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UNIVERSITY OF THE
WITWATERSRAND,
JOHANNESBURG

An assessment and evaluation of dissolved methane concentrations at a natural gas extraction site in the Free State Province, South Africa.

A research report submitted to the Faculty of Science in fulfilment of the requirements for the degree of Master of Science by coursework and research project

School of Animal, Plant and Environmental Sciences

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DECLARATION

I declare that this research is my own, unaided work. It is submitted in fulfilment for the requirements for the degree of Master of Science at the University of the Witwatersrand. It has not been submitted previously for any degree or examination at any other University.



Khalid Patel

30 October 2018

ABSTRACT

A worldwide concern associated with natural gas exploration and extraction is the potential for contamination of shallow groundwater. A natural gas extraction operation is underway near Virginia in the Free State Province of South Africa. The aim of this study is to determine whether ongoing gas extraction activity has affected the chemical composition of surrounding groundwater. This was achieved through re-sampling of boreholes (water wells) previously sampled in 2015 by the operator, prior to gas extraction.

Dissolved methane (CH_4) above the laboratory limit of detection was present in six out of seven re-sampled boreholes, at distances between 153 and 1538 m from the production well. Dissolved CH_4 concentrations ranged from < 0.007 to 3.16 mgCH_4/l, with an average of 0.234 mg/l. Dissolved CH_4 concentrations were positively correlated with manganese (*r=0.347, n=55, p=0.010*) and negatively correlated with bromide (*r=-0.338, n=55, p=0.012*), calcium (*r=-0.303, n=55, p=0.024*), sulfate (*r=-363, n=55, p=0.006*) and electrical conductivity (*r=-0.266, n=55, p=0.049*).

No statistically significant correlation was observed between dissolved CH_4 concentrations and proximity to the gas well (*r = 0.221, n = 55, p = 0.105*), elevation relative to the production well (*r = 0.190, n = 55, p = 0.165*) or sampling depth (*r = .330, n = 55, p = 0.469*). The small observed decrease in the mean concentration of dissolved CH_4 between 2015 and 2017 was not statistically significant (*p = 0.812)*. Thus, no evidence was found that the gas extraction operation has contributed to increased concentrations of CH_4 in groundwater by means by stray gas migration from the production well. The methane in the sampled wells is believed to be of biogenic origin, based on the positive correlation between dissolved CH_4 and NH_4 (*p=0.045*) and the non-detection of higher-chain hydrocarbons.

Comparison of pre- and during-production analyses for 24 water quality variables identified several statistically-significant changes over time: increases in pH (*0.195* units), arsenic (*0.002 mg/l*), lead (*0.001 mg/l*), potassium (*0.875 mg/l*) and dissolved organic carbon (*7.647 mg/l*). The South African drinking quality guidelines were exceeded, both before and during gas production, for electrical conductivity, chloride and manganese.

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1. INTRODUCTION

Natural gas is a fossil fuel found in oil fields, natural gas fields and coal beds. Natural gas originates from three predominant formation processes namely, thermogenic, biogenic and abiogenic processes (Gold, 1985). Natural gas is a versatile and cleaner burning fossil fuel with a wide variety of energy applications (Demirbas, 2006). As a result of these properties, natural gas has emerged as a preferred fossil energy source from both an environmental and political perspective (Rozel and Reaven, 2012).

Increasing global energy demands, coupled with the economics of energy use and an emphasis on cleaner burning fuels has resulted in increasing natural gas exploration and extraction activity globally (Osborn et al, 2011). This increase in natural gas exploration and extraction has highlighted several concerns over the potential impact of natural gas, in particular the contamination of shallow groundwater aquifers used predominantly for drinking water (Fontenot et al, 2013).

Instances of groundwater contamination have been recorded in areas allowing the use of horizontal drilling and hydraulic fracturing (McPhillips et al, 2014). Contamination of groundwater resources from natural gas extraction activities includes the risks associated with high-pressure injections of large volumes of fracturing fluids, methane migration from failed well casings into aquifers used for drinking water and the migration of produced water into freshwater aquifers (Vidic et al, 2013).

In South Africa, methane emissions from subsurface are common occurrences in the Karoo with historic and present-day anecdotal evidence available of explosive gas present in boreholes. Dissolved methane has been detected in both shallow and deep boreholes throughout areas representative of Karoo geology (Talma and Esterhuyse, 2015). As a result, the presence of naturally occurring dissolved methane is a common in boreholes and spring water associated with areas underlain by Karoo geology (Talma and Esterhuyse, 2015).

Current research undertaken on methane contamination of groundwater from natural gas extraction is focussed on the use of horizontal drilling and hydraulic fracturing techniques which are applied to low permeability organic shale formations and “tight-sand” reservoirs (Osborn et al, 2011). This research has been undertaken almost exclusively in the United States of America resulting in limited research

on groundwater contamination that may arise from other extractive techniques undertaken across the globe.

An unconventional natural gas extraction operation is currently underway, near the town of Virginia in the Free State Province South Africa. The operation entails the extraction of natural gas from gas bearing fractures and faults (Venmyn Deloitte, 2016). The operation provides a unique opportunity to study the potential impact of a non-hydraulic fracturing natural gas extraction operation on groundwater quality in adjacent aquifers.

Thus, the aim of the research is to determine if current extraction activities at a single gas extraction site has affected groundwater quality parameters, specifically dissolved methane concentrations in aquifers adjacent to the operation. This research is particularly topical as South Africa has recently completed a strategic environmental assessment (CSIR, 2016) on the impact and feasibility of developing gas resources and in particular, shale gas resources in the Karoo.

2. LITERATURE REVIEW

2.1 Natural gas origins and formation processes

Natural gas is a fossil fuel found in geological formations such as coal beds, shale deposits and tight-sand formations. It is a naturally-occurring hydrocarbon rich gaseous mixture composed primarily of methane (CH_4) as well as ethane and propane. Depending on its origin, natural gas may also contain other components such as C_2+ hydrocarbons, carbon dioxide (CO_2), helium (He), hydrogen sulfide (H_2S), nitrogen (N_2) and noble gasses (Faramawy et al, 2016).

In its pure state, natural gas is a colourless, odourless and combustible gas which releases approximately 50 – 55 megajoules (MJ) per kilogram (kg) of energy when burned (Faramawy et al, 2016). Natural gas originates from three predominant formation processes, namely abiogenic, biogenic and thermogenic (Gold, 1985).

2.1.1 Abiogenic processes

The formation of natural gas by abiogenic processes is primarily through the reduction of CO_2 and is thought to occur during magma cooling.

Evidence for the abiogenic formation of natural gas is supported by the discovery of CH_4 at a hydrothermal vent located in the East Pacific Rise and in other crustal fluids (Lollar et al, 2002).

The abiogenic formation of natural gas is thought to commonly occur in hydrothermal systems during water-rock interactions such as the metamorphism of graphite-carbonate bearing lithological units (Kenney et al, 2002), surface-catalysed polymerisation (Foustoukos and Seyfried, 2004) and other gas-water-rock reactions such as the serpentinization of ultramafic lithological units (Lollar et al, 2006).

The contribution of abiogenic hydrocarbons to economic hydrocarbon reserves has proved difficult to quantify. This is due to obscuring of abiogenic isotopic signatures as a result of mixing with CH_4 of microbial origin (Lollar et al, 2006) as well as uncertainty in carbon isotopic signatures for abiogenic versus thermogenic hydrocarbons (Horita and Berndt, 1999). Regardless, data obtained from four sites in Canada and South Africa strongly suggest that abiogenic natural gas is more common place than previously believed. Its contribution to globally significant abiogenic reserves remains uncertain (Lollar et al, 2006).

2.1.2 Biogenic processes

The formation of natural gas by biogenic processes occurs through the actions of methanogenic bacteria on organic material during the deposition of sediment in the early stage of its burial (Rice, 1992). The production of CH_4 from oil or coal involves different processes by differing groups of micro-organisms (Aitken et al, 2004). These processes include acidogenesis, acetogenesis and methanogenesis (Faramawy et al, 2016).

Acidogenesis occurs through the actions of heterotrophic bacteria that hydrolyze complex organic polymers into simple, soluble organic materials such as alcohols, sugars and volatile fatty acids (Faramawy et al, 2016). Acidogenesis is followed by acetogenesis. Acetogenesis involves fermentation by syntrophic bacteria of the simple, soluble organic material produced by hydrolyses during acidogenesis. Acetogenesis results in the production of acetate, CO_2, hydrogen (H_2) and formate (Faramawy et al, 2016). Fermented product, namely acetic acid and H_2, is then consumed by Archea which produce CH_4 and CO_2 (Faramawy et al, 2016).

As a result, biogenic gas is predominantly composed of CH_4 and CO_2 (Schoell, 1980) with a lesser proportion of higher chain hydrocarbons

such as C_4H_{10} (Butane), C_2H_6 (Ethane), C_5H_{12} (Pentane) and C_3H_8 (Propane).

2.1.3 Thermogenic processes

Natural gas of thermogenic origin forms as a result of the slow and incomplete decomposition of organic material in anaerobic environments such as sedimentary basins (Durand, 1993). This residual, incompletely decomposed material accumulates in sediments as kerogen, a complex macromolecule (Durand, 1993). The increased temperature and pressure of associated depth allow for the thermal degradation of kerogen which produces both hydrocarbon and non-hydrocarbon compounds as well as pyrobitumen (Speight, 2007, Tissot and Welte, 1984).

This process of kerogen conversion is referred to as maturation and results in the formation first of oil and then thermal gas. Thermal gas is primarily derived from two types of kerogen namely labile and refractory kerogen (Clayton, 1991). Labile kerogen degradation generates both oil and gas within a temperature range of 100 - 150° C while refractory kerogen degradation generates only gas within a temperature range of 150 – 200 ° C (Clayton, 1991). Thermogenic gas contains a greater proportion of higher chain hydrocarbons such as C_4H_{10}, C_2H_6, C_5H_{12}, and C_3H_8 (Schoell, 1980).

2.2 Classification of natural gas

Natural gas accumulates in gas reservoirs, naturally occurring storage areas consisting of porous and permeable rock surrounded by a further layer of impermeable rock (Speight, 2007). Natural gas migrates along preferential pathways such as faults, fissures and fractures until reaching a reservoir where it accumulates. In general, the porous rock in the reservoir contains the gas which is prevented from escaping upward or laterally by the layer of impermeable rock acting as a naturally occurring seal (Speight, 2007). Natural gas encountered in reservoirs is classified according to either its origin or chemical composition (Tagliabue et al, 2009).

2.2.1 Conventional gas – classification via origin

Conventional gas is linked to deep reservoirs associated with crude oil or reservoirs that contain very little or no crude oil (Speight, 2007). Natural gas associated with crude oil is referred to as associated gas or wet gas and coexists with oil in the reservoir rock. Associated gas is present in various forms such as “solution gas” dissolved in crude oil or as “gas-cap gas” lying above the crude oil reservoir (Faramawy et al, 2016). Associate gas is generally leaner in CH_4 and richer in terms of higher molecular weight hydrocarbons (Speight, 2015).

Natural gas from reservoirs containing very little or no crude oil is referred to as non-associated gas or dry gas. Non-associated gas is produced from geological formations that contains small volumes, if any, of crude oil or hydrocarbons with a higher boiling point than CH_4 (Faramawy et al, 2016). Non-associated gas is generally richer in CH_4 content and leaner in terms of higher molecular weight hydrocarbons It often contains non-hydrocarbon gasses such as CO_2 and H_2S_2 (Speight, 2015).

2.2.2 Unconventional gas – classification via origin

Several forms of unconventional gas are known to occur. They include coal bed methane, deep aquifer gas, gas hydrates and shale gas (Faramawy et al, 2016). Coal bed methane is associated with coal seams and formed during coalification by either thermogenic or biogenic processes (Ritter et al, 2015). The composition of coal bed methane is primarily CH_4 with other minor constituents such as C_2H_6, CO_2, N(Nitrogen), H_2S_2 and SO_2 (Sulfur Dioxide) (Moore et al, 2012).

Deep aquifer gas occurs due to the migration of gas through aquifers and into reservoir rocks resulting in the saturation of aquifers with CH_4 (Faramawy et al, 2016). CH_4 solubility in water is low. As a result, aquifer gas content is heavily influenced by temperature, pressure and salinity (Faramawy et al, 2016).

Gas hydrates are crystalline cells of hydrogen bonded water molecules that serve to trap gas molecules (Faramawy et al, 2016). CH_4 hydrate is primarily formed through the microbial reduction of CO_2 from available organic matter in shallow sedimentary basins (Kvenvolden, 1995).CH_4 hydrates are found in deep lake sediments, terrestrial deposits located in sediments beneath permafrost and in the marine environment (Speight, 2007).

Shale gas is associated with low permeability organic shales and impermeable sandstone (Speight, 2013). CH_4 produced from shale gas reservoirs is not associated with crude oil and originates from either thermogenic, biogenic or a mixture of these formation processes (Prinzhofer and Battani, 2003).

2.2.3 Hydrocarbon content – classification via chemical composition

Natural gas is also classified according to the content of hydrocarbons present in produced gas. Non-associated gas (dry gas) typically consists of mostly CH_4 with very little or no components of C_2+ hydrocarbons. Associate gas (wet gas) is distinguished from non-associate gas due to the presence of C_2+ hydrocarbons in volumes higher than 10% of total produced gas (Rojey et al, 1997).

2.2.4 Sulfur content – classification via chemical composition

In addition to classification by hydrocarbon content, natural gas is also classified according to the presence of sulfur in produced gas (Speight, 2015). Using this form of classification, natural gas is classified into either sweet or sour gas which is dependent on sulfur content primarily in the form of H_2S (Kidnay et al, 2011). Sweet gas contains no or trace amounts of sulfur whereas sour gas contains H_2S in amounts of more than 5 (mg/Nm^3) (Maddox, 1974).

2.3 Composition of natural gas

The composition of natural gas is variable and is based primarily on its formation process and the reservoir from which it is extracted (Speight, 2015). In general, natural gas is comprised of many different hydrocarbon and non-hydrocarbon components and is never consistent (Faramawy et al, 2016). The general composition of natural gas, both wet and dry, is illustrated in Table 1.

Table 1: General composition of wet and dry natural gas (adapted from Speight, 2015).

Constituents	Composition (vol%)	
	Wet	Dry
Hydrocarbons		
Methane	84.6	96.0
Ethane	6.4	2.0
Propane	5.3	0.6
Isobutane	1.2	0.18
n-butane	1.4	0.12
Isopentane	0.4	0.14
n-pentane	0.2	0.06
Hexanes	0.4	0.10
Heptanes	0.1	0.80
Non-hydrocarbons		
Carbon dioxide	<5.0	
Helium	<0.5	
Hydrogen sulfide	<5	
Nitrogen	<10	
Argon	<0.05	
Radon, Krypton, Xenon	Traces	

2.3.1 Hydrocarbon components

The hydrocarbon components of natural gas include CH_4 and associate alkanes such as C_4H_{10}, C_2H_6 and C_3H_8 in addition to a small proportion of C_5+ hydrocarbons. In addition, other hydrocarbon components may also include polycyclic aromatic compounds such as toluene, benzene and xylene (Mokhatab et al, 2006).

2.3.2 Non-hydrocarbon components

The non-hydrocarbon components of natural gas include components referred to as contaminants, diluents and solid matter (Kidnay et al, 2011). Contaminants are components considered detrimental to gas extraction and treatment equipment and are known pollutants (Faramawy et al, 2016).

Contaminants include sulfur species that are formed by biochemical mechanisms involving the reduction of sulfate ions in sulfates dissolved in water through the actions of sulfur reducing bacteria (Kidnay et al,

2011). Sulfur contaminants may also be formed through the thermal degradation of kerogen at depths (Kidnay et al, 2011). Contaminant sulfur species typically include carbon disulphide (CS_2), carbonyl sulfide (COS), elemental sulfur (S), hydrogen sulfide (H_2S) and mercaptans (Younger, 2004).

In addition to sulfur species, other contaminants include arsenic (Caumette et al, 2009) and mercury (Fitzgerald and Lamborg, 2003). Arsenic (As) found in natural gas is thought to be the result of geological gas formation and is found in different forms in natural gas as well as condensate (Caumette et al, 2009). Mercury (Hg) is formed as a result of the reduction or thermal degradation of mercury sulfide (HgS) in contact with hydrocarbons and is present in numerous forms including inorganic mercury (Fitzgerald and Lamborg, 2003).

Diluent components include non-combustible gasses that reduce the heating value of natural gas (Speight, 2014). Diluents include CO_2, He and N_2. CO_2 components occur as a result of anaerobic bacterial degradation or organic material (Strapoc et al, 2011), the reactions of residues from kerogen degradation with water at depth (Machel, 2001) and the thermal decomposition of carbonates at temperatures exceeding 200° C (Hunt, 1979).

Helium (He) diluent components originates from outgassing of the mantle or through the radioactive decay of minerals deep within the earth's crust (Johnson and Rydjord, 2001). Lastly, N diluent components are produced as a result of bacterial reduction of nitrates dissolved in water, trapped air or thermal degradation of organic material (Rojey et al, 1997).

Lastly, solid matter may also be present in natural gas primarily in the form of fine silica and scaling from iron sulfides and iron oxides. Scaling components may also include barium sulfate, calcium carbonate, lead sulfides and oxides and zinc sulfides (Godoy et al, 2005).

2.4 Preference for and uses of natural gas

Natural gas is a versatile and relatively cleaner burning fossil fuel with a wide variety of applications (Demirbas, 2006). As a result, natural gas has emerged as a preferred fossil energy source from both an environmental and political perspective (Rozel and Reaven 2012).

The preference for natural gas is driven by the opportunity it provides to countries to reduce their reliance on net energy imports and enhance domestic energy independence (Rozel and Reaven 2012). In addition,

the use of natural gas as an energy source may potentially assist in the reduction of the global carbon energy footprint of energy provision (when compared to other fossil fuels) as well as reduce emissions of criteria pollutants associated with conventional fossil fuel use (Rozel and Reaven, 2012).

2.4.1 Natural gas emissions

Emissions from vehicles and power generation are the primary sources of urban air pollution and global greenhouse gas contributions. (Xu and Chen, 2016). A reduction in the emissions from these sectors is anticipated to improve urban air quality and contribute to the global reduction of greenhouse gasses (Xu and Chen, 2016).

As natural gas is the cleanest burning fossil fuel available (Liang et al, 2012), the substitution of traditional fossil fuels such as oil and coal with natural gas is further anticipated to result in less air pollution and a reduction in greenhouse emissions (Xu and Chen, 2016). In comparison to coal fired power stations, natural gas fired power stations produce approximately 50% less CO_2, 70% less nitrogen oxides (NO_x), 99% less sulfur oxides (SO_x) and insignificant amounts of mercury compounds (Xu and Chen, 2016).

In general, the primary products of natural gas combustion are CO_2 and water vapor as well as trace amounts of carbon monoxide (CO) significantly less pollutants such as NOx and SO_2 and almost no particulate matter (Liang et al, 2012). Table 2 provides a comparison of typical emissions from the combustion of various fossil fuels.

Table 2: Comparison of emissions of fossil fuels (adapted from EIA, 1998). 1 British Thermal Unit (Btu) = 0.00105587 Megajoules (MJ)

Pollutant (pounds per billion Btu of energy input)	Natural gas	Oil	Coal
Carbon dioxide	117,000	164,000	208,000
Carbon monoxide	40	33	208
Nitrogen oxides	92	448	457
Sulfur dioxide	1	1,122	2,591
Particulates	7	84	2,744
Mercury	0.000	0.007	0.016

The global substitution of traditional fossil fuels with natural gas has resulted in gas replacing oil as the second largest fuel used for power generation (IEA, 2014). As a result, the use of natural gas for power generation activities rose from 12.1% in 1973 to 22.5% in 2012 (IEA, 2014).

In addition to the displacement of oil, natural gas has also displaced the use of coal in power generation, reducing the emissions of CO_2 from fuel combustion by the world's two largest emitters of air pollution, namely the United States (US) and China (Xu and Chen, 2016).

