# Chemical variability of groundwater samples collected from a Coal Seam Gas exploration well, Maramarua, New Zealand

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**Keywords**: Coal seam gas (CSG), coalbed methane (CBM), groundwater, Waikato, hydrochemistry, geochemical modelling

## Abstract

A pilot study has produced 31 groundwater samples from a coal seam gas (CSG) exploration well located in Maramarua, New Zealand. This paper describes sources of CSG water chemistry variations, and makes sampling and analytical recommendations to minimize these variations. The hydrochemical character of these samples is studied using factor analysis, geochemical modelling, and a sparging experiment. Factor analysis unveils carbon dioxide ($CO_2$) degassing as the principal cause of sample variation (about 33%). Geochemical modelling corroborates these results and identifies minor precipitation of carbonate minerals with degassing. The sparging experiment confirms the effect of $CO_2$ degassing by showing a steady rise in pH while maintaining constant alkalinity. Factor analysis correlates variations in the major ion composition (about 17%) to changes in the pumping regime and to aquifer chemistry variations due to cation exchange reactions with argillaceous minerals. An effective CSG water sampling program can be put into practice by measuring pH at the well head and alkalinity at the laboratory; these data can later be used to calculate the carbonate speciation at the time the sample was collected. In addition, TDS variations can be reduced considerably if a correct drying temperature of 180°C is consistently implemented.

# 1. Introduction

Coal Seam Gas (CSG) constitutes an emerging source of natural gas currently under exploration and development in countries like the US and Australia. Similarly, CSG exploration has been taking place in New Zealand with trial production pods in Huntly, Taranaki, and Kaitangata (CRL Energy Ltd, 2010). Although in both Australia and New Zealand CSG exploration and development has been taking place at a considerable pace, there is concern about potential environmental problems that could arise as a consequence of these operations (Taulis, 2010).

CSG is mainly methane gas stored in underground coal seams saturated with groundwater. The methane gas is adsorbed within the micropore structure of the coals held in by potentiometric pressure. To extract this gas, producers depressurize the coal seams by extracting large amounts of water (typically around 40 $m^3$/day but sometimes up to 100 $m^3$/day). Therefore, water production is critical for the success of CSG operations. In addition, CSG water chemistry is important as an exploration tool and to assess potential environmental implications arising from disposal issues.

The geochemical signature of CSG waters has been defined by Van Voast (2003) by analysing the CSG hydrochemistry for different producing basins in the US. The signature consists of high sodium and bicarbonate concentrations with low calcium and magnesium, and almost nil sulphate. In addition, high chloride concentrations are possible, and particularly in coal beds that are intimately associated with marine beds. In general, CSG waters have high alkalinity with circumneutral pH and their salinity tends to be in the brackish range (2000 < TDS <10,000 mg/L).

A few studies have investigated the hydrochemical nature of CSG waters. For example, Bartos and Ogle (2002) sampled springs, aquifers and CSG wells completed in coal seam aquifers within the Wyodak-Anderson coal zone to characterize recharge and groundwater flow processes within the Powder River Basin (PRB). McBeth et al. (2003a; 2003b) studied the water chemistry and trace element concentrations in discharge points and holding ponds in three Wyoming watersheds. Rice (2003) studied the chemical and isotopic composition of CSG waters sampled from 3 producing

53 fields targeting the Ferron Sandstone in Utah and noted hydrochemical differences which she
54 attributed to separate recharge areas, differences in flow paths, and various solute sources. Patz et
55 al. (2006; 2004) examined the interaction of CSG discharge water with semi-arid ephemeral stream
56 channels. This was done by sampling three discharge wells and seven sampling sites within the
57 stream. Similarly, Jackson and Reddy (2007a, b) collected CSG water samples from outfalls and
58 discharge points from five different Wyoming watersheds and carried out a geochemical analysis to
59 assess salinity and sodicity implications. In Australia, Golding et al (2010) studied the hydrochemistry
60 and isotopic composition of CSG waters from Permian coal beds within the Bowen Basin in
61 Queensland; this enabled them to infer the origin of the water based on the proximity to recharge
62 areas while considering the effect of folding and faulting. While in all of these studies the
63 hydrochemistry of CSG waters fits the geochemical signature as described by Van Voast (2003), none
64 of these focus on understanding the transient variations of samples taken from a single well over
65 time.

66 Decker (1987) presented the hydrochemistry of 30 CSG water samples from a well
67 completed in East Divide Creek Unit, Piceance Basin, Colorado collected between 1985 and 1987.
68 These samples fit the geochemical signature of CSG waters but also exhibit noteworthy
69 hydrochemical variations over time. Decker (1987) studied these variations using Piper diagrams,
70 and inferred that they were caused by a combination of true composition changes and random
71 errors (e.g. sampling and analysis).

72 The Maramarua coalfield is located in the north-eastern part of the Waikato Coal Region, in
73 New Zealand's North Island. This region is renowned for holding important coal resources within
74 the Waikato Coal Measures. Since 2003, significant CSG exploration activity has been undertaken in
75 this region by both the L&M Group and Solid Energy. In 2004, a CSG exploration borehole (C1) in
76 Maramarua was converted into a CSG pilot test by L&M, and active pumping from this well resulted
77 in 31 CSG water samples. A preliminary analysis of these samples was presented by Taulis and Milke

(2007) but no conclusions as to the nature of hydrochemical variations were presented in that work. Therefore, the aim of this article is to unveil the nature of CSG water sample variations from the Maramarua C1 well and to explore the potential implications this could have on co-produced water sampling and characterization.

# 2. Materials and Methods

## 2.1 Study Area and CSG Exploration

The Maramarua coalfield is bounded by the Maungaroa Fault to the West and by a series of NE trending normal faults separating it into sectors (Mangatangi, Puketoka, Kopuku, Clifton, and Maby sectors) (Edbrooke, 1981). The main coal resources are contained within the Waikato Coal Measures (WCM), deposited in the Eocene, and consisting of carbonaceous mudstones (clay and shales), sandstone conglomerates, fresh limestone, and sub-bituminous coals. The WCM (0-240m deep) forms the basement part of the Te Kuiti Group (180 to 600mm thick) which includes estuarine and shallow marine deposits overlying the WCM (Hall et al., 2006). In August 2003, exploration bore C1 was drilled in the Kupakupa seam within the Clifton Sector (Figure 1). In June 2004, exploration hole C1 was fitted with steel casing to carry out the pilot gas test. The casing was set with grout to about 2 m above the Kupakupa coal seam to isolate it from overlying units (L&M Coal Seam Gas Ltd, 2005) but no screen or gravel pack were fitted at the open interval.

Between August and October 2004 pilot testing of the Maramarua C1 borehole produced 22 CSG water samples that were analysed at the EEL (Environmental Engineering Laboratory, University of Canterbury) . In this particular operation, a “sucker rod” pump was used to pump CSG water to the surface in order to depressurize the Kupakupa seam. Pumping took place continuously except for a few interruptions due to pump break downs. Water samples were collected whenever pumping was resumed and had been ongoing for some period of time. Whenever there was a pump break down, the water level could remain stagnant inside the well for up to several days; the water level

would then slowly rise inside the well (due to artesian pressure), but it would decrease as soon as the pump was repaired and depressurization operations were resumed. However, pumping operations were suspended in November 2004 due to ongoing pump problems. Pump testing was resumed in April 2005 when a Progressive Cavity pump was installed in C1 and, between April and June 2005, 9 more samples were collected using this pump.

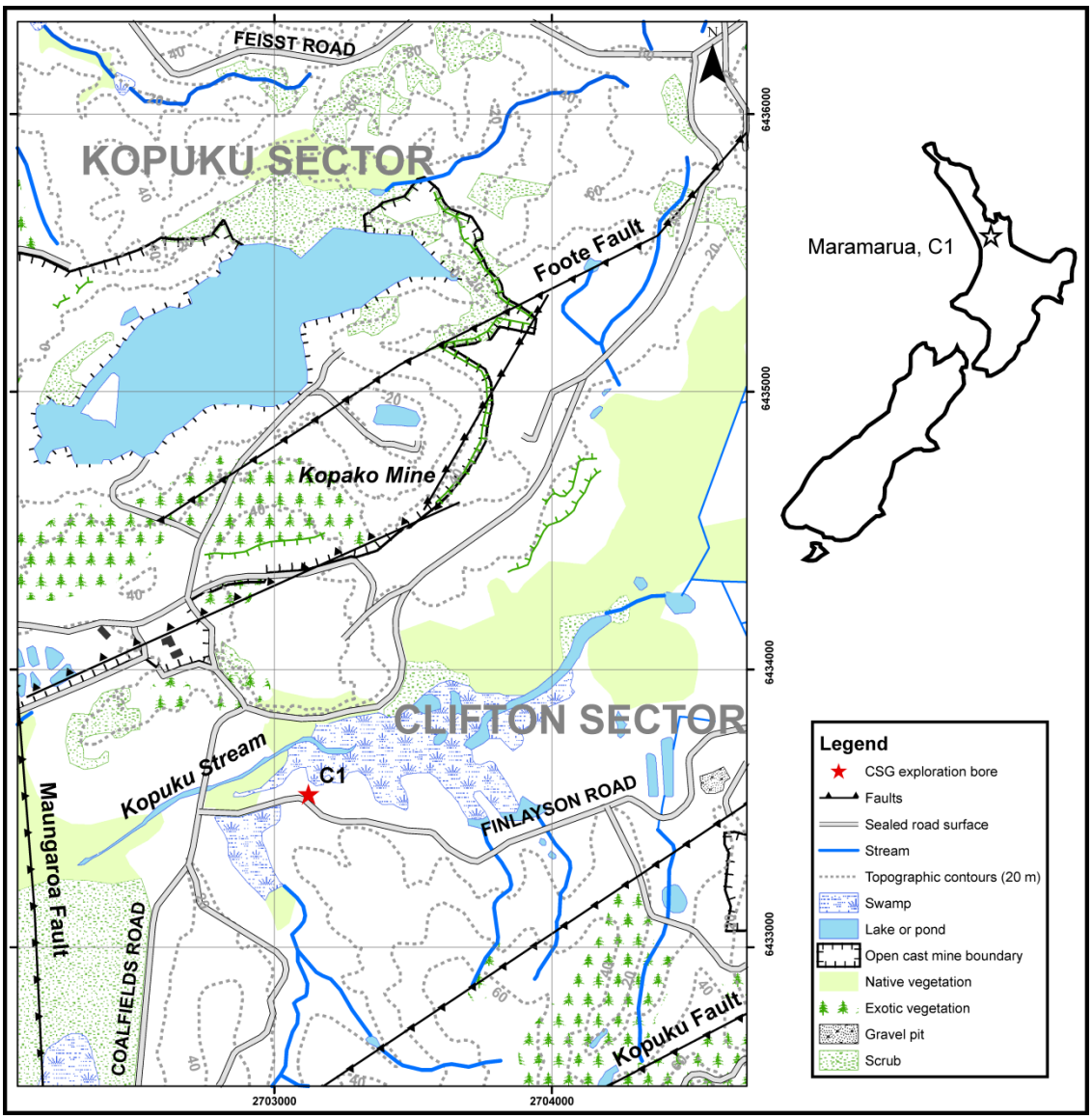


**Figure 1. Location of Maramarua C1 well (sourced from Topographic Map BB33 and BC33 North Island, Crown Copyright Reserved and after Edbrooke (1981))**

## 2.2 Sampling and Analysis

Common standards for sampling wells usually involve purging the well and taking the sample only after removing about 3 well volumes of stagnant water. In the case of C1, the well was purged continuously throughout the gas test because the aim of the test was to lower the water level (to a level just above the coal seam). Prior to sample collection, Electrical Conductivity, Dissolved Oxygen, pH, and Temperature were measured at the wellhead with a YSI-556 calibrated meter. On average these values were 1274 μS/cm, 24.6%, 7.8, and 18.3°C. Sample collection was carried out in untreated 1-liter polyethylene sample bottles. Bottles were prewashed and then rinsed three times with sample water before collecting each sample. No acidification was carried out because this would have modified the alkalinity and pH of the samples, and this would have impaired the subsequent laboratory work for non-metal constituents.

