CSG waters. These samples were taken consecutively over a period of three months (August-October) in 2004 and three months (April-June) in 2005. Again, these samples exhibit low concentrations of calcium and magnesium accompanied by high concentrations of bicarbonate and chloride. Sodium concentrations are consistently high, averaging 313.3 mg/L and exhibiting minor variation ($\delta = 7.8$ mg/L). Sulphate levels are generally very low (<2mg/L) except for the first two samples of the second round (38 and 14 mg/L). The low sulphate levels, low calcium and magnesium levels, and high bicarbonate levels match the typical geochemical signature for CSG water and provide a good indication for this well's potential for methane. Specific conductance (1253-1424 mS/cm) is fairly high but within expectations. The major ions are sodium, bicarbonate and chloride, thus classifying this water as of the Na-HCO₃⁻-Cl type. This can be observed graphically by the use of a Piper diagram (Fig. 4). All of the 2004 samples are plotted at approximately the same place in the diagram, while the 2003 sample is plotted at a considerable distance from these values.

Schoeller diagrams can also be used to study the geochemical signature of these samples (Fig. 5). The differences between the 2003 and 2004/05 samples can be seen clearly in this diagram. CSG water from Maramarua samples has the same proportion of major and minor ions than water from CSG producing basins in the U.S.A. (Fig. 6). Maramarua CSG water is very similar

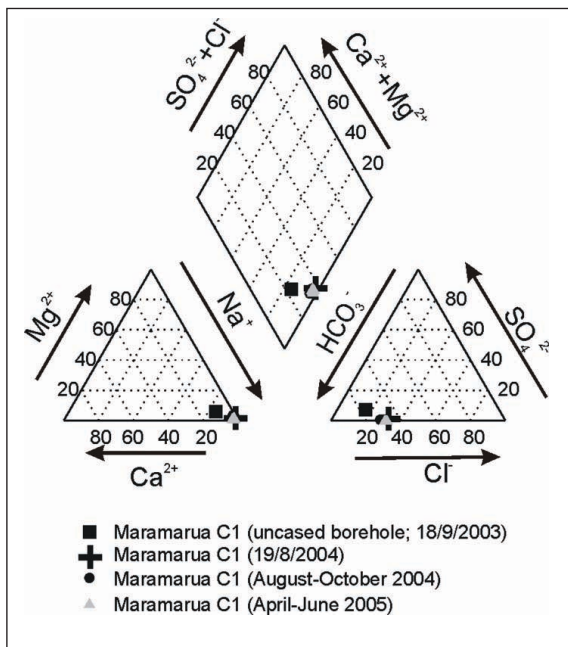


Figure 4. Piper diagram for Maramarua data

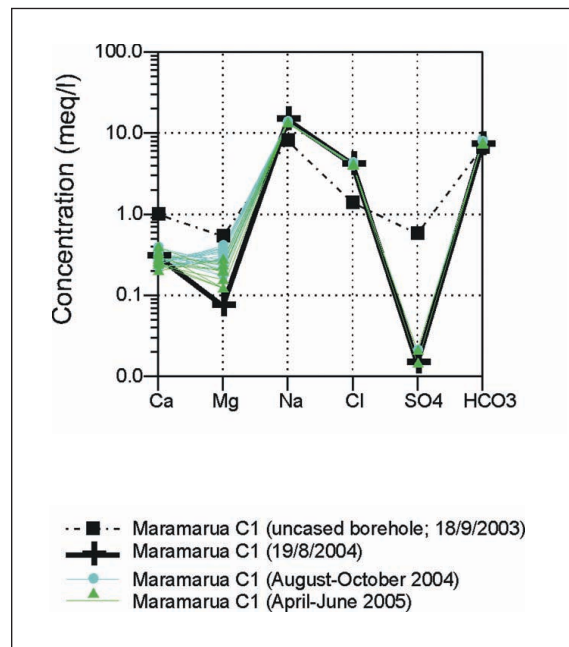


Figure 5. Schoeller diagram for Maramarua C-1 well

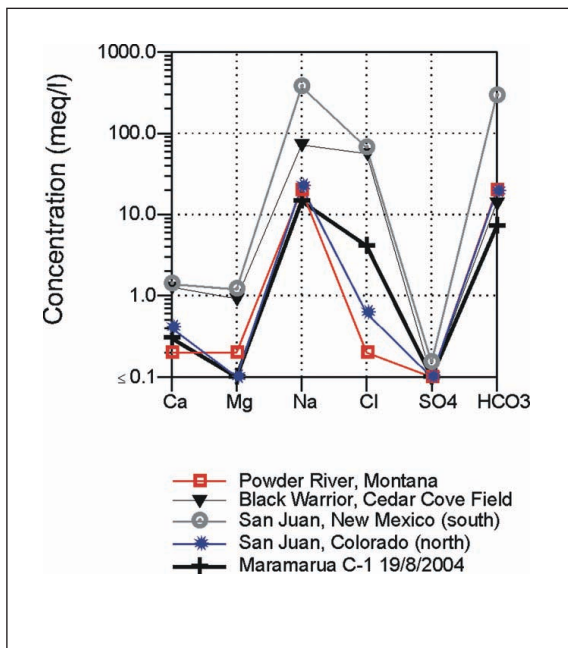


Figure 6. Maramarua CSG water compared against CBM samples from U.S. basins. Sources: CRL Energy Ltd. and (Van Voast, 2003).