In the US, the displacement of coal is due to the implementation of clean air policies and the increasing affordability of natural gas. Conversion to gas has resulted in a reduction of 200 mega tonnes (Mt) of CO_2 emitted from power generation activities in 2012 (Environment Canada, 2013). By 2040, the displacement of coal with natural gas is projected to result in a further 30% reduction in coal fired power plants in the US (IEA, 2014).

In China, deteriorating air quality due to the use of coal and oil fuelled power generation has significantly impacted human health and sectors such as tourism (Xu and Chen, 2016). In order to improve ambient air quality, the Chinese government has promulgated legislation and a set of stringent regulations aimed at improving air quality (Xu and Chen, 2016). In this regard, the phasing out of coal fired power generation and coal fired heating and replacing it with natural gas is identified as a priority. Through the conversion of coal fired power stations to natural gas fired power stations, the city of Beijing alone is expected to reduce its annual emissions of CO_2 by 30 million tonnes, SO_2 by 10000 tonnes, NO_x by 19000 tonnes and particulate matter by 3 000 tonnes (Bloomberg, 2015).

As a cleaner-burning fossil fuel, natural gas is also viewed as a bridging or transition fuel that will facilitate the shift from coal to renewable energy and thereby reduce the emissions of heat trapping gasses and criteria pollutants (Vidic et al, 2013). However, natural gas is comprised primarily of CH_4, considered the second most important anthropogenic greenhouse gas is emitted to the atmosphere. CH_4 has a Global Warming Potential (GWP) of 25, in other words the emission of 1 tonne of CH_4 is the equivalent, from a global warming point of view, to 25 tonnes of CO_2, when integrated over a time horizon of 100 years. This is because CH_4 is more short-lived than CO_2, it traps more heat per molecule than CO_2 (Boucher, et al, 2009). As such, the exploitation and use of natural gas is best used to bridge to more sustainable and renewable energy sources while reducing the global carbon budget of current energy provision.

2.4.2 Natural gas demand and consumption

Current global population growth rates of 1% per annum are projected to result in a global population of approximately 8.2 billion people by 2025 (FAO, 2013) of which most growth is anticipated in the developing world (Masters and Ela, 2008). Population growth, rapid urbanisation and economic development are expected to increase the global energy demand by a further 58% by the year 2025 (FAO, 2008).

By 2040 demand for oil and gas is projected to increase to 104 million barrels per day (Mb/d) and 5.4 trillion cubic meters (tcm) respectively (IEA, 2014). As a result, a growing global demand for natural gas is anticipated due to the availability of the resource, its associated cost and potential environmental benefits (Balat and Ozdemir, 2005).

In 2012, the global production of natural gas amounted to 3.5 tcm (USEIA, 2014). Major natural gas producers include the Organisation for Economic Co-operation and Development (OECD) countries as well as non-OECD countries in Europe and Asia (USEIA, 2014). In addition, non-OECD countries in Africa, the Americas, Asia (excluding China) and the Middle East showed a significant increase in terms of the global production of natural gas during the last 40 years (IEA, 2014).

Globally, the US remains the largest producer of natural gas and contributes 20% of total global production amounting to 689 billion cubic meters (bcm) (IEA, 2014). In addition to being the largest producer, the US is also the largest consumer of natural gas making the country a net importer of approximately 37 bcm in order to meet its energy demands (IEA, 2014). Russia is the second largest producer of natural gas and unlike the US is a net exporter, exporting approximately 30% of its annual production volume of 671 bcm (IEA, 2014). In terms of natural gas imports, the largest importers are Germany, Italy, Korea and Japan. Globally, natural gas production is further projected to increase in every other major region with the US remaining as the world's largest natural gas producer (IEA, 2014).

The primary demand for natural gas is due to power generation as well as heating and industrial applications (Balat, 2009). In 2004, natural gas consumption by sector included industry at 37.5%, non-energy at 9.0%, transport at 5.6% and various other sectors such as agriculture, residential and non-specified at 48% (Balat, 2009).

In addition to the various applications for which natural gas is suited, it may also act as a base ingredient for a wide variety of products such

as anti-freeze, fabrics, fertiliser and plastics (Balat, 2007). The demand and consumption of natural gas is driven by the interlinked aspects related to its affordability, ability to meet growing energy demands, combating emissions and the suitability of natural gas for various applications ranging from power generation to industrial use (Osborn et al, 2011).

2.4.3 Natural gas applications

Natural gas is used predominantly for power generation and is the second largest source of fuel for global power generation (Balat, 2009). When used as a feed stock in newer, more energy efficient power plants natural gas emits approximately 60% less CO_2 per unit of energy generated relative to conventional coalfired power plants. As a result, an increase in the utilisation of natural gas-powered power plants has been estimated to reduce the electricity sectors carbon emissions by 22% in the short term (MIT, 2011). In addition, the use of natural gas for electricity generation emits virtually no SO_x and comparably very little NO_x, the two gasses responsible for acid rain (Demirbas, 2006).

However, generating electricity from natural gas is usually more expensive than utilising coal due to increased fuel costs such as those related to transport from wellhead to pipeline and pipeline to plant (Balat, 2006). Recent breakthroughs in combined cycle gas turbine technology (CCGT) have helped to offset this cost as CCGT plants require lower capital investment and shorter installation times in comparison to coal fired power plants (Balat, 2009).

The efforts of pipeline companies to spread their costs across industrial, residential and commercial consumers, combined with breakthroughs in CCGT technology have resulted in the improved affordability of natural gas to residential consumers (Balat, 2007). In addition to being affordable, the use of natural gas by residential consumers also confers other benefits such as natural gas cooking and heating (Balat, 2007). Commercial uses of natural gas are similar to those of residential consumers but vary by scale and include requirements for larger scale cooling, space and water heating (Balat, 2009).

Natural gas is also used as a gasoline or diesel substitute in natural gas vehicles (Xu and Chen, 2016). Used as a transportation fuel, natural gas emits almost 20% less heat trapping gasses than conventional fuels (Werpy et al, 2010) for the same number of tonne-kilometers of transport services. This includes approximate reductions of CO by 70%, non-methane gas emissions by 89% and oxides of nitrogen by 87%.

Furthermore, vehicles utilising natural gas produce little or no evaporative emissions during use or re-fuelling (Demirbas, 2006).

Despite producing fewer pollutants than traditional vehicles, the share of natural gas vehicles is only 1.3% globally (Werpy et al, 2010). Obstacles to the adoption of natural gas vehicles include higher capital costs, longer refuelling times and shorter driving distances (Werpy et al, 2010). Despite these obstacles to market penetration, natural gas consumption for natural gas vehicles has grown three-fold in the last 40 years (USEIA, 2015) to accommodate a 22% increase in the use of natural gas vehicles most notably in the Asia-Pacific region (NGV Global, 2015).

As a relatively cleaner-burning fossil fuel with a wide variety of applications, natural gas is best used to bridge to a more renewable energy source in applications such as power or thermal generation and as fuel in vehicles reducing the global carbon budget of current energy provision (Vidic et al, 2013).

2.5 Concerns regarding natural gas extraction

Increasing global energy demand combined with the economics of energy use and policy emphasis on cleaner burning fuels have resulted in a global increase in natural gas exploration and extraction activities (Osborn et al, 2011). Despite producing comparably lower CO_2 emissions and other criteria pollutants, the increase in natural gas extraction activities has highlighted several concerns regarding the exploitation of natural gas, in particular the risk of contamination of shallow ground water aquifers used primarily to obtain drinking water, is a widespread concern (Fontenot et al, 2013).

Research undertaken on the risk to ground water from natural gas exploitation has focussed mostly on possible contamination resulting from the use of horizontal drilling techniques and the application of hydraulic fracturing in low permeability organic shale formations and “tight-sand” reservoirs located almost exclusively in the US (Osborn et al, 2011).

Possible ground water contamination arising from natural gas extraction includes the risk associated with high-pressure injections of large volumes of fracturing fluids resulting in aquifer contamination, stray gas and fluid migration from inadequately constructed or failed well casings, the creation of improved hydraulic connectivity between deep saline aquifers and shallow freshwater aquifers as well as contamination originating from produced water(Vidic et al, 2013).

Combined, all these potential risks contribute to growing concerns regarding water quality of shallow freshwater aquifers used primarily for drinking and domestic purposes (Fontenot et al, 2013).

Instances of ground water contamination have been recorded in areas where natural gas extraction operations use both horizontal drilling techniques and well stimulation via hydraulic fracturing (McPhillips et al, 2014). In the state of Pennsylvania – USA, two major cases of gas migration into shallow ground water aquifers were reported in 2008 and 2011. The migration of stray gas affected more than 15 drinking water wells but neither of these cases was specifically linked to horizontal drilling or hydraulic fracturing. Instead they were attributed to incorrectly cased gas wells (Considine et al, 2012).

However, a further study on aquifers overlying the Marcellus and Utica shale formations in Pennsylvania and New York documented systematic CH_4 contamination in drinking water wells associated with hydraulic fracturing activities used to extract natural gas (Osborn et al, 2011). Results from the study indicated increases in average and maximum dissolved CH_4 concentrations in drinking water wells in close proximity (< 1 km) to gas wells, with some concentrations high enough to be considered an explosive hazard (Osborn et al, 2011). In contrast, the concentration of dissolved CH_4 in drinking water wells not considered to be in close proximity to gas wells (> 1km) indicated significantly less, but not the complete absence of, dissolved CH_4 present (Osborn et al, 2011). Despite the increased concentrations of dissolved CH_4 recorded in drinking water wells, the study found no evidence of further chemical contamination of ground water by drilling fluids (Osborn et al, 2011). Drinking water wells sampled for the study were located within similar geological formations and hydrogeological regimes, suggesting that natural gas extraction activities and the use of hydraulic fracturing were responsible for the increases in dissolved CH_4 observed (Osborn et al, 2011).

The results of the study by Osborn et al (2011) have been contested by several replying papers (McPhillips et al, 2014). The responses contest the conclusion that dissolved CH_4 concentrations were the result of hydraulic fracturing. Important criticisms of the study highlighted the lack of baseline data and that most of the sampling occurred in the Dimock region of Pennsylvania, an area known to have stray gas migrations concerns due to incorrectly cased gas wells (Davies, 2011; Saba and Orzechowski, 2011 and Schon, 2011).

In response to these criticisms, a follow up study was undertaken that included a more extensive dataset distributed across several counties in northeast Pennsylvania (Jackson et al, 2013). The study sampled 141

drinking water wells, examined dissolved gas concentrations and their isotopic signatures in relation to gas well proximity (Jackson et al, 2013). The study recorded dissolved CH_4 in 82% of drinking water wells sampled with average concentrations six times higher for locations less than 1 km from gas wells (Jackson et al, 2013)

In addition, C_3H_8 was detected in 10 drinking water wells, also within 1 km from gas wells (Jackson et al, 2013). The study indicated that distance to gas wells was highly significant for dissolved CH_4 concentrations (P = 0,007) whereas distances to valley bottoms (topography) and tectonic formation were not significant (P = 0, 27 and P = 0, 11 respectively). The results of the study strongly suggest that drinking water wells < 1km from gas wells have water contaminated by stray gas (Jackson et al, 2013).

However, a further study undertaken by Siegel et al (2015) found there to be no statistically significant relationship between dissolved CH_4 concentrations in drinking water wells and their proximity to gas wells. The data set for this study included 11,300 samples, two orders of magnitude larger than the datasets used by previous studies undertaken by Osborn et al (2011) and Jackson et al (2013). In addition, the dataset incorporated ground water samples obtained near 661 pre-existing gas and oil wells of which, 92% are unconventional wells where either horizontal drilling or hydraulic fracturing has been applied (Siegel et al, 2015). The results of the study indicated that there is no evidence to suggest that increasing concentrations of CH_4 in ground water are a function of proximity to gas wells (Siegel et al, 2015).

In 2011, the U.S. Environmental Protection Agency (USEPA) found evidence of groundwater contamination, in the form of hydraulic fracturing chemicals in the drinking water wells of Pavilion, Wyoming, an area considerably different than the Marcellus shale region of the eastern United States of America (USEPA, 2011). While in the Fayetteville shale region of Arkansas, a geochemical study found no evidence that CH_4 or major ion chemistry found in shallow groundwater has been impacted on or influenced by gas extraction activities (Kresse et al, 2012 and Warner et al, 2013). Two further studies undertaken by Boyer et al (2012) and Molofsky et al (2013) found no evidence of increased methane in drinking well water as a result of natural gas extraction activities (McPhillips et al, 2014). However, one study observed changes in water quality from samples taken pre-drilling and post drilling (Boyer et al, 2012).

McPhillips et al (2014) undertook a further study across the Chenango County in New York to assess dissolved CH_4 patterns within groundwater. The study collected and analysed 113 groundwater

samples located in areas of active and non-active gas extraction. The results of the study indicated that most dissolved solids and CH_4 concentrations were well below the action levels of federal drinking water standards (McPhillips et al, 2014). Statistical analyses of geochemical data indicated that higher CH_4 concentrations are associated with groundwater classified as sodium-chloride, sodium-bicarbonate-chloride and sodium-bicarbonate. The study highlighted the importance of furthering the understanding of natural fractures and patterns of connectivity among geological units as well as the importance of collecting baseline data from individual drinking water wells indicating the naturally occurring presence of dissolved CH_4 in groundwater (McPhillips et al, 2014).

A more comprehensive analyses and interpretation of 19,278 predrilling groundwater samples from the Appalachian Basin, collected from 2009 to 2012 observed that 22,9% of predrilling sampling naturally exceeded the analytical detection limit for dissolved CH_4 (Siegel et al, 2015) . The study observed that the concentration of dissolved CH_4 broadly relates to the water bearing geological unit through which the drinking water well is sunk, hydro-chemical facies, topography, whether the drinking water well intersects restricted or confined saline zones and where the drinking water well is commissioned within groundwater circulation pathways (Siegel et al, 2015). The study also determined that dissolved CH_4 in shallow groundwater in this location commonly occurs in sodium dominated groundwater types, originating from surrounding and underlying rocks or from deeper connate brines commonly found in valley settings at shallow depths (Siegel et al, 2015).

As a result of the concerns over natural gas extraction and the use of horizontal drilling techniques and hydraulic fracturing, the USEPA undertook and completed a study on the impacts of hydraulic fracturing on drinking water in the US (USEPA, 2016). The aim of the assessment was to assess the potential of impacts to impact ground water resources and identify features that affect the frequency and significance of impacts determined (USEPA, 2016).

The study identified a combination of activities considered likely to result in frequent and significant impacts to groundwater quality and quantity. These impacts include the injection of hydraulic fluids into wells with inadequately constructed casing of cementation, the injection of hydraulic fluids directly into groundwater, spills of hydraulic fluids, chemicals and produced water and water withdrawals (USEPA, 2016). The impacts identified varied in severity from temporary changes in water quality to severe water quality deterioration that

rendered water in private drinking wells unfit for drinking purposes (USEPA, 2016).

In contrast to the draft study (USEPA, 2015), in later work the EPA removed the finding that no evidence of systematic or widespread impact was observed because of hydraulic fracturing (USEPA, 2016). The removal of the finding from the amended study (USEPPA, 2016) was based on the lack of quantitative support offered by analysed data and the inherent uncertainty involved in estimating the frequency of impacts arising from hydraulic fracturing (USEPA, 2016). Regardless, the number of incidents where drinking water wells have been contaminated remain relatively small in comparison to the number of gas wells, including those hydraulically fractured (USEPA, 2016).

In summary, research to date has largely occurred in the USA and provide evidence for the potential contamination of groundwater by natural gas extraction activities and in particular contamination of ground water resources by stray gas migration. The studies also emphasise that the presence of dissolved CH_4 may be naturally occurring and associated with geological and hydrological regimes. The complexity of the subsurface environment makes understanding the impact of gas extraction on ground water resources challenging (USEPA, 2016). The collection of baseline information is of critical importance in understanding pre-extraction conditions and the variability of naturally occurring methane (Siegel et al, 2015).

2.6 Natural gas extraction in South Africa

In South Africa, detectable CH_4 occurrence in boreholes (water wells) and spring water is widespread in areas representative of Karoo Basin geology. Dissolved CH_4 has been recorded in both shallow and deep boreholes, as well as waters associated with thermal springs (Talma and Esterhuyse, 2015). In addition, CH_4 emissions from subsurface are also fairly common with frequent anecdotal evidence of gas present in volumes large enough to be considered an explosive hazard (Talma and Esterhuyse, 2015).

Isotopic analyses of CH_4 found in the Central Karoo Basin indicate that it is predominantly of thermogenic origin (Talma and Esterhuyse, 2015). Towards the far northern and eastern fringes of the Basin, there are indications of microbial origin (Talma and Esterhuyse, 2015). Helium (He) is associated with CH_4 in the Basin, strongly suggesting that both gasses are present as a result of preferential pathways from depth (Talma and Esyerhuyse, 2015). Considerable interest has been directed

towards the Karoo due to its potential to harbour significant shale gas resources which may contribute to potential energy and economic benefits for South Africa (CSIR, 2016).

As a potentially significant source of shale gas, natural gas extraction in the Karoo is based on the application of both horizontal drilling techniques and hydraulic fracturing required to produce economically viable natural gas (de Kock et al, 2017). However, the proposed development of shale gas in South Africa is a divisive topic riddled with uncertainty and inadequately informed by available scientific evidence (CSIR, 2016), further exacerbated by public framing of the topic as a choice between either economic development or environmental protection.

In order to address this uncertainty and critically evaluate the proposed development of shale gas in the Karoo, the Council for Scientific and Industrial Research (CSIR) undertook and completed a Strategic Environmental Assessment (SEA) to determine the impact of several shale gas development scenarios on the receiving environment (CSIR, 2016). As part of the SEA, the anticipated impact of shale gas development on ground and surface water resources were evaluated. Impacts identified in the SEA include the risk of contamination of water resources arising from surface spills and discharge, failed well integrity and the creation of preferential pathways from hydraulic fracturing as well as a reduction in the availability of water resources for people and other economic activities (CSIR, 2016). In addition, the SEA highlighted the fact that the Karoo is water scarce and that water availability for shale gas development is significantly constrained (CSIR, 2016).

In order to best mitigate these impacts to water resources, the SEA advocated the use of setbacks and exclusion areas to guide the location of proposed shale gas development. Those areas where shale gas development could pose a probable and significant impact to water resources would be excluded (CSIR, 2016). As a result of the constraint mapping undertaken in the SEA, a limited area is identified as suitable for shale gas development i.e. where anticipated impacts are unlikely to result in significant negative, long-term impacts (CSIR, 2016). Unique features of South African geology such as the intrusion of dolerite dykes into native country rocks (Hobbs et al, 2016), complex shallow fractured rock aquifer systems (Esterhuyse et al, 2014) and regional water scarcity warrant a precautionary approach (Esterhuyse, 2017).

The SEA further emphasises the importance of water resource monitoring and in particular pre- shale gas development (baseline) monitoring (CSIR, 2016). The location, quantification and characterisation of CH_4 resources in the Central Karoo Basin is

considered to be of critical importance, along with establishment of a detailed baseline of gas origins and naturally occurring concentrations in water resources. The characterisation and development of this baseline will allow for an evidence-based resolution of potential disputes over contamination issues resulting from anticipated shale gas exploration and extraction (Talma and Esyerhuyse, 2015).

Enthusiasm over the potential size of shale gas reserves in the Karoo has been curbed as a result of revised estimates of the size of the likely resource. Initial estimates varied between 13-390 trillion cubic feet (tcf) (Econometrix, 2012). These early estimates are considered speculative at best, as they are not based on actual measurements but rather on a combination of proxy factors used to infer the size of the resource. These factors include the area, depth, thermal maturity, carbonaceous shale thickness and total organic carbon content of the 30 m thick Whitehill formation of the Ecca Group (de Kock et al, 2017).

Using actual measurements from samples obtained from two deep exploration boreholes de Kock et al (2017) determined that there is virtually no desorbed or residual gas present, despite the high total organic carbon content of the shales. This finding they attribute to the metamorphosed and overmature state of the Ecca Group. In addition, the organic carbon present in the shale remains predominantly unbound to H with little hydrocarbon generation potential (de Kock et al, 2017).