The analytical methods used throughout this study were based on APHA standards for most of the parameters being analysed, except for Sulphate and Chloride which were analysed using HACH methods. Magnesium was calculated from known hardness and calcium concentrations, and the carbonate species were obtained by solving the carbonate equilibrium equations using alkalinity, pH, and specific conductance. In addition, a sample collected on 19/8/2004 was sent to certified laboratories for a complete analysis including minor ions and trace elements. This sample was collected in a 1-liter untreated polyethylene bottle for major constituents, and in an acidified 250 ml bottle for dissolved metals. For the analytical determination of TDS by evaporation, samples were dried at 180°C (APHA, 1999) but were also dried at 103°-105° C for comparison purposes.

The 31 water samples analysed at the EEL are presented in Table 1. These samples exhibit low concentrations of calcium and magnesium accompanied by high concentrations of bicarbonate and chloride. Also, the sodium concentrations for these samples are consistently high (average = 313 mg/L). Sulphate levels are generally very low (<2mg/L) and below the detection limit. Specific conductance (1284-1424 μS/cm) is fairly high, and TDS values are in the range of 702-814 mg/L. The

low sulphate levels, along with the Na-$HCO_3$-Cl chemical signature, is indicative of this well's potential to produce methane gas (Van Voast, 2003).

Figure 2 shows a Piper diagram for these samples. On this diagram, the samples appear clustered together in specific regions. Figure 3 shows significant variations in calcium and magnesium concentrations but there are no grounds for discarding these samples as sampling errors.

146 **Table 1. Samples collected during Maramarua pilot gas test (August, 2004 - June, 2005)**

| | # | Date | Elapsed time (days) | pH | Sp Cond µS/cm T=25°C | TDS mg/L | Alkalinity mg/L as $CaCO_3$ | Hardness mg/L as $CaCO_3$ | $Ca^{2+}$ mg/L | $Mg^{2+}$ mg/L | $Cl^-$ mg/L | $SO_4^{2-}$ mg/L | $HCO_3^-$ mg/L | $CO_3^{2-}$ mg/L | $CO_{2\,(aq)}$ mg/L | $Na^+$ mg/L | WL mbgl |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| First sampling round | 1 | 01/08/2004 | 0 | 7.9 | 1424 | 798 | 428 | 27.3 | 7.39 | 2.13 | 140 | < 2 | 509.0 | 2.9 | 21 | 326 | 25 |
| | 2 | 06/08/2004 | 5 | 7.9 | 1390 | 814 | 425 | 29.0 | 4.48 | 4.34 | 142 | < 2 | 512.0 | 2.9 | 22 | 327 | 40 |
| | 3 | 07/08/2004 | 6 | 7.8 | 1354 | 786 | 416 | 25.0 | 4.80 | 3.16 | 142 | < 2 | 502.6 | 2.3 | 26 | 325 | 60 |
| | 4 | 08/08/2004 | 7 | 7.8 | 1389 | 772 | 413 | 23.0 | 4.90 | 2.62 | 145 | < 2 | 498.2 | 2.3 | 26 | 317 | 65 |
| | 5 | 09/08/2004 | 8 | 7.8 | 1386 | 774 | 421 | 25.3 | 5.32 | 2.91 | 142 | < 2 | 509.0 | 2.2 | 29 | 316 | 70 |
| | 6 | 10/08/2004 | 9 | 7.8 | 1390 | 702 | 410 | 24.8 | 4.56 | 3.25 | 142 | < 2 | 495.6 | 2.0 | 29 | 317 | 80 |
| | 7 | 16/08/2004 | 15 | 7.8 | 1391 | 800 | 394 | 23.3 | 5.79 | 2.13 | 142 | < 2 | 475.9 | 2.0 | 28 | 311 | 126 |
| | 8 | 20/08/2004 | 19 | 7.9 | 1357 | 740 | 394 | 32.0 | 7.79 | 3.05 | 143 | < 2 | 474.5 | 2.6 | 20 | 308 | 55 |
| | 9 | 12/09/2004 | 41 | 7.7 | 1325 | 742 | 391 | 32.7 | 5.40 | 4.67 | 143 | < 2 | 473.4 | 1.7 | 32 | 313 | 66 |
| | 10 | 13/09/2004 | 42 | 7.7 | 1358 | 768 | 388 | 32.0 | 5.20 | 4.63 | 141 | < 2 | 468.9 | 1.7 | 31 | 308 | 91 |
| | 11 | 14/09/2004 | 43 | 7.7 | 1380 | 766 | 385 | 30.5 | 5.20 | 4.26 | 141 | < 2 | 465.8 | 1.7 | 31 | 305 | 100 |
| | 12 | 17/09/2004 | 46 | 7.7 | 1410 | 786 | 390 | 30.5 | 5.60 | 4.02 | 140 | < 2 | 471.9 | 1.7 | 31 | 314 | 46 |
| | 13 | 18/09/2004 | 47 | 7.8 | 1396 | 734 | 390 | 32.5 | 4.80 | 5.00 | 144 | < 2 | 471.4 | 2.0 | 27 | 311 | 62 |
| | 14 | 18/09/2004 | 47 | 7.8 | 1418 | 746 | 390 | 31.0 | 5.00 | 4.51 | 142 | < 2 | 471.0 | 2.1 | 25 | 320 | 64 |
| | 15 | 18/09/2004 | 47 | 7.7 | 1325 | 772 | 390 | 25.0 | 4.40 | 3.41 | 146 | < 2 | 471.9 | 1.7 | 32 | 306 | 70 |
| | 16 | 19/09/2004 | 48 | 7.6 | 1338 | 770 | 388 | 26.5 | 4.40 | 3.78 | 142 | < 2 | 469.6 | 1.3 | 40 | 309 | 100 |
| | 17 | 20/09/2004 | 49 | 7.6 | 1361 | 786 | 390 | 26.5 | 6.39 | 2.56 | 146 | < 2 | 472.6 | 1.3 | 40 | 317 | 105 |
| | 18 | 21/09/2004 | 50 | 7.6 | 1284 | 792 | 395 | 31.5 | 7.19 | 3.29 | 144 | < 2 | 478.7 | 1.4 | 40 | 320 | 120 |
| | 19 | 04/10/2004 | 63 | 7.9 | 1326 | 766 | 390 | 30.0 | 6.39 | 3.41 | 141 | < 2 | 469.9 | 2.7 | 20 | 318 | 140 |
| | 20 | 05/10/2004 | 64 | 7.9 | 1380 | 784 | 393 | 28.0 | 5.99 | 3.17 | 148 | < 2 | 472.9 | 2.7 | 20 | 317 | 150 |
| | 21 | 20/10/2004 | 79 | 7.6 | 1390 | 746 | 390 | 28.0 | 5.99 | 3.17 | 145 | < 2 | 472.6 | 1.4 | 40 | 317 | 130 |
| | 22 | 21/10/2004 | 80 | 7.7 | 1385 | 743 | 390 | 27.0 | 5.60 | 3.17 | 151 | < 2 | 471.9 | 1.7 | 32 | 318 | 144 |
| Second sampling round | 23 | 25/04/2005 | 264 | 7.2 | 1270 | 828 | 365 | 28.0 | 6.40 | 2.90 | 145 | < 2 | 443.9 | 0.5 | 94 | 313 | 70 |
| | 24 | 27/04/2005 | 266 | 7.4 | 1309 | 812 | 375 | 23.0 | 6.70 | 1.50 | 144 | < 2 | 455.4 | 0.8 | 61 | 313 | 90 |
| | 25 | 29/04/2005 | 268 | 7.4 | 1296 | 826 | 378 | 24.0 | 5.60 | 2.40 | 148 | < 2 | 459.1 | 0.8 | 61 | 308 | 110 |
| | 26 | 3/05/2005 | 272 | 7.5 | 1309 | 782 | 383 | 19.0 | 5.20 | 1.50 | 143 | < 2 | 464.7 | 1.0 | 49 | 307 | 130 |
| | 27 | 10/05/2005 | 279 | 7.5 | 1305 | 784 | 375 | 20.0 | 4.80 | 1.90 | 148 | < 2 | 455.0 | 1.0 | 48 | 314 | 145 |
| | 28 | 23/05/2005 | 292 | 7.7 | 1318 | 780 | 383 | 18.0 | 4.80 | 1.50 | 143 | < 2 | 463.4 | 1.7 | 31 | 312 | 180 |
| | 29 | 24/05/2005 | 293 | 7.4 | 1296 | 822 | 380 | 29.0 | 7.90 | 2.40 | 143 | < 2 | 461.5 | 0.8 | 62 | 306 | 60 |
| | 30 | 10/06/2005 | 309 | 7.7 | 1317 | 844 | 380 | 24.0 | 4.00 | 3.40 | 145 | < 2 | 459.8 | 1.6 | 31 | 313 | 170 |
| | 31 | 11/06/2005 | 310 | 7.4 | 1314 | 792 | 380 | 22.3 | 4.80 | 2.50 | NA | < 2 | 461.5 | 0.8 | 62 | NA | 180 |

