



# Assessing the potential impacts of hydraulic fracturing on water and soil quality in the vicinity of well sites in the Surat Basin, Queensland

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Hydraulic fracturing operations in Central Queensland (photograph by GISERA).

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# Abbreviations/Acronyms

Abbreviation / Acronym	Description
ADWG	Australian drinking water guideline
AEM	Dilute-acid extractable metal
AFS	Atomic fluorescence spectrometry
ANSTO	Australian Nuclear Science and Technology Organisation
ANZG	Australian and New Zealand Governments
BTEX	Benzene, toluene, ethylbenzene, xylenes
CMIT	5-chloro-2- methyl-1,2-thiazol-3(2H)-one
CRM	Certified reference material
CSG	Coal seam gas
CSIRO	Commonwealth Scientific and Industrial Research Organisation
DFBA	Difluorobenzoic acid
DGV	Default guideline value
DO	Dissolved oxygen
DOC	Dissolved organic carbon
Dup	Duplicate
FBA	Fluorobenzoic acid
FEP	Fluorinated ethylene propylene
FLPE	Fluorinated high density polyethylene
GC-MS	Gas chromatography-mass spectrometry
GISERA	Gas Industry Social and Environmental Research Alliance
HSE	Health, safety and environment
HF	Hydraulic fracturing
HF fluid	Hydraulic fracturing fluid
MilliQ	High purity deionised water
ICP-AES	Inductively coupled plasma atomic emission spectrometry
IPC-MS	Inductively coupled plasma mass spectrometry
LDPE	Low density polyethylene
LOD	Limit of detection
LOR	Limit of reporting
MCL	Maximum contaminant level
MIT	2-methyl-1,2-thiazol-3(2H)-one
NATA	National Association of Testing Authorities
NEPM	National Environmental Protection Measure
NMI	National Measurement Institute
PAH	Polycyclic aromatic hydrocarbon
QA/QC	Quality assurance/quality control
Rep	Replicate
RO	Reverse osmosis
Std. dev	Standard deviation
TDS	Total dissolved solids
TEA	Triethanolamine (also known as 2,2',2''-nitrilotri(ethan-1-ol))
THM	Trihalomethane
TOC	Total organic carbon
TRH	Total recoverable hydrocarbons
TRM	Total recoverable metal
TSS	Total suspended solids
TTFBA	Tetrafluorobenzoic acid

USEPA	United States Environmental Protection Agency
WHO	World Health Organisation
WTF	Water treatment facility

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This report was supported by the Gas Industry Social and Environmental Research Alliance (GISERA). GISERA is a collaboration between CSIRO, Commonwealth and state governments and industry established to undertake publicly-reported independent research. The purpose of GISERA is to provide quality assured scientific research and information to communities living in gas development regions focusing on social and environmental topics including groundwater and surface water, biodiversity, land management, the marine environment, and socio-economic impacts. The governance structure for GISERA is designed to provide for and protect research independence and transparency of research. Visit [gisera.csiro.au](https://gisera.csiro.au) for more information about GISERA's governance structure, projects and research findings.

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## Executive summary

Coal seam gas (CSG) production has grown exponentially in Australia over the last two decades and it is estimated there are now around 19,000 productive wells with several thousand more planned (OGIA, 2016). CSG extraction in Australia involves drilling a network of wells across the designated gas field to depths that intersect the target coal seams. The evolved gas is piped to the surface and then via distribution network to a local processing facility. Some of the gas is supplied into domestic markets, however the majority is piped to the coast for liquefaction and overseas distribution. In order to increase the yield of gas (methane), some wells undergo a stimulation process known as hydraulic fracturing (HF).

HF involves the high pressure injection of a large volume of fluids into a well in order to fracture targeted coal seams so that fracture pathways open for gas and fluids to flow into the well. The fractures created are kept open by fine solids (proppants), usually sand, which are added to the injected HF fluids. HF are typically 90% water, 8-9% sand proppant with 1-2% of chemical additives (e.g. gelling agents, biocides, corrosion inhibitors) which are added to optimise the HF fluid performance.

The greatest number of CSG wells are found in southern and central Queensland and estimates suggest that around 10- 40% of the wells in the Surat Basin, Qld will be hydraulically fractured during their 25 to 30 year lifetime (DES 2014).

Despite significant monitoring by industry and intense regulatory oversight of the industry at both State and Federal levels, there is still widespread public concern about the environmental impacts of HF, in particular the threats posed by the use of chemicals. Community concerns centre around the nature and toxicity of chemicals used in the HF operations, potential mobilization of chemicals used in HF and contaminants from coal seams, into groundwater and the potential for impacts on human health and the environment.

Aside from the industrial chemicals used in HF operations, coal seams and surrounding rock formations are also known to contain a number of naturally-occurring chemical constituents (referred to as geogenic chemicals) that have the potential to be mobilised during HF activities (Ziemkiewicz and He 2015, Harrison et al. 2017). These geogenic chemicals include trace elements (e.g. arsenic, manganese, barium, boron and zinc), radionuclides (e.g. isotopes of radium, thorium, and uranium) and organic chemicals such as hydrocarbons and phenols. Mobilisation can occur because some HF chemicals have the potential to facilitate the release these chemicals from the coal seams and surrounding strata, through the effects of, for example, chelating agents, acids, surfactants, and solvents. Their release into waters introduced into, or naturally present in coal seams raises concerns for their potential impacts both in natural groundwater and in flowback water that is brought to the surface.

In order to address the above concerns, CSIRO has undertaken a comprehensive investigation of the impacts of HF on air, soil and water quality at two locations in the Surat Basin, Qld. The impacts of HF on air quality are provided in a separate report by Dunne et al. (2019). The study reported here involved measuring the concentration of a comprehensive range of chemicals before, during and after HF in surface waters, groundwater bores and soils in close proximity to

the wells undergoing HF and examination of the flowback and produced waters generated by the HF and gas generation processes. To the best of our knowledge this is the most extensive study conducted in the world to date on this topic. A total of 113 water samples and 40 soil samples were collected with these samples undergoing 22 analytical procedures to determine the concentration of more than 150 potential contaminants including organics, inorganics and radionuclides. The study targeted six wells which were sampled periodically up to 6 months from the time of HF, a local creek and groundwater bores located within the zone of HF activities. Water samples from Origin Energy's Reedy Creek Water Treatment Facility (WTF) were also taken in order to check the efficacy of reverse osmosis (RO) treatment in removing chemicals from combined wastewaters (including produced waters) generated by CSG operations in this region of the Surat Basin. The study did not cover the treatment of flowback waters and well flush waters generated prior to well commissioning as these waters are not treated at the WTF but are transported offsite to a licenced waste treatment facility where they are processed.

The objectives of this study were to:

1. Assess the concentrations of HF chemicals and geogenic chemicals in flowback and produced waters resulting from CSG HF operations.
2. Quantify the impacts of HF operations on the concentrations of potential contaminants in nearby surface waters, groundwater and soils.
3. Assess chemical concentrations in the collected water and soil samples against relevant Australian water and soil quality guideline values.
4. Conduct a laboratory assessment of various spill scenarios involving spillage of HF fluid and produced waters onto various soils types representative of the Surat Basin.

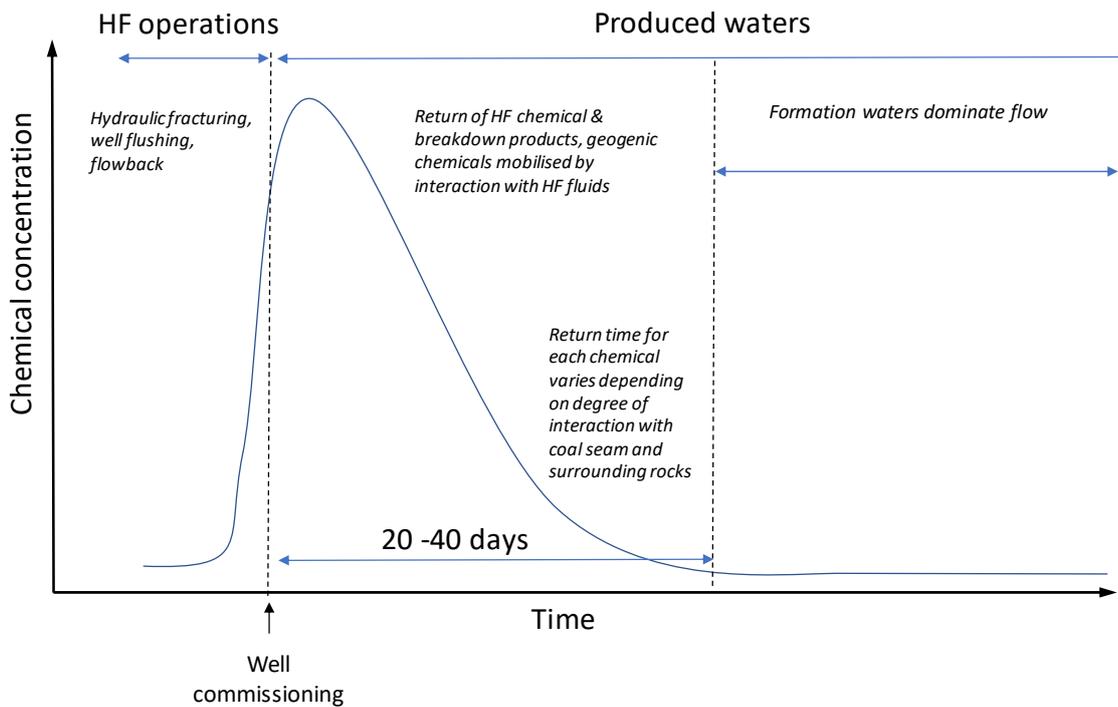
The chemical spill study (objective 4) was conducted as a parallel investigation (Kookana et al. 2020). This involved deliberately exposing soil samples from various locations in the Surat Basin to HF fluids and flowback waters and measurement of effects. Spills of HF fluids and produced water on soils are among the most polluting and plausible pathways of exposure to contaminants. Since the occurrence of spills is unpredictable, conducting a field-based soil contamination study is unlikely to yield meaningful information that can be extrapolated to other locations. Mimicking the exposure via spills of HF fluid and produced water in the laboratory (under controlled conditions) was therefore a more appropriate approach, as this would generate more broadly applicable information on the potential fate and effects of HF fluid chemicals in soils that could be used to inform future management of spills.

In this report, the concentrations of chemicals measured in CSG waters were compared against accepted environmental benchmarks. A large number of chemicals have been measured in this study and in order to gain some appreciation of the environmental relevance of the chemicals, measured concentrations were compared to accepted water and soil quality guidelines. These comparisons are not intended to make assessments of regulatory significance, but to use these benchmarks as tool to identify contaminants of potential concern. The main set of guidelines

used were the Australian and New Zealand default guidelines for freshwater quality (ANZG 2018) as these guidelines are toxicologically-derived and provide scientifically defensible thresholds against which contaminant concentrations may be assessed. Given that they are intended for the protection of freshwater aquatic organisms, they are far more stringent than guidelines set for irrigation or other purposes. This worst case assessment approach allows chemicals of potential concern to be identified and importantly allows chemicals to be screened out if their concentration levels fall below these stringent benchmark values. Other Australian and international guidelines were used where applicable. This included the ANZG guidelines for irrigation and livestock drinking (ANZG 2018) and for groundwater bore samples the Australian drinking water guidelines (ADWG 2011) were used. In order to place the levels of radioactivity measured into perspective, CSG waters data was also compared to international drinking water guidelines (USEPA MCL) which are the most stringent radiological guidelines available.

The findings of the study were as follows:

1. Water sampling was conducted at six wells in the Surat Basin during hydraulic fracturing operations and periodically for up to 6 months post HF. The suite of HF chemicals used at the wells sites was relatively simple and comprised 9 chemicals plus guar gum and gelatine. The chemicals were ethylene glycol, sodium tetraborate, boric acid, hydrochloric acid, triethanolamine, potassium chloride, CMIT & MIT (both biocides) and diammonium peroxydisulfate. Additives (proppant plus chemicals) comprised typically 9% of the total injected volume. The water composition of well flowback and produced waters was found to be dominated mainly by geogenic chemicals with HF fluid-derived chemicals (e.g. triethanolamine and MIT, a biocide) only being detected during the early stages of well operations.
2. Chemical concentrations in the flowback and produced waters were dynamic and changed with time. Peak concentrations of many chemicals were observed during well commissioning and the first few days of produced water flow which is the duration over which most of the waters injected during HF are returned to the surface. After this period, the concentrations of the chemicals declined over a period of 20 to 40 days with occasional spikes in concentrations. The relatively stable concentrations observed toward the end of the sampling program were assumed to represent formation water quality whereas the increased concentrations during flowback reflect the interaction of HF fluids with coal seam materials and subsequent release of geogenic contaminants. A conceptual model of chemical behaviour with time is presented in Figure ES1. With time, the concentrations of synthetic chemicals in HF fluids that are not present in nature should eventually drop to zero, whereas the concentration of geogenic chemicals and trace elements such as boron, will decline until they reach the concentration found in the formation waters from the area.