As a result of these findings, de Kock et al (2017) concluded that the smallest of the resource estimates, namely 13 tcf is the most realistic estimation of shale gas reserves in the Karoo Basin. Nonetheless, the low estimate, 13 tcf still represents a significant resource in terms of its developmental potential for South Africa. For the resource to be considered economically viable, the study strongly suggests that shale gas development would need to be confined to a small, clearly delineated area in the southern section of the Karoo Basin (de Kock et al, 2017).

As is the case internationally, South African research on the impact of natural gas extraction is focussed almost exclusively on the impact of shale gas development using horizontal drilling and hydraulic fracturing. In comparison, very little research has been undertaken on unconventional natural gas reserves outside the USA, extracted using conventional drilling techniques and the potential CH_4 contamination that may occur from these operations.

An unconventional natural gas extraction operation is currently underway near the town of Virginia in the Free State Province of South Africa (Renergen, 2017). A map of the location of the operation is shown

in Figure 1. The gas is thought to originate from the Witwatersrand Supergroup or shallow Karoo which suggests that the gas is likely to be a mantle mix derived from abiogenic and biogenic hydrocarbons (Venmyn Deloitte , 2016). Proved and probable natural gas reserves of the field have been estimated at 100 million cubic feet (mcf) (Venmyn Deloitte , 2016).

Natural gas extracted from the field also contains a high concentration of He, which ranges from 2.5 to 7% across the reserve (Renergen, 2017). The underlying geology of the field and low-pressure gas flows allows for low-cost extraction via conventionally drilled vertical wells (Renergen, 2017).

At present natural gas is extracted from one well (diameter 10 cm), following which it is compressed and dispensed on site. The extraction well was conventionally drilled with a combination of diamond and percussion drill rigs to a depth of approximately 450 m, where it intercepts the gas bearing fracture (Renergen, 2017). The extraction well is fitted with a series of telescopic casing, is cemented in place to ensure stability as well as isolate the well from the surrounding geology (Renergen, 2017). The extraction well and compression plant is located approximately 1 km south of the Doorn River and is surrounded by 9 boreholes located at varying distances from the extraction well (Renergen, 2017).

Natural gas extraction at the operation began in 2016 (Renergen, 2017). In order to determine baseline water qualities, the operators began water quality monitoring in 2015 (Renergen, 2017). The parameters identified for monitoring during the baseline monitoring period included dissolved CH_4 concentrations as well as a variety of other parameters indicative of stray gas migration, saline water intrusion and contamination by drilling fluids used (Renergen, 2017). As such, the baseline samples represent a “snapshot” of pre-existing water qualities of the surrounding groundwater resource.

The nature of the operation and collection of pre-gas extraction water quality samples provides a unique opportunity to evaluate potential change following gas extraction operations. The operations used conventional extraction methods (i.e. vertical drilling without well stimulation), thus the ongoing monitoring during the operational also allows for the evaluation of change that may occur as a result of operations employing conventional extraction methods.

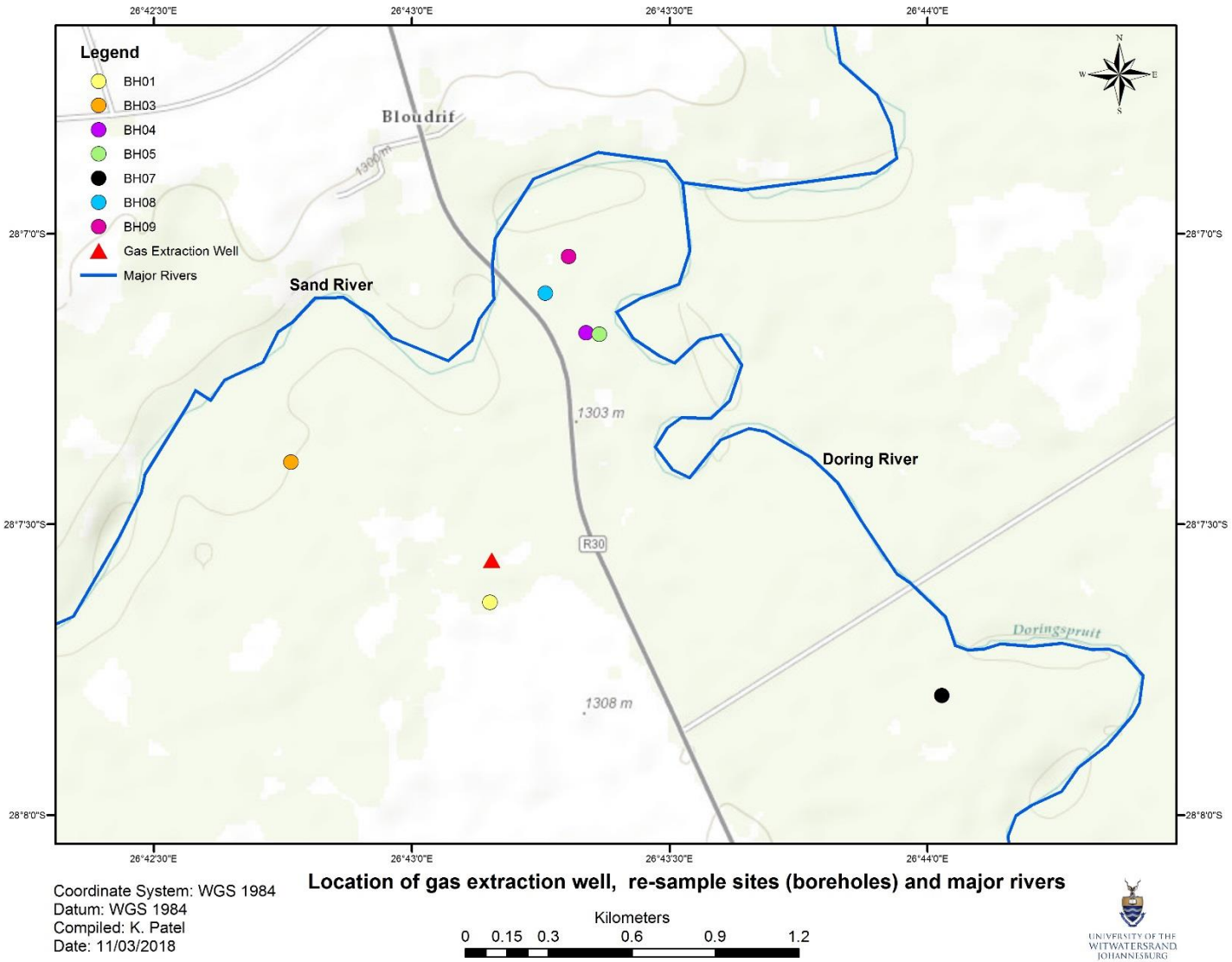


Figure 1:Location of gas extraction well, re-sample sites and major rivers

3. RESEARCH METHOD

3.1 Aim and objective

The research aims to determine whether ongoing gas extraction activity near Virginia, South Africa has affected the chemical composition of surrounding groundwater. The objective is to assess and evaluate changes since the onset of gas extraction activities in 2015 in several chemical parameters, with emphasis placed on dissolved CH_4 concentration, within the adjacent aquifer.

The aim and objective of the research will be achieved through a re-sampling programme from seven boreholes between 150 and 1500 m from the single gas extraction well and follow up laboratory analyses of groundwater samples, obtained from locations previously sampled by the gas production operator in 2015.

3.2 Study site

The study site is located approximately 13 km south west of the town of Virginia in the Matjhabeng Local Municipality of the Free State Province (MLM IDP, 2015). Dominant land uses within the municipality include agriculture and gold mining (MLM IDP, 2015). The study area is also comprised predominantly of agricultural land (grazing with some maize cropping) with extensive gold mining land uses to the north and south. The study site forms part of the larger Middle Vaal Water Management Area (WMA) and is located in quaternary catchments C42K (DWAF, 2003). Rivers and stream present within the study area include the Sand, Doring and Boschluisspruit Rivers (DWAF, 2003). The location of the study site and major rivers present are shown in Figure 1.

3.2.1 Geology

The regional geology of the study area is comprised of rocks from the Witwatersrand, Ventersdorp and Karoo Supergroups. Surface geology is comprised of aeolian sand and associated outcrops, alluvium, Karoo dolerite, sandstones and shales (Johnson et al, 2006). The Witwatersrand Supergroup is comprised of sedimentary formations consisting of shale, quartzite and conglomerate as well as gold bearing reefs that are extensively mined within the area (Johnson et al, 2006). The Ventersdorp Supergroup is comprised of pyroclastic rocks, quartzite, conglomerate, lava and clastic sediments (Johnson et al, 2006). The Ventersdorp Supergroup provides for a unique volcano-sedimentary supercrustal record that contains the largest and most widespread sequence of volcanic rocks present in the Kaapvaal Craton (Johnson et al, 2006). The Karoo Supergroup is comprised of conglomerate, mudstone, shale, siltstone, sandstone associated with extensive flood basalts and doleritic dykes and sills (Johnson et al, 2006). In terms of surface geology, aeolian sands cover much of the study area and are interspersed with calcrete and ferricrete with alluvium, consisting of interbedded sand and gravel with lenses of clay material (Johnson et al, 2006).

3.2.2 Hydrogeology

Exploitable aquifers are found in alluvial deposits associated with streams and rivers as well as the Witwatersrand, Ventersdorp and Karoo Supergroups (DWAF, 2003). Shallow primary aquifer systems are associated with alluvial deposits and exhibit high permeability, porosity and variation in yield. Due to their unconfined nature and high permeability, shallow primary aquifers are vulnerable to surface sources of contamination (Steyl et al, 2012).

Secondary aquifer systems are associated with Karoo deposits and typically occur within the upper 150 m of the geological sequence but have been recorded within the upper 300 m as well (Steyl et al, 2012). These aquifers are further associated with fracturing in shales and sandstones of the Karoo Supergroup sediments as well as dolerite intrusions. These aquifer systems also vary significantly in yield (Barnard, 2000). The aquifer systems associated with alluvial and Karoo deposits are most often exploited and play an important role in water supply for surrounding agricultural activities.

Below a depth of 300 m, aquifer systems are associated with Witwatersrand and Ventersdorp sediments. In these aquifer systems, groundwater quality deteriorates rapidly and the permeability of water bearing formations decreases by orders of magnitude (Steyl et al, 2012). These deep aquifer systems are generally confined, highly saline and exhibit limited natural connection between the overlying, exploitable shallow aquifers systems (Steyl et al, 2012). As such, these deeper aquifer systems are not suitable for agricultural or domestic activities and seldom exploited (Steyl et al, 2012).

Regardless, both shallow and deeper groundwater resources within the catchment tend to be naturally saline (DWAF,2003). Increasing salinity in shallow groundwater resources is attributable to the excess evaporation over precipitation in endorheic pans which are commonly found in this landscape, while deeper groundwater resources originate from the Ecca formation and are mostly Na-Cl dominated waters found in sediments resulting from past marine deposition (DWAF,2003). In general, pollution of the groundwater resources in the WMA originate primarily from gold mining and agriculture (DWAF, 2003).

3.2.3 Groundwater monitoring sites

Known boreholes sampled prior to gas extraction in 2015 were re-sampled in 2017. Re-sample site ID, coordinates, borehole depth, approximate elevation and distance from the gas extraction well are provided in Table 3:

Table 3: Re-sample site information. DD means 'decimal degrees'. A negative latitude denotes South of the equator, a positive longitude is East of the Greenwich Meridian.

Site ID	Coordinates (DD)		Borehole depth (m)	Elevation (masl)	Distance from gas well (m)
	Latitude	Longitude			
BH01	-28.127213	26.719194	37	1299	153.4
BH03	-28.123210	26.712767	40	1291	676.7
BH04	-28.119499	26.722305	51	1294	777.6
BH05	-28.119538	26.722728	24	1292	792.1
BH07	-28.129905	26.733792	33	1298	1523.9
BH08	-28.118371	26.720983	41	1290	853.9
BH09	-28.117312	26.721737	40	1293	985.6

A map of the study site and location of re-sample sites in relation to the gas extraction well is shown in Figure 1.

Sample borehole were drilled by landowners and land occupiers. As such, detailed information on borehole construction, stratigraphy, water strikes encountered as well as physico-chemical parameters encountered during drilling are unavailable and therefore represent a study limitation.

3.3 Selection of groundwater quality parameters

The selection of chemical parameters for sampling and analyses is based on a review of related scientific literature (CSIR, 2016; CWERC, 2014; Entrekin et al, 2011 and USEPA, 2016) and the parameters sampled for in 2015 as part of the pre-extraction water quality baseline determination.

Reviewed scientific literature identifies a selection of chemical parameters that may be affected by natural gas extraction and includes parameters related to the release of contaminants from deep aquifers and contaminants from the use of drilling fluids and other chemical additives (Entrekin et al, 2011 and Molofsky et al, 2013). Identified chemical parameters were then linked to those sampled for and analysed during 2015 to ensure appropriate comparisons of pre and post extraction water qualities. The chemical parameters identified for re-sampling and analyses are provided in Table 4:

Table 4:Identified sampling parameters (adapted from CSIR, 2016; CWERC, 2014; Entrekin et al, 2011; and USEPA, 2016)

Sampling parameters	Symbol	Unit
General water quality indicators		
Dissolved organic carbon	DoC	mg/l
Dissolved oxygen	DO	mg/l
Dissolved inorganic carbon	DiC	mg/l
Electrical conductivity	EC	mS/m
Acidity (Negative log [H^+])	pH	Value at 25°C
Total suspended solids	TSS	mg/l
Major Ions		
Ammonia	NH_4^+	mg/l
Bromide	Br^-	mg/l
Calcium	Ca^{+2}	mg/l
Chloride	Cl^-	mg/l
Potassium	K^{+1}	mg/l
Sodium	Na^+	mg/l
Sulfate	SO_4^{-2}	mg/l
Metals		
Arsenic	As	mg/l
Barium	Ba	mg/l
Boron	Bo	mg/l
Lead	Pb	mg/l
Lithium	Li	mg/l
Manganese	Mn	mg/l
Rubidium	Rb	mg/l
Strontium	Sr	mg/l
Uranium	U	mg/l
Dissolved gasses		
Methane	CH_4	mg/l
Ethane	C_2H_6	mg/l

3.4 Groundwater re-sampling methodology

The aim of a groundwater sampling programme is the collection of a representative sample of current parameters obtained from a known or specified volume of water derived from within an aquifer (USEPA, 2002). In order to obtain a representative sample of within aquifer parameters, the sampling technique must be selected to ensure that possible chemical and physical alteration of the sample is avoided and also

consider aspects such as borehole construction, equipment, sample handling and transport (USEPA, 2002).

To obtain a representative groundwater sample of within aquifer parameters, re-sampling was undertaken using the low flow/low stress purging and sampling technique (USEPA, 1996). The low flow technique is based on the premise that pumping at a low rate within the screened zone will prevent the drawdown of stagnant water in the column above and its accidental inclusion in the sample (Puls and Barcelona, 1989).

Key to the use of the low flow technique for representative sample collection is the minimisation of drawdown during pumping at approximate recovery rates as well as the stabilisation of water levels and water quality indicator parameters such as dissolved oxygen, pH, temperature, turbidity, oxidation-reduction potential and electrical conductivity (Puls and Barcelona, 1989). Once draw down is minimised and stabilisation is achieved, groundwater samples can be extracted directly from the water bearing formation through the bore screen (Sundaram et al, 2009).

In addition to allowing for the collection of a representative sample of groundwater from the water bearing formation, further benefits of the low flow technique include: minimisation of hydraulic stress between borehole and aquifer interfaces, reduction in entrained sediment and is less time consuming than traditional borehole purging methods as the volume of water to be pumped and then disposed of is significantly reduced (Sundaram et al, 2009).

The use of the low flow purging and sampling technique allows for the collection of a representative groundwater sample from the water bearing formation within little or no alteration to its physical or chemical parameters (Sundaram et al, 2009). In addition, samples collected using the low technique are appropriate for the collection of dissolved gasses, mobile organics and inorganics, volatiles and other naturally occurring parameters (USEPA, 1996). The re-sampling programme undertaken in 2017 was done exclusively using the low flow technique.

3.4.1 Equipment and materials

Equipment and materials used during the 2017 re-sampling programme are listed below and includes:

- Solinst Temperature, Level and Conductivity (TLC) meter – model 107;

- Aquaread probe – model AP2000;
- Aquameter handheld display panel – model AM200;
- Reel with rope;
- Solinst bladder pump – model 407;
- Generator;
- Teflon lined polyethylene tubing;
- Air compressor;
- Purge container;
- Flow through cell;
- 500 ml laboratory provided plastic sample bottles for subsequent analyses of inorganic chemical components;
- 500 ml laboratory provided glass sample bottles for subsequent analyses of organic chemical components;
- 40 ml laboratory provided glass vials with Teflon faced silicone septa for subsequent analyses of dissolved gasses;
- 2 l glass beaker;
- 20 l distilled water;
- 30 l cooler box; and
- Powder free latex gloves.

All equipment and materials that come into contact with samples are limited to inert materials such as glass, stainless steel and Teflon (USEPA, 2002).

3.4.2 Re-sampling procedure

The 2017 low flow re-sampling procedure applied to each borehole is described in point form below (Sundaram et al, 2009; Puls and Barcelona, 1996; Smart and Worthington, 2012; USEPA, 1996; USEPA, 2002 and WRC, 2007):

a) Measure and record static water level to approximate groundwater level under undisturbed and no pumping conditions;

b) Lower TLC meter into borehole and record results obtained at every 1 m interval;

c) Continue to lower TLC meter until the bottom of the borehole is reached taking care to avoid disturbing settled sediment;

d) Record temperature, level and EC readings. A sudden and significant spike in EC is assumed to indicate optimal sampling depth as it is related to the borehole and aquifer interface where water flows directly out from the formation;

e) Lower bladder pump and tubing slowly into the borehole using the reel and rope. Ensure that the pump intake is placed at appropriate depth, determined by the previously recorded EC profile;

f) Establish connections between submerged bladder pump, air compressor, generator, Aquaread and flow through cell;

g) Connect bladder pump discharge line to flow through cell in order to collect water for turbidity measurements and direct discharge line from flow through cell to dedicated purge container;

h) Begin pumping the borehole at a low rate of 0.2 to 0.5 litres per minute while slowly increasing the pumping rate until a drawdown of < than 0.33 feet (10 cm) per minute is achieved. If a drawdown rate of 0.33 feet cannot be achieved, a predetermined pump setting, based on borehole depth versus pump rate, is instead selected;

i) Start Aquaread probe as soon as water begins to enter the flow through cell. Ensure that a minimum of one tubing volume is purged before recording water stabilisation indicator parameters;

j) Following a purge of one tubing volume from the flow through cell, record water stabilisation indicator parameters every minute.

Stabilization criteria are based on three successive readings of indicator parameters as described in Table 5 and obtained from the Aquaread probe:

Table 5: Stabilization criteria (adapted from Puls and Barcelona, 1996 and Wilde et al, 1998).

Sampling parameters	Stabilization criteria
pH	+/- 0.1 pH units
Specific electrical conductance (SEC)	+/- 3% S/cm
Oxidation-reduction potential	+/- 10 millivolts
Turbidity	+/- Nephelometric Turbidity Unit (NTU)
Dissolved oxygen	+/- 0.3 milligrams per litre

k) Once stabilization criteria are obtained, the Aquaread probe is switched off and the in-situ measurements indicating stabilization are recorded;

l) Maintain the pumping rates to avoid disturbance to the overlying stagnant water column and collect sample directly from the discharge port of the pump tube prior to it passing through the flow through cell;

m) Ensure that all sample containers are filled from the discharge port of the pump tube with minimal turbulence by allowing water to gently flow from the tubing and into the container; and

n) Ensure that samples for dissolved gasses and volatiles are collected when the pump tubing is completely full of groundwater to prevent aeration;

o) For dissolved gasses and volatiles place glass vials into the beaker while groundwater flows into it from the pump tube and fill the vials while they are completely submerged and with zero headspace;

p) Place the vials with Teflon coated septa into the beaker and dislodge any air trapped by tapping it. Remove the pump tube from the glass vial and secure the vial underwater without allowing

water in the vial to come into contact with air to prevent contamination and degassing;

q) Remove bladder pump from borehole and disconnect all connection tubes ensuring that the valves on the air compressor cylinder are closed;

r) Disconnect the pump tube from the pump and connect it to the open-ended line to the cylinder connection. Slowly release compressed air into the pump tube to remove remaining water trapped within; and

s) Decontaminate the flow through cell and Aquaread probe in distilled water, towel dry and store.