Sp Cond = Specific Conductance
WL =depth to water level measured from the surface
mbgl = meters below ground level

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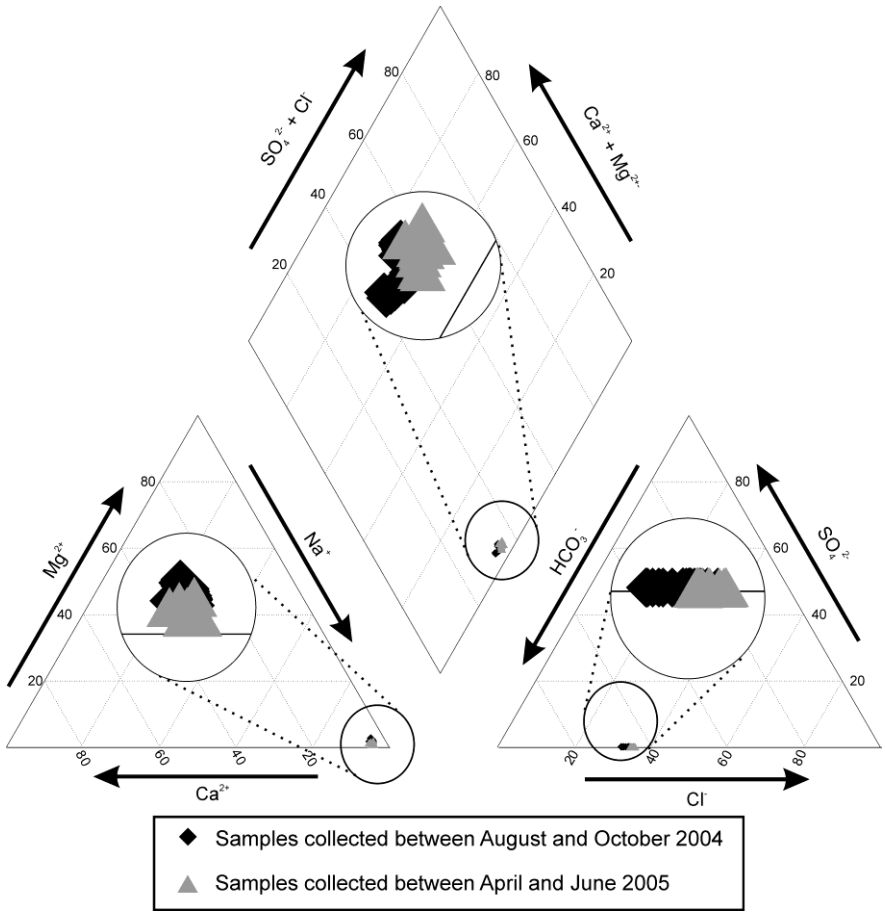


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149 **Figure 2. Piper diagram for Maramarua C1 samples collected between August, 2004**

150 **and June, 2005. Sulphate concentrations are plotted as half the detection limit (1 mg/L).**

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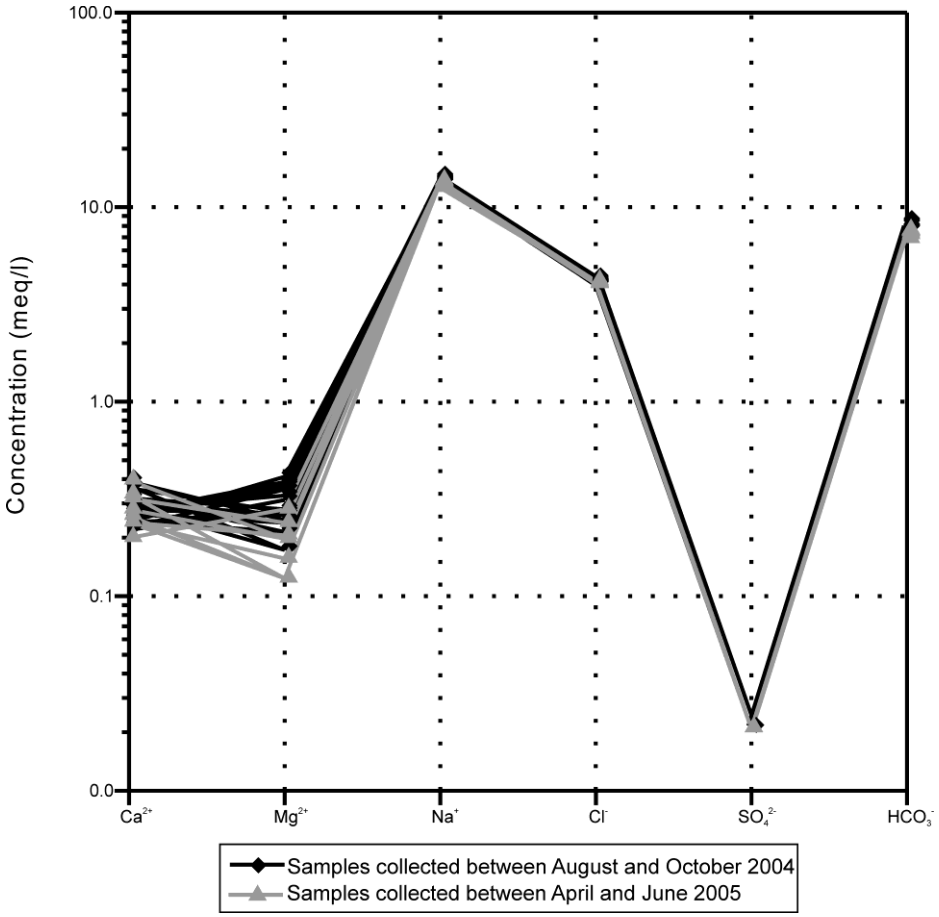
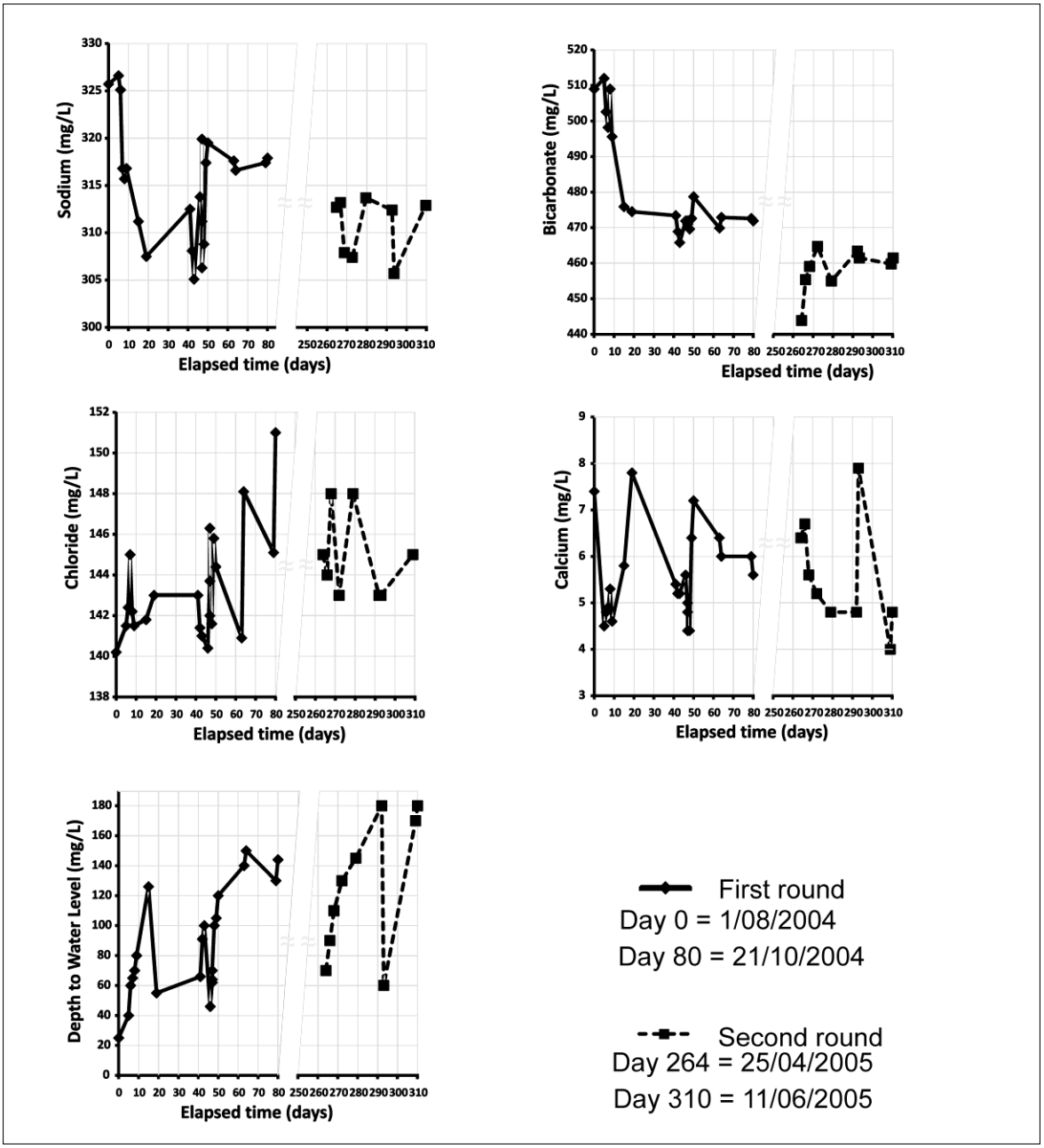



**Figure 3. Schoeller diagram for Maramarua C1 samples collected between August, 2004 and June, 2005. Sulphate concentrations are plotted as half the detection limit (1 mg/L).**

Figure 4 presents the sodium, bicarbonate, chloride, calcium concentrations in water samples along with a plot of water levels, measured during sample collection. An analytical trend analysis of the data presented here is not straight forward because samples were not collected at equally spaced intervals. In such situations, trend or time-series analysis becomes complicated, and the computation of autocorrelation coefficients is impaired (Chatfield, 1996).

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161 **Figure 4. Time plots for selected CSG water ions and depth to water level (measured**

162 **from the surface)**

163 An idealized representation of the 31 samples collected is presented in Table 2. This table is

164 based on average major ion concentrations for the 31 samples presented in Table 1, but with minor

165 ions and trace elements from the sample collected on 19/8/2004.