**Figure ES1 Conceptual model of chemical concentrations observed in CSG well waters**

3. Water quality data for the six wells was compared to Australian surface water quality guideline values (DGVs) in order to identify contaminants of potential concern. Based on their concentrations and their comparison with surface water quality guidelines, geogenic chemicals were the main potential contaminants identified. The chemicals measured at concentrations above Australian default guideline values (DGVs) for freshwaters were ammonia, boron and seven trace metals: chromium, copper, manganese, lead, nickel, silver and zinc. Many of the exceedances were marginal and were mainly confined to the early stages of well production, an exception being boron which was consistently present at concentrations above the Australian DGV of 0.37 mg/L. Any treatment processes applied to CSG well waters need to reduce the concentrations of these chemicals to below acceptable levels which are determined by the final use of the water. RO treatment was found to be effective in reducing the concentrations of the identified contaminants of concern to below the very stringent Australian guidelines for freshwaters.

4. The activities of seven radionuclides were measured in water and soil samples. All radionuclides were below the existing levels of regulatory concern that apply in Australia throughout the HF process and beyond. Radium-226 was the most abundant radionuclide in water. Aside from selected water samples taken during the first 20 days of well operation, Ra-226 activities were very low, and were even below the very stringent international guideline levels for drinking water.

5. Concentrations of dissolved organic carbon (DOC) reached concentrations in excess of 100 mg C/L during the early stages of well production. However, the organic compounds that were able to be specifically identified (e.g. hydrocarbons, HF fluid chemicals) typically only comprised a small fraction (<5%) of the total DOC and the remaining pool of carbon is currently uncharacterised. It is likely that the breakdown products of guar gum contribute to DOC concentrations during the early phases of well operation.

6. Sampling of nearby groundwater bores for an extensive range of potential contaminants did not indicate any impacts of CSG operations on water quality.
7. Water samples from a local creek adjacent to one of the study areas did not indicate signs of contamination relating to CSG activities. However, the creek's water quality showed evidence of impacts from hydrocarbon and trace metals contamination arising from non-CSG related sources (e.g. sewage treatment works discharges) upstream of the CSG operations.
8. Water sampling of a CSG water treatment facility indicated the treatment procedures for produced waters which incorporate reverse osmosis were effective in removing or lowering the concentrations CSG-related chemicals to below acceptable regulatory levels from the wastewater stream. This included all of the chemicals of potential concern identified in the CSG well waters. As expected, the highest concentration of chemicals were observed in samples of the concentrated brines (the waste product of the treatment process) which are stored in ponds on site.
9. Soil sampling from across drill leases and nearby background) sites did not reveal any contamination that could be associated with CSG activities during HF operations. This finding was expected as there were no spills of HF chemicals reported over the time of the study. Given that the probability of capturing a spill event in the field is low, a companion laboratory study was conducted where spills of HF fluid chemicals and produced waters were simulated in the laboratory and residues measured over time. Readers are referred to the final report by Kookana et al. (2020) for more information.

# 1 Introduction

Coal seam gas (CSG) production has grown exponentially in Australia over the last two decades and it is estimated there are now around 19,000 productive wells in operation with several thousand more planned (OGIA, 2016). CSG extraction in Australia involves drilling a network of wells across the designated gas field to depths that intersect the target coal seams. The evolved gas is piped to the surface and then via distribution network to a local processing facility and then piped to coast facilities for liquefaction and overseas distribution. In order to increase the yield of methane, some wells undergo a stimulation process known as hydraulic fracturing (HF). Estimates suggest that around 10- 40% of the wells in the Surat Basin will be hydraulically fractured during their 25 to 30 year lifetime (DES 2014).

Community concerns centre around the nature and toxicity of chemicals used in the HF operations; potential mobilization of chemicals from the coal seams and the potential for impacts on human health and the environment.

In addition, coal seams and surrounding rock formations are also known to contain a number of chemical constituents that have the potential to be mobilised during hydraulic fracturing activities (Ziemkiewicz and He 2015, Harrison et al. 2017). Mobilisation can occur because some HF chemicals have the potential to release naturally occurring chemicals from the coal seams and surrounding strata, through the effects of, for example, chelating agents, acids, surfactants, and solvents. The concentrations of the so-called geogenic chemicals mobilised from coal and surrounding strata also depends on groundwater composition and the nature of the geological strata undergoing gas extraction. Geogenic chemicals include trace elements (e.g. arsenic, manganese, barium, boron and zinc), radionuclides (e.g. isotopes of radium, thorium, and uranium) and organic chemicals such as hydrocarbons and phenols. Their release into flowback and produced waters raises concerns for their potential impacts on both natural groundwater and surface waters and soils.

Despite significant monitoring by industry and intense regulatory oversight of the industry at both State and Federal levels, there is still widespread public concern about the environmental impacts of HF, in particular the threats posed by the use of chemicals. Securing a social licence to operate for the unconventional gas industry has been hampered by the lack of independent scientific studies on the impacts of HF, leading to distrust by the general public.

In order to address the above concerns, CSIRO has undertaken this comprehensive investigation of the impacts of HF on air, soil and water quality at two locations in the Surat Basin, Qld. The study involved measuring the concentration of a comprehensive range of chemicals before, during and after HF in surface waters and groundwater bores in close proximity to the wells undergoing HF and examination of the flowback and produced waters generated by the HF and gas generation processes. To the best of our knowledge this is the most extensive study conducted in the world to date on CSG-related chemicals. A total of 113 water samples and 40 soil samples were collected with these samples undergoing 22 analytical procedures to determine the concentration of more than 150 potential contaminants including organics, inorganics and radionuclides. The study targeted six wells which were sampled periodically for up to 6 months from the time of HF, a local

creek and groundwater bores. Water samples from Origin Energy's Reedy Creek Water Treatment Facility were also taken in order to check the efficacy of reverse osmosis (RO) treatment in removing chemicals from combined wastewaters (including produced waters) generated by CSG operations in this region of the Surat Basin.

This report provides an overview of the water and soil study and provides detailed interpretation of the data. A number of associated reports which provide supporting information, are also available (Table 1). A complementary air quality investigation was conducted separately by CSIRO Oceans & Atmosphere and the outcomes of this study are detailed in a separate report (Dunne et al. 2019).

The objectives this study were to:

1. Assess the concentrations of HF chemicals and geogenic chemicals in flowback and produced waters resulting from CSG HF operations.
2. Quantify the impacts of HF operations on the concentrations of potential contaminants in nearby surface waters, groundwater and soils.
3. Assess chemical concentrations in the collected water and soil samples against relevant Australian water and soil quality guideline values.
4. Conduct a laboratory assessment of various spill scenarios involving spillage of HF fluid and produced waters onto various soils types representative of the Surat Basin.

The chemical spill study (objective 4) was conducted as a parallel investigation (Kookana et al. 2020). This involved deliberately exposing soil samples from various locations in the Surat Basin to HF fluids and flowback waters and measurement of effects. Spills of HF fluids and produced water on soils are among the most polluting and plausible pathways of exposure to contaminants. Since the occurrence of spills is unpredictable, conducting a field-based soil contamination study is unlikely to yield meaningful information that can be extrapolated to other locations. Mimicking the exposure via spills of HF fluid and produced water in the laboratory (under controlled conditions) was therefore a more appropriate approach, as this would generate more broadly applicable information on the potential fate and effects of HF fluid chemicals in soils that could be used to inform future management of spills.

The following topics were out of scope of the project:

**Long-term impacts of hydraulic stimulation:** Given the short timeframe of this study (maximum 6 months post stimulation monitoring), the long-term impacts of hydraulic stimulation (if any) on water quality was not covered.

**Efficacy of the treatment of flowback water and well flushing waters:** These water types were collected and transported offsite to a licenced waste treatment facility for treatment.

**Impacts of drilling and well construction:** This was not possible as the wells at the proposed study sites were drilled in 2015 and 2016.

**Impacts of HF on deep groundwater:** There were no means of accessing deep groundwater samples from the study sites.

**Groundwater contamination with methane:** This topic is the subject of other investigations conducted by GISERA.

**Ecological risk assessment:** The study was not designed to provide an ecotoxicological assessment of chemicals or to deliver a formal risk assessment.

**Impacts of HF on human health:** The study was not designed to determine the impacts of HF on human health.

**National or regional assessment of HF impacts:** This study assessed the impact of HF on water and soil quality at two locations in the Surat Basin. It was not intended to be a national or regional assessment. However, with proper contextualisation and consideration of differences between locations and differences in industry practices, the outcomes of the study may provide insights into likely impacts at other locations.

**Table 1 Supporting reports associated with this study**

<b>Report title</b>	<b>Topic</b>	<b>Citation</b>
Combabula site familiarisation visit	Site visit report	Apte, S.C. and Williams M. (2017a)
Potential impacts of hydraulic fracturing on air, soil and water quality in the vicinity of coal seam gas well sites in the Surat Basin, Queensland: water and soil monitoring plan	Details of the sampling plan	Apte, S.C., Kookana, R.S. and Williams, M. (2017b).
Water and soil quality field sampling report	Detailed description of the sampling campaign including sampling procedures and sample processing methodologies	Apte, S.C., Craig, A., King, J.J., Angel, B.M., Williams, M. and Kookana, R.S. (2018a)
Water and soil sample analysis: data report	Analytical data reports for analyses conducted on water and soil samples including replicates and quality control information. All data is also available for in spreadsheet format for download	Apte, S.C., Williams, M., King, J.J., Angel, B.M., Kookana, R.S. and Craig, A., (2018b).
Pre-hydraulic fracturing water and soil quality data summary	Review of Origin Energy's baseline water quality data for the two study sites	Apte, S.C., Craig, A., King, J.J., Angel, B.M., Williams, M. and Kookana, R.S. (2018c)
Measurements of air quality at a hydraulic fracturing site in the Surat Basin, Queensland	Companion report on air quality	Dunne et al. 2019

## 2 Background to hydraulic fracturing

Hydraulic fracturing is a well stimulation process that is used to increase the flow of gas from a well. It involves the high pressure injection of a large volume of fluids into a well in order to fracture targeted coal seams so that fracture pathways open for gas and fluids to flow into the well. The fractures created are kept open by fine solids (proppants), usually sand, which are added to the injected fluids. A photograph illustrating the typical field set up for HF of a CSG well is provided in Figure 1.

In order to facilitate the HF process, holes are produced in the well casing at exact depths in the well that target specific coal seams. These holes are typically created using perforating guns that consist of a string of shaped explosive charges that, when set off, shoot an explosively generated jet that penetrates the steel casing and surrounding cement jacket to a distance of typically 20 to 40 cm into the coal seam (Jeffrey 2012).

Hydraulic fracturing is then performed by isolating the perforated section, typically by installing a plug inside the casing that presses against the casing to hold itself in place. Pumping fluid down the well then pressurises the perforated section. The fluid pressure is increased until the *in situ* stress and strength of the rock are exceeded, resulting in formation of a fracture. This fracture is extended by continuing to pump the fracturing fluid into the well. The size and extent of the fracture network are dependent on a number of parameters including the properties of the coal seam. HF treatments typically create fractures extending horizontally to between 100 and 300 m in coal seams (Jeffrey 2012).

Both the volume of HF fluid injected and the pressures applied during HF are dependent on the characteristics of the site and the well stimulation design. HF can involve the injection of several hundred thousand to over a million litres of fluids per well (CSIRO 2015). Injection pressures depend on the depth of the interval being fractured and typically range from 10 MPa to 40 MPa with an average pressure of around 25 MPa (Jeffrey 2012).

In the case of CSG extraction, the injected fluids are predominantly water and proppant (typically 97–98 % of the total volume) with a small amount of chemical additives used to optimise the HF fluid performance and enhance well production. Groundwater accessed from local bores or surface water are the usual sources of water used for HF.

The composition of HF fluid is variable and formulations are regularly re-optimised to suit the characteristics of the wells undergoing HF. The typical components of HF fluid commonly used in the CGS operations are summarised in Table 2. In order to maintain the proppant in suspension, HF fluids usually take the form of a viscous gel. Commonly, guar gum is used to form linear gels. If required, more viscous, crosslinked gels are formed by addition of formulations containing reagents such as borate salts, ethylene glycol, and potassium hydroxide. Elimination of microbial activity in the wells is essential in order to prevent corrosion of the downhole pipe, formation of hydrogen sulphide gas and general clogging of the hydraulic fracture network. This is achieved through the addition of biocides such as 2-methyl-1,2-thiazol-3(2H)-one (MIT) plus 5-chloro-2-methyl-1,2-thiazol-3(2H)-one (CMIT) to the HF fluid. Additional reagents are added for pH control (e.g. hydrochloric acid), clay management (e.g. potassium chloride) and corrosion inhibition (e.g. gelatines) to prevent corrosion of well casings and equipment. Once the proppant

has been satisfactorily inserted into the fractures, gel breakers such as ammonium peroxydisulfate or nitroethanol are added to reduce fluid viscosity and maximise recovery of HF fluids during flowback.