All collected samples are stored and transported in a cooler box at near ambient but stabilised temperature while on site. Once sample collection is complete, samples are delivered directly to accredited laboratories within 24 hours to avoid analyte loss (Nielsen, 1991).

3.5 Issues associated with sampling procedure

The numerical comparison between baseline and re-sampled data assumes identical treatment of the samples. These considerations include the potential for non-standardisation of the sampling technique between the sequential sampling dates or locations, difference in the number of samples taken during baseline and subsequent samples, and differences in the parameters analysed or the methods used for analysis. Details of these limitations as they apply to this study are discussed in the sections below.

3.5.1 Sampling and analysis in the baseline study

Baseline sample data was collected in 2015 by the gas well operator's appointed environmental assessment consultants. It consisted of three successive sampling events in April 2015 and two in May 2015. Two boreholes in addition to those resampled in 2017, were sampled in 2015 but have subsequently collapsed (BH03) and run dry (BH06) and thus could not be resampled in 2017.

The sampling technique used during baseline sample collection was a combination of traditional borehole purging and low flow purging, using both a bailer and bladder pump. No documentation from the consultants responsible for collecting the baseline samples was available to indicate which boreholes were subject to the various purging and sampling techniques.

The baseline sampling programme included a much wider array of parameters for assessment, beyond those primarily related to natural gas extraction. Finally, it was noted that there was occasional alteration of the parameter detection limits relating to the laboratory analysis of baseline samples. The points of non-standardisation noted above represent potentially substantive limitations that must be considered when evaluating baseline data against re-sampled data.

The combination of unsuitable sample size, inconsistent use of purging and sampling techniques and possible degassing and/or sample contamination provide evidence that the baseline results of 2015 are uncertain at best and for certain parameters – notably those prone to outgassing- and are unlikely to reliably represent pre-gas extraction values within the aquifer.

3.5.2 Sample collection in 2017

The re-sample reported this study data was collected in 2017 by the author. It consisted of five successive re-sampling events during the months of February, April, June, August and October 2017.

The re-sampling programme undertaken in 2017 was standardised across all boreholes. It was done exclusively using the low flow purging and sampling technique. Sampling was done using a bladder pump as opposed to a bailer.

The re-sampling programme focussed exclusively on within-aquifer parameters which on the basis of reviewed literature were potentially altered by natural gas extraction activities. It excluded those not considered related to gas extraction, resulting in a more focussed analysis of selected parameters.

The use of an appropriate, standardised purging and sampling technique in the 2017 re-sampling programme provides for a more robust sampling programme and a reproducible approach. The re-sampling results are therefore more representative of the aquifer water chemistry.

3.6 Analyses performed on water samples

Baseline and re-sample data were sent to South African National Accreditation System (SANAS) laboratories for analyses. The laboratories responsible for 2015 baseline sample analyses were:

- M and L Laboratory (Pty) Ltd; and
- UIS Organic Laboratory (Pty) Ltd

Laboratories responsible for 2017 re-sampling analyses were:

- M and L Laboratory (Pty) Ltd (40 Modulus Road, Ormonde, Johannesburg, 2190);
- UIS Organic Laboratory (Pty) Ltd (13 Sovereign Drive, Route 21 Corporate Park, Pretoria, 0062); and
- X Lab Earth Science (Pty) Ltd (259 Kent Avenue, Ferndale, Johannesburg, 2194).

The parameters analysed by the various laboratories are shown in Table 6. The various methods used by the laboratories to analyse parameters are also shown in Table 6. Laboratory results are included in Appendix 1.

Table 6:Parameter analyses by laboratory and analytical method applied (APHA, 1992; APHA, 1997; APHA, 2005; USEPA, 1994; USEPA, 1997; USEPA, 2001; USEPA, 2003; USEPA, 2005; USEPA, 2007; USEPA, 2010 and USEPA, 2014)

Sampling parameters	Responsible Laboratory	Laboratory Analytical Method
General water quality indicators		
Dissolved organic carbon	M and L / X Lab Earth Science	EPA 415.3
Dissolved oxygen	M and L / X Lab Earth Science	
Dissolved inorganic carbon	M and L / X Lab Earth Science	
Electrical conductivity	M and L / X Lab Earth Science	ME-AN 007 based on APH 2510
Acidity	M and L / X Lab Earth Science	ME-AN 016 based on APHA 4500- H B
Total suspended solids	M and L / X Lab Earth Science	ME-AN 009 based on APHA 2540D
Major ions		
Ammonia	M and L / X Lab Earth Science	Discrete analyser
Bromide	M and L / X Lab Earth Science	ME-AN 014 based on EPA 300.1 and APHA 4110 B
Chloride	M and L / X Lab Earth Science	
Sulfate	M and L / X Lab Earth Science	
Calcium	M and L / X Lab Earth Science	ME-AN 027 based on EPA 200.7 and APHA 3120
Potassium	M and L / X Lab Earth Science	
Sodium	M and L / X Lab Earth Science	
Metals		
Arsenic	M and L / X Lab Earth Science	ME-AN 026 based on EPA 200.8 and APHA 3030 B
Barium	M and L / X Lab Earth Science	
Boron	M and L / X Lab Earth Science	
Lead	M and L / X Lab Earth Science	
Lithium	M and L / X Lab Earth Science	
Manganese	M and L / X Lab Earth Science	
Rubidium	M and L / X Lab Earth Science	
Strontium	M and L / X Lab Earth Science	
Uranium	M and L / X Lab Earth Science	
Dissolved gasses		
Methane	UIS Organic Laboratory (Pty) Ltd	Headspace GC-FID based on EPA 8015d and EPA 5021a
Ethane	UIS Organic Laboratory (Pty) Ltd	

4. RESULTS

4.1 Values used when below the limit of detection

Laboratory analytical methods are limited in terms of their ability to accurately measure low concentrations of chemical parameters. The concentrations that are too low to be accurately measured are referred to as either Below Detection Limit (BDL) or Below the Limit of Detection (LOD) values in laboratory reporting (Croghan and Egeghy, 2003).

LOD values are commonplace and are often either censored or substituted by a constant value to allow for statistical analyses. However, the censoring or substitution of LOD values can result in unreliable statistics (Croghan and Egeghy, 2003). Numerous options exist to manipulate censored data for statistical analyses and includes options for extrapolation, maximum likelihood estimation and simple replacement (Hornung and Reed, 1990 and Finkelstein and Verma, 2001).

The most common and easily reproduced option is to use simple replacement, where the LOD values are replaced with either zero, a fraction of the detection limit or the laboratory detection limit itself (Croghan and Egeghy, 2003). Simple LOD replacement techniques are only adequate if a relatively small percentage of sample values are replaced, since both error rates and relative difference in means increase significantly once the percentage of censored values exceeds 25% (Croghan and Egeghy, 2003). The differences between overall error rate for various replacement techniques are provided in Table 7:

Table 7: Difference in error rate for different replacement methods (adapted from Croghan and Egeghy, 2003).

Replacement value				
Level	**ZERO**	**LOD/2**	**$LOD/\sqrt{2}$**	**Overall**
05	0.00	0.00	0.00	0.00
10	1.27	0.00	0.00	0.42
25	33.33	11.60	0.00	14.98
50	70.07	66.67	33.27	56.67
75	100.00	66.67	71.20	79.29
Overall	40.93	28.99	20.90	30.27

For this study, 1320 total samples (N) were collected across the seven boreholes. Of these, 283 censored values were recorded (21.4%).

Replacement of censored values with the $LOD/\sqrt{2}$ was applied in this study as the preferred approach due to it having the smallest overall error rate (21%) in relation to other replacement methods and the ease with which it can be reproduced (Croghan and Egeghy, 2003).

4.2 Sampling results

The combined sampling results (baseline of 2015 and re-sampling of 2017) for each borehole and each chemical parameter are provided in Tables 8 - 14 below. Censored values which have been replaced with the LOD divided by 1.414 ($LOD/\sqrt{2}$) are indicated in red italic font.

Table 8:Borehole 1 results (baseline and re-sampling)

	Symbol	Unit	Baseline Sample 2015			Re-samples 2017				
			Sample date			Sample date				
			01/04/2015	13/05/2015	29/05/2015	03/02/2017	05/04/2017	19/06/2017	25/08/2017	27/10/2017
BH01	NH_4	mg/l	*0.071*	*0.071*	*0.071*	*0.071*	*0.071*	0.480	0.110	0.270
	As	mg/l	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	0.010	0.005
	Ba	mg/l	0.110	0.240	0.290	0.220	0.300	0.280	0.240	0.350
	Bo	mg/l	0.460	0.200	0.200	0.120	0.100	0.140	0.220	0.180
	Br	mg/l	1.020	2.240	1.870	3.680	4.700	4.300	0.071	7.000
	Ca	mg/l	40.000	83.000	96.000	102.000	88.000	121.000	90.000	95.000
	Cl	mg/l	151.000	253.000	233.000	322.000	298.000	329.000	288.000	281.000
	C_2H_6	mg/l	*0.009*	*0.009*	*0.009*	*0.009*	*0.009*	*0.009*	*0.009*	0.009
	DiC	mg/l	48.000	33.000	34.000	43.080	44.000	48.100	44.220	45.000
	CH_4	mg/l	0.090	*0.005*	*0.005*	*0.005*	*0.005*	*0.005*	0.190	0.068
	DoC	mg/l	*0.071*	*0.071*	1.900	*0.071*	16.000	11.000	*0.071*	*0.071*
	O_2	mg/l	7.600	5.600	6.300	6.820	9.710	10.300	12.320	9.200
	EC	mg/l	90.200	139.000	143.000	170.000	160.900	176.700	144.000	152.000
	Pb	mg/l	*0.001*	*0.001*	*0.001*	*0.001*	0.034	*0.001*	*0.001*	0.001
	Li	mg/l	0.030	0.020	0.030	0.021	0.033	0.034	0.030	0.022
	Mn	mg/l	0.090	0.030	0.020	0.024	0.079	0.640	0.220	0.430
	K	mg/l	1.100	1.400	1.500	1.670	1.700	1.870	2.300	2.600
	pH	Value at 25°C	7.600	7.300	7.400	8.000	7.400	7.500	7.600	7.700
	Rb	mg/l	*0.001*	0.010	0.040	0.030	0.055	0.041	*0.001*	*0.001*
	Na	mg/l	140.000	154.000	151.000	157.000	190.000	188.000	164.000	167.000
	Sr	mg/l	0.560	1.100	1.300	1.100	1.630	1.770	1.300	1.300
	SO_4	mg/l	43.000	65.000	36.000	38.000	39.000	30.000	29.000	29.000
	TSS	mg/l	16.000	120.000	0.707	245.000	147.000	225.000	0.707	604.000
	U	mg/l	*0.003*	*0.003*	*0.003*	*0.003*	*0.003*	*0.003*	0.010	0.006

Table 9: Borehole 3 results (baseline and re-sampling)

	Symbol	Unit	Baseline Sample 2015			Re-samples 2017				
			Sample date			Sample date				
			01/04/2015	13/05/2015	29/05/2015	03/02/2017	05/04/2017	19/06/2017	25/08/2017	27/10/2017
BH03	NH_4	mg/l	NS	0.100	0.200	0.071	0.100	*0.071*	0.550	0.012
	As	mg/l	NS	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	0.004
	Ba	mg/l	NS	0.150	0.180	0.210	0.110	0.250	0.200	0.220
	Bo	mg/l	NS	0.200	0.500	0.140	0.140	0.190	0.260	0.130
	Br	mg/l	NS	*0.071*	*0.071*	2.970	*0.071*	1.000	*0.071*	1.700
	Ca	mg/l	NS	25.000	28.000	72.000	23.000	64.000	55.000	89.000
	Cl	mg/l	NS	33.000	28.000	78.000	37.000	90.000	94.000	100.000
	C_2H_6	mg/l	NS	*0.009*	*0.009*	*0.009*	*0.009*	*0.009*	*0.009*	*0.009*
	DiC	mg/l	NS	43.000	36.000	30.600	27.000	29.900	36.360	32.000
	CH_4	mg/l	NS	0.170	0.140	*0.005*	0.818	0.086	0.336	0.095
	DoC	mg/l	NS	*0.071*	1.000	*0.071*	11.000	4.900	15.360	*0.071*
	O_2	mg/l	NS	6.400	6.000	4.490	5.820	9.900	11.980	9.000
	EC	mg/l	NS	56.700	55.500	81.200	52.700	93.000	90.000	300.000
	Pb	mg/l	NS	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*
	Li	mg/l	NS	0.020	0.030	0.019	0.025	0.028	0.030	0.015
	Mn	mg/l	NS	0.070	0.070	0.150	0.056	0.290	0.150	0.014
	K	mg/l	NS	0.870	0.950	1.100	1.000	1.290	1.900	1.600
	pH	Value at 25°C	NS	7.600	7.900	7.300	8.200	7.500	7.800	7.500
	Rb	mg/l	NS	*0.001*	0.008	0.011	0.025	0.007	*0.001*	*0.001*
	Na	mg/l	NS	92.000	96.000	86.000	93.000	96.000	110.000	77.000
	Sr	mg/l	NS	0.530	0.610	0.720	0.540	1.100	1.300	0.850
	SO_4	mg/l	NS	32.000	13.500	55.000	15.800	43.000	29.000	67.000
	TSS	mg/l	NS	30.000	2.000	205.000	50.000	315.000	326.000	*0.707*
	U	mg/l	NS	*0.003*	*0.003*	*0.003*	*0.003*	*0.003*	*0.003*	*0.003*

Table 10: Borehole 4 results (baseline and re-sampling)

	Symbol	Unit	Baseline Sample 2015			Re-samples 2017				
			Sample date			Sample date				
			01/04/2015	13/05/2015	29/05/2015	03/02/2017	05/04/2017	19/06/2017	25/08/2017	27/10/2017
BH04	NH_4	mg/l	1.100	0.900	0.900	1.000	1.000	0.610	1.300	0.710
	As	mg/l	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	0.007
	Ba	mg/l	0.560	0.610	0.800	0.560	0.510	0.560	0.570	0.640
	Bo	mg/l	0.150	0.100	0.120	0.120	0.048	0.140	0.180	0.150
	Br	mg/l	1.990	1.920	2.420	3.460	4.210	4.700	*0.071*	1.600
	Ca	mg/l	143.000	140.000	127.000	144.000	98.000	131.000	108.000	116.000
	Cl	mg/l	495.000	394.000	477.000	497.000	464.000	489.000	444.000	570.000
	C_2H_6	mg/l	*0.009*	*0.009*	*0.009*	*0.009*	*0.009*	*0.009*	*0.009*	*0.009*
	DiC	mg/l	69.000	46.000	47.000	40.320	40.000	40.500	43.260	41.000
	CH_4	mg/l	0.340	0.340	*0.005*	*0.005*	*0.005*	*0.005*	0.238	*0.005*
	DoC	mg/l	1.100	*0.071*	*0.071*	*0.071*	11.000	8.100	21.380	*0.071*
	O_2	mg/l	7.400	6.600	6.700	3.600	4.180	9.500	11.300	10.700
	EC	mg/l	197.200	213.000	216.000	207.000	192.500	211.300	195.000	207.000
	Pb	mg/l	*0.001*	*0.001*	*0.001*	*0.001*	0.008	*0.001*	*0.001*	*0.001*
	Li	mg/l	0.080	0.060	0.070	0.061	0.076	0.079	0.070	0.065
	Mn	mg/l	1.200	1.300	1.600	1.100	1.140	0.990	1.300	0.870
	K	mg/l	2.500	2.500	2.500	1.100	2.400	2.570	3.800	4.400
	pH	Value at 25°C	7.400	7.200	7.600	7.800	7.900	7.700	7.700	7.600
	Rb	mg/l	0.020	0.030	0.040	0.038	0.070	0.041	0.001	0.001
	Na	mg/l	204.000	202.000	191.000	201.000	206.000	196.000	201.000	225.000
	Sr	mg/l	4.100	3.500	4.200	2.700	3.300	3.370	3.400	2.900
	SO_4	mg/l	42.000	91.000	34.000	29.000	28.000	27.000	24.000	26.000
	TSS	mg/l	40.000	197.000	4.000	330.000	187.000	400.000	*0.707*	*0.707*
	U	mg/l	*0.003*	*0.003*	*0.003*	*0.003*	*0.003*	*0.003*	*0.003*	*0.003*

Table 11: Borehole 5 results (baseline and re-sampling)

	Symbol	Unit	Baseline Sample 2015			Re-samples 2017				
			Sample date			Sample date				
			01/04/2015	13/05/2015	29/05/2015	03/02/2017	05/04/2017	19/06/2017	25/08/2017	27/10/2017
BH05	NH_4	mg/l	0.710	0.600	0.710	0.800	0.710	0.630	0.800	0.670
	As	mg/l	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	0.008
	Ba	mg/l	3.500	0.800	0.990	0.680	0.680	0.730	0.540	0.790
	Bo	mg/l	0.040	0.030	0.070	0.065	0.004	0.110	0.090	0.089
	Br	mg/l	2.500	*0.071*	2.550	1.500	4.500	4.600	*0.071*	1.700
	Ca	mg/l	119.000	186.000	152.000	160.000	128.000	186.000	133.000	167.000
	Cl	mg/l	505.000	501.000	500.000	503.000	481.000	513.000	392.000	503.000
	C_2H_6	mg/l	0.760	*0.009*	*0.009*	*0.009*	*0.009*	*0.009*	*0.009*	*0.009*
	DiC	mg/l	27.000	49.000	25.000	37.200	36.000	34.800	38.880	39.000
	CH_4	mg/l	3.160	*0.005*	*0.005*	0.194	0.826	0.074	0.106	0.016
	DoC	mg/l	*0.071*	*0.071*	3.000	*0.071*	12.000	8.300	32.040	*0.071*
	O_2	mg/l	5.600	6.600	6.200	3.900	3.670	9.400	14.190	8.100
	EC	mg/l	167.100	222.000	220.000	205.000	190.700	215.800	187.000	168.000
	Pb	mg/l	*0.001*	*0.001*	*0.001*	*0.001*	0.008	*0.001*	*0.001*	*0.001*
	Li	mg/l	0.006	0.007	0.008	0.006	0.006	0.008	0.010	0.006
	Mn	mg/l	1.300	3.500	4.200	2.850	3.000	3.290	2.200	1.300
	K	mg/l	2.800	2.300	1.900	2.300	2.300	7.440	4.300	3.800
	pH	Value at 25°C	7.100	7.100	7.200	7.500	7.400	7.400	7.500	7.200
	Rb	mg/l	*0.001*	0.002	0.003	0.037	0.072	*0.001*	*0.001*	*0.001*
	Na	mg/l	137.000	152.000	161.000	130.000	135.000	140.000	121.000	146.000
	Sr	mg/l	1.400	1.000	1.300	0.880	1.700	1.100	1.300	0.980
	SO_4	mg/l	16.500	84.000	39.000	28.000	26.000	32.000	27.000	32.000
	TSS	mg/l	38.000	233.000	24.000	345.000	290.000	400.000	*0.707*	*0.707*
	U	mg/l	*0.003*	*0.003*	*0.003*	*0.003*	*0.003*	*0.003*	*0.003*	*0.003*

Table 12: Borehole 7 results (baseline and re-sampling)