**Table 2. Idealized sample using averages of major ions but with minor ions and trace elements from certified laboratory analyses.**

| | | Idealized Sample |
|---|---|---|
| pH | | 7.8 [(1)] |
| Specific Conductance (T=25ºC) | µS/cm | 1351 [(2)] |
| TDS | mg/L | 776 [(2)] |
| Hardness | mg/L as $CaCO_3$ | 26.7 [(2)] |
| Alkalinity | mg/L as $CaCO_3$ | 392 [(2)] |
| Bicarbonate ($HCO_3^-$) | mg/L | 474 [(2,3)] |
| Carbonate ($CO_3^{2-}$) | mg/L | 1.72 [(2,3)] |
| Carbon dioxide ($CO_{2\,(aq)}$) | mg/L | 36.8 [(2,3)] |
| Calcium ($Ca^{2+}$) | mg/L | 6 [(4)] |
| Magnesium ($Mg^{2+}$) | mg/L | 0.9 [(4)] |
| Sodium ($Na^+$) | mg/L | 314.1 [(2)] |
| Potassium (K) | mg/L | 3 [(4)] |
| Chloride ($Cl^-$) | mg/L | 143.7 [(2)] |
| Sulphate ($SO_4^{2-}$) | mg/L | 0.7 [(1)] |
| Fluoride (F) | mg/L | 0.79 [(4)] |
| Boron (B) | mg/L | 2.5 [(4)] |
| Silica ($SiO_2$) | mg/L | 10.7 [(4)] |
| Total Iron (Fe) | mg/L | 0.4 [(4)] |
| Barium ($Ba^{2+}$) | mg/L | 0.024 [(4)] |
| Zinc ($Zn^{2+}$) | mg/L | 1.28 [(4)] |

[(1)] Analysed at CRL Energy Ltd Laboratory, Wellington, NZ.
[(2)] Average of 31 samples presented in Table 1
[(3)] Calculated from carbonate equilibrium.
[(4)] Sample was analysed by Hill Laboratories, Hamilton, and NZ.

## 2.3 Factor Analysis of hydrochemical data

The hydrochemistry of the Maramarua CSG samples was analysed using a form of multivariate analysis known as Factor Analysis. Some examples of the application of Factor Analysis to hydrochemical studies are given by Liu (2003), Love (2004), and Olmez (1994). Jackson and Reddy (2007a) used multi-factor Analysis of Variance to analyse CSG water samples collected from both outfalls and discharge ponds to identify differences in physio-chemical properties and ion concentrations between watersheds and years, but did not conduct factor analysis to identify combinations of variables that control variability.

An underlying assumption of factor analysis is that the multivariate data are normally distributed (Davis, 2002). Prior to the analysis the data were tested for normality and, in cases where the Maramarua CSG water quality data did not follow a normal distribution, transformations

were applied so that the data could be analysed using this technique. The Factor Analysis of Maramarua CSG water quality data was carried out using the MINITAB statistical software package.

Maramarua CSG water samples considered for Factor Analysis comprise 31 observations (samples 1-22 and 23-31 in Table 1). The variables are the chemical properties and constituents listed in Table 1, including the water levels, but excluding sulphate. However, some of these variables are either not independent variables or are strongly related to each other (e.g. bicarbonate and alkalinity, hardness and magnesium) so only independent variables were selected for this analysis.

## 2.4 Experimental Sparging

A laboratory experiment consisted of sparging the Maramarua CSG water sample collected on 11/06/2005 to measure hydrochemical changes with degassing. The sample was carefully analysed (avoiding unnecessary agitation) for specific conductance, alkalinity, pH, hardness, and calcium. Special provisions were made to measure calcium and hardness – samples were centrifuged and filtered (using 0.22 μ filters) to ensure that only soluble ions were measured. Once the sample was analysed, a 1.5 L sample was placed in a 2 L Erlenmeyer flask. The flask and the water were weighted prior to starting the sparging experiment. A porous hollow coil was then introduced inside the flask, and air was continuously pumped through it. A sketch of this experimental setup is presented in Figure 5. The aim of this experiment was to generate enough air bubbles in order to cause agitation and accelerate the carbon dioxide degassing process. While the experiment was being carried out, an open glass column with circulating cold water going through an inner glass coil ("cold finger") was introduced into the flask to a level just above the water level mark. This cold finger acted as a trap for water vapour leaving the system. Water particles leaving the system condensed on the cold finger and then slowly dripped back into the sample. The opening on top of the flask was sealed around the cold finger to avoid losses. This sparging experiment was run for 6 hours at a temperature of 20°C. After this time, the flask was weighed and the specific conductance

of the sparged water was recorded. Any discrepancies, due mainly to water vapour escaping the system, were corrected by adding deionized water.

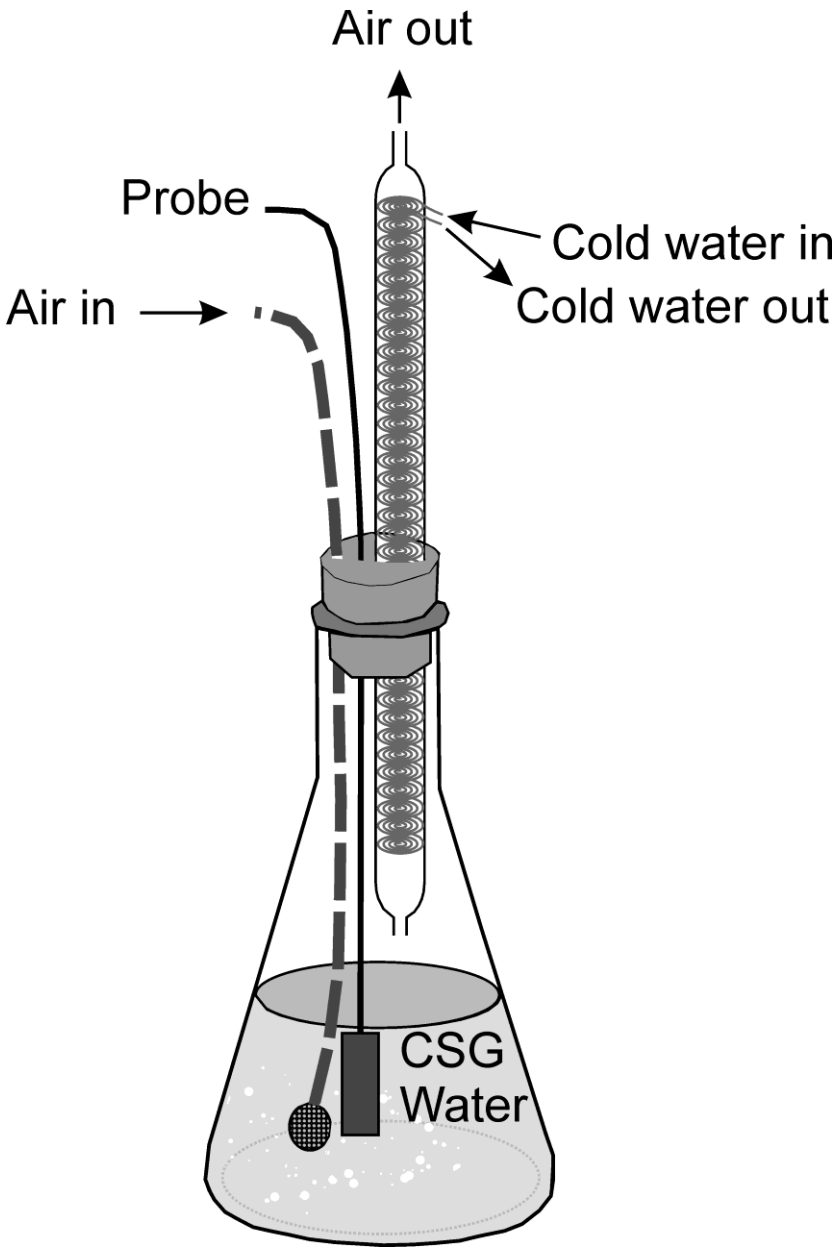



**Figure 5. Experimental setup for CSG sparging experiment.**

## 2.5 Geochemical Modelling

Geochemical modelling of the experimental sparging was carried out using a chemical speciation model, Visual MINTEQ v. 3.0 (U.S. Environmental Protection Agency, 2005). The idealized

sample presented in Table 2 was used as input for the model but using the initial and final pH values recorded during the sparging experiment.

# 3. RESULTS

## 3.1 Factor Analysis of hydrochemical data

The first 5 eigenvalues account for 90.9% of the total variance, therefore, only 5 factors were extracted. Therefore, a Factor Analysis with varimax rotation was carried out on 5 extracted eigenvalues resulting from a traditional Principal Component Analysis (PCA). The sum of the calculated communalities resulting from the factor extraction process is 90.9% (Table 3), which is the total variance after the five factors had been extracted and rotated. However, the variance has been redistributed among these factors so that, for example, the first factor contains 33% of the variance while the first PCA eigenvalue had 45%. These five factor score coefficients are shown graphically in Figure 6.

**Table 3. Eigenvalues after five factors are extracted**

| Factor Score N° | Eigenvalue (λ) [(1)] | Contribution | Cumulative |
|---|---|---|---|
| $B_1$ | 3.283 | 32.8% | 32.8% |
| $B_2$ | 1.653 | 16.5% | 49.3% |
| $B_3$ | 1.596 | 16.0% | 65.3% |
| $B_4$ | 1.332 | 13.3% | 78.6% |
| $B_5$ | 1.226 | 12.3% | 90.9% |
| Total | 9.09 | 90.9% | |