Following the completion of the HF stage, the coal seam is depressurised and the fluids are allowed to flow from the well to the surface. Initially, flowback fluid will contain a mixture of HF fluid, proppant and groundwater from the coal seam. At the surface, flowback waters are initially stored on site either in storage tanks, in on-site ponds and subsequently transferred by tanker to a water treatment facility.

Well completion is the next step which is conducted separately by another rig. This involves flushing the well to remove any excess HF fluid gel and debris and installing the production tubing, water pump and drive rods. The final stage is well head installation and connection of the well to the gas and produced water gathering equipment including a water pump drive head.

Both the well flushings and flowback waters are collected in holding tanks and subsequently transported offsite for treatment at a licenced water treatment facility. During the production phase, produced waters are separated from gas at the wellhead and removed by a pipeline gathering network to a water treatment facility.



**Figure 1 Hydraulic fracturing of a well in the Surat Basin**

Table 2 Typical components of HF fluid and their role (adapted from NICNAS 2017)

Type / Purpose	Example Chemicals	Comments
Gelling agents (GA)	Guar gum; hydroxy-propyl guar,	Thickens the fluid
GA crosslinkers	Borate salts, monoethanolamine,	Maintains fluid viscosity
GA breakers	Sodium / ammonium persulfate	When added, turns the gel into solution
Friction reducers	Polyacrylamide, solvents,	Minimises friction
Biocides	Glutaraldehyde, sodium hypochlorite	Eliminates bacteria
pH adjusting agents	Sodium / potassium carbonate, HCl,	Keeps other components effective
Iron control	Citric acid	Prevents metal oxide precipitation
Acids	Acetic acid, hydrochloric acid	Dissolves minerals
Surfactants	Isopropanol, terpenoids, sweet orange oil	Increases fluid viscosity
Corrosion inhibitor	N-N,dimethyl formamide, gelatine	Prevents pipe corrosion
Scale inhibitors	Ethylene glycol	Prevents scale deposits
Proppant	Quartz sand, silica	Keeps fractures open

### 3 Background to the study sites

The study was conducted in the Surat Basin, Queensland, Australia at the established gas fields of Condabri and Combabula. The Surat Basin (Figure 2) is an area of intensive CSG extraction in Australia (OGIA 2016, Mallants et al. 2018).

During the planning phase of the study, two sites operated by Origin Energy in the Surat Basin at Condabri and Combabula were selected for investigation (Apte et al. 2017a). A peer-reviewed sampling and monitoring plan was subsequently developed (Apte et al. 2017b) and the field sampling program executed from July 2017 to April 2018 (Apte et al. 2018a). The main characteristics of two study sites are described below.

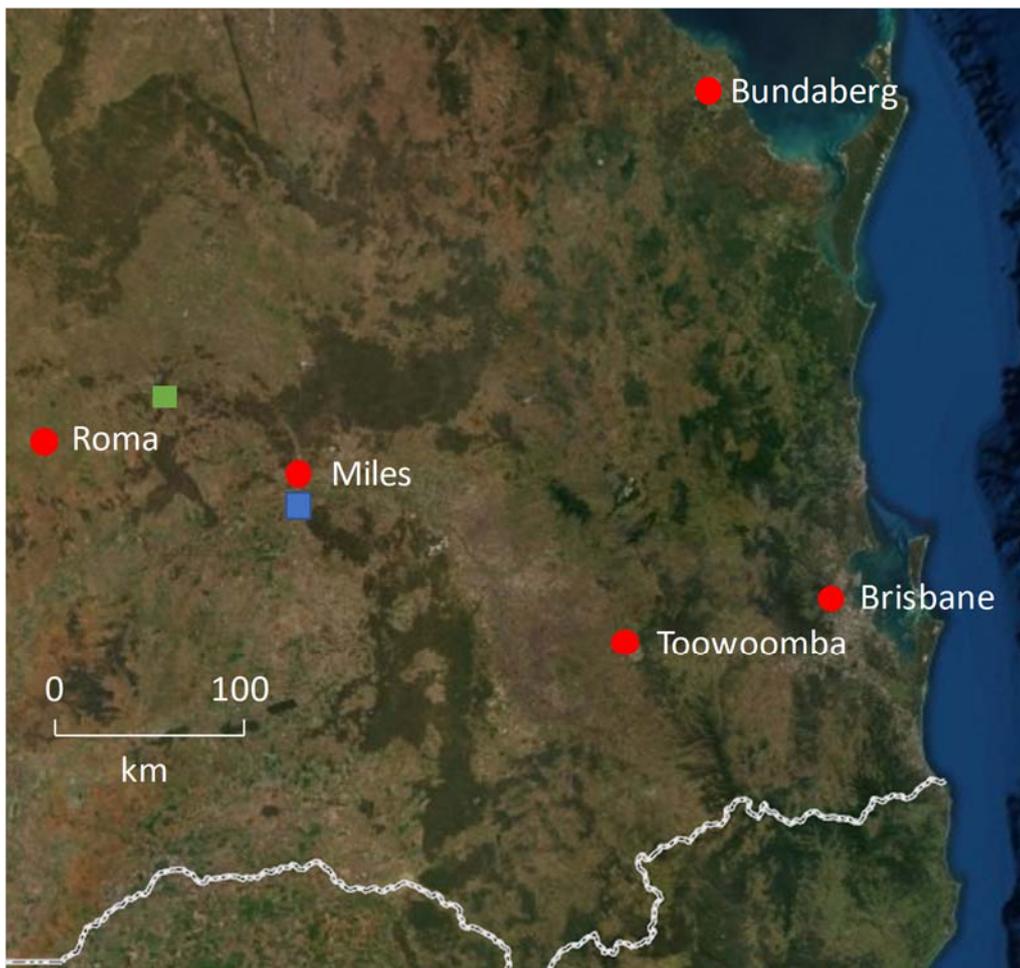


Figure 2 Map of the region showing the approximate locations of the Condabri (blue) and Combabula (green) study sites

#### Condabri

The study site (26°45'21" S, 150°10'49" E) was a farmland property of approximately 1030 ha area located between the towns of Miles and Condamine. The property is predominantly a flat, semi-arid open grassland with stands of native tree vegetation (Figure 3). Dogwood Creek, an ephemeral surface waterway borders the western boundary of the property and the Leichhardt

Highway borders the eastern boundary. The area to the west of Dogwood Creek is dominated by farmland with 5 CSG wells within a 5 km distance west of the Creek.

A site familiarisation visit was undertaken by CSIRO staff on 12 April 2017 in order to inspect the study area and organise field work logistics. The property contained 19 CSG wells, grid spaced at approximately 600 – 700 m intervals. Rig release dates indicate that the wells were drilled and constructed between August and September 2015, with an additional well constructed in August 2016 (Source: Queensland Globe). Well depths range from 740 to 860 m and target the Walloon coal measures. Twelve of the wells underwent some form of well bore stimulation in June and July 2017 after which they were brought on-line and connected to the gas and water pipeline network. The wells in this area are serviced by a network of pipelines and vents, which connect to the Condabri Central Gas Processing Facility which is approximately 5 km to the south of the study site.

The predominant soil types are typical of the Surat Basin (Table 3). The majority of these soils have formed from quaternary alluvium containing sand, silt mud and gravel (Chinchilla 1:250,000 geology sheet SG56-9). In total, six main soil types were noted to be present at the Condabri site. These included Dermosol, Sodosol, Hydrosol, Kandosol, Rudosol and Vertosol (Figure 4).

The locations of the six wells selected for sampling at Condabri are shown in Figure 3. Further details on sampling site selection at this site and the sampling program in general may be found in the report by Apte et al. (2017b).

**Table 3 Soil types at the well pad sampling sites**

<b>Well</b>	<b>Soil Type</b>
CNN204	Dermosol
CNN207	Vertosol
CNN209	Dermosol
CNN210	Rudosol
CNN218	Rudosol
CON382	Rudosol



**Figure 3** Map showing the location of the Condabri field site. The red dots are the CSG wells sampled for both waters and soils. The green dots denote the sites where only soils were sampled

### **Combabula**

The site (26°16'46" S, 149°33'22" E) is a farmland property located approximately 100 km northwest of Miles. Similar to the Condabri site, the property is a semi-arid open grassland with stands of native tree vegetation (Figure 5). An ephemeral creek runs through the property, however, as noted during the site inspection visit (Apte et al. 2017c), there were no conspicuous surface water features.

The property has over 30 drilled wells, grid spaced at approximately 600 – 700 m intervals. Twenty-three of the wells underwent some form of well bore stimulation between August and October 2017 after which they were brought on-line and connected to the gas and water pipeline network. The wells in this area are serviced by a network of pipelines and vents, which connect to the nearby Reedy Creek central Gas Processing Facility. The locations of the three wells selected

for sampling are shown in Figure 5. Further details on sampling site selection at this site and the sampling program in general may be found in the reports by Apte et al. (2017a and 2017b).

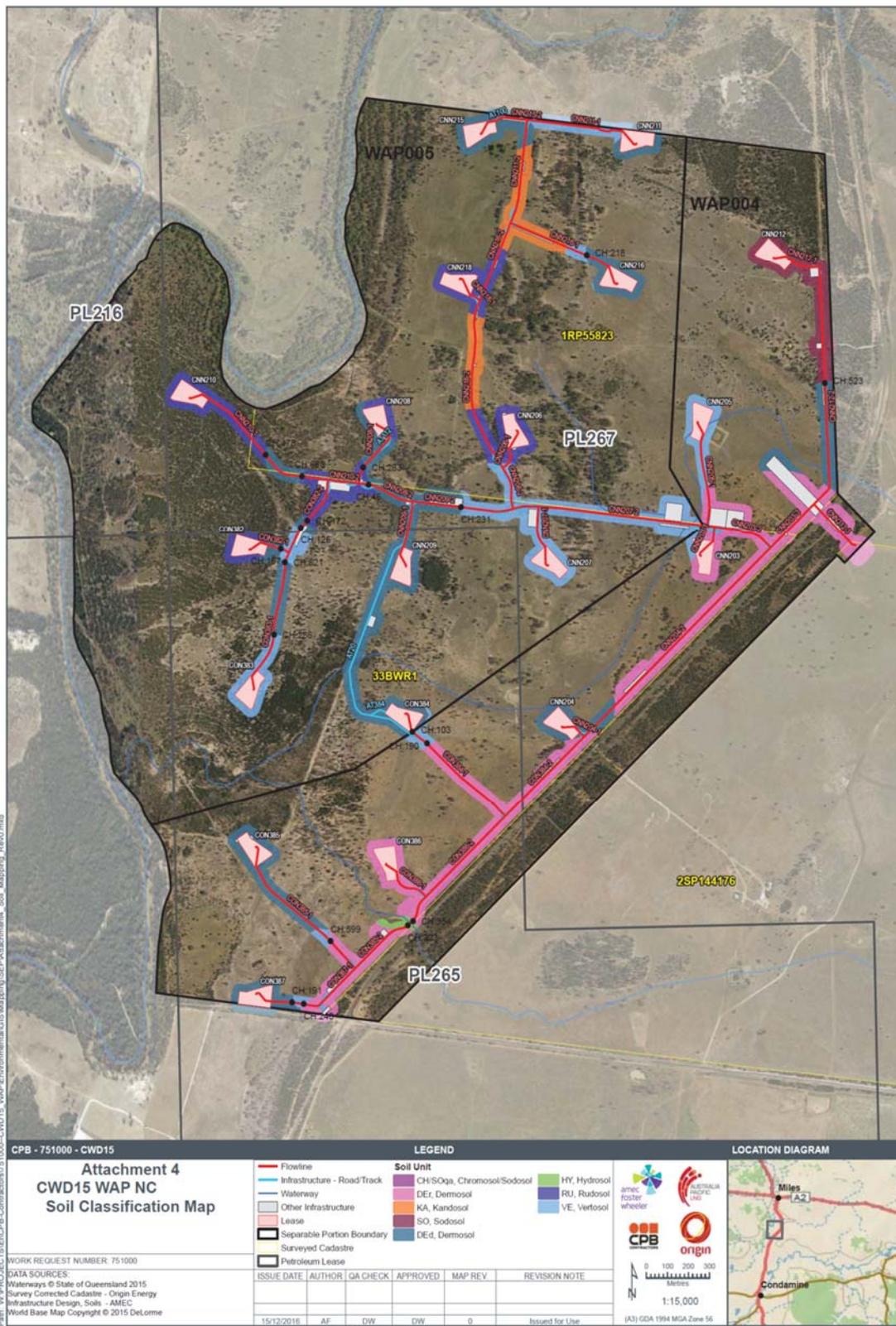
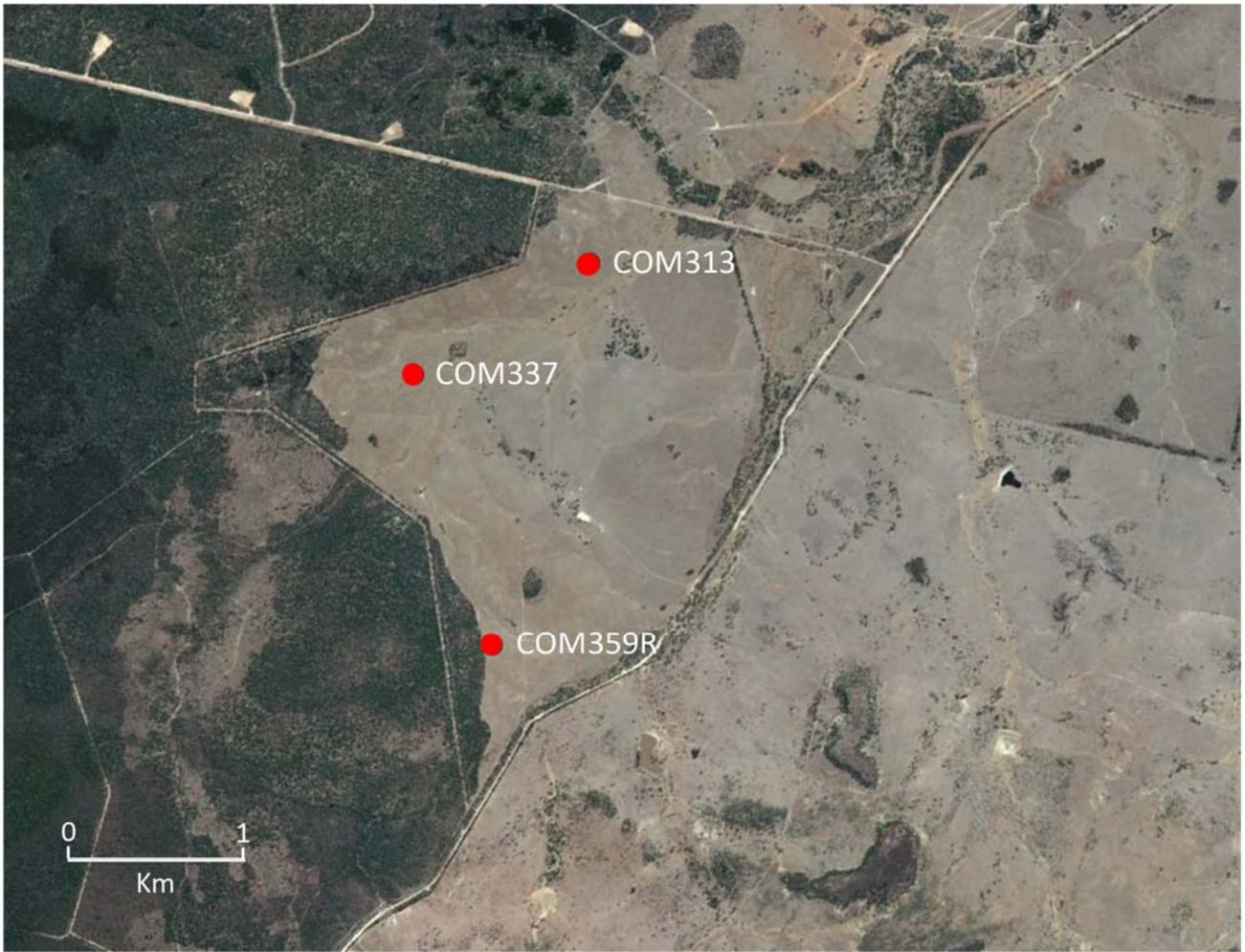