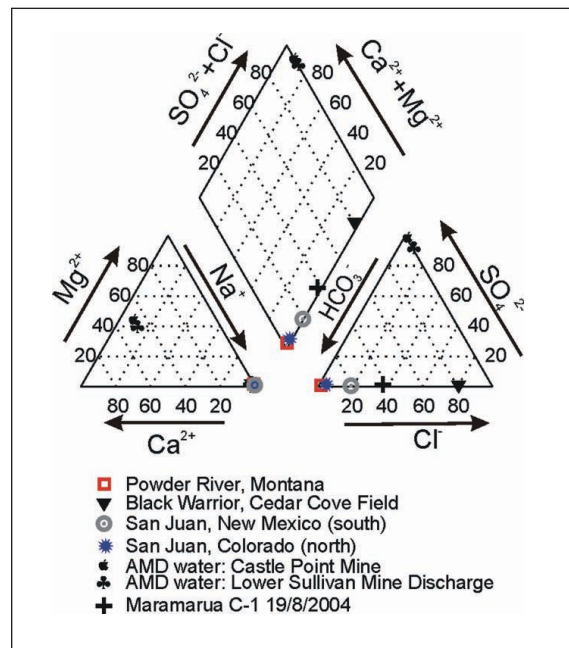


Figure 7. Piper diagram grouping CSG water samples from Maramarua, typical CSG samples from selected U.S. basins, and samples from AMD sites in the New Zealand West Coast region. Sources: CRL Energy Ltd. and (Van Voast, 2003).

to water from the PRB (Montana) and San Juan basin (Colorado) with the exception of higher chloride content. On the other hand, Maramarua CSG water is less mineralised, containing significantly less sodium, bicarbonate, and chloride, than typical water from the Black Warrior basin (Cedar Cove field) and San Juan basin (New Mexico side). However, in all of these basins, the proportion of ions remains the same: low calcium, low magnesium, high sodium, high bicarbonate, high chloride, and low sulphate.

The similarities between the Maramarua CSG water and selected basins in the U.S.A. can also be visualised by grouping these data according to their major anions and cations with the use of

a Piper diagram (Fig. 7). All of the CSG sites plot on the lower right corner of the cation triangle because sodium is the major cation, and calcium and magnesium concentrations are very low. The data plot on the lower left corner of the anion triangle; however some points tend to plot towards the right of the triangle because of high chloride concentrations San Juan (NM), Maramarua, and Black Warrior (Cedar Cove field)).

Acid mine drainage (AMD) waters in New Zealand have traditionally been associated with coal mining operations (Trumm et al., 2005). AMD results when minerals like pyrite and marcasite, sometimes present in coal measures, come in contact with water and air (oxygen). Oxidation reactions occur which result in the dissolution of iron and sulphate, and a net increase in acidity. Water that has come in contact with coal under oxidising conditions generally exhibits a low pH, metals dissolved in solution (iron, manganese, and aluminium), and high sulphate concentrations. CSG waters are generated in an anoxic environment and therefore do not oxidise sulphur-bearing minerals within the coal seam. The biogenic processes of CSG formation produce water with a fairly neutral pH, little or no dissolved metals, and very low sulphate concentrations. To illustrate the difference between AMD and CSG water, typical New Zealand AMD water samples have been plotted alongside CSG samples in Fig. 7. AMD samples plot at the exact opposite position from CSG samples in both the cation and anion triangles. AMD water has almost nil bicarbonate concentrations, low sodium, and low chloride concentrations. These differences suggest that CSG waters could even be used to neutralise AMD waters if CSG and AMD producing sites are relatively close.

Conclusion

CSG waters have a common geochemical signature which is independent of the basin location. Whether in the U.S.A. or in Maramarua, CSG waters have high sodium, high bicarbonate, low calcium, low magnesium, and low sulphate concentrations. Also, CSG waters can have high chloride concentrations if the coal measures were deposited in a marine environment. CSG waters generally have alkaline pH values and their dissolved salt content can be high or low depending on the well location within the basin (i.e. distance from recharge areas).

The correct characterisation of CSG waters requires adequate well completion and sampling procedures. Maramarua C-1 samples exhibit a water quality of the Na-HCO₃-Cl type with alkaline pH (7.8) and moderate salinity (EC = 1310 mS/cm). The highest ion concentration is sodium (334 mg/L) which may constrain the use of CSG waters as a resource. Overall, CSG waters from this part of Maramarua have the same proportion of major and minor ions than CSG waters from CSG basins in the U.S.A. This is evident with both Schoeller and Piper diagrams. Some basins are more mineralised than the Maramarua C-1 water quality, but others like the PRB (Montana) have similar concentrations.

CSG waters should not be regarded as a waste, but instead should be regarded as a resource. If adequately managed, CSG waters can be used in a variety of applications, including irrigation and watering stock. However, because CSG water quality varies throughout different basins and within individual basins, each CSG discharge should be assessed individually.

Acknowledgements

This research is a direct result of a TIF project funded by FRST through The University of Canterbury, L&M Coal Seam Gas, and CRL Energy. Without the TIF funding this work would not have been possible. Additional thanks to L&M for providing data and funding, especially to Mick Ryan (L&M) who diligently collected water samples and data from the gas flow testing. Integrated Mapping (MapToaster Topo/NZ) deserves a special thank you for permitting the publication of the map on Fig. 3.

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