[(1)] Eigenvalues for extracted factor score coefficients after varimax rotation

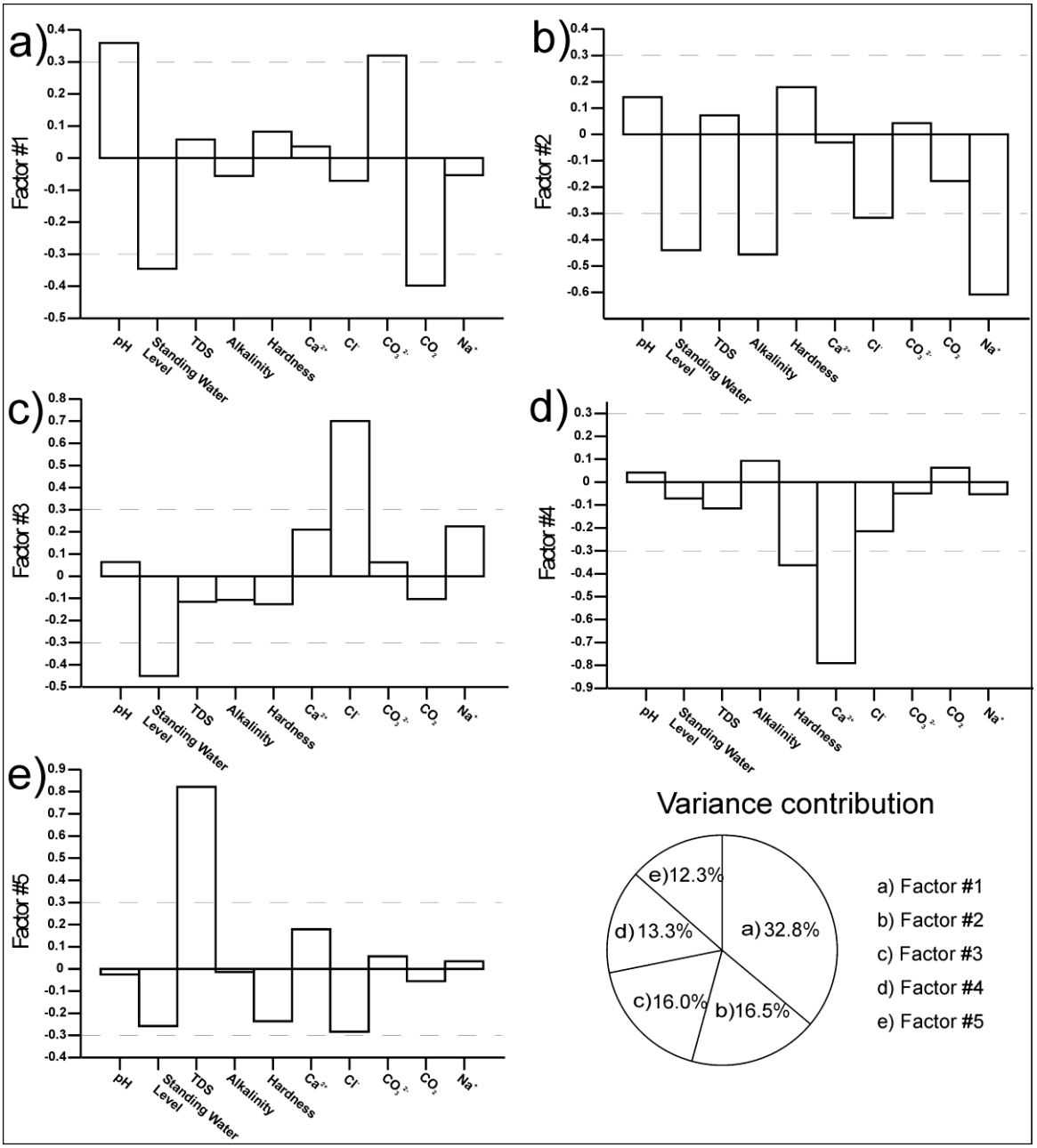



**Figure 6. Plot components for factor score coefficients (5 Factors, total variance = 90.9%)**

Factor #1

The components of the factor score coefficients for the first factor are distributed in such a way that only the components for carbon dioxide, pH, water level, and carbonate (in order of importance) are significant (e.g. > + 0.3 or < - 0,3; Figure 6a). This figure indicates that a strong decrease in dissolved carbon dioxide tends to be associated with a significant lowering of the water

level inside the well together with a considerable increase in pH and carbonate concentrations. This description fits the carbonate speciation model defined by solving the classical carbonate equilibrium equations (Freeze and Cherry, 1979; Snoeyink and Jenkins, 1980). To illustrate this point, these equations were solved for the 31 samples collected, and the resulting species distribution was plotted on a diagram constructed for different pH values (Figure 7). This plot shows that, for pH values greater than 7, carbonate concentrations tend to increase with increasing pH values while carbon dioxide concentrations tend to decrease. The 31 samples do not follow a specific pattern (some of the earliest samples are clustered together with later samples) and degassing is strongly correlated against pH. Therefore, the first factor score coefficient represents changes in pH values resulting from the carbon dioxide degassing process.

As the well is depressurized, different samples are collected under different degassing and agitation conditions. This water may remain inside the well (for a brief period of time) before it is collected, and the different water levels induce pressure changes, $CO_2$ degassing, and changes in hydrochemistry. On the other hand, degassing can also occur by water agitation inside the well (e.g. turbulent flow due to the absence of a gravel pack) which occurs when the pump is operating at maximum capacity (e.g. low standing water level), hence the negative value for the component representing the water level inside the well. Conversely, a low flow rate and a high water level inside the well could help keep $CO_2$ in solution as water pressure at the pump intake, located at the bottom of the well, helps prevent degassing. Therefore, water level variations induce changes in hydraulic pressure and have a direct impact on $CO_2$ degassing. During sampling, CSG water samples were carefully collected by completely filling polyethylene bottles with sample water (to avoid air gaps) and by sealing the bottles with an air-tight lid. However, when the sample is in a bottle, $CO_2$ degassing, carbonate precipitation, and a rise in pH could still occur if the seal is broken or becomes loose during transport (APHA, 1999). Consequently, the first factor shows that about 33% of the hydrochemical variations are due to this degassing process either during the sampling of co-produced water or subsequently during sampling storage and handling.

In addition, solving the carbonate system of equations can help describe the degassing process at the aquifer level. The lowest pH value detected in the Maramarua CSG water samples was 7.2 (25/04/2005). Assuming this is the pH of CSG water in the actual coal seam aquifer, the carbonate equilibrium equations can be solved with this pH value to calculate aquifer $CO_2$ partial pressure ($pCO_2$). Using this calculation procedure, it is possible to calculate a $pCO_2$ of at least 0.012577 atm for the Kupakupa seam at this location. Once this water is exposed to the surface, the pressure drops to normal atmospheric levels. Near the coast of New Zealand, for example, the atmospheric $pCO_2$ at standard conditions is around 0.000356 atm (Currie et al., 2011). However, these changes do not occur instantaneously as revealed by the different pH values in the Maramarua CSG water samples.

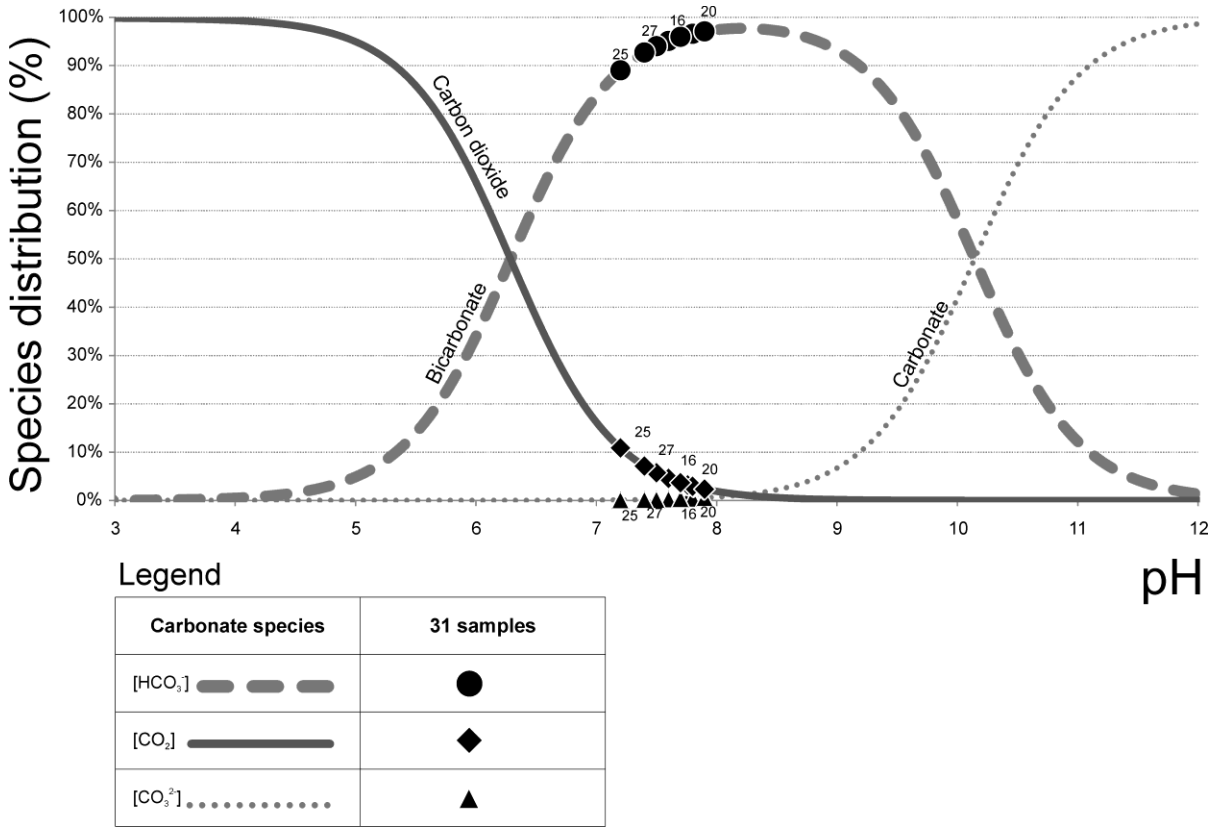



**Figure 7. Distribution of major species of dissolved inorganic carbon for the 31 samples collected during this study**

Factor #2

The major components in the second factor, which accounts for 16.5% of the variance, are standing water level inside the well, sodium, alkalinity (equivalent to bicarbonate for the studied pH range), and chloride (Figure 6b). These ions are the major ions in the CSG water samples collected throughout the study (water of the Na-$HCO_3$-Cl type as illustrated in Figure 2), so this factor is showing the correlation between the major ion composition and the water level inside the well. More specifically, this factor shows that with ongoing pumping and thus a low standing water level, the major ions will have lower concentrations. The second factor is a reflection of mixing processes, but can also reflect the pumping induced movement of waters of varying composition into the well. Factor #2 does not contain a TDS (laboratory measurement) term thus indicating that these variations are not significant enough to affect TDS determinations directly.

Figure 8 shows the 31 samples plotted for the first two factors. The symbols represent sample pH and are labelled according to the major ion contribution to TDS discounting $CO_2$ loss (TDS*), divided in 4 groups. This figure shows that the first factor is strongly linked to pH (from degassing, see the analysis of Factor #1); pH increases with increasing values for the first factor scores. The second factor picks up on slight variations in hydrochemistry that occur independently of pH. Here, factor scores linked to samples with lower TDS* (Groups I and II) tend to have a positive value and plot above groups III and IV. These variations in TDS* are relatively minor but noticeable enough to explain the significance of the second factor — this factor reveals a correlation between major ions once corrected for variations due to degassing.