	Symbol	Unit	Baseline Sample 2015			Re-samples 2017				
			Sample date			Sample date				
			01/04/2015	13/05/2015	29/05/2015	03/02/2017	05/04/2017	19/06/2017	25/08/2017	27/10/2017
BH07	NH_4	mg/l	0.300	0.200	0.100	1.600	0.500	0.350	0.190	0.089
	As	mg/l	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*
	Ba	mg/l	0.090	0.090	0.110	0.085	0.081	0.180	0.170	0.140
	Bo	mg/l	0.030	0.004	0.004	0.012	0.004	0.006	0.030	0.024
	Br	mg/l	0.760	*0.071*	1.370	4.460	4.500	1.900	*0.071*	1.000
	Ca	mg/l	173.000	163.000	132.000	161.000	136.000	184.000	145.000	157.000
	Cl	mg/l	299.000	290.000	280.000	290.000	272.000	297.000	313.000	338.000
	C_2H_6	mg/l	*0.009*	*0.009*	*0.009*	*0.009*	*0.009*	*0.009*	*0.009*	*0.009*
	DiC	mg/l	55.000	49.000	74.000	55.920	54.000	53.600	55.560	56.000
	CH_4	mg/l	0.130	0.220	0.280	0.027	0.037	0.159	0.035	0.012
	DoC	mg/l	*0.071*	*0.071*	1.500	*0.071*	12.000	11.900	23.450	*0.071*
	O_2	mg/l	7.200	6.300	6.200	5.410	4.110	9.100	12.940	6.900
	EC	mg/l	154.200	171.000	172.000	172.000	156.600	174.100	167.000	161.000
	Pb	mg/l	*0.001*	*0.001*	*0.001*	0.002	0.004	*0.001*	*0.001*	*0.001*
	Li	mg/l	0.030	0.020	0.040	0.021	0.024	0.028	0.020	0.023
	Mn	mg/l	0.170	0.190	0.220	0.130	0.130	0.180	0.130	0.084
	K	mg/l	0.980	1.100	0.800	1.200	1.200	1.290	1.300	1.400
	pH	Value at 25°C	7.000	7.000	7.000	7.200	7.000	7.100	7.300	7.100
	Rb	mg/l	*0.001*	0.020	0.040	0.036	0.057	0.045	*0.001*	*0.001*
	Na	mg/l	57.000	65.000	61.000	57.000	63.000	62.000	60.000	60.000
	Sr	mg/l	1.700	1.500	1.800	1.300	1.610	1.700	1.900	1.500
	SO_4	mg/l	60.000	73.000	44.000	31.000	40.000	33.000	36.000	39.000
	TSS	mg/l	20.000	170.000	6.000	230.000	200.000	255.000	*0.707*	*0.707*
	U	mg/l	*0.003*	*0.003*	*0.003*	*0.003*	*0.003*	*0.003*	0.010	0.004

Table 13: Borehole 8 results (baseline and re-sampling)

	Symbol	Unit	Baseline Sample 2015			Re-samples 2017				
			Sample date			Sample date				
			01/04/2015	13/05/2015	29/05/2015	03/02/2017	05/04/2017	19/06/2017	25/08/2017	27/10/2017
BH08	NH_4	mg/l	*0.071*	*0.071*	*0.071*	*0.071*	*0.071*	*0.071*	0.130	*0.071*
	As	mg/l	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	0.010	0.013
	Ba	mg/l	0.100	0.100	0.130	0.100	0.098	0.097	0.120	0.160
	Bo	mg/l	0.090	0.020	0.070	0.080	0.004	0.085	0.140	0.100
	Br	mg/l	3.550	2.820	4.160	2.220	5.000	2.500	*0.071*	78.000
	Ca	mg/l	205.000	198.000	183.000	178.000	150.000	192.000	233.000	322.000
	Cl	mg/l	479.000	443.000	183.000	446.000	436.000	407.000	679.000	589.000
	C_2H_6	mg/l	*0.009*	*0.009*	*0.009*	*0.009*	*0.009*	*0.009*	*0.009*	*0.009*
	DiC	mg/l	44.000	38.000	35.000	37.320	44.000	37.700	38.700	49.000
	CH_4	mg/l	*0.005*	*0.005*	*0.005*	*0.005*	*0.005*	*0.005*	*0.005*	*0.005*
	DoC	mg/l	*0.071*	*0.071*	*0.071*	*0.071*	44.000	8.800	*0.071*	*0.071*
	O_2	mg/l	7.800	6.400	7.600	5.560	3.940	12.000	7.140	7.700
	EC	mg/l	210.400	243.000	273.000	217.000	210.000	220.000	270.000	325.000
	Pb	mg/l	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*
	Li	mg/l	0.070	0.060	0.080	0.057	0.069	0.075	0.090	0.076
	Mn	mg/l	0.002	0.010	0.010	0.013	0.008	0.007	0.024	0.013
	K	mg/l	5.900	5.500	5.500	5.300	5.400	5.370	9.200	13.000
	pH	Value at 25°C	7.200	7.400	7.200	7.300	7.500	7.400	7.400	7.800
	Rb	mg/l	0.010	0.010	0.030	0.023	0.075	0.048	*0.001*	*0.001*
	Na	mg/l	141.000	151.000	189.000	131.000	144.000	134.000	167.000	192.000
	Sr	mg/l	2.600	2.500	3.300	1.990	2.380	2.410	4.000	3.200
	SO_4	mg/l	214.000	200.000	212.000	159.000	187.000	144.000	152.000	264.000
	TSS	mg/l	0.707	253.000	8.000	310.000	287.000	330.000	22.000	*0.707*
	U	mg/l	*0.003*	*0.003*	*0.003*	*0.003*	*0.003*	*0.003*	*0.003*	*0.003*

Table 14:Borehole 9 results (baseline and re-sampling)

	Symbol	Unit	Baseline Sample 2015			Re-samples 2017				
			Sample date			Sample date				
			01/04/2015	13/05/2015	29/05/2015	03/02/2017	05/04/2017	19/06/2017	25/08/2017	27/10/2017
BH09	NH_4	mg/l	0.200	*0.071*	0.100	0.600	0.710	1.480	0.920	0.410
	As	mg/l	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	0.014
	Ba	mg/l	0.250	0.260	0.340	0.310	0.280	0.350	0.300	0.330
	Bo	mg/l	0.360	0.300	0.032	0.260	0.170	0.310	0.420	0.420
	Br	mg/l	3.240	*0.071*	3.310	1.140	2.900	2.900	*0.071*	2.300
	Ca	mg/l	178.000	181.000	153.000	143.000	112.000	144.000	118.000	126.000
	Cl	mg/l	538.000	594.000	561.000	544.000	533.000	520.000	443.000	427.000
	C_2H_6	mg/l	*0.009*	*0.009*	*0.009*	*0.009*	*0.009*	*0.009*	*0.009*	*0.009*
	DiC	mg/l	29.000	45.000	32.000	39.480	40.000	40.300	39.600	44.000
	CH_4	mg/l	0.087	0.140	0.230	0.234	1.485	0.406	1.130	0.843
	DoC	mg/l	*0.071*	*0.071*	*0.071*	*0.071*	12.000	6.900	13.230	*0.071*
	O_2	mg/l	7.800	4.600	6.700	3.580	2.280	7.300	6.930	5.000
	EC	mg/l	213.400	251.000	252.000	229.000	210.600	225.700	199.000	195.000
	Pb	mg/l	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*
	Li	mg/l	0.110	0.090	0.110	0.092	0.110	0.120	0.090	0.095
	Mn	mg/l	0.350	0.430	0.560	0.450	0.520	0.560	0.310	0.110
	K	mg/l	3.900	3.800	3.500	3.400	3.500	3.940	5.200	5.500
	pH	Value at 25°C	7.500	7.300	7.300	7.600	7.500	7.600	7.600	8.000
	Rb	mg/l	0.003	0.008	0.020	0.011	0.056	0.038	*0.001*	*0.001*
	Na	mg/l	217.000	254.000	247.000	226.000	244.000	245.000	202.000	220.000
	Sr	mg/l	3.700	3.300	4.000	2.800	3.400	3.420	3.300	2.700
	SO_4	mg/l	99.000	107.000	94.000	68.000	54.000	35.000	54.000	51.000
	TSS	mg/l	48.000	227.000	0.707	290.000	290.000	345.000	62.000	0.707
	U	mg/l	*0.003*	*0.003*	*0.003*	*0.003*	*0.003*	*0.003*	*0.003*	0.0023

4.3 Descriptive statistics

Replacement of censored values with $LOD/\sqrt{2}$ allows for the calculation of descriptive statistics of the various chemical parameter concentrations in each borehole sampled. As an example, boxplots for dissolved CH_4 concentrations by proximity to the gas well are shown in Figure 2, since this is the most important parameter to monitor in relation to a production natural gas well. Full descriptive statistics for all chemical parameters in each sampled borehole are provided in Appendix 2 and include minimum (Min), maximum (Max), Mean, Median, Range, Standard Deviation (SD) and Coefficient of Variation (CV).

Notable observations which occurred *across all boreholes* include the high variation among several major ions (Ca, Cl, Na and SO_4) and some general water quality indicators (DiC, DOC, dissolved O_2 and TSS). The variability among these parameters means that estimates of central tendency are less reliable, and higher sample numbers are required to determine the mean values of these chemical parameters within each borehole, to a given level of accuracy. Nevertheless, the results corroborate the prior observation that both shallow and deeper groundwater resources within the catchment tend to be naturally saline (DWAF, 2003).

Lower variation was observed *across all boreholes* for dissolved gasses (C_2H_6 and CH_4), metals (As, Ba, Bo, Pb, Li, Mn, Rb, Sr and U), pH and select major ions (NH_4 and Br). The lower variation among these parameters indicates that despite the small number of samples analysed, the descriptions of central tendency are more reliable.

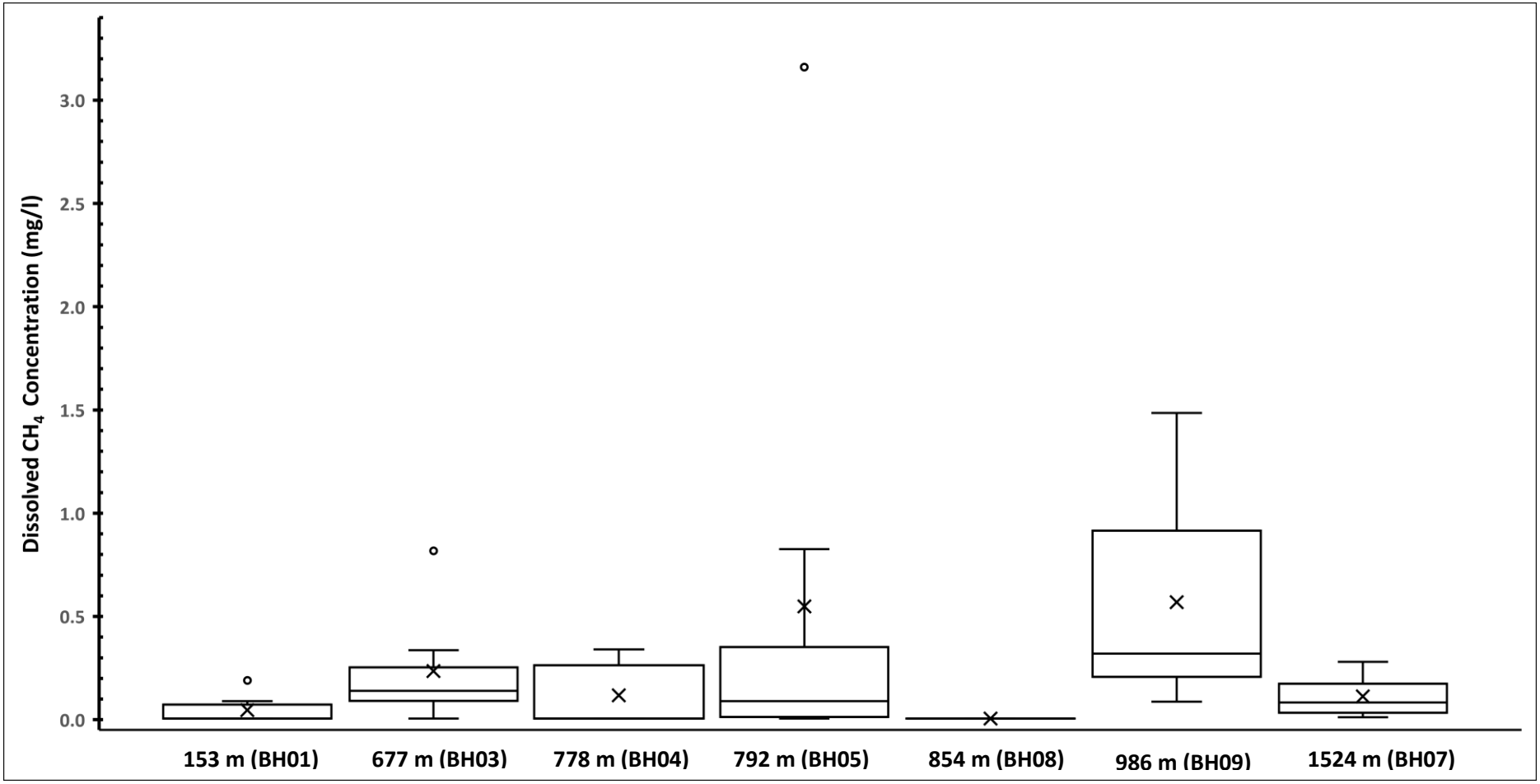


Figure 2: Boxplots of dissolved CH_4 concentrations by proximity to production well. All boxplots show the mean as an x, the median as the line within the box which represents the 1st and 3rd quartiles and whiskers indicating 1.5 times the interquartile range with points representing outliers.

4.4 Dissolved CH_4 concentration trends over time

Linear regression is used in the section below to model the relationship between dissolved CH_4 concentrations (dependant variable) and time (explanatory variable) for each borehole sampled. The coefficient of determination (R^2) value for the model is also provided and indicates how close the observed data fit the observed trend-line. An alpha (α) of 0.05 is used as the cut-off for statistical significance.

4.4.1 Borehole 1

Dissolved CH_4 concentration trends in BH01 are shown in Figure 3 below. BH01 is upstream and approximately 153m from the gas extraction well. CH_4 concentration trends over time are indicated with a green linear trend-line.

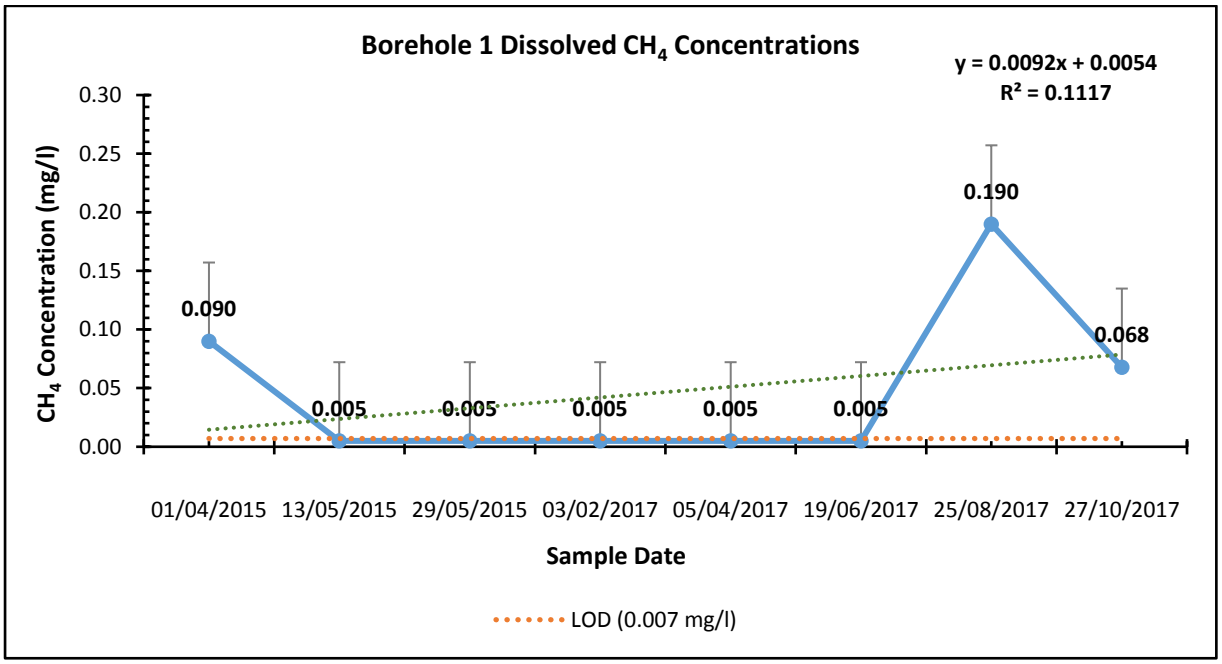


Figure 3: Borehole 1 dissolved CH_4 concentrations over time

Dissolved CH_4 concentrations within BH01 (*n=8*) range from 0.005 mg/l (LOD replacement value) to 0.190 mg/l during the 2015 to 2017 sampling period. A maximum observed dissolved CH_4 concentration of 0.190 mg/l was observed during the month of August 2017, during ongoing gas extraction activity at the well. Nearly two thirds of samples collected and analysed within BH01 recorded concentrations below the laboratory LOD (0.007 mg/l).

The mean dissolved CH_4 concentration observed within BH01 during the 2015 to 2017 sampling period was 0.047 mg/l (*SD=0.067*). The relatively low dispersion of dissolved CH_4 sample data within BH01 suggests that the mean is a reliable indicator of central tendency for expected dissolved CH_4 concentrations within the borehole.

Comparison of mean dissolved CH_4 concentrations pre-extraction (2015) and during ongoing gas extraction (2017), indicate an increase of 0.022 mg/l over the two-year sampling period. BH01 displays a marginal but non-significant increasing trend ($R^2=0.11$, $n = 8$, $p = 0.631$) in terms of dissolved CH_4 concentrations over time.

4.4.2 Borehole 3

Dissolved CH_4 concentration trends in BH03 are shown in Figure 4 below. BH03 is downstream and approximately 677m from the gas extraction well. CH_4 concentration trends over time are indicated with a green linear trendline.

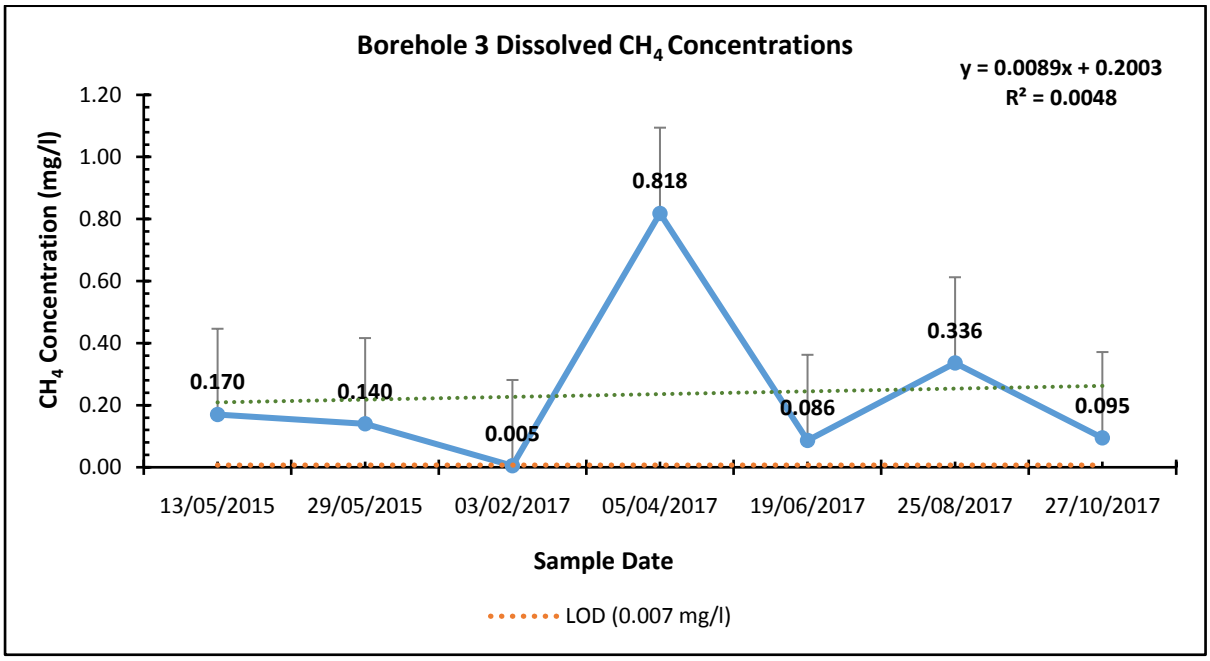


Figure 4: Borehole 3 dissolved CH_4 concentrations over time

Dissolved CH_4 concentrations within BH03 (*n=7*) range from 0.005 mg/l (LOD replacement value) to 0.818 mg/l during the 2015 to 2017 sampling period. A maximum observed dissolved CH_4 concentration of 0.818 mg/l was observed during the month of April 2017, during ongoing gas extraction activity at the well. Concentrations below the laboratory LOD (0.007 mg/l) were reported for 13% of samples within BH03.