Figure 4 Soil classification map of the Condabri study area



**Figure 5 Map showing the location of the Combabula site CSG wells that were sampled**

## 4 Methods

Full details of the field sampling program and sampling procedures employed in the study can be found in the report by Apte et al. (2018a). Only a brief overview will be given here.

Field activities at the two study sites (Condabri and Combabula), including sample collection, were conducted in the second half of 2017 and early 2018. All water and soil samples were collected using internationally accepted sampling and sample processing protocols.

A summary of the water and soil samples collected is presented in Table 4. The sample log detailing all water and soil samples collected is provided in the report by Apte et al. (2018a).

Sample processing (i.e. sample preservation, filtration and extraction of trace organic compounds) was conducted at on-site laboratories at the Condabri Operations Centre and Reedy Creek Operations Centre prior to shipping samples to CSIRO or NMI. Full details of these procedures may be found in Apte et al. (2018a).

### 4.1 Sample collection

#### 4.1.1 Hydraulic fracturing fluid

Samples of HF fluid used at the five of the six wells monitored during this study were provided by the on-site HF teams (Table 4). Note that the fluid formulation can be changed as the HF operations progress. The phases of the HF operation are termed zones and there were typically 8 to 10 zones per HF operation. Samples of fluid from each HF zone were provided. The samples were refrigerated and then transferred to the CSIRO laboratory in Adelaide for subsequent analysis. Semi-quantitative analysis was performed to confirm the composition of the fluids as compared to the data provided by the HF operators.

#### 4.1.2 Flowback and produced waters

Six wells were monitored during the course of the study over a period of six months commencing at the start of HF operations. These comprised three wells at the Condabri site: CNN218, CON382, CNN204 and three at the Combabula site: COM313, COM337 and COM359R. Owing to safety considerations, water samples from each well were collected by the Origin Pilots team with sample bottles and detailed sampling instructions supplied by CSIRO. A typical drill lease/well pad from which samples were taken is shown in Figure 6.

Following HF, a separate rig was deployed (well completions rig) to flush the well. The well was then either connected directly to the distribution system or in the case of CNN218, flowed back into a holding pond for a period of time prior to connection. Well flushing samples (samples collected on behalf of CSIRO by the well completions rig team) were obtained from all wells apart from CNN218 where flowback samples were taken by CSIRO staff.

The sampling design employed involved initial intensive (daily) sampling immediately after the well had been hydraulically fractured, then weekly sampling for the first month, followed by monthly sampling for the following six months. This design was adopted following a review of

published work that shows that the most rapid changes in water quality are likely occur during and soon after HF operations and well completion.



**Figure 6 A well pad under construction at Combabula**

### **4.1.3 Water-treatment facility (WTF) waters**

The Reedy Creek Water Treatment Facility (WTF) receives produced waters from approximately 600 CSG wells across the Combabula and Reedy Creek gas fields. As noted earlier, flowback waters and well flushings are treated separately at an off-site licenced water treatment facility. The WTF utilises initial screening and filtration, chloramination disinfection, membrane filtration and RO to treat produced and associated waters, prior to re-injection into groundwater aquifers (APLNG 2010a; APLNG 2018). The treated CSG water is also utilised onsite at major infrastructure locations such as site camps, gas production facilities and administration facilities (APLNG 2014). Prior to re-injection the treated waters are conditioned to adjust dissolved oxygen levels to those found in groundwater from the region. The brine reject from the RO plant is transferred to evaporation ponds (APLNG 2010b). The Reedy Creek WTF has the capacity to treat up to 40 ML of CSG-associated water per day.

Samples of raw water, post-treatment water and reject brines were collected by CSIRO staff from the Reedy Creek WTF on three occasions over the study period (Table 4). Photographs of the sampling locations within the treatment plant are shown in Figure 7 and Figure 8. It should be noted that the WTF receives and treats water from a network of CSG wells situated across the

Reedy Creek and Combabula gas fields. The samples therefore provided an integrated view of water quality across the gas fields.



**Figure 7 WTF plant input and output water sampling locations**



**Figure 8 WTF reject brine sampling location**

#### **4.1.4 Surface water samples**

The most significant surface water feature within the Condabri study area is Dogwood Creek, which borders the western side of the study area (Figure 9). Upstream of the study site, Dogwood Creek flows through the township of Miles and receives inputs from the town's sewage treatment works. In order to take into account the possibility of contaminants originating from the Miles area which are not associated with HF operations, Dogwood Creek water samples were collected at sites upstream and downstream (Figure 10) of the study area on the same day within one hour of each other. This paired sampling approach minimised the influence of any variations in upstream sample water quality and flow regime. The upstream water sample was taken from a jetty at Gil Weir campground (26°42'30.31"S, 150°10'44.26"E). The downstream site was located on Origin Energy property close to Miles Airport (26°47'57.15"S, 150° 8'41.51"E). There were five sampling events: three during HF operations, one shortly after the cessation of HF and one several months after operations had ceased (Table 4).

The original intent was to sample surface water dams at Condabri and Combabula, however, this plan was abandoned owing to the lack of suitable sampling sites. The absence of surface water at Combabula was noted in the site familiarisation visit report (Apte et al. 2017c).



**Figure 9 Dogwood Creek upstream (top photo) and downstream (bottom photo) sampling locations**



Figure 10. Map showing the locations of the Dogwood Creek sampling sites

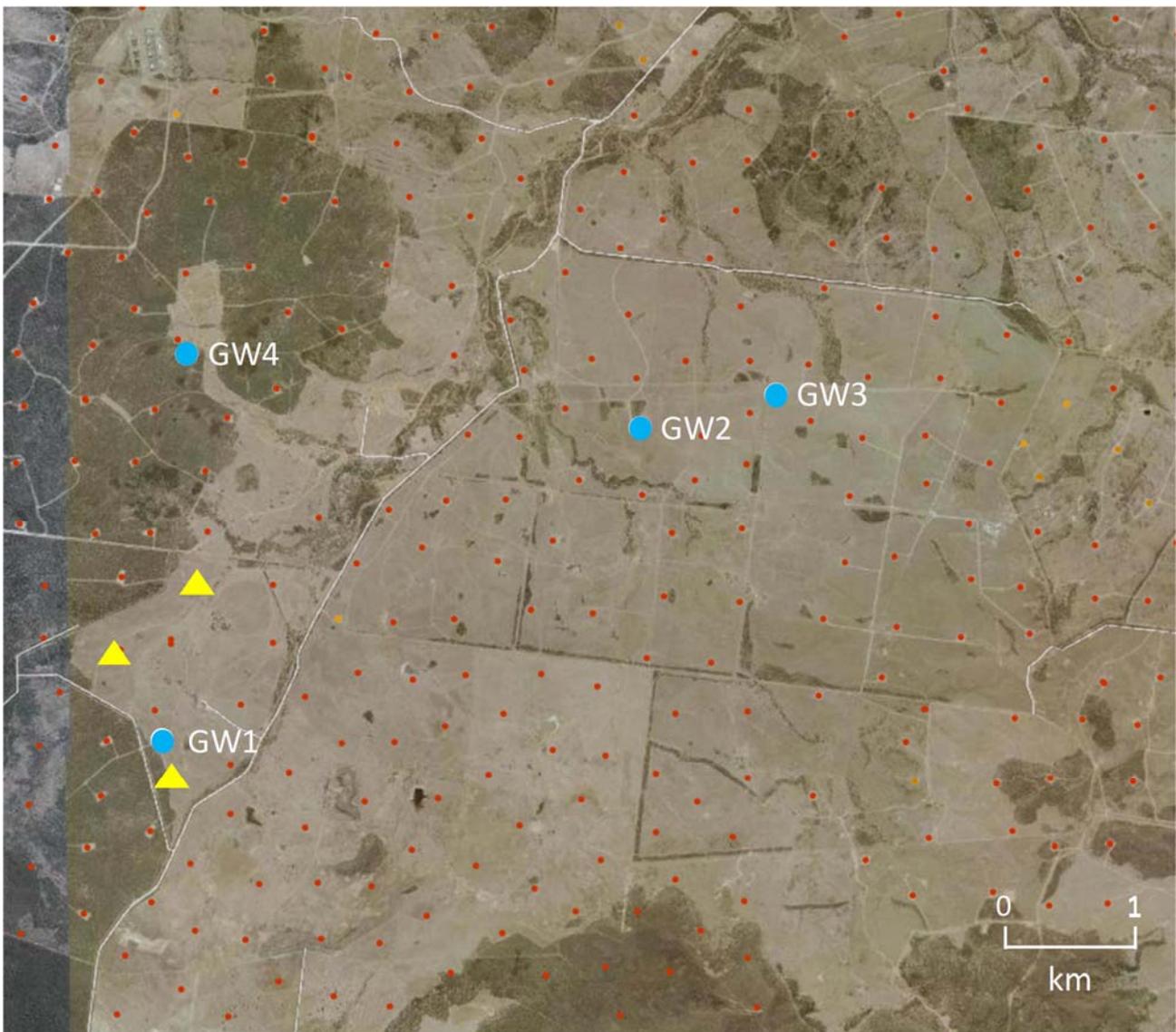
#### 4.1.5 Groundwater bore samples

Registered water bores, for use as potable water sources, watering livestock and irrigation, are found across the Surat Basin.