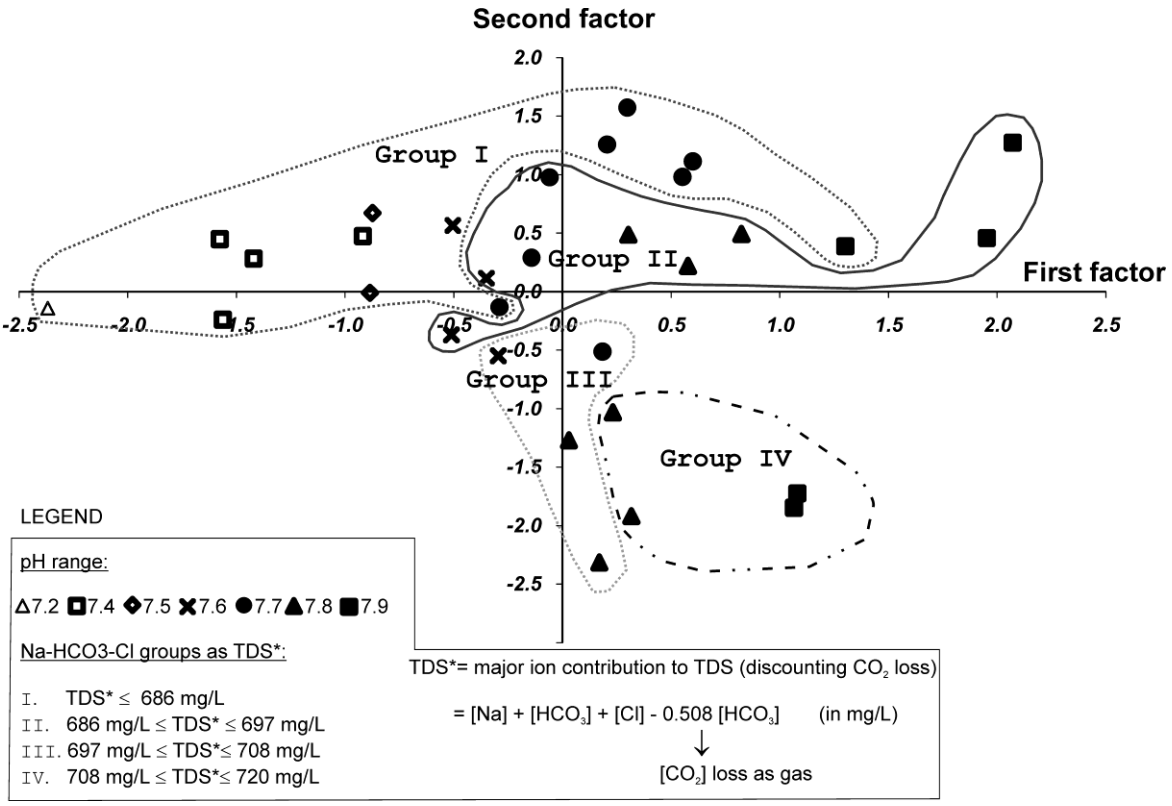



**Figure 8. Plot of factor scores for the first two factors.**

Factor #3

The third factor (variance contribution =16%) shows a negative correlation between chloride and standing water levels in the well (Figure 6c). This complements the interpretation of the second factor which showed a positive correlation between chloride and standing water level indicating that chloride is one of the major ions present in CSG samples. However, in the case of the third factor, the negative correlation between chloride and standing water level would indicate that chloride concentrations are high with standing water level decline which is exactly the opposite. Therefore, the second and third factors reflect that, although chloride concentrations tend to remain constant throughout pumping operations (the relative standard deviation for the 31 samples is 1.8%), some variations with pumping are expected. Further chloride variations are likely due to random errors associated with analytical determinations (relative error of 1.4% associated with the measuring

technique). This factor also reflects the fact that chloride in this CSG water was a less significant anion (average 4.1 q meq/L) than $Na^+$ (13.7 meq/L) and $HCO_3^-$ (7.8 meq/L). This aligns with the stronger weighting on sodium and alkalinity than chloride in factor #2.

Factor #4

Factor #4 (Figure 6d) shows a strong correlation between calcium and hardness. This is not unexpected as the value for hardness includes the value for calcium plus the value for magnesium. Therefore, a strong change in calcium concentrations would cause a change in hardness. The calcium coefficient for this factor is more heavily weighted than the hardness one (which also includes magnesium), so calcium is the main source of variation associated to this component. Calcium concentrations could vary significantly with calcium carbonate precipitation, which occurs with CSG water degassing. However, factor #4 does not include heavily weighted coefficients for any of the components associated to calcium carbonate precipitation (pH, standing water level, carbonate, or carbon dioxide). Since there are no other high-value coefficients for this factor, the calcium variation expressed by this factor could be attributed to natural variations in calcium in the CSG water (independent of degassing and the main mineralization processes reflected in Factors #1 and #2) or to the analytical determination of calcium. APHA (1999) reports a relative standard deviation of 9.2% associated to this technique, but laboratory titrations conducted could have been as high as 17%.

Factor #5

In factor #5 (Figure 6e) the only significant component is TDS. Therefore, this factor represents an independent source of variation associated with the TDS content of the Maramarua CSG water samples. This variation would be linked to the analytical technique used to measure TDS rather than to an actual process in the aquifer or within the well. This is because one would expect a strong correspondence between TDS and the coefficients for the major ions present in the samples ($Na\text{-}HCO_3\text{-}Cl$), but these coefficients are too low in factor #5. The relative error of TDS

333 determinations could be as high as 7%, so there is a high uncertainty surrounding TDS
334 determinations. Consequently, factor #5, which represents 12.3% of the variance, most likely
335 represents the uncertainty associated to this measuring procedure.

## 336 3.2 Experimental Sparging
337

338 Results for the laboratory sparging experiment are presented in Table 4. After sparging, the
339 water was left undisturbed in a closed container for about 8 hours. After this period of time, large
340 light grey fragments were observed at the bottom of the bottle. The sample volume was corrected
341 by adding 5.57 mL of deionized water to account for water losses through evaporation (0.26%).
342 Initial and final conditions after sparging differ mainly in pH, hardness, and calcium concentrations.

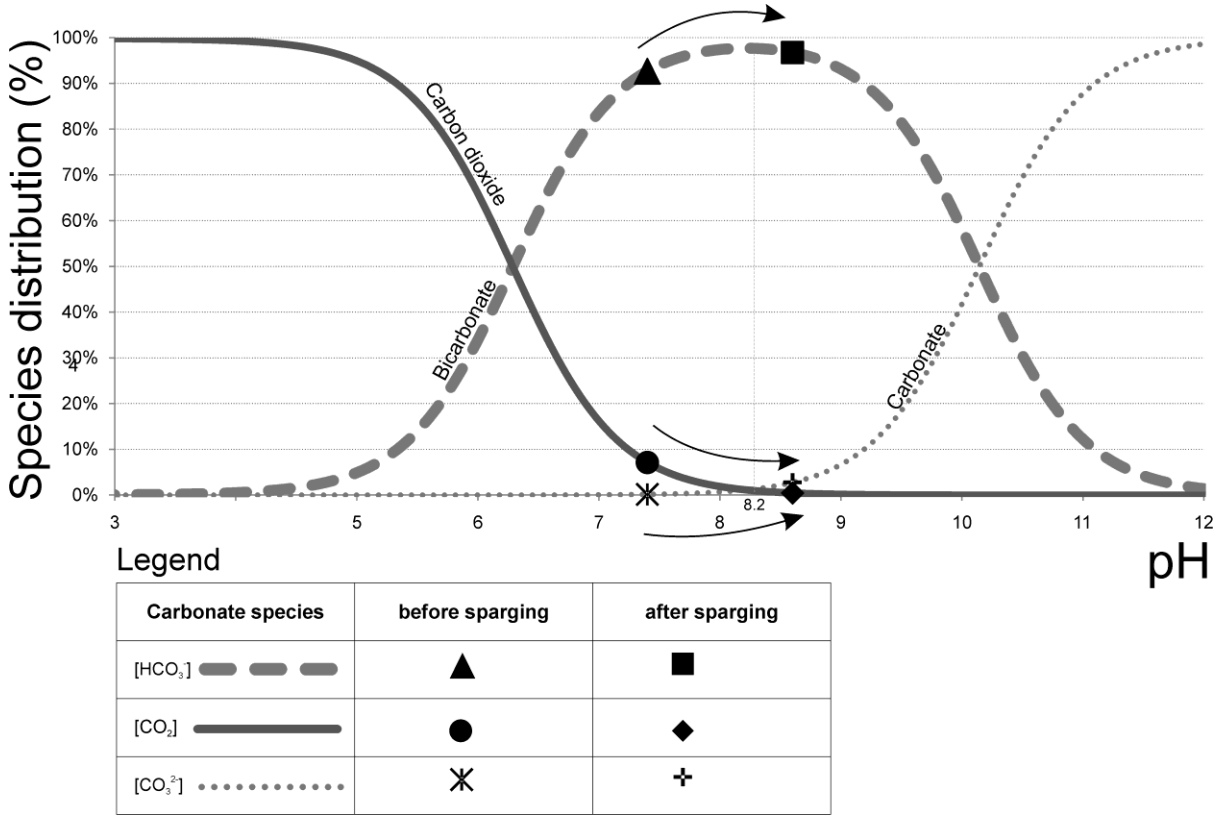
343 **Table 4. Sparging experiment results on CSG water sample collected on 11/06/2005**

| Parameters | units | prior to sparging | after sparging |
|---|---|---|---|
| Weight (water + flask) | grams | 2136.88 | 2131.31 |
| pH | pH units | 7.4 | 8.6 |
| Specific Conductance | µS/cm | 1314 | 1315 |
| Alkalinity | as mg/L $CaCO_3$ | 380 | 380 |
| Hardness | as mg/L $CaCO_3$ | 22.3 | 14.7 |
| $Ca^{2+}$ | mg/L | 4.8 | 2.9 |
| $Mg^{2+}$ | mg/L | 2.5 | 1.9 |
| $HCO_3^-$ | mg/L | 461.5 | 437.7 |
| $CO_3^{2-}$ | mg/L | 0.8 | 12.4 |
| $CO_{2\,(aq)}$ | mg/L | 61.7 | 3.7 |
| $H_2CO_3$ | mg/L | 0.098 | 0.006 |
| $H_2CO_3^*$ | mg/L | 61.8 | 3.7 |
| Saturation Index | pH units | -0.95 | 0.29 |

344

345 The immediate results from the sparging experiment indicate a rise in pH from 7.4 to 8.6,
346 and calcium precipitation in the order of 40%. Hardness is reduced by 34% after sparging, and this is
347 mainly a consequence of calcium precipitation. Magnesium precipitation could have also taken place
348 (25% at the most), but it is not possible to determine this with certainty because the APHA
349 measuring procedure is not sufficiently accurate at such low concentrations.