The mean dissolved CH_4 concentration observed within BH03 during the 2015 to 2017 sampling period was 0.236 mg/l (*SD=0.276*). The relatively high dispersion of dissolved CH_4 sample data within BH03 suggests that the reported mean is an unreliable indicator of central tendency for expected dissolved CH_4 concentrations within the borehole.

Comparison of mean dissolved CH_4 concentrations pre-extraction (2015) and during ongoing gas extraction (2017), indicate a non-significant increase of 0.113 mg/l ($R^2 = 0.00$, $n = 7$, $p = 0.644$) over the two-year sampling period.

4.4.3 Borehole 4

Dissolved CH_4 concentration trends in BH05 are shown in Figure 7 below. BH04 is downstream and 778m from the gas extraction well. CH_4 concentration trends over time are indicated with a green linear trendline.

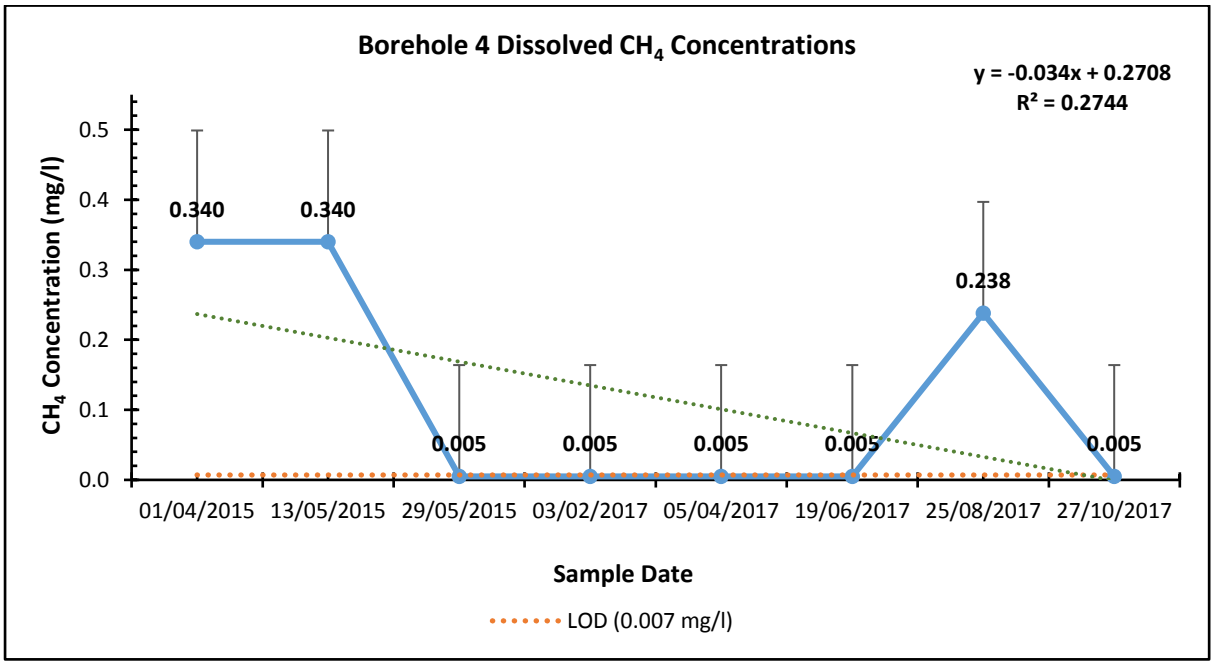


Figure 5: Borehole 4 dissolved CH_4 concentrations over time

Dissolved CH_4 concentrations within BH04 (*n=8*) range from 0.005 mg/l (LOD replacement value) to 0.340 mg/l during the 2015 to 2017 sampling period. A Maximum observed dissolved CH_4 concentration of 0.340 mg/l was observed during the months of April and May 2015, prior to gas extraction activity at the well. Half of the samples collected and analysed within BH04 recorded concentrations below the laboratory LOD (0.007 mg/l).

The mean dissolved CH_4 concentration observed within BH04 during the 2015 to 2017 sampling period was 0.118 mg/l (*SD=0.159*). The relatively high dispersion of dissolved CH_4 sample data within BH04 suggests that the mean is an unreliable indicator of central tendency for expected dissolved CH_4 concentrations within the borehole.

Comparison of mean dissolved CH_4 concentrations pre-extraction (2015) and during ongoing gas extraction (2017), indicate a decrease of 0.176 mg/l over the two-year sampling period. BH04 displays non-significant decreasing trend *($R^2 = 0.27$, $n = 8$, $p = 0.124$)* in terms of dissolved CH_4 concentrations over time.

4.4.4 Borehole 5

Dissolved CH_4 concentration trends in BH05 are shown in Figure 6 below. BH05 is downstream and 792m from the gas extraction well. CH_4 concentration trends over time are indicated with a green linear trend line.

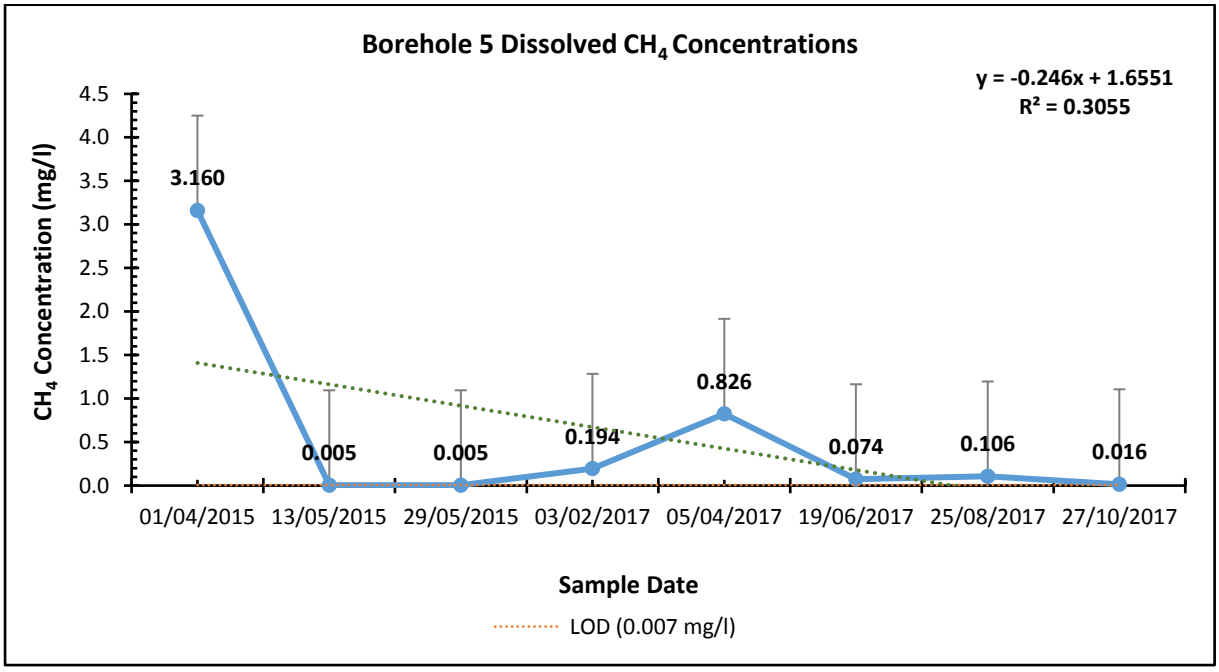


Figure 6: Borehole 5 dissolved CH_4 concentrations over time

Dissolved CH_4 concentrations within BH05 (*n=8*) range from 0.005 mg/l (LOD replacement value) to 3.160 mg/l during the 2015 to 2017 sampling period. A maximum observed dissolved CH_4 concentration of 3.160 mg/l was observed during the month of April 2015, prior to gas extraction activity at the well. A quarter of the samples collected and analysed for BH05 recorded concentrations below the laboratory LOD (0.007 mg/l).

The mean dissolved CH_4 concentration observed within BH05 during the 2015 to 2017 sampling period was 0.548 mg/l (*SD=1.090*). The relatively high dispersion of dissolved CH_4 sample data within BH05 suggests that the mean is an unreliable indicator of central tendency for expected dissolved CH_4 concentrations within the borehole.

Comparison of mean dissolved CH_4 concentrations pre-extraction (2015) and during ongoing gas extraction (2017), indicate a decrease of 0.814 mg/l over the two-year sampling period. BH05 displays a non-significant decreasing trend (R^2*=0.30, n = 8, p = 0.315)* in terms of dissolved CH_4 concentrations over time.

4.4.5 Borehole 7

Dissolved CH_4 concentration trends in BH07 are shown in Figure 7 below. BH07 is upstream and 1524m from the gas extraction well. CH_4 concentration trends over time are indicated with a green linear trend line.

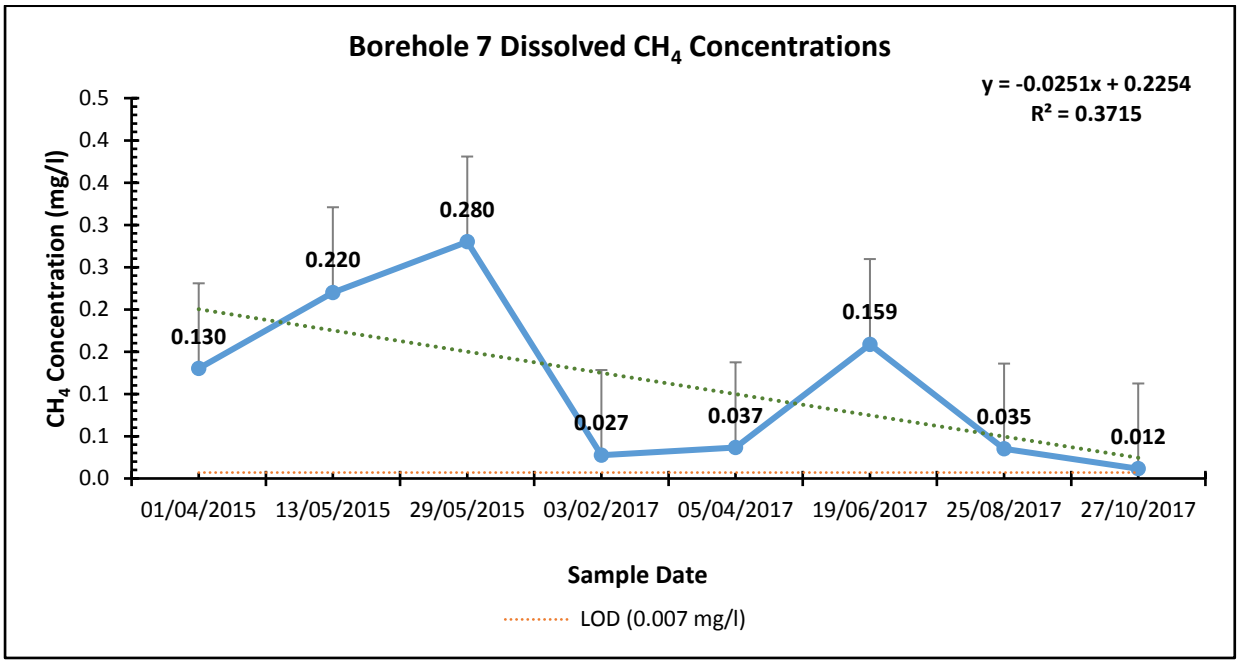


Figure 7: Borehole 7 dissolved CH_4 concentrations over time

Dissolved CH_4 concentrations within BH07 (*n=8*) range from 0.012 mg/l to 0.280 mg/l during the 2015 to 2017 sampling period. A maximum observed dissolved CH_4 concentration of 0.280 mg/l was observed during the month of May 2015, prior to gas extraction activity at the well. None of samples collected and analysed within BH07 recorded concentrations below the laboratory LOD (0.007 mg/l).

The mean dissolved CH_4 concentration observed within BH07 during the 2015 to 2017 sampling period was 0.112 mg/l (*SD=0.101*). The relatively low dispersion of dissolved CH_4 sample data within BH07 suggests that the mean is a reliable indicator of central tendency for expected dissolved CH_4 concentrations within the borehole.

Comparison of mean dissolved CH_4 concentrations pre-extraction (2015) and during ongoing gas extraction (2017), indicate a decrease of 0.156 mg/l over the two-year sampling period. BH07 displays a significant decreasing trend ($R^2 = 0.37$, $n = 8$, $p = 0.01$) in terms of dissolved CH_4 concentrations over time.

4.4.6 Borehole 8

Dissolved CH_4 concentration trends in BH08 are shown in Figure 8 below. BH08 is downstream stream 854m from the gas extraction well.

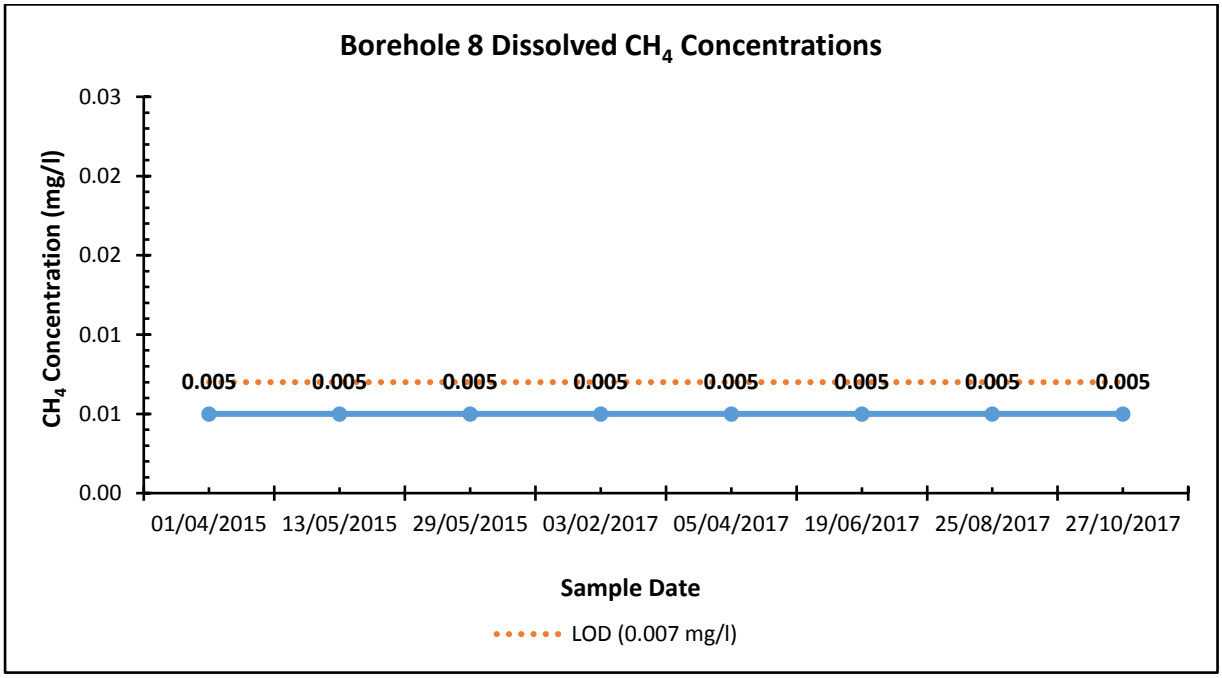


Figure 8: Borehole 8 dissolved CH_4 concentrations over time

Dissolved CH_4 concentrations within BH08 (*n=8*) were all observed to be below the laboratory LOD (0.007 mg/l) during the 2015 to 2017 sampling period. All of the samples collected and analysed within BH08 recorded concentrations below the laboratory LOD (0.007 mg/l), thus nothing useful can be said except that dissolved CH_4 was undetectable at this site, both before and after the commencement of gas production.

4.4.7 Borehole 9

Dissolved CH_4 concentration trends in BH09 are shown in Figure 9 below. BH09 is downstream stream 986m from the gas extraction well. CH_4 concentration trends over time are indicated with a green linear trend line.

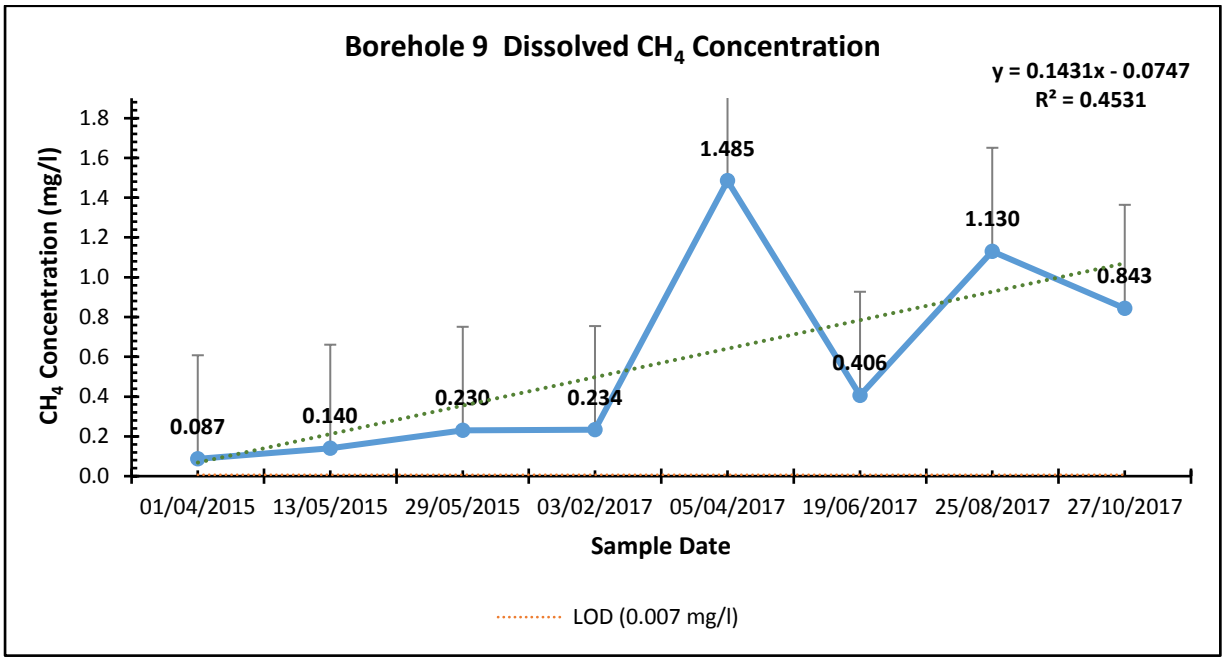


Figure 9: Borehole 9 dissolved CH_4 concentrations over time

Dissolved CH_4 concentrations within BH09 (*n=8*) range from 0.087 mg/l to 1.485 mg/l during the 2015 to 2017 sampling period. A maximum observed dissolved CH_4 concentration of 1.485 mg/l was observed during the month of April 2017, during ongoing gas extraction activity at the production well. None of samples collected and analysed within BH09 recorded concentrations below the laboratory LOD (0.007 mg/l).

The mean dissolved CH_4 concentration observed within BH09 during the 2015 to 2017 sampling period was 0.569 mg/l (*SD=0.521*). The relatively high dispersion of dissolved CH_4 sample data within BH09 suggests that the mean is an unreliable indicator of central tendency for expected dissolved CH_4 concentrations within the borehole.

Comparison of mean dissolved CH_4 concentrations pre-extraction (2015) and during ongoing gas extraction (2017), indicate an increase of 0.668 mg/l over the two-year sampling period. BH09 displays a non-significant increasing trend ($R^2 = 0.45$, $n = 8$, $p = 0.07$) in terms of dissolved CH_4 concentrations over time.