Three registered bores at the Combabula study site were sampled on four occasions (Table 4). The location of the bores is shown in Figure 11. The first two sampling events were during HF operations and the last two after operations had ceased. Towards the end of the groundwater bore sampling program, bore GW3 became inaccessible due to pump failure. Consequently, in the last groundwater sampling campaign (February 2018), a nearby bore, Pine Dam Bore (GW4) was sampled as an alternative.

The depths of the groundwater bores ranged from 70 m to 194 m. This compares to depths of between 443 m and 850 m for the coal seams targeted by the CSG wells that were monitored at the Combabula site. The groundwater bores are relatively shallow and do not intersect any of the coal seams which are found at much deeper depths. Instantaneous contamination of the groundwater boreholes during HF is highly unlikely during HF given the time required for chemicals to pass through rocks and travel upwards to the shallow bores.

Pre-HF baseline data for these bores were also provided by Origin Energy (Apte et al. 2018c). Sampling was conducted by CSIRO staff with assistance from Origin Energy staff. Sampling of the western supply bore (GW1), is shown in Figure 12.



**Figure 11** Map showing the location of groundwater bores at Combabula that were sampled. The red dots indicate the location of all CSG wells in the area and the yellow triangles the CSG wells that were sampled during the study



**Figure 12 Sampling from the western supply bore (GW1) at the Combabula study site**

#### **4.1.6 Soil sampling at Condabri**

A common practice in the industry when preparing a well pad is to scrape the surface soils (generally to a depth of 20-30 cm) and store them for later rehabilitation of the well pad. Therefore, the subsoil on the well pad has a greater exposure to any spills during HF operations.

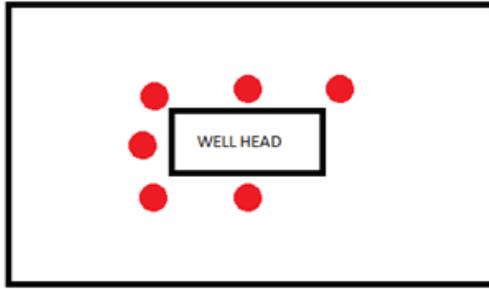
Based on the rehabilitation plans for the study sites by Origin Energy (e.g. not using drilling mud for rehabilitation), it was considered more appropriate to collect soil samples once all HF-related and well commissioning operations on the well-lease area had been completed. Soil samples were therefore collected once the site was fully rehabilitated and was ready to be handed back to the owner. Cores were taken in order to assess the quality of sub-surface soils that may have been exposed to contaminants during HF operations.

Six wells CON382, CNN204, CNN207, CNN209, CNN210 and CNN218 were selected for soil sampling. Samples were collected by CSIRO team members with the assistance of Origin Energy staff who provided hydraulic coring equipment for collection of soil cores. A hand auger was used to collect additional samples near CNN210. The soil types found at each site are shown in Table 3.

Soil cores were collected at five to six points around the well lease area within the drill lease excluding areas containing gas and/or water pipelines and also from a nearby reference site which was deemed to be undisturbed by the HF and associated operations. The sampling approach is illustrated in Figure 13. The cores collected from each site were sectioned into depths of 0-20, 20-40 and 40-60 cm and the layers from each of the replicates cores combined and mixed to obtain one sample per depth. Due to extensive clearing of trees at CON382 reference site, the site was considered as highly disturbed and hence no background samples were taken for this site.

A total of 36 composite soil samples were generated. The samples were shipped to the CSIRO laboratory in Adelaide for analyses. Soil samples from each well were archived at -18°C for potential further analysis (if required).

Well pad Site



Undisturbed Site; away from well pad and activities



Figure 13 Example of soil sample collection locations within well pad site (red dots) and undisturbed site (green dots) with same soil type

**Table 4 Summary of the water and soil sampling program**

<b>Sample type</b>	<b>Samples to be collected</b>	<b>Proposed number of samples</b>	<b>Actual no. samples taken</b>	<b>Notes</b>
<b>Dogwood Creek</b>	Surface water	16	10	Samples collected upstream and downstream of the Condabri study area. Five sampling events: 3 during and 2 after HF operations
<b>Farm dams</b>	Surface water	12	0	Samples not taken owing to lack of suitable sampling sites
<b>Water bores</b>	Groundwater	12	12	Three registered bores at the Combabula study site sampled on four occasions. The first two sampling events were during HF operations and the last two after operations had ceased.
<b>Hydraulic fracturing</b>	HF fluid samples	6	46	Frac zone samples from 5 wells (typically between 8 and 10 zones) were obtained
<b>Stimulation, flow back and production phases</b>	Flushing, produced & flowback waters	68	76	Six wells were monitored over a period of up to six months commencing at the start of HF operations. Three wells at the Condabri site: CNN218, CON382, CNN204 and three at the Combabula site: COM313, COM337, COM359R. Well flushing, flowback and produced waters sampled
<b>Wastewater treatment facility</b>	Incoming water	3	4	Samples taken at the Reedy Creek WTF on 3 occasions over a four month period
<b>Post-treatment</b>	RO-treated water	3	3	Samples taken at the Reedy Creek WTF on 3 occasions over a four month period
<b>Membrane rejects</b>	Brine	3	3	Samples taken at the Reedy Creek WTF on 3 occasions over a four month period
<b>TOTAL</b>		<b>123</b>	<b>154</b>	
<b>Soils</b>	Soil samples from the well pad and adjacent areas	40	36	Soil cores (0-20, 20-40 and 40-60 cm depth) at Condabri site were collected at 6 points on six drill leases after HF activities had ceased. Adjacent to each drill lease, paired reference samples were collected. Additional soil samples were collected from each drill lease and reference site and archived for potential later analysis (if required).

## 4.2 Sample analysis

Summary details of the chemical analyses performed on the water samples collected are given in Table 5 and for soil samples in Table 6. Full details of the analytical procedures employed in the study are the subject of a separate report (Apte et al. 2018b).

This list of chemicals to be analysed was developed following a review of relevant published literature on CSG operations. The list covers both inorganic and organic chemicals and radionuclides that may be potential contaminants of soil and waters. A list of specific organic compounds analysed is provided in Table 7. These organic compounds are referred to as 'target compounds' as they have been 'targeted' for analysis and are the subject of specific analytical methods developed for their detection. However, complex environmental samples will also contain a wide range of other unknown organic compounds of varying composition. The identification of some, or all of these compounds is referred to as 'non-target' analysis and involves chromatographic separation and mass spectrometric detection of individual compounds. The identities of the compounds are obtained through the interpretation of their mass spectra. Non-target analysis is a specialist, non-routine activity and can be very time consuming and was beyond the scope of this study.

The list of organic compounds included isomers/derivatives of fluorobenzoic acid which are added to the HF fluids by the operators to provide a means of tracing the progress of the injected fluids in the well for post-HF analysis of the HF operation.

Wherever possible, sample analyses were conducted in NATA (National Association of Testing Authorities, Australia) accredited laboratories. The quality control (QA/QC) program adopted in the study included field duplicates, laboratory replicates, blanks, spike recovery tests and where available analysis of certified reference materials (Apte et al 2018b).

Analysis for organic target compounds was conducted by the National Measurement Institute, Sydney (NMI). All radiochemical analyses were conducted by the Australian Nuclear Science and Technology Organisation (ANSTO) who are the lead agency in Australia for environmental radioactivity measurement. Analysis of non-target organics was conducted at the CSIRO Land and Water laboratory in Adelaide.

Soil samples were analysed by NATA-accredited laboratories (namely NMI for organic chemicals and by CSIRO for inorganic chemicals).

**Table 5 Water quality parameters analysed**

Parameter	Description	Typical Limit of Detection (3σ)
<b>Dissolved:</b> Al, Ag, As, Ba, Be, Bi, Cd, Ca, Ce, Co, Cr, Cu, Cs, Dy, Er, Eu, Fe, Ga, Gd, Hf, Ho, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Os, Pd, Pt, Pr, Rb, Re, Rh, Ru, S, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, W, Y, Yb, V, Zn & Zr	Sample filtered through a 0.45 µm membrane filter. Analysis by both inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectrometry (ICP-AES)	0.01-1 µg/L
<b>Total:</b> Al, Ag, As, Ba, Be, Bi, Cd, Ca, Ce, Co, Cr, Cu, Cs, Dy, Er, Eu, Fe, Ga, Gd, Hf, Ho, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Os, Pd, Pt, Pr, Rb, Re, Rh, Ru, S, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, W, Y, Yb, V, Zn & Zr	Acid digestion and analysis by both ICP-MS and ICP-AES	0.01-1 µg/L
Total Hg	Cold vapour atomic fluorescence spectrometry (CV-AFS)	1 ng/L
Dissolved Organic Carbon (DOC)	Shimadzu Combustion Analyser	0.5 mg/L
Alkalinity as CaCO <sub>3</sub>	Titration	5 mg/L
Sulfate and chloride	Ion chromatography	1 mg/L
Phosphate, nitrate, nitrite, ammonia	Ion chromatography	1 mg/L
Electrical conductivity	Conductivity meter	
Ra-226, Ra-228	Alpha counting (ANSTO)	1 mBq/L
U-234, U-238, Th-230 and Th-232	Alpha counting (ANSTO)	1 mBq/L
Gross alpha and beta	Alpha and Beta counting (ANSTO)	50 mBq/L
Total suspended sediment (TSS) and pH	Gravimetry, ISE	1 mg/L
HF additives, e.g. fluorobenzoic acid tracers; butoxyethanol, biocides etc., depending on the HF fluid composition	Dissolved phase (filtration, solid phase extraction) liquid chromatography- quadrupole time of flight mass spectrometry (CSIRO Laboratory- LC-QTOF-MS)	low µg/L
Geogenic organic chemicals: Phenols (phenol, methylphenols, dimethylphenols)	CSIRO Laboratory (LC-QTOF-MS) and GC-MS at NMI (NATA-accredited laboratory)	low µg/L
PAHs (naphthalene and substituted naphthalenes, acenaphthene, anthracene, benzopyrenes, fluoranthene, fluorene, phenanthrene)		
VOCs- Volatile organic carbons (including BTEX compounds), TRHs- Total recoverable hydrocarbons, THMs -Trihalomethanes		

**Table 6 Soil quality parameters analysed**

Parameter	Description	Typical Limit of Detection (3σ)
<b>Total:</b> Al, Ag, As, Ba, Be, Bi, Cd, Ca, Ce, Co, Cr, Cu, Cs, Dy, Er, Eu, Fe, Ga, Gd, Hf, Hg, Ho, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Os, Pd, Pt, Pr, Rb, Re, Rh, Ru, S, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, W, Y, Yb, V, Zn & Zr	Acid digestion and analysis by both ICP-MS and ICP-AES	0.01-1 µg/g
Ra-226, Ra-228, U-234, U-238, Th-230 and Th-232	Alpha counting (ANSTO)	1 Bq/kg
Geogenic organic chemicals: Phenols (phenol, methylphenols, dimethylphenols) PAHs (naphthalene and substituted naphthalenes, acenaphthene, anthracene, benzopyrenes, fluoranthene, fluorene, phenanthrene)	Sample extraction by various methods. CSIRO Laboratory (LC-QTOF-MS) and GC-MS at NMI (NATA-accredited laboratory)	low µg/g

### 4.3 Benchmarking of data

In this report, the concentrations of chemicals measured in CSG waters are compared against accepted environmental benchmarks. A large number of chemicals have been measured in this study and in order to gain some appreciation of the environmental relevance of the chemicals, measured concentrations were compared to accepted water quality guidelines. These comparisons are not intended to make assessments of regulatory significance, but to identify contaminants of potential concern. The main set of guidelines used were the Australian and New Zealand default guidelines for freshwater quality (ANZG 2018) as these guidelines are toxicologically-derived and provide scientifically defensible thresholds against which contaminant concentrations may be assessed. Given that they are intended for the protection of freshwater aquatic organisms, they are far more stringent than guidelines set for irrigation or other purposes. This worst case assessment allows chemicals of potential concern to be identified and importantly allows chemicals to be screened out if their concentration levels fall below these stringent benchmark values.

Other Australian and international guidelines were used as applicable. This included the ANZG guidelines for irrigation and livestock drinking, and for groundwater bore samples the Australian drinking water guidelines (ADWG 2011) were used. In order to place the levels of radioactivity measured into perspective, there is comparison of CSG waters data to international drinking water guidelines which are the most stringent radiological guidelines available.