The carbonate species and properties for the 11/06/2005 sample before and after sparging are presented in Table 4. Before sparging, the major carbonate species was bicarbonate (462 mg/L) followed by dissolved carbon dioxide (62 mg/L). The calculated $CaCO_3$ saturation index for this sample is negative (-0.95) which means this sample is not precipitating calcium carbonate. Once the sample was sparged, the carbon dioxide degassing process was accelerated because the sample was exposed to the open atmosphere and to a lower atmospheric pressure. As a consequence, the pH rose from 7.4 to 8.6, and the carbonate speciation changed (Table 4). This time, dissolved carbon dioxide concentrations were very low (3.7 mg/L), and carbonate concentrations increased to 12 mg/L; the major carbonate ion continued to be bicarbonate, but its concentration decreased to 438 mg/L. In general, these results can be interpreted graphically using Figure 9. This figure shows the shift in the carbonate species' concentrations due to sample sparging. At a pH of about 8.2, the sparged sample reaches a maximum bicarbonate content in relation to the remaining carbonate species. As sparging continues, bicarbonate percentage decreases while carbonate increases. Another significant consequence resulting from sample sparging is the saturation index (Table 4), which in this case resulted in a positive value (0.29) indicating slight super saturation at the end of the experiment.




366

367 **Figure 9. Carbonate species prior and after sample sparging**

368

## 3.3 Geochemical Modelling

MINTEQ results are presented in Table 5. The original sample had a pH of 7.4 and, according to MINTEQ, presented some carbonate and zinc precipitation in the form of smithsonite. Calcite, carbonate, siderite, and smithsonite precipitation are significant when running the model with a pH of 8.6, which corresponds to the pH of the 11/06/2005 sample after the sparging experiment.

**Table 5. MINTEQ modelling results**

| **Modelling of idealized sample with pH = 7.4** | | | | |
|---|---|---|---|---|
| **Parameter** | **total dissolved** | **%dissolved** | **total precipitated** | **% precipitated** |
| Carbonate | $3.90 \cdot 10^{-3}$ | 99.7 | $1.25 \cdot 10^{-5}$ | 0.3 (1) |
| Zinc | $7.08 \cdot 10^{-6}$ | 36.1 | $1.25 \cdot 10^{-5}$ | 63.9 (1) |
| **Modelling of idealized sample with pH = 8.6** | | | | |
| **Parameter** | **total dissolved** | **%dissolved** | **total precipitated** | **% precipitated** |
| Calcium | $1.0170 \cdot 10^{-4}$ | 67.9 | $4.50 \cdot 10^{-5}$ | 32.1 (2) |
| Carbonate | $3.8551 \cdot 10^{-3}$ | 98.4 | $6.18 \cdot 10^{-5}$ | 1.6 (1,2) |
| Iron | $8.2663 \cdot 10^{-7}$ | 11.5 | $6.34 \cdot 10^{-6}$ | 88.5 (3) |
| Zinc | $1.0100 \cdot 10^{-6}$ | 5.2 | $1.86 \cdot 10^{-5}$ | 94.8 (1) |

(1) Precipitates as smithsonite ($ZnCO_3$)
(2) Precipitates as calcite ($CaCO_3$)
(3) Precipitates as siderite ($FeCO_3$)

MINTEQ predicted precipitation of calcium (32%), iron ( 89%), and zinc (95%) at pH 8.6. MINTEQ shows that CSG waters are undersaturated with respect to carbonate minerals at the wellhead (pH =7.4), which suggests these waters do not tend to precipitate carbonate minerals in the aquifer. However, once CSG waters reach equilibrium with the atmosphere (pH =8.6), the saturation index for most of these minerals (e.g. calcite) increases, and CSG waters tend to precipitate carbonate minerals and other minerals (e.g., Fe and Zn) when present.

# 4. Discussion

As evidenced by Factor #1, when CSG waters are in the aquifer, the aquifer $pCO_2$ can be up to two orders of magnitude greater than atmospheric $pCO_2$ at the surface, and the carbonate system behaves as a closed system. At this pressure, carbon dioxide will remain dissolved in the water, and

386 the dominant carbonate species will be bicarbonate. Furthermore, CSG waters will be just saturated
387 or undersaturated. However, once CSG waters are pumped to the surface, the lower atmospheric
388 pressure will cause carbon dioxide gas to come out of solution and the carbonate equilibrium will
389 start to change. This observation is in agreement with a study by Patz et al. (2006) in which $CO_2$
390 degassing from CSG water was identified as the likely cause of pH increase in discharge channels
391 open to the atmosphere.

392 Unless special provisions are taken when collecting a sample (like the use of micropurge sampling
393 and pressurized flow cells) it is practically impossible to avoid the degassing process.

394 The sample collected on 11/06/2005 from the Maramarua C1 well had unavoidably lost
395 some carbon dioxide as the water was being pumped to the surface. However, because this sample
396 was stored in a closed plastic bottle which had been completely filled with CSG water (leaving no air
397 gaps), the degassing effect was controlled (Saturation Index of -0.95). The saturation index (0.29)
398 resulting from sample sparging is close to zero because most of the calcite precipitated as carbon
399 dioxide degassed (it must have been higher at some point but then decreased as calcite
400 precipitated). This was verified by measuring calcium concentrations before and after sparging with
401 differences of 40%. In addition, MINTEQ modelling with the idealized sample at pH = 8.6 has resulted
402 in a positive saturation index, which corroborates the calculated positive saturation index value for
403 the 11/06/2005 sample after sparging. This shift in the Saturation Index is in agreement with a study
404 by Jackson and Reddy (2007a) where a decrease in calcium concentrations (e.g. due to calcite
405 precipitation) was detected in CSG water flowing from outfalls to discharge ponds.

406 Factor analysis shows a correlation between the carbonate precipitation process and water
407 level fluctuations. In this case, lower water levels imply less hydraulic pressure to keep the $CO_2$ in
408 solution. Higher pumping rates lead to both lower water levels and more turbulence, which induces
409 degassing. Turbulent flow in the zone adjacent to the well and through the pump intake results as a
410 consequence of well losses. Well losses are generally considered to be proportional to the square of

411 the pumping rate (Jacob, 1946), and these are magnified in absence of a gravel pack which is the
412 case here.

413 These results highlight the large variations one might find with CSG water due to degassing.
414 For this CSG water, the true aquifer pH could be as low as 6.6 with a $pCO_2$ of 0.037885 atm because
415 at this pH/$pCO_2$ value, MINTEQ predicts no mineral precipitation. However, when CSG water is
416 abstracted, the pH inside the well immediately begins to rise because of the pressure loss. When
417 samples are collected, pH could rise further with sample handling. Even if the sample bottle is full
418 with no air space, degassing will resume upon analysis. The overall time for degassing to occur varies
419 greatly based on $CO_2$ concentrations, temperature, and agitation during storage and transit (APHA,
420 1999); however, under rigorous sampling and analytical protocols, an analyst might be able to keep
421 these variations at less than 33%. With poor or variable sampling of CSG water, the resulting data
422 could have large variations wholly dependent on sampling, analysis procedures, and the amount of
423 degassing allowed for each sample. To minimize variations due to $CO_2$ degassing, APHA (1999)
424 recommends carrying out laboratory examinations as soon as possible and to analyse samples
425 promptly after opening the sample container while avoiding vigorous sample agitation. Further
426 measures can be taken by using a pressurized chamber (e.g. at a pressure equal to the aquifer $pCO_2$)
427 and to minimize temperature effects (e.g. by keeping the sample at a lower temperature than the
428 one measured when it was collected).

429 When solving the carbonate system of equations for CSG waters, it is valuable to note that
430 the addition or removal of carbon dioxide does not influence the final alkalinity value (Snoeyink and
431 Jenkins, 1980), and this confirms the experimental result in Table 4. Alkalinity could decrease with
432 calcium carbonate precipitation but calcium concentrations are low in CSG waters to begin with. This
433 result has further implications for sampling CSG waters – when sampling, it is necessary to measure
434 pH at the wellhead because this value changes with degassing. Samples can be analysed for alkalinity
435 at a later stage in the laboratory since this value will not change as carbon dioxide is lost. By

436 measuring alkalinity in the laboratory, and pH in the field, the analyst can reconstruct the true
437 concentrations before and after degassing. However, pH meters need to be properly calibrated
438 because, at high alkalinity values (> 400 mg as $CaCO_3$/L), pH inaccuracies of 0.1 can result in high
439 errors (10-15 mg/L for $CO_2$) when solving the carbonate equilibrium equations (APHA, 1999).

440 Factor #2 reflects changes in major ion composition with ongoing pumping and lower
441 standing water levels inside the CSG well. In particular, sodium concentrations tend to decrease with
442 lower water levels. This is explained by taking into account the different lithologies that give rise to
443 heterogeneity and confining conditions within the WCM. The WCM are confined by claystones and
444 present coal seams interbedded with various mudstones (Taulis and Milke, 2007). These
445 sedimentary rocks contain clay minerals having a significant cation exchange capacity (Domenico
446 and Schwartz, 1998) hence these minerals tend to adsorb $Ca^{2+}$ ions and release $Na^{+}$ ions, which
447 results in CSG waters having high $Na^{+}$ concentrations (Van Voast, 2003). Decker (1987) has described
448 a diffuse layer of cations with high ionic potential (e.g. $Ca^{2+}$ and $Mg^{2+}$) bound to clay minerals within
449 coal measures; in turn, anions with high ionic potential (e.g. $CO_3^{2-}$ and $SO_4^{2-}$) will be held more tightly
450 in the diffuse layer. Because the system must be electrically neutral, this layer will have lower
451 concentrations of lower ionic potential ions (e.g. sodium, bicarbonate, and chloride). At greater
452 distances from the diffuse layer, the coal seam aquifer water will not be directly influenced by the
453 cation exchange capacity of these minerals and the diffuse layer will not be present. When the
454 pumping rate is increased, after continuous pumping, the standing water level inside the well drops
455 and the drawdown cone expands. This enables new sites within the coal seam to be accessed and, in
456 particular, sites adjacent to clay-bearing minerals will be accessed first. Therefore, the diffuse layer
457 within these sites will be drawn into the well and will mix with other CSG waters. This cation
458 exchange mechanism could give rise to CSG water having a slightly lower concentration of sodium,
459 bicarbonate, and chloride but with insignificant changes in salinity (e.g. TDS) as seen with factor #2;
460 variations due to this effect could be as high as 16.5% independently of degassing effects.