4.4.8 Dissolved CH_4 and distance from gas well

The mean dissolved CH_4 concentrations in relation to distance from the gas extraction well is shown in Figure 10 below. CH_4 concentration trends in relation to distance from the gas well are indicated with a green linear trendline.

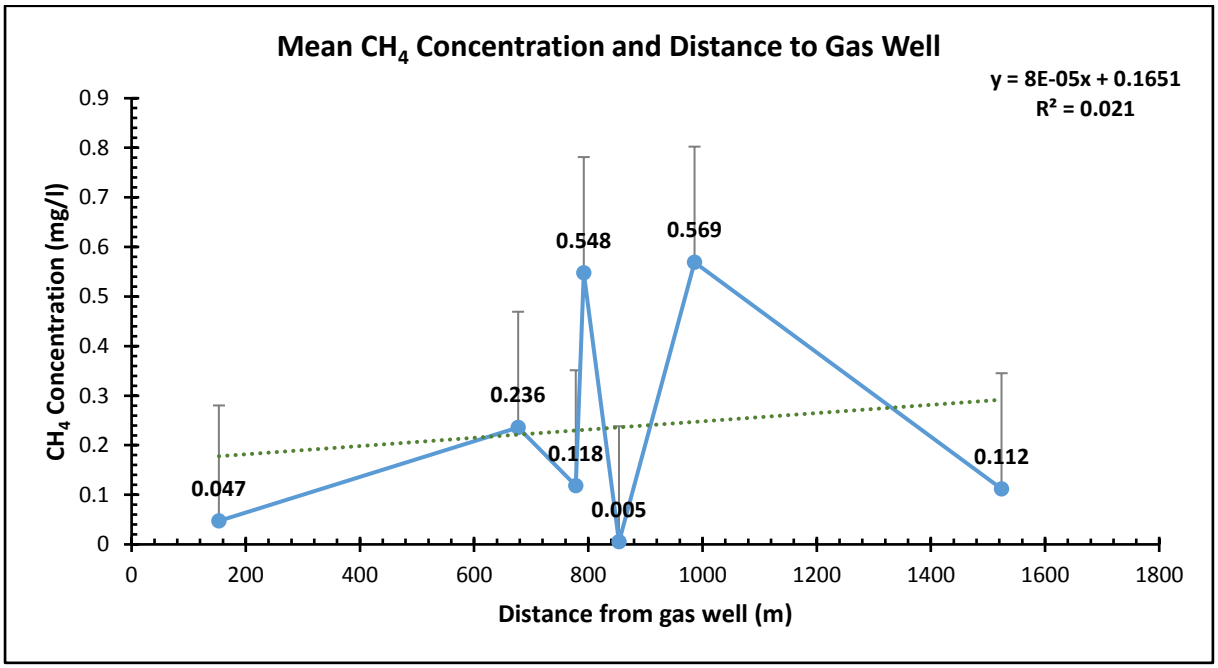


Figure 10: Mean CH_4 concentrations and distance to gas well

Mean dissolved CH_4 concentrations range from 0.005 (LOD replacement value) to 0.569 mg/l within the boreholes sampled. The highest mean dissolved CH_4 concentration (0.569 mg/l) was observed at BH09 which is approximately a kilometre from the gas extraction well.

The lowest mean dissolved CH_4 concentration (LOD replacement value of 0.005 mg/l) was observed at BH08 which is 854m from the gas extraction well. The apparent increasing trend of CH_4 concentration with distance from the production well is not significant ($R^2 = 0.02$, $n = 7$, $p = 0.756$).

4.4.9 Dissolved CH_4 and elevation relative to the production well

The mean dissolved CH_4 concentrations relative to elevation of the production well is shown in Figure 11 below. CH_4 concentration trends in relation to relative elevation are indicated with a green linear trendline.

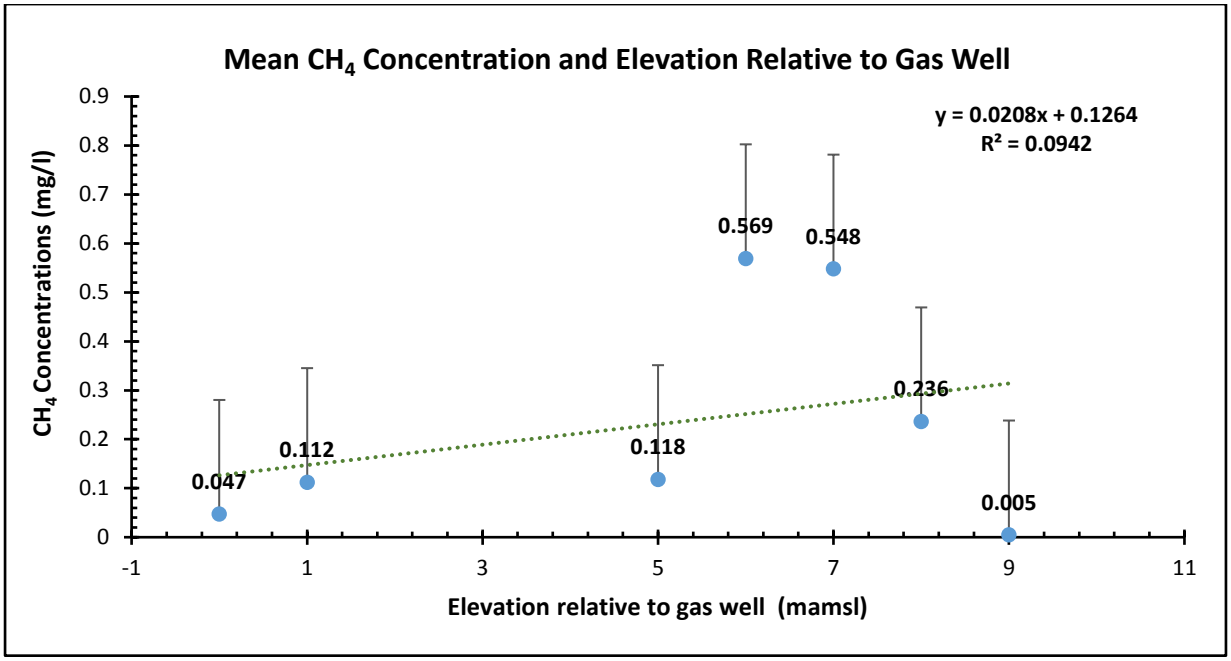


Figure 11: Mean CH_4 concentrations and elevation relative to production well.

Mean dissolved CH_4 concentrations range from 0.005 (LOD replacement value) to 0.569 mg/l within the boreholes sampled. The highest mean dissolved CH_4 concentration (0.569 mg/l) was observed within BH09 located 6 m below production well elevation (1299 m) at 1293 meters above mean sea level (mamsl).

The lowest mean dissolved CH_4 concentration (LOD replacement value of 0.005 mg/l) was observed within BH08 located 9 m below the production well elevation (1299 m) at 1290 mamsl. No significant trend was observed ($R^2 = 0.09$, $n = 7$, $p = 0.149$)

4.4.10 Dissolved CH_4 and sampling depth

The mean dissolved CH_4 concentrations in relation to sampling depth below the ground level in each well is shown in Figure 12 below. CH_4 concentration trends in relation to sampling depth are indicated with a green linear trend line.

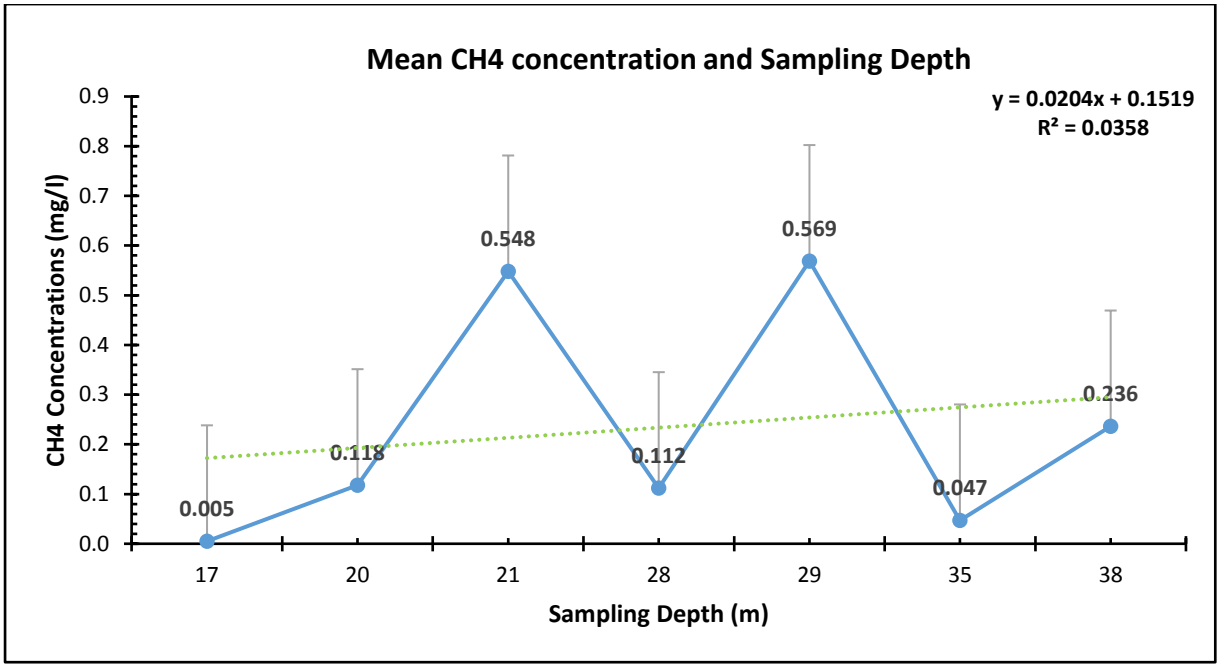


Figure 12: Mean CH_4 concentrations and sampling depth

Mean dissolved CH_4 concentrations range from 0.005 (LOD replacement value) to 0.569 mg/l within the boreholes sampled. The highest mean dissolved CH_4 concentration (0.569 mg/l) was sampled at a depth of 29 m and the lowest (LOD replacement value of 0.005 mg/l) was sampled at a depth of 17 m. The apparent increasing trend with sampling depth was not significant ($R^2 = 0.03$, $n = 7$, $p = 0.955$).

4.5 Statistical analyses

4.5.1 Pre-analysis data transformation

All the data, from both the baseline (2015) and re-sample period (2017) exhibited skewness values ranging from < -1 to > 1 and were therefore not normally distributed. As the data was skewed and not normally distributed, water quality parameter measurements were transformed by means of a natural logarithm (Grabow et al, 1998):

- Parameter X → LN(X)

Once the data was log transformed, residuals from regression analyses were normally distributed and had a constant variance allowing for parametric statistical analyses (Grabow et al, 1998).

As the data (with and without log transforms) is monotonic, the use of non-parametric means of analyses will yield similar results to

parametric analyses. However, the use of parametric analyses on the log transformed data explicitly allows for the analyses of groups with unequal variance and is more suitable to a small, absolute *n* size. In addition, parametric analyses is able to provide more information than non-parametric analyses which will only indicate if any differences observed are significant or not. As such, parametric analyses on the log transformed data was undertaken.

4.5.2 Comparison of pre and post gas extraction mean parameter concentrations

A two-sided Student t-test for paired samples was undertaken to compare the means of various parameter sample data prior to gas extraction (2015) and during ongoing gas extraction (2017) conditions (the mean across all boreholes for each parameter for the 2015 sampling versus the 2017 sampling). The results of the Student t-test are indicated in Table 15 below.

Table 15: Results of parameter mean comparison. The t-test is for the hypothesis that the difference between sampling periods is zero, i.e. no change between periods. A low value for *p* suggests that is unlikely that an observable difference could have been obtained by chance, statistically-significant differences at the 95% confidence level are highlighted in red

Parameter[1]	n Values		Mean[2]		SD[3]		Mean difference in the ln(X) value	*P* Value
	2015	2017	2015	2017	2015	2017		
NH_4	20	35	0.322	0.494	0.353	0.345	0.40234	0.228
As	20	35	0.001	0.003	0.000	0.001	0.48424	*0.007*
Ba	20	35	0.470	0.327	0.601	0.219	-0.09000	0.484
Bo	20	35	0.159	0.134	0.131	0.096	-0.01356	0.943
Br	20	35	1.721	4.600	1.102	5.778	0.47971	0.158
Ca	20	35	130.071	133.457	59.305	48.893	0.10930	0.430
Cl	20	35	346.071	380.200	184.860	160.506	0.2290	0.143
C_2H_6	20	35	0.045	0.009	0.095	0.000	-0.21121	0.356
DiC	20	35	42.738	41.611	9.859	7.307	-0.00315	0.965
CH_4	20	35	0.268	0.214	0.690	0.363	-0.12374	0.812
DoC	20	35	0.481	8.128	0.344	2.123	2.02453	*≤0.001*
O_2	20	35	6.562	7.656	0.402	1.389	0.06650	0.450
EC	20	35	176.943	186.623	67.444	40.501	0.09945	0.334

Parameter[1]	n Values		Mean[2]		SD[3]		Mean difference in the ln(X) value	*P* Value
	2015	2017	2015	2017	2015	2017		
Pb	20	35	0.001	0.002	0.000	0.002	0.27899	*0.039*
Li	20	35	0.047	0.047	0.034	0.035	-0.03089	0.424
Mn	20	35	0.733	0.650	1.107	0.900	0.19574	0.470
K	20	35	2.486	3.361	1.714	2.239	0.27731	*0.004*
pH	20	35	7.336	7.531	0.240	0.209	0.02627	*0.011*
Rb	20	35	0.014	0.024	0.010	0.007	0.03530	0.889
Na	20	35	150.286	149.600	59.927	59.503	-0.00769	0.815
Sr	20	35	2.122	2.204	1.343	0.960	0.04473	0.667
SO_4	20	35	77.226	57.166	62.394	55.369	-0.28434	0.128
TSS	20	35	69.244	191.345	29.487	32.219	0.81395	0.111
U	20	35	0.003	0.003	0.000	0.001	0.08970	0.222

[1] a natural log transformation was applied to all variables to reduce skewness.

[2] untransformed $\bar{x}$ provided.

[3] untransformed SD provided.

In most instances, the mean of the re-sampled parameters (2017) was higher than the mean of baseline parameters (2015). Statistically significant differences in the mean concentrations of various parameters prior to and during ongoing gas extraction conditions were identified and include:

- Arsenic (As) prior to gas extraction ($\bar{x}$ *= 0.001, SD = 0)* and during ongoing gas extraction ($\bar{x}$ *= 0.003, SD=0.001*) conditions; *t (6) = 3.97, p = 0.007*;

- Dissolved Organic Carbon (DoC) prior to gas extraction ($\bar{x}$*= 0.481, SD = 0.344*) and during ongoing gas extraction ($\bar{x}$*= 8.128, SD = 2.123*) conditions; *t (6) = 8.71, p = ≤0.001*;

- Lead (Pb) prior to gas extraction (($\bar{x}$ *= 0.001, SD = 0*) and during ongoing gas extraction (($\bar{x}$ *= 0.002, SD = 0.002*) conditions; *t (6) = 2.63, p = 0.039*;

- Potassium (K) prior to gas extraction (($\bar{x}$ *= 2.486, SD = 1.714*) and during ongoing gas extraction (($\bar{x}$ *= 3.361, SD = 2.239*) conditions; *t (6) = 4.64, p = 0.004*; and

- pH prior to gas extraction (($\bar{x}$ *= 7.336, SD = 0.240*) and during ongoing gas extraction (($\bar{x}$ *= 7.531, SD = 0.209*) conditions; *t (6) = 3.66, p = 0.01*.

The difference between the mean concentration of dissolved CH_4 prior to gas extraction (($\bar{x}$ *= 0.268, SD = 0.690*) and during ongoing gas extraction ($\bar{x}$ *= 0.214, SD = 0.363*), was not statistically significant; *t (6) = - 0.24, p = 0.812*.

Although statistically significant differences were observed in the means concentrations of As, DoC and Pb, it is important to note that more than half of these measurements are censored values replaced with $\mathrm{LOD}/\sqrt{2}$ to obtain a discrete measurement of a possible range of actual concentrations. The use of replacement values is likely to complicate calculation of and comparison of means, both prior to and during ongoing gas extraction. As such, the results of the t-test are likely to be influenced by these replacement values.

4.5.3 Relationship between CH_4 and other chemical parameters

Pearson's product-moment correlation coefficients were calculated to evaluate the possible relationships between dissolved CH_4 concentrations and various other chemical parameters that may be affected by natural gas extraction. The results of the correlation analyses are shown in Table 16 below.

Table 16: Pooled correlations between dissolved CH_4 and other parameters.

Parameter [1]	n Values		Correlation coefficient	*P* Value
	2015	2017		
NH_4	20	35	*.272*	*0.045*
As	20	35	-0.064	0.642
Ba	20	35	0.236	0.083
Bo	20	35	0.075	0.585
Br	20	35	*-.338*	*0.012*
Ca	20	35	*-.303*	*0.024*
Cl	20	35	-0.193	0.159
C_2H_6	20	35	*.292*	*0.030*
DiC	20	35	-0.038	0.781
DoC	20	35	0.126	0.358
O_2	20	35	-0.154	0.263
EC	20	35	*-.266*	*0.049*
Pb	20	35	-0.108	0.431
Li	20	35	-0.078	0.570
Mn	20	35	*.347*	*0.010*
K	20	35	-0.162	0.239
pH	20	35	0.056	0.683
Rb	20	35	-0.174	0.203
Na	20	35	-0.086	0.531
Sr	20	35	-0.101	0.465

Parameter [1]	n Values		Correlation coefficient	*P* Value
	2015	2017		
SO_4	20	35	*-.363*	*0.006*
TSS	20	35	0.024	0.861
U	20	35	0.015	0.911
[1] a natural log transformation was applied to all variables to reduce skewness.				

Several statistically significant correlations were identified through the analyses. Statistically significant correlations identified include:

- A weak positive association between NH_4 and CH_4 (*r=0.272, n=55, p=0.045*);
- A weak positive association between C_2H_6 and CH_4 (*r=0.292, n=55, p=0.030*);
- A moderate positive association between Mn and CH_4 (*r=0.347, n=55, p=0.010*);
- A weak negative association between EC and CH_4 (*r=-0.266, n=55, p=0.049*);
- A moderate negative association between Br and CH_4 (*r=-0.338, n=55, p=0.012*);
- A moderate negative association between Ca and CH_4 (*r=-0.303, n=55, p=0.024*); and
- A moderate negative association between SO_4 and CH_4 (*r=-363, n=55, p=0.006*)

5. DISCUSSION

5.1 Sampling challenges

The use of differing sampling procedures during the 2015 baseline sampling and 2017 re- sampling periods has been noted in the methods section. Baseline sample data collected was undertaken using a combination of traditional borehole purging and low flow purging, employing both a bailer and bladder pump, with no record of what technique was used on which borehole and time. Re-sampling was undertaken using a bladder pump and the low flow purging and sampling technique consistently across all boreholes.

The use of the low flow purging and sampling technique was selected for re-sampling due to its ability to minimise hydraulic stress through the maintenance of low-level drawdowns and its suitability for dissolved gas and volatile analyses (Puls and Barcelona, 1989). In addition, the consistent use of the low flow purging and sampling technique assists in the minimisation of sample variability (USEPA, 1996).

Baseline samples may have been compromised because of possible degassing and/or sample contamination. In this regard, the baseline samples may be an unreliable indication of groundwater conditions prior to gas extraction. This is an important consideration and limitation when attempting to compare baseline and re-sampling results. Furthermore, this finding emphasises the need to apply a consistent and appropriate sampling method throughout future monitoring.

5.2 Unbalanced sample numbers and values below the detection limit

Baseline data collected consisted of three successive sampling events. Re-sample data collected consisted of five successive re-sampling events.

The difference in the number of repeat measurements complicated the statistical analysis, since it precludes certain standard tests for paired data (such as the non-parametric Wilcoxon test) which assume equal numbers in the before-and-after samples. The t-tests applied here are somewhat robust to small differences in sample size but had to be applied to log-transformed data in order to remove non-normality in the raw data, thus sacrificing some power.