Table 7 Organic compounds analysed

Category/compound
<b>Phenols</b>
Phenol, 2-chlorophenol, 2-methylphenol, 3- & 4-methylphenols, 2,4-dimethylphenol, 2-nitrophenol, 4-nitrophenol, 2,4-dichlorophenol, 2,6-dichlorophenol, 4-chloro-3-methylphenol, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol, 2,3,4,6-tetrachlorophenol, pentachlorophenol
<b>Total recoverable hydrocarbons (TRHs)</b>
TRH C6-C9, TRH C10-C14, TRH C15-C28, TRH C29-C36
NEPM (TRHs): TRH C6-C10, TRH>C10-C16, TRH>C16-C34, TRH>C34-C40
<b>Monocyclic aromatic hydrocarbons</b>
Benzene, toluene, ethylbenzene, m&p-xylenes, o-xylene, styrene, waters only: isopropylbenzene, n-propylbenzene, 1,3,5-trimethylbenzene, tert-butylbenzene, 1,2,4-trimethylbenzene, sec-butylbenzene, 4-isopropyltoluene, n-butylbenzene
<b>Polycyclic aromatic hydrocarbons (PAHs)</b>
Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)&(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenz(ah)anthracene, benzo(ghi)perylene
<b>Halogenated aliphatic hydrocarbons (waters only)</b>
Chloromethane, vinyl chloride, bromomethane, chloroethane, trichlorofluoromethane, 1,1-dichloroethane, dichloromethane, trans-1,2-dichloroethene, 1,1-dichloroethene, 2,2-dichloropropane, cis-1,2-dichloroethene, bromochloromethane, 1,1,1-trichloroethane, carbon tetrachloride, 1,1-dichloropropene, 1,2-dichloroethane, trichloroethene, 1,2-dichloropropane, dibromomethane, cis-1,3-dichloropropene, trans-1,3-dichloropropene, 1,1,2-trichloroethane, tetrachloroethene, 1,3-dichloropropane, 1,2-dibromoethane, 1,1,1,2-tetrachloroethane, 1,1,2,2-tetrachloroethane, 1,2,3-trichloropropane, 1,2-dibromo-3-chloropropane, hexachlorobutadiene
<b>Halogenated aromatic hydrocarbons (waters only)</b>
Chlorobenzene, bromobenzene, 2-chlorotoluene, 4-chlorotoluene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, 1,2,3-trichlorobenzene, 1,2,3,4-tetrachlorobenzene
<b>Trihalomethanes (waters only)</b>
Chloroform, bromodichloromethane, dibromochloromethane, bromoform, dichlorobromomethane, tribromomethane, trichloromethane
<b>Others (waters only)</b>
Acetone, vinylacetate, 2-butanone (MEK), 4-methyl-2-pentanone (MIBK), 2-hexanone (MBK), Methyl tert-butyl ether (MTBE), Carbon disulfide

## 5 Results

### 5.1 Overview of field operations and chemical analysis

The water and soil sampling campaigns were carried out successfully over a period of 9 months (July 2017 to April 2018). Some minor modifications to the original sampling plan were necessary owing to delays caused by bad weather and operational issues (e.g. HF equipment breakdown). The planned finish date was late December 2017/early 2018, however, the sampling program actually finished in early April 2018.

A total of 154 water and HF fluid samples were collected compared to 123 planned (Table 4). Soil sampling sample numbers were close to the planned number (36 samples collected compared to 40 planned).

Detailed analytical data including replicates, field blanks and quality control data are available in a separate report (Apte et al. 2018b). Spreadsheet compilations of the analytical data generated including the quality control data are available for download from the project data repository. The key summary data are provided in this report along with interpretation.

### 5.2 Summary of the HF operations

HF operations are complex and require a number of pieces of equipment including above-ground water storage ponds, mixing units, high pressure pumps, cranes, chemical and proppant storage trailers, flowback tanks, control vans and a coiled tubing unit to convey HF fluids down the well (Figure 1). Hydraulic Fracturing took approximately 1 to 3 days per well. Well completion including flushing, installation of production equipment and connection to surface infrastructure (pumps, separators, and pipelines) took approximately 1 to 2 days per well.

A summary of the HF operations at the two study sites is provided in Table 8. The total volume of fluid injected per well varied from 358,000 to 840,000 litres (for reference an Olympic sized swimming pool contains 2,500,000 litres of water).

Information on the HF chemicals used at each well and volumes of water/chemicals is provided in Table 9. It is noteworthy that similar chemical formulations were used at each site. The suite of HF chemicals used at the wells sites was relatively simple and comprised 9 chemicals plus guar gum and gelatine. The chemicals were ethylene glycol, sodium tetraborate, boric acid, hydrochloric acid, triethanolamine, potassium chloride, CMIT & MIT (both biocides) and diammonium peroxydisulfate. Additives (proppant plus chemicals) comprised typically 9% of the total injected volume. Fluorobenzoic acid (FBA) tracers were added by the HF operations team to the HF fluid used at CON382 and CNN204. The FBA tracers are not a usual HF additive but are added in small quantities to selected wells to provide a diagnostic of HF performance.

Produced water samples were collected for the following durations: CNN218: 161 days, CON382: 73 days, CNN204: 148 days, COM313: 166 days and COM359R: 161 days. CON382 was taken offline after 10 weeks as the well started to produce crude oil. COM337 was suspended (pending maintenance) after 3 days of operation because of down-bore pump failure. The volumes of produced waters produced by the wells over the sampling period are shown in Figure 14. The

Combabula wells generally produced more water than the wells at Condabri. The flow versus time plots varied markedly between wells. CNN204 and CNN218 flows increased with time to a plateau. CON382 and COM359R were fairly consistent across the sampling period. COM313 exhibited a maximum and then a steady decline.

Comparison of the well HFF injection volumes in Table 8 with the cumulative produced water data plots in Figure 14 indicated that the approximate durations taken for HFF fluid to be returned to the surface varied from 22 to 48 days (CNN204: 48 days, CON382: 41 days, COM359R: 22 days, COM313 29 days). Note these values are upper estimates as the waters returned during well flushing are not included (data not available at the time of writing). Owing to gaps in the produced water and flowback water data, CNN218 was not included in this comparison.

Table 8 Drilling and HF data for the wells

Well	Latitude	Longitude	Well depth (m)	Drilling completion date	HF dates	Well completion dates
<b>Condabri</b>						
CNN218 <sup>1</sup>	-26.738331	150.181954	763.20	15 August 2015	8-18 July 2017	29-30 July 2017
CNN204	-26.756619	150.186385	781.20	1 September 2015	25 July – 10 August 2017	10-12 August 2017
CON382	-26.749025	150.171566	821.20	29 September 2015	21-23 July 2017	25-26 July 2017
<b>Combabula</b>						
COM 313	-26.294406	149.515117	826.2	14 August 2017	6-7 October 2017	9-11 October 2017
COM 337	-26.301183	149.505875	833.2	18 August 2017	9-10 October 2017	11-13 October 2017
COM 359R	-26.314511	149.512078	876.2	21 March 2016	14 October 2017	16-20 October 2017

<sup>1</sup>Well was flowed back from 19 to 24 July

Table 9 Summary of hydraulic fracturing chemicals information

Location Well	Condabri			Combabula		
	CNN218	CON 382	CNN 204	COM313	COM337	COM359R
Number of frac zones	8	10	10	10	8	7
Total injected fluid (L)	747734	358421	343999	765781	839279	552253
Fresh water (L)	674286	331150	311811	695826	761018	495580
Wet chemical constituents (L)	7301	5950	5377	1727	2801	8208
Dry chemical constituents (L)	8181	4371	4428	10528	10997	7345
Proppant 20/40 (L)	52943	14156	18993	56631	62845	40392
Proppant 40/70 (L)	5023	2794	3390	1069	1618	728
Additives by volume (%)	9.82	7.6	9.4	9.1	9.3	10.3
Chemicals by volume (%)	2.07	2.88	2.85	1.60	1.64	2.82
Proppant by volume (%)	7.75	4.73	6.51	7.53	7.68	7.45
<b>Wet Chemical Constituents</b>						
J604 Crosslinker (ethylene glycol, sodium tetraborate, boric acid)	Y	Y	N	Y	Y	Y
HCl	Y	Y	Y	Y	Y	Y
J318 breaker aid (triethanolamine)	Y	Y	Y	Y	Y	Y
<b>Dry Chemical Constituents</b>						
KCl clay control	Y	Y	Y	Y	Y	Y
M275 biocide (3:1 mixture of CMIT &MIT)	Y	Y	Y	Y	Y	Y
J218 Breaker (diammonium peroxydisulfate)	Y	Y	Y	Y	Y	Y
J479 encapsulated breaker (diammonium peroxydisulfate)	Y	Y	Y	Y	Y	Y
J580 guar gum	Y	Y	Y	Y	Y	Y
B499 corrosion Inhibitor (gelatine)	Y	Y	Y	Y	Y	Y
<b>FBA Chemical tracers</b>						
2-FBA	N	Y	Y	N	N	N
3-FBA	N	Y	Y	N	N	N
4-FBA	N	Y	Y	N	N	N
2,3-DFBA	N	Y	Y	N	N	N
2,4-DFBA	N	Y	Y	N	N	N
2,5-DFBA	N	Y	Y	N	N	N
2,6-DFBA	N	Y	Y	N	N	N
3,5-DFBA	N	Y	Y	N	N	N
3,4-DFBA	N	Y	Y	N	N	N
2,3,4,5-TTFBA	N	Y	Y	N	N	N

Y = included, N= not included

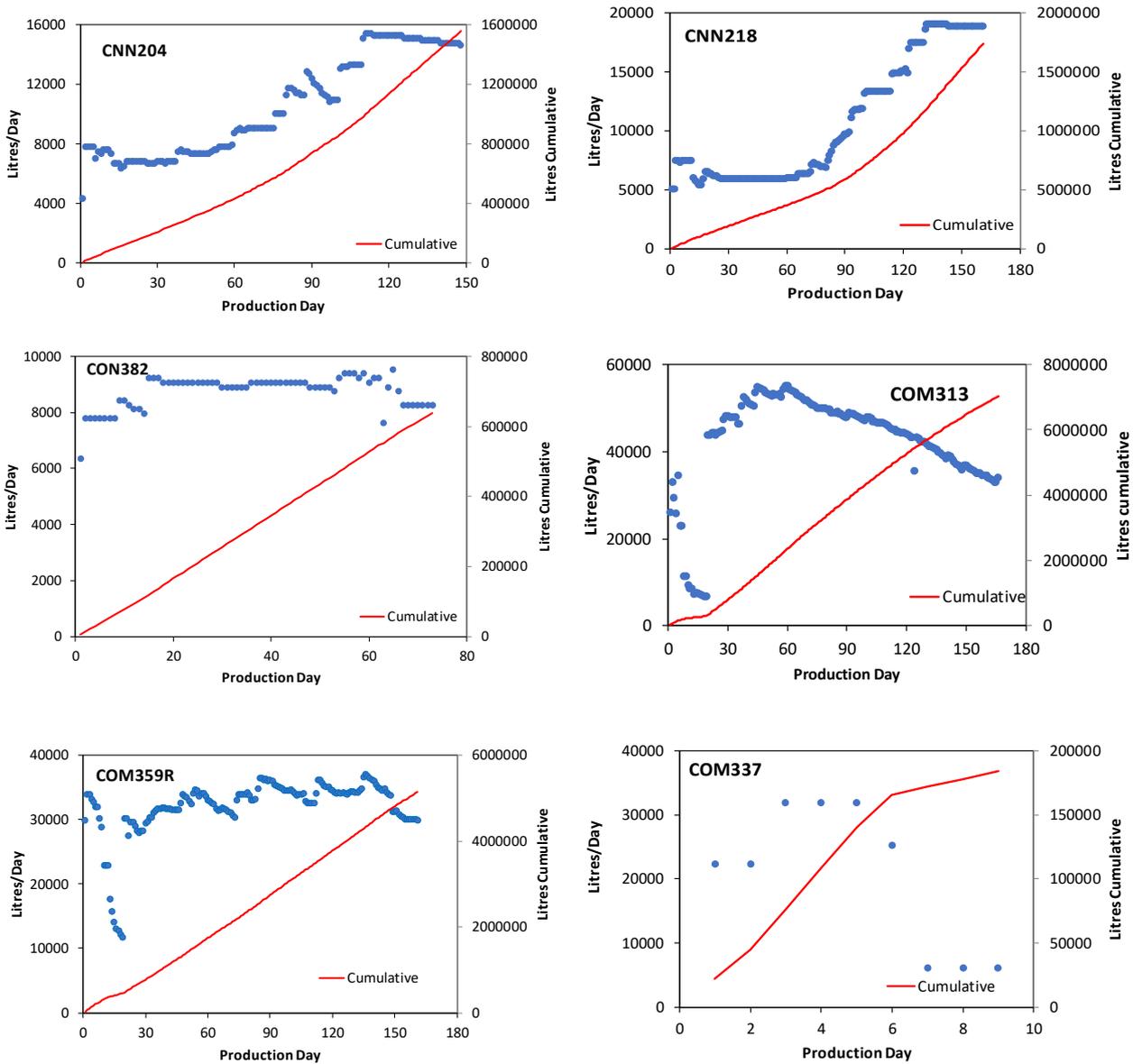


Figure 14 Produced water yields for the Condabri and Combabula wells over the study period

## 5.3 Produced and flowback water: inorganics

### 5.3.1 General water quality parameters & major cations and anions

General water quality parameters for the well samples are summarised in Table 10 to Table 15. Water pH ranged from 6.23 to 8.94, except for the first flowback water sample in COM359R, which had a pH of 4.52. As shown in Figure 16, the pH increased for up to 70 days post-HF, after which, it generally stabilised.