Factor#5 has highlighted an important consideration to be taken into account when carrying out TDS determinations by evaporation. Van Voast (2003) has previously reported laboratory inconsistencies in the determination of TDS by calculation — the $CO_2$ that is lost due to evaporation (about half of the bicarbonate) is not always discounted. When carrying out TDS determinations by evaporation, APHA (1999) specifies drying temperatures of 180°C for TDS because, when the sample is dried, $CO_2$ and $H_2O$ are lost and bicarbonates are converted to carbonates. However, at temperatures below 180°C this reaction may not go to completion. This is particularly important when analysing CSG waters because of the high bicarbonate content present in these waters. Some laboratories tend to have a relaxed attitude about the drying temperature for TDS and often use 103°-105° C instead of 180°C. This generally would pose no problems in low bicarbonate waters but, with highly carbonated CSG waters, overestimation of TDS is definitely a possibility. Throughout these study, samples were dried up at both 103°-105° C and 180°C. It was discovered that TDS values decreased in about 74% of the samples when using 180°C with values decreasing in about 6% on average and up to 10% in some cases. Although in this study TDS determinations were carried out at 180°C, random variations in oven temperature or humidity interferences while drying could have impacted on TDS determinations as shown by factor #5.

MINTEQ modelling for the CSG water at this well revealed that degassing is likely to cause calcium precipitation as calcium carbonate ($CaCO_3$) and zinc precipitation as smithsonite ($ZnCO_3$). This last result is in agreement with a study by McBeth et al (2003a) which identified smithsonite precipitation from CSG water in holding ponds located in the Powder River Basin, Wyoming. According to MINTEQ, zinc precipitation could be as high as 95% and, in the case of the idealized sample, which had a zinc concentration of 1.28 mg/L, this could represent a significant reduction (1.22 mg/L) if the CSG water is exposed to the open atmosphere for some period of time.

## 5. Conclusions

A pilot CSG well in Maramarua (NZ) has produced water samples exhibiting noteworthy variations over time. These hydrochemical variations are a product of composition changes induced by pumping (as high as 50%) and random errors due to sample handling and analysis (as high as 42%).

CSG water composition changes induced by pumping are a consequence of both $CO_2$ degassing (about 33%) and the mixing of aquifer waters of varying major ion (Na-$HCO_3$-Cl) composition (about 17%). Degassing is an inherent process of pumping but can be controlled with good production and completion techniques (e.g. gravel pack, continuous pumping, and water level above the well screen) to promote laminar flow into the well. Continuous pumping at a constant rate can help minimize variations in major ion composition as water of homogeneous composition will be drawn into the producing well. Sampling degassing may also occur but these variations can be minimized by collecting samples with minimum agitation, by filling sample containers completely, and by using air-tight seals. Degassing prior to analysis can be controlled by transporting the sample at a low temperature (lower than when it was collected) and by carrying out the analysis as soon as possible, immediately after opening the sample container.

At this well, carbonate minerals likely to precipitate with CSG water degassing were calcium carbonate ($CaCO_3$), smithsonite ($ZnCO_3$), and siderite ($FeCO_3$). However, concentrations of Ca, Zn, and Fe tend to be low in CSG waters. Effective sampling of CSG waters can be carried out by measuring pH with a properly calibrated meter at the well head while carrying out alkalinity determinations later in the laboratory. These data can then be used to recreate the exact state of the carbonate species at the time of sample collection. In addition, it is possible to use these data to infer the $pCO_2$ in the aquifer; in the case of Maramarua C1 this pressure could have been at least two orders of magnitude higher than atmospheric $pCO_2$.

508 Random errors due to sample handling and analysis are evident in the determinations of $Cl^-$
509 (16% at the most), $Ca^{2+}$ (as high as 13%), and TDS (as high as 12%). Chloride variations could also be
510 an indication of variations with different pumping regimes, and calcium variations due to this effect
511 could also be expected. In the determination of TDS by evaporation, it is important to evaporate
512 samples using the correct drying temperature of 180°C, recommended by APHA (1999), to avoid an
513 overestimation (as high as 10%) of this parameter. At lower temperatures, bicarbonates may not
514 completely convert into carbonates, and the evaporation of water and loss of $CO_2$ may not fully take
515 place.

516 CSG waters from Maramarua C1 have a high bicarbonate concentration, which plays an
517 important role in shaping their hydrochemistry once abstracted. Once exposed to atmospheric $pCO_2$,
518 CSG water pH rises considerably, but bicarbonate concentrations will rise while carbon dioxide gas is
519 vented and carbonate minerals are precipitated. Consequently, different pumping rates, along with
520 changes in pressure, will yield a continuously changing hydrochemistry.

521

# References


American Public Health Association, American Water Works Association, and Water Environment Federation., 1999, Standard methods for the examination of water and wastewater: Washington, D.C., American Public Health Association, 1 computer optical disc p.

Bartos, T.T., and Ogle, K.M., 2002, Water quality and environmental isotopic analyses of ground-water samples collected from the Wasatch and Fort Union formations in areas of coalbead methane development : implications to recharge and ground-water flow, eastern Powder River Basin, Wyoming. , Water-resources investigations report ; 02-4045: Cheyenne, Wyo; Denver, CO, U.S. Dept. of the Interior U.S. Geological Survey, p. vi, 88 , (4 folded).

Chatfield, C., 1996, The analysis of time series : an introduction: London, Chapman & Hall, xii, 283 p.

CRL Energy Ltd, 2010, Annual Review 2010: Wellington.

Currie, K.I., Reid, M.R., and Hunter, K.A., 2011, Interannual variability of carbon dioxide drawdown by subantarctic surface water near New Zealand: Biogeochemistry, v. 104, p. 23-34.

Davis, J.C., 2002, Statistics and data analysis in geology: New York, J. Wiley, xvi, 638 p. p.

Decker, A.D., Klusman, R., Horner, D.M., and Anonymous, 1987, Geochemical techniques applied to the identification and disposal of connate coal water: Proceedings - International Coalbed Methane Symposium, v. 1987, p. 229-242.

Domenico, P.A., and Schwartz, F.W., 1998, Physical and chemical hydrogeology: New York, Wiley, xiii, 506 p.

Edbrooke, S.W., 1981, Maramarua Coalfield: assessment of exploration 1977-1980., New Zealand Geological Survey.

Freeze, R.A., and Cherry, J.A., 1979, Groundwater: Englewood Cliffs, N.J., Prentice-Hall, xvi, 604 p.

Golding, S.D., Kinnon, E.C.P., Boreham, C.J., Baublys, K.A., and Esterle, J.S., 2010, Stable isotope and water quality analysis of coal bed methane production waters and gases from the Bowen Basin, Australia: International Journal of Coal Geology, v. 82, p. 219-231.

Hall, S.L., Nicol, A., Moore, T.A., and Bassett, K.N., 2006, Timing of normal faulting in the Waikato Coal Measures, New Zealand, and its implications for coal-seam geometry: New Zealand Journal of Geology and Geophysics, v. 49, p. 101-113.

Jackson, R.E., and Reddy, K.J., 2007a, Geochemistry of coalbed natural gas (CBNG) produced water in powder river basin, wyoming: Salinity and sodicity: Water Air and Soil Pollution, v. 184, p. 49-61.

Jackson, R.E., and Reddy, K.J., 2007b, Trace element chemistry of coal bed natural gas produced water in the Powder River Basin, Wyoming: Environmental Science & Technology, v. 41, p. 5953-5959.

Jacob, C.E., 1946, Drawdown Test to Determine Effective Radius of Artesian Well: Proceeding, American Society of Civil Engineers, v. 72.

558 L&M Coal Seam Gas Ltd, 2005, PEP 38608 Maramarua Project Report, Ministry of Economic
559 Development New Zealand. Unpublished Petroleum Report 3212.

560 Liu, C.-W., Lin, K.-H., and Kuo, Y.-M., 2003, Application of factor analysis in the assessment of
561 groundwater quality in a blackfoot disease area in Taiwan: Science of The Total
562 Environment, v. 313, p. 77-89.

563 Love, D., Hallbauer, D., Amos, A., and Hranova, R., 2004, Factor analysis as a tool in groundwater
564 quality management: two southern African case studies: Physics and Chemistry of the Earth,
565 Parts A/B/C, v. 29, p. 1135-1143.

566 McBeth, I., Reddy, K.J., and Skinner, Q.D., 2003a, Chemistry of trace elements in coalbed methane
567 product water: Water Research, v. 37, p. 884-890.

568 McBeth, I.H., Reddy, K.J., and Skinner, Q.D., 2003b, Coalbed methane product water chemistry in
569 three Wyoming watersheds: Journal of the American Water Resources Association, v. 39, p.
570 575-585.

571 Olmez, I., Beal, J.W., and Villaume, J.F., 1994, A new approach to understanding multiple-source
572 groundwater contamination: Factor analysis and chemical mass balances: Water Research, v.
573 28, p. 1095-1101.

574 Patz, M.J., Reddy, K., and Skinner, Q.D., 2006, Trace elements in coalbed methane produced water
575 interacting with semi-arid ephemeral stream channels: Water Air and Soil Pollution, v. 170,
576 p. 55-67.

577 Patz, M.J., Reddy, K.J., and Skinner, Q.D., 2004, Chemistry of coalbed methane discharge water
578 interacting with semi-arid ephemeral stream channels: Journal of the American Water
579 Resources Association, v. 40, p. 1247-1255.

580 Rice, C.A., 2003, Production waters associated with the Ferron coalbed methane fields, central Utah:
581 chemical and isotopic composition and volumes: International Journal of Coal Geology, v. 56,
582 p. 141-169.

583 Snoeyink, V.L., and Jenkins, D., 1980, Water chemistry: New York, Wiley, xiii, 463 p.

584 Taulis, M.E., 2010, Australia and New Zealand CBNG Development and Environmental Implications,
585 *in* Reddy, K.J., ed., Coalbed natural gas : energy and environment: Energy science,
586 engineering and technology series.: New York, Nova Science Publishers, p. xxi, 511.

587 Taulis, M.E., and Milke, M.W., 2007, Coal seam gas water from Maramarua, New Zealand:
588 Characterisation and comparison to United States analogues: Journal of Hydrology (New
589 Zealand), p. p1-17.

590 U.S. Environmental Protection Agency, 2005, Exposure Assessment Models, U.S. Environmental
591 Protection Agency, p. web page.

592 Van Voast, W.A., 2003, Geochemical signature of formation waters associated with coalbed
593 methane: Aapg Bulletin, v. 87, p. 667-676.

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