During both baseline and re-sampling periods, numerous parameters returned below LOD values. Replacement of these censored values with $\mathrm{LOD}/\sqrt{2}$ allowed for the calculation of descriptive statistics for the various chemical parameters. However, the use of $\mathrm{LOD}/\sqrt{2}$ replacement technique is imprecise (Croghan and Egeghy, 2003).

Lastly, all data collected rejected normality with absolute skewness values ranging between < -1 and > 1.0. Thus, the water quality parameter measurements were transformed by means of a natural logarithm to allow for a normal data distribution and parametric statistical analyses suitable for small sample sizes with unequal variance (Grabow et al, 1998).

5.3 Evaluation of dissolved CH_4 concentrations

5.3.1 Presence of dissolved CH_4 concentrations in groundwater samples

Dissolved CH_4 concentrations above the laboratory LOD were recorded in 6 of the 7 boreholes sampled (86%) prior to and during ongoing gas extraction. The pooled average dissolved CH_4 concentration was 0.234 mg/l with a range of < 0.007 mg/l (LOD) to 3.16 mg/l.

There were no statistically significant trends in CH_4 concentrations, between pre- and during-production, or with distance to the production well, altitude relative to the production well or sampling depth. Peak dissolved CH_4 concentrations were observed to occur mostly within the months of April and August, during both the baseline (2015) and re-sampling (2017) period. The cause of these apparent peaks is unknown and outside the focus of this study but they may be the result of seasonal aquifer recharge dynamics.

5.3.2 Association between saline water and dissolved CH_4

All borehole waters sampled tended to be naturally saline. They exhibit elevated concentrations of Cl ($\bar{x}$ *= 373.52 mg/l, SD = 163.34*) and Na ($\bar{x}$ *= 150.87 mg/l, SD = 57.18*) attributed to surface pan evaporation and past marine deposition (DWAF, 2003). The association of elevated dissolved CH_4 concentrations in groundwater characterised as saline (Cl > 20 mg/l) is well documented (McPhillips et al, 2014; Molofsky et al, 2013 and Warner et al, 2012) and is thought to be indicative of

interaction between deeper, saline aquifers and overlying, shallow, freshwater aquifers.

Deep, saline groundwater is subject to longer groundwater residence times than shallow, freshwater bodies, leading to protracted rock-water interactions and/or are in contact with Na-Cl rich waters found in underlying geological formations (Molofsky et al, 2013). The mixing of fresh water and Na-Cl rich water from deeper aquifers and the progressive ion exchange between Ca, Mn and K results in the liberation of Na in groundwater with consequent increases in Ba, Bo, Cl, Li and Sr concentrations (Kresse et al, 2012).

Longer rock-water interactions are also associated with anaerobic conditions due to microbial consumption of O_2 and other electron acceptors such as SO_4, iron oxides and Mn oxides (Kresse et al, 2012). Evidence of these redox reactions typically include increased concentrations of K, Mn and decreased concentrations of SO_4 present in groundwater (Kresse et al, 2012).

The results of this study are consistent with those of Molofsky et al (2013) and McPhillips et al (2014) as dissolved CH_4 concentrations were positively correlated to Mn (*r=0.347, n=55, p=0.010*) and negatively correlated to Br (*r=-0.338, n=55, p=0.012*), Ca (*r=-0.303, n=55, p=0.024*) and SO_4 (*r=-363, n=55, p=0.006*). In addition, dissolved CH_4 was observed to negatively correlate to EC (*r=-0.266, n=55, p=0.049*), most likely related to the redox reactions resulting in the decrease of SO_4 (Kresse et al, 2012).

In general, the deep, saline aquifers within the study area are confined, restricting vertical connectivity with the overlying shallow, freshwater aquifers (Steyl et al, 2012). However, limited but naturally occurring hydraulic connectivity is known to occur due to the intrusion of dolerite dykes into native country rocks (Hobbs et al, 2016). This limited but naturally occurring vertical connectivity allows for naturally occurring Na-Cl rich water and shallow, freshwater interaction which is accompanied by the associated increase in concentrations of dissolved CH_4 (Esterhuyse et al, 2014).

The continued presence of dissolved CH_4 prior to and during ongoing gas extraction, as well as the relatively high variability (*SD= 0.501*) of concentration data within the boreholes is evidence that CH_4 is likely a common constituent with variable concentrations in groundwater within the area which is representative of Karoo geology (Talma and Esterhuyse, 2015).

5.3.3 Distance, elevation and sampling depth effects

Reports of an association between dissolved CH_4 concentrations and distance to gas wells, principally in production wellfields in the USA, have been heavily contested (Davies, 2011; Jackson et al, 2013, McPhillips et al, 2014; Osborn et al, 2011, Saba and Orzechowski, 2011; Schon, 2011 and Siegel et al, 2015). Osborn et al (2011) and Jackson et al (2013) reported increases in average and maximum dissolved CH_4 concentrations of boreholes in close proximity to (< 1km) to gas wells whereas McPhillips et al (2014) and Siegel et al (2015), found there to be no statistically significant relationship between CH_4 concentrations and its proximity to gas wells.

The results of this study near Virgina in South Africa are consistent with those of McPhillips et al (2014) and Siegel et al (2015), as no statistically significant correlation was observed between dissolved CH_4 concentrations and proximity to the gas well ($r = 0.221$, $n = 55$, $p = 0.105$). This finding provides further evidence that observed dissolved CH_4 concentrations are likely a function of the underlying geology rather than proximity to gas wells.

It may be that horizontal distance to the production well is less important than the elevation of the sampled aquifer relative to the source of methane i.e. production well. However, no statistically significant relationship was observed between dissolved CH_4 concentrations and elevation relative to production well ($r = 0.190$, $n = 55$, $p = 0.165$) were found in this case. These results are contrary to the results of Heisig and Scot (2013) and Molofsky et al (2013) who observed statistically significant inverse correlations between topography and dissolved CH_4 concentrations i.e. lower elevation is associated with higher dissolved CH_4 concentrations.

No statistically significant relationship was observed between dissolved CH_4 concentrations and the depth at which groundwater sampling occurred ($r = .330$, $n = 55$, $p = 0.469$); contrary to the results of Nicot et al (2017) and Humez et al (2016). Both these studies reported significantly higher dissolved CH_4 concentrations with sampling undertaken at increasing well depth.

However, in order to better understand the relationship between distance, elevation and sampling depth effects on dissolved CH_4 concentrations, a detailed understanding of the site geology and geohydrology is required. As this information was not available it is important to underscore this as a limitation of the study as analyses

and interpretation of results is likely significantly influenced by these two features.

5.3.4 Gas origin

Dissolved CH_4 concentrations were observed to positively correlate to NH_4 ($r=0.272$, $n=55$, $p=0.045$) and C_2H_6 ($r=0.292$, $n=55$, $p=0.030$). The positive correlation of these parameters is important as it provides some supporting evidence of the origin of the gas.

Elevated concentrations of NH_4 are indicative of the biogenic origin of dissolved CH_4 detected. This is because NH_4 commonly occurs as a by-product of the methanogenic decomposition of organic material (Griffioen et al, 2013). Although C_2H_6 was also correlated to dissolved CH_4 concentrations, this result was based on the single sample which reported dissolved C_2H6 above the laboratory LOD (0.013 mg/l). Other long-chain hydrocarbons, which could be expected to be associated with CH_4, including Polycyclic Aromatic Compounds (< 0.1 µg/l), Total Petroleum Hydrocarbons within the $C^{10} – C^{40}$ range (< 382 µg/) and Total Oil and Grease (< 1 mg/l), showed no association with observed CH_4 in either 2015 or 2017. These results are strong evidence for the dissolved CH_4 having a biogenic origin (Osborn et al, 2011).

In order to confirm the origin of the dissolved CH_4 present, it is recommended that isotopic analyses be undertaken of the $\delta^{13}C$ and $\delta^{2}H$ isotopes of the gas present in groundwater. As He has been identified as a major gas component in the operators reserve determination (Renergen, 2017), it is further recommended that analyses of $^{3}He/^{4}He$ ratios should be undertaken to determine if there is a deep, mantle component of the dissolved CH_4 present in groundwater.

5.3.5 Water quality before and during ongoing gas extraction

Comparison of the various water quality parameters identified several statistically significant increases during ongoing gas extraction. Significant increases in were observed for pH ($p = 0.01$), As ($p = 0.007$), Pb ($p = 0.039$), K ($p = 0.004$) and DoC ($p = <0.00$)

The increase in mean pH values is likely due to the oxidation of CH_4 and the associated reduction in oxidizing reactants such as Mn and SO_4 (Molofsky et al, 2013). The increase in mean pH toward slightly above neutral ($\bar{x} = 7.43$, $SD = 0.205$) may also be related to the mean increase

in As and Pb concentrations observed during ongoing gas extraction. Sorption of As and Pb occurs near neutral pH and weakens rapidly above pH 9.3 (Fontenot et al, 2013). Increases in pH toward values slightly above neutral but not alkaline, give rise to concentrations of As and Pb through desorption from iron oxides and mobilisation via the oxidation of pyrite (Fontenot et al, 2013). The increase in mean concentrations of As and Pb are therefore likely due to the lowering of the water table from either groundwater withdrawals or drought resulting in the oxidation of exposed pyrites (Gates et al, 2011).

The increase in mean K concentrations is attributed to redox reactions resulting from microbial consumption of electron receptors such as O_2 and SO_4. These reactions occur under anaerobic conditions which are prevalent in groundwater with protracted rock-water interactions i.e. longer residence times, evident by the high mean Cl values across all boreholes sampled (Molofsky et al, 2013).

The increase in mean DoC concentrations may be related to the use of septic tanks and agricultural activity which is widespread throughout the study area. The baseline (2015) samples were collected during the months of April and May, which may correspond to underground septic tank drainage or low season for agricultural activity. The re-sampling in in 2017 occurred between February to October and may have included some events of DoC contamination originating from either source.

No significant change in dissolved CH_4 concentrations were observed before and during gas extraction. The difference in the observed mean concentration of dissolved CH_4 reported in this study prior to gas extraction ($\bar{x} = 0.268, SD = 0.690$) and during ongoing gas extraction ($\bar{x} = 0.214, SD = 0.363$) was not statistically significant; $t\ (6) = -0.24, p = 0.812$. With no significant difference in the means of CH_4 prior to and during ongoing gas extraction, it is likely that the changes to water quality are the result of naturally occurring biogeochemical processes and not from stray gas originating from the extraction well.

5.4 Water quality and fitness for use

Groundwater within the study area is used for a variety of purposes ranging from domestic to agricultural and mining uses (DWAF, 2003b). In terms of drinking water, three parameters exceed the South African National Standards 241: 2015 Drinking Water Standards (SANS, 2015). Exceedances of the SANS 241: 2015 Drinking Water Standard are highlighted in red and provided in Table 18 below.

Table 17: Comparison against SANS 241:2015 drinking water standard

Parameter	Unit	Threshold	Mean		SD		Pooled Mean Result
			2015	2017	2015	2017	
DoC	mg/l	≤ 10	0.481	8.128	0.344	2.123	5.35
DO	mg/l	-	6.562	7.656	0.402	1.389	7.27
DiC	mg/l	-	42.738	41.611	9.859	7.307	42.08
EC	mS/m	≤ 170	176.943	186.623	67.444	40.501	185.30
pH	Value at 25°C	≤ 5 - ≤ 9.7	7.336	7.531	0.240	0.209	7.5
TSS	mg/l	< 1200	69.244	191.345	29.487	32.219	147.91
NH_4	mg/l	≤ 1.5	0.322	0.494	0.353	0.345	0.435
Br	mg/l	-	1.721	4.600	1.102	5.778	3.58
Ca	mg/l	≤ 150	130.071	133.457	59.305	48.893	134.12
Cl	mg/l	≤ 300	346.071	380.200	184.860	160.506	373.52
K	mg/l	≤ 50	2.486	3.361	1.714	2.239	3.07
Na	mg/l	≤ 200	150.286	149.600	59.927	59.503	150.87
SO_4	mg/l	≤ 250	77.226	57.166	62.394	55.369	65.45
As	mg/l	≤ 0.01	0.001	0.003	0.000	0.001	0.002
Ba	mg/l	≤ 0.7	0.470	0.327	0.601	0.219	0.384
Bo	mg/l	≤ 2.4	0.159	0.134	0.131	0.096	0.139
Pb	mg/l	≤ 0.01	0.001	0.002	0.000	0.002	0.002
Li	mg/l	-	0.047	0.047	0.034	0.035	0.047
Mn	mg/l	≤ 0.01	0.733	0.650	1.107	0.900	0.69
Rb	mg/l	-	0.014	0.024	0.010	0.007	0.021
Sr	mg/l	-	2.122	2.204	1.343	0.960	2.08
U	mg/l	≤ 0.03	0.003	0.003	0.000	0.001	0.003
CH_4	mg/l	-	0.268	0.214	0.690	0.363	0.234
C_2H_6	mg/l	-	0.045	0.009	0.095	0.000	0.023

At present South African has no stipulated threshold for dissolved CH_4 concentrations for either drinking water use (SANS 2015), domestic use (DWAF, 1996), irrigation (DWAF, 1996) or livestock watering use (DWAF, 1996). No dissolved CH_4 concentrations observed in baseline and re-sample data exceeded the 10 mg/l "action level" as defined by the US Office of Surface Mining (Eltshlager et al, 2001).

The presence of dissolved CH_4 is known to alter the concentration of some groundwater chemical parameters (Molofsky et al, 2013). The oxidation of CH_4 is known to result in the reduction of oxidizing reactants (K, iron oxides, Mn oxides and SO_4), increases in bicarbonate, Mn and Fe concentrations and pH values as well as decreases in oxidation-reduction potentials, all of which have the potential to impact the fitness for use of groundwater for water users (Kelly and Matishoff, 1985).

Among the exceedances, the most concerning is Mn. Mean Mn concentrations far exceed the South African drinking water standards (SANS, 2015). Mn is a trace metal present in soils and common in drinking water. At low concentrations Mn is essential for human health (Keen et al, 1994). However, in excess Mn is a known neurotoxicant (Bouchard et all, 2011).

Numerous studies have reported on associations between excess Mn in groundwater and adverse implications for human health (Homoncik et al, 2010). These include impaired intellectual function of children (Wasserman et al, 2006), increased hyperactivity in children (Bouchard et al, 2011), various neurological symptom in both adults and children and general manganism (Kondakis et al, 1989).

5.5 Recommendations

To improve the robustness of future monitoring it is recommended that a single, standardised sampling method, appropriate for the collection of dissolved gasses and other volatiles is implemented and strictly adhered to. The standardised sampling method must be strictly followed prior to, during and post gas extraction with additional parameters added for further analyses where necessary.

Additional dedicated groundwater monitoring boreholes should be drilled near the gas extraction site. This will allow for more accurate determination of CH_4 concentration trends and their relationship to extraction activity over time. The use of dedicated monitoring

boreholes is preferred as many landowners may choose to equip their existing boreholes with pumps, making them unsuitable for future sampling.

The placement of dedicated monitoring boreholes should be informed by conceptual models of local geology and geohydrology. These models should also consider features such as structural controls, the confined or unconfined nature of aquifers and identify preferential flow-paths. Based on the above, a wider placement of dedicated monitoring boreholes, that may potentially extend up to 5 km from the production well, both upstream and downstream is recommended.

Ongoing monitoring should place special emphasis on NH_4, Mn, Br, Ca, SO_4 and EC concentrations. In addition, ongoing monitoring should also include iron concentrations due to the oxidation of CH_4, which is known to result in the reduction of oxidizing reactants such as iron oxides.

Over time, analysis of these parameters should confirm or refute the relationships identified with dissolved CH_4 in this study. In addition, pH, As, Pb, K and DoC should continue to be monitored as they are good indications of the presence or absence of dissolved CH_4 and its ability to alter water quality parameters and therefore future fitness of use.

In order to confirm the origin of the dissolved CH_4 present, it is recommended that isotopic analyses be undertaken of the $\delta^{13}C$ and $\delta^{2}H$ isotopes of the gas present in groundwater (Schoell, 1980). The isotopes of He should also be analysed as He was identified as a major gas component in the operators reserve determination (Renergen, 2017) and may provide a further indication of the deep or shallow origin of dissolved CH_4 present in groundwater. Lastly, as He is associated with the decomposition of uranium and thorium, radioactive isotope analyses should be undertaken as water emanating from the site may be radioactive and potentially harmful to downstream users.

Confirmation of the origin will allow for the streamlining of a future water monitoring programme, whereby parameters for monitoring are selected based on gas origin and composition. Lastly, the peak increases in dissolved CH_4 observed to occur the months of April and August should be investigated to determine if they are the result of aquifer recharge dynamics or other sub-surface events.

5.6 Conclusion

The aim of this study was to assess and evaluate changes in within aquifer chemical parameters from seven boreholes located near a single active natural gas extraction well. This aim was achieved through re-sampling of boreholes previously sampled by the operator in 2015 and prior to gas extraction (Renergen, 2017).

Comparison of baseline (2015) and re-sample (2017) data indicated that dissolved CH_4 concentrations above the laboratory detection limit were recorded in six of the seven of boreholes sampled *both* prior to (2015) and during ongoing gas extraction (2017). Dissolved CH_4 concentrations were positively correlated to Mn ($p = 0.010$) and negatively correlated to Br ($p = 0.012$), Ca ($p = 0.024$), SO_4 ($p = 0.024$) and EC ($p = 0.049$). No statistically significant correlation was observed between dissolved CH_4 concentrations and proximity to the gas well ($p = 0.105$) or elevation relative to production well ($p = 0.165$). Clues to the biogenic origin of the gas were also observed, including a positive correlation between dissolved CH_4 and NH_4 ($p=0.045$), which is typically a by-product of methanogenic decomposition of organic material (Griffioen et al, 2013). There was an absence of detectable higher chain hydrocarbons.

Comparison of pre and ongoing gas extraction mean water quality parameters identified several statistically significant increases during the period of ongoing gas extraction. These mean increases include pH (*0.195 units*), As (*0.002 mg/l*), Pb (*0.001 mg/l*), K (*0.875 mg/l*) and DoC (*7.647 mg/l*). The reported small difference between the concentration of dissolved CH_4 prior to gas extraction and during ongoing gas extraction was not statistically significant ($p = 0.812$).

All boreholes sampled were naturally saline with elevated concentrations of Cl and Na. The presence of dissolved CH_4 is strongly associated with groundwater characterised as saline (McPhillips et al, 2014 and Molofsky et al, 2013). CH_4 may be a common occurrence in groundwater within the study area and its prevalence is due to the underlying geology and not gas extraction activities. The increases observed in various other parameters during ongoing gas extraction are also likely the result of naturally occurring biogeochemical processes resulting from limited but naturally occurring hydraulic connectivity between deep and shallow aquifers as well as land uses such as agriculture. No evidence was found of increasing CH_4 concentrations as a result of gas extraction operations.

The presence of dissolved CH_4 is known to alter the concentration of some groundwater chemical parameters (Molofsky et al, 2013). The

oxidation of CH_4 is known to result in the reduction of oxidizing reactants (K, iron oxides, Mn oxides and SO_4), increases in bicarbonate concentrations, Mn and Fe and pH values as well as decreases in oxidation-reduction potentials, all of which have the potential to impact the fitness for use of groundwater for water users (Kelly and Matishoff, 1985). This is of particular importance as the presence of dissolved CH_4, due to either natural hydraulic connectivity or increased stray gas abundance may lead to further deterioration of water already not suitable for drinking.

Recommendations include standardisation of the sampling method, introduction of dedicated monitoring sites (the placement of which must be considered in relation to conceptual geological and geohydrological models), ongoing monitoring of those parameters which correlate significantly to dissolved CH_4 concentrations, ongoing monitoring of those parameters that can be altered in the presence of dissolved CH_4, isotope analyses to confirm the origin of the gas and investigation of apparent peaks of CH_4 concentration during the months of April and August.

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APPENDIX 1: LABORATORY RESULTS

APPENDIX 2: DESCRIPTIVE STATISTICS FOR SAMPLED PARAMTERS