Most chemical parameters exhibited a concentration peak a few days into the produced water phase followed by a significant decrease over the following 40 days or longer. The conductivity of the well samples, which is an indicator of major ion concentration, was generally in the range 8.17-35 mS/cm, with a few samples from wells CNN218 and CNN204 having much higher peak

values up to 219 mS/cm. For comparative purposes, seawater has a typical conductivity of 50 mS/cm. For all wells except COM382, the conductivity decreased rapidly post-HF, stabilising after approximately 50 days. The initial conductivity of COM382 post-HF was not as elevated as the other wells, and it exhibited a more gradual decrease over time than the other wells.

Alkalinity was in the range 117-1640 mg CaCO<sub>3</sub>/L, except for the first flowback water sample of COM359R, which had a low pH of 4.52 and consequently a low alkalinity of 8 mg CaCO<sub>3</sub>/L. Alkalinity increased steadily over time for the Condabri wells CNN218, CON382 and CNN204, whereas for the Combabula wells COM313 and COM359R, it increased rapidly to a peak after 1-2 days of produced water, after which, it decreased over the remaining duration of measurement.

The chloride, sulfate and nitrate (as N) concentrations were in the range 1700-77000, <0.1-1200 and <0.005-0.77 mg/L respectively. The concentration of chloride and sulfate generally decreased over the duration of measurements, with some chloride concentrations increasing above this trend in the first few days of produced water. The concentration of nitrate in most samples was <0.005 mg/L.

The dissolved organic carbon (DOC) and total organic carbon (TOC) concentrations were in the range 1.34-1140 and 1.73-1100 mg/L, respectively. The DOC comprised a large proportion of the TOC, with the mean being 80%. As illustrated in Figure 16, DOC decreased over time; over a few days for wells CNN204 and COM359R, over 30 to 50 days for CON382 and COM313, and over 70 days for CNN218. Residual guar gum and its breakdown products are also likely to contribute to organic carbon concentrations during the early stages of well production. At some wells, occasional high spikes in TOC concentrations were observed that were associated with the presence of particulate forms of carbon (determined by the difference between TOC and DOC). Examples include the sample from well CNN218 collected on 8/8/2017 (particulate carbon: 333 mg/L), and from well CON382 collected on 8/8/2017 (particulate carbon: 189 mg/L). These high particulate carbon concentrations are consistent with the observation of coal fragments in some samples which would have contributed significantly to their carbon content.

Total ammonium concentrations were generally elevated in the well samples. The highest value recorded was 44 mg N/L in a well flush sample from COM359R (Table 14). Total ammonia comprises two chemical forms in aqueous solution: the ammonium (NH<sub>4</sub><sup>+</sup>) ion and unionised ammonia (NH<sub>3</sub>). The two forms are in pH-dependent chemical equilibrium with the proportion present as unionised ammonia increasing as pH becomes more alkaline. The speciation of total ammonia is highly significant with respect to ammonia toxicity to aquatic organisms as the toxic form of ammonia is the unionised form (the ammonium ion is not regarded as being toxic). Consequently, ammonia toxicity varies with pH, increasing as solutions become more alkaline. The ANZG default water quality guideline values for total ammonia take these factors into account and vary with pH (ANZG 2019). The measured concentrations of total ammonia are compared with the pH dependent guideline values in Figure 15. The graph indicates that there were 70 out of 78 samples where total ammonia concentrations exceeded the pH-dependent guideline value for freshwaters (Figure 15). This graph also indicated that total ammonia concentrations are generally higher in lower pH samples.

The concentrations of dissolved boron are shown in Table 16 and Table 17, with the time series data being plotted in Figure 16. Boron concentrations were elevated in the well samples and exceeded the ANZG DGV for 95% species protection of 0.37 mg/L in all but two samples from

Combabula. Aside from contributions from HF fluids, boron concentrations are elevated in formation waters from coal seams. Boron concentrations at the wells followed a similar pattern to other major ions at most wells with the highest concentrations occurring during well commissioning and the first few days of production and then a tailing off to much lower concentrations. It is highly likely that the initial high concentrations of boron in the well waters originate from the J604 cross linker in the HF fluid (Table 9). This interpretation is supported by the data from well CNN204 where no boron-containing cross linker was used. The boron concentrations in returned waters were much lower and only displayed a slight increase in concentration during the early days of well operation. Boron concentrations were marginally above the ANZG DGV at this site in all samples collected reflecting the naturally elevated concentrations of this element in coal seam formation waters.

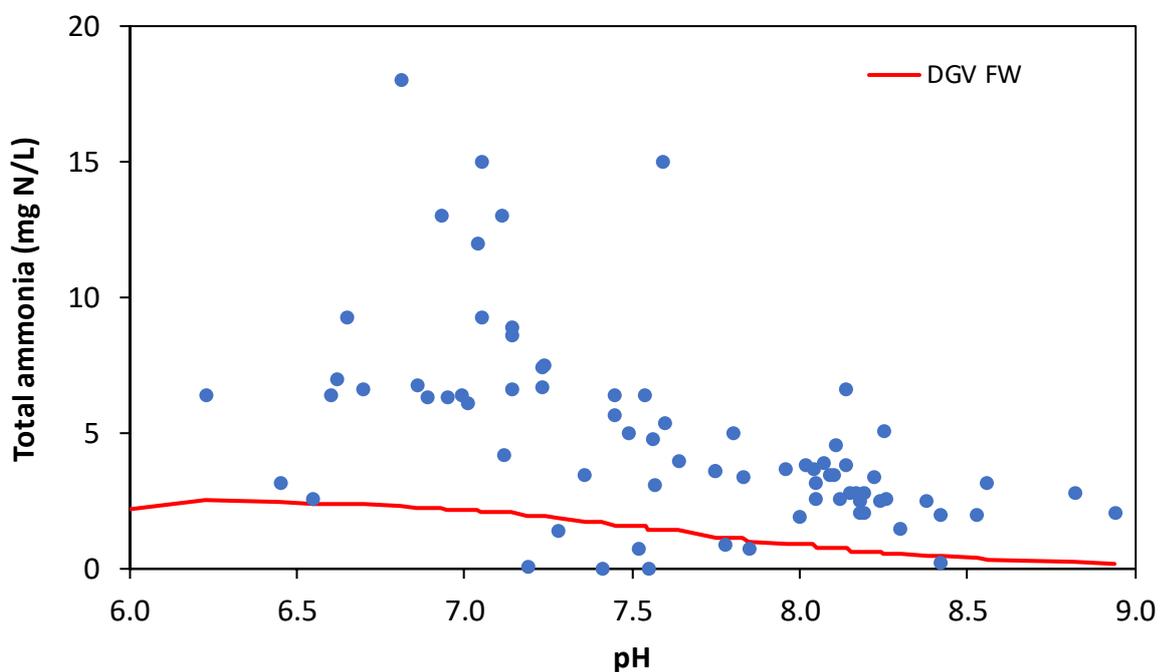


Figure 15 Total ammonia concentrations in well samples versus pH. The red line represents the ANZG default guideline values for freshwaters

Table 10 General water quality parameters and major anions measured in well CNN218 water samples

Date	Production day	Water type	pH	Conductivity mS/cm	TSS mg/L	Alkalinity mg CaCO <sub>3</sub> /L	TOC mg/L	DOC mg/L	Chloride mg/L	Sulfate mg/L	Phosphate mg P/L	Nitrate mg N/L	Nitrite mg N/L	Total Ammonia mg N/L
19/07/2017	-13	F	6.81	26.54	347	248	950	852	9400	440	0.21	0.82	0.77	18
20/07/2017	-12	F	6.65	21.89	122	117	606	602	7300	160	0.013	0.25	0.005	9.3
20/07/2017	-12	F	6.60	20.71	160	149	553	499	6900	110	<0.005	1.7	<0.005	6.4
21/07/2017	-11	F	6.45	20.01	110	291	449	393	4500	96	<0.005	0.53	<0.005	3.2
22/07/2017	-10	F	6.55	18.79	158	761	359	339	6400	75	<0.005	0.018	0.006	2.6
1/08/2017	0	P	7.04	219.4	307	214	192	185	77000	1200	0.025	23	0.14	12
3/08/2017	2	P	6.93	58.31	207	675	351	323	13000	96	<0.005	0.011	0.007	13
4/08/2017	3	P	7.05	49.00	145	718	352	326	11000	55	<0.005	0.037	0.016	15
8/08/2017	7	P	7.11	32.75	138	870	372	39	11000	<0.5	<0.005	0.010	<0.005	13
16/08/2017	15	P	7.23	24.31	329	843	263	20	5800	7.1	0.012	0.11	<0.005	7.4
22/08/2017	21	P	7.56	18.29	287	844	117	109	3700	0.2	<0.005	0.10	<0.005	4.8
14/09/2017	44	P	8.22	12.83	3640	818	41	7	2900	<0.1	0.010	0.82	<0.005	3.4
10/10/2017	70	P	8.56	10.54	57	1110	5	2	1700	<0.1	<0.005	0.017	<0.005	3.2
12/12/2017	133	P	8.18	8.778	38	1290	2	1	2700	<1	<0.005	0.8	<0.005	2.1
9/01/2018	161	P	8.19	8.171	38	1250	2	1	2200	<1	<0.005	0.01	0.009	2.1
<b>Minimum</b>	-	-	<b>6.45</b>	<b>8.17</b>	<b>38</b>	<b>117</b>	<b>1.75</b>	<b>1.34</b>	<b>1700</b>	<b>0.20</b>	<b>&lt;0.005</b>	<b>0.01</b>	<b>&lt;0.005</b>	<b>2.10</b>
<b>Maximum</b>	-	-	<b>8.56</b>	<b>219</b>	<b>3640</b>	<b>1290</b>	<b>950</b>	<b>852</b>	<b>77000</b>	<b>1200</b>	<b>0.21</b>	<b>23.0</b>	<b>0.77</b>	<b>18.0</b>

F=flowback, P=produced water

Table 11 General water quality parameters and major anions measured in well CNN204 water samples

Date	Production day	Water type	pH	Conductivity mS/cm	TSS mg/L	Alkalinity mg CaCO <sub>3</sub> /L	TOC mg/L	DOC mg/L	Chloride mg/L	Sulfate mg/L	Phosphate mg P/L	Nitrate mg N/L	Nitrite mg N/L	Total Ammonia mg N/L
12/08/2017	-2	WF	7.19	31.70	60	283	39	31	6500	24	<0.005	<0.005	<0.005	0.052
12/08/2017	-2	WF	8.82	31.67	1415	195	198	92	9300	67	<0.005	0.036	0.037	2.8
14/08/2017	0	P	7.28	109.3	192	156	52	34	24000	540	<0.005	6.6	0.033	1.4
15/08/2017	1	P	7.24	41.94	190	509	78	53	8200	79	<0.005	0.012	0.006	7.5
16/08/2017	2	P	6.70	34.35	138	547	153	158	5700	27	<0.005	0.006	<0.005	6.6
22/08/2017	8	P	7.12	18.05	258	702	20	7	5600	1.8	<0.005	0.80	<0.005	4.2
29/08/2017	15	P	7.36	13.71	44	839	16	5	2700	0.1	<0.005	<0.005	<0.005	3.5
5/09/2017	22	P	7.57	11.48	285	935	76	5	2700	0.6	<0.005	0.28	<0.005	3.1
13/09/2017	30	P	8.05	10.39	329	993	51	7	1700	<0.1	0.017	0.78	<0.005	2.6
10/10/2017	57	P	8.94	8.15	76	1532	3	2	1900	3.5	0.011	0.021	<0.005	2.1
15/11/2017	93	P	8.00	7.87	20	1584	1	2	2200	<1	<0.005	0.036	<0.005	1.9
12/12/2017	120	P	8.38	7.94	73	1644	4	2	2000	<1	0.030	0.31	<0.005	2.5
9/01/2018	148	P	8.30	7.91	21	1637	2	1	1900	<1	<0.005	0.013	<0.005	1.5
<b>Minimum</b>	-	-	<b>6.70</b>	<b>7.87</b>	<b>21</b>	<b>156</b>	<b>1.39</b>	<b>1.25</b>	<b>1700</b>	<b>0.10</b>	<b>&lt;0.005</b>	<b>0.01</b>	<b>&lt;0.005</b>	<b>0.05</b>
<b>Maximum</b>	-	-	<b>8.94</b>	<b>109</b>	<b>1415</b>	<b>1644</b>	<b>198</b>	<b>158</b>	<b>24000</b>	<b>540</b>	<b>0.03</b>	<b>6.60</b>	<b>0.04</b>	<b>7.50</b>

WF=well flushing, P=produced water

Table 12 General water quality parameters and major anions measured in well CON382 water samples

Date	Production day	Water type	pH	Conductivity mS/cm	TSS mg/L	Alkalinity mg CaCO <sub>3</sub> /L	TOC mg/L	DOC mg/L	Chloride mg/L	Sulfate mg/L	Phosphate mg P/L	Nitrate mg N/L	Nitrite mg N/L	Total ammonia mg N/L
26/07/2017	-3	WF	6.86	20.14	1090	727	221	249	6300	36	<0.005	0.18	0.018	6.8
26/07/2017	-3	WF	6.23	23.71	898	589	383	363	8000	93	<0.005	<0.005	0.021	6.4
29/07/2017	0	P	6.89	19.72	148	801	263	171	3000	<0.1	<0.005	0.014	<0.005	6.3
30/07/2017	1	P	6.95	19.43	160	824	273	200	3600	<0.1	<0.005	0.005	<0.005	6.3
31/07/2017	2	P	6.99	19.45	142	825	236	139	3100	<0.1	0.006	0.012	<0.005	6.4
1/08/2017	3	P	7.01	18.98	92	831	244	145	2800	<0.1	<0.005	0.012	<0.005	6.1
3/08/2017	5	P	7.14	18.00	133	855	263	194	4900	<0.1	0.013	0.012	<0.005	6.6
4/08/2017	6	P	7.23	17.74	201	799	255	135	3400	<0.1	0.028	0.012	<0.005	6.7
8/08/2017	10	P	7.59	17.26	151	913	267	78	4100	<0.5	<0.005	0.011	<0.005	15
16/08/2017	18	P	8.11	14.10	97	932	129	128	2000	<0.1	<0.005	<0.005	<0.005	4.6
22/08/2017	24	P	7.75	12.37	87	989	43	41	2800	<0.1	0.005	0.63	<0.005	3.6
22/08/2017 dup	24	P	7.75	12.23	95	995	39	35	2900	<0.1	<0.005	0.10	<0.005	3.6
14/09/2017	47	P	8.19	9.42	75	1010	23	5	1800	<0.1	0.024	1.70	<0.005	2.8
10/10/2017	73	P	8.42	8.12	56	1450	14	13	2200	<0.1	<0.005	<0.005	<0.005	2.0
<b>Minimum</b>	-	-	<b>6.23</b>	<b>8.20</b>	<b>56</b>	<b>589</b>	<b>14</b>	<b>5</b>	<b>1800</b>	<b>&lt;0.1</b>	<b>&lt;0.005</b>	<b>&lt;0.005</b>	<b>&lt;0.005</b>	<b>2.00</b>
<b>Maximum</b>	-	-	<b>8.42</b>	<b>24.0</b>	<b>1093</b>	<b>1450</b>	<b>383</b>	<b>363</b>	<b>8000</b>	<b>93</b>	<b>0.03</b>	<b>1.70</b>	<b>0.02</b>	<b>15</b>

WF=well flushing, P=produced water

Table 13 General water quality parameters and major anions measured in well COM313 water samples

Date	Production day	Water type	pH	Conductivity mS/cm	TSS mg/L	Alkalinity mg CaCO <sub>3</sub> /L	TOC mg/L	DOC mg/L	Chloride mg/L	Sulfate mg/L	Phosphate mg P/L	Nitrate mg N/L	Nitrite mg N/L	Total Ammonia mg N/L
10/10/2017	-9	WF	7.41	27.71	61	451	44	41	7600	49	0.053	0.25	<0.005	0.02
10/10/2017	-9	WF	7.52	29.63	112	516	27	25	7800	71	<0.005	<0.005	<0.005	0.77
19/10/2017	0	P	8.53	32.68	173	548	18	14	11000	37	0.13	0.008	<0.005	2.0
20/10/2017	1	P	7.45	19.12	684	1551	165	137	6200	<1	0.017	2.9	<0.005	6.4
21/10/2017	2	P	7.54	16.10	239	1366	204	194	5000	<1	0.010	2.3	<0.005	6.4
26/10/2017	7	P	7.80	13.72	83	1295	115	110	4200	<1	0.017	2.9	0.007	5.0
31/10/2017	12	P	7.64	13.20	76	1266	68	65	3800	<1	0.012	2.6	<0.005	4.0
8/11/2017	20	P	8.14	11.43	100	1237	40	36	3500	<1	0.006	0.011	<0.005	3.8
14/11/2017	26	P	7.83	11.32	61	1254	24	23	2900	<1	<0.005	0.008	<0.005	3.4
12/12/2017	54	P	8.05	9.49	77	1254	7	3	2800	<1	<0.005	1.1	0.011	3.2
9/01/2018	82	P	8.26	9.64	18	1194	5	7	2500	<1	<0.005	0.011	0.006	2.6
12/02/2018	116	P	8.17	9.57	1280	1116	13	6	3100	<1	<0.005	<0.005	<0.005	2.8
12/03/2018	144	P	8.15	10.03	17	1084	2	2	3200	<1	<0.005	<0.005	<0.005	2.8
12/03/2018 dup	144	P	8.12	10.38	25	1077	2	2	3600	<1	<0.005	<0.005	<0.005	2.6
3/04/2018	166	P	8.18	10.15	9	1064	2	3	2800	<1	<0.005	0.006	0.005	2.5
3/04/2018 dup	166	P	8.24	10.74	11	1061	2	3	2900	<1	<0.005	<0.005	0.005	2.5
<b>Minimum</b>	-	-	<b>7.41</b>	<b>9.49</b>	<b>9</b>	<b>451</b>	<b>2</b>	<b>2</b>	<b>2500</b>	<b>&lt;1</b>	<b>&lt;0.005</b>	<b>&lt;0.005</b>	<b>&lt;0.005</b>	<b>0.02</b>
<b>Maximum</b>	-	-	<b>8.53</b>	<b>32.68</b>	<b>1280</b>	<b>1550</b>	<b>204</b>	<b>194</b>	<b>11000</b>	<b>71</b>	<b>0.13</b>	<b>2.90</b>	<b>0.011</b>	<b>6.4</b>

WF=well flushing, P=produced water

Table 14 General water quality parameters and major anions measured in well COM359R water samples

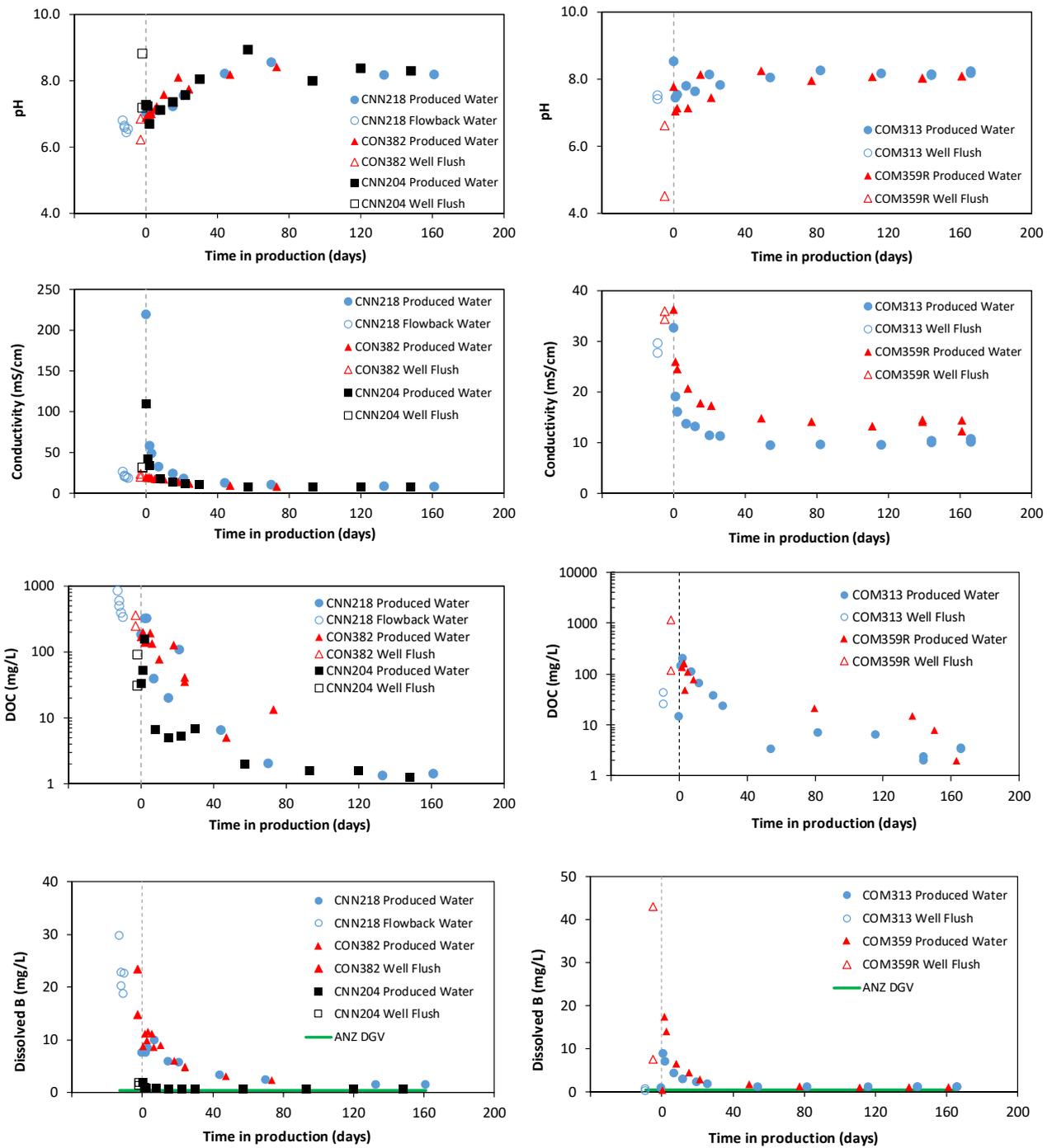
Date	Production day	Water type	pH	Conductivity mS/cm	TSS mg/L	Alkalinity mg CaCO <sub>3</sub> /L	TOC mg/L	DOC mg/L	Chloride mg/L	Sulfate mg/L	Phosphate mg P/L	Nitrate mg N/L	Nitrite mg N/L	Total Ammonia mg/L
19/10/2017	-5	WF	4.52	35.96	660	8	1100	1140	13400	360	1.6	0.17	0.021	44
19/10/2017	-5	WF	6.62	34.39	139	366	130	116	10500	86	0.11	2.4	0.094	7.0
24/10/2017	0	P	7.78	36.28	80	484	30	32	11000	50	0.090	3.9	0.027	0.88
25/10/2017	1	P	7.05	25.98	316	1400	324	303	8100	<1	0.007	5.3	0.006	9.3
26/10/2017	2	P	7.14	24.55	314	1440	178	163	7300	<1	0.012	3.5	<0.005	8.9
1/11/2017	8	P	7.14	20.70	110	1240	157	150	5400	<1	0.020	3.3	<0.005	8.6
8/11/2017	15	P	8.14	17.80	94	1260	139	137	5800	<1	0.019	0.018	<0.005	6.6
14/11/2017	21	P	7.45	17.31	70	1230	80	79	5100	<1	0.023	0.007	<0.005	5.7
12/12/2017	49	P	8.25	14.80	92	1220	12	3	4900	<1	<0.005	3.2	<0.005	5.1
9/01/2018	77	P	7.96	14.16	66	1260	6	8	4400	<1	0.007	0.014	<0.005	3.7
12/02/2018	111	P	8.07	13.25	1770	1300	15	5	4100	<0.1	<0.005	0.008	<0.005	3.9
12/03/2018	139	P	8.02	14.16	123	1280	2	2	4200	<1	<0.005	0.006	<0.005	3.8
12/03/2018 dup	139	P	8.04	14.52	98	1280	2	2	4900	<1	<0.005	0.007	<0.005	3.7
3/04/2018	161	P	8.10	14.43	11	1330	2	2	4700	<1	<0.005	<0.005	<0.005	3.5
3/04/2018 dup	161	P	8.09	12.26	41	1310	2	3	4500	<1	<0.005	0.009	<0.005	3.5
<b>Minimum</b>	-	-	<b>4.52</b>	<b>12.26</b>	<b>11</b>	<b>8</b>	<b>2</b>	<b>2</b>	<b>4100</b>	<b>&lt;1</b>	<b>&lt;0.005</b>	<b>0.01</b>	<b>&lt;0.005</b>	<b>0.88</b>
<b>Maximum</b>	-	-	<b>8.25</b>	<b>36.28</b>	<b>1770</b>	<b>1440</b>	<b>1100</b>	<b>1140</b>	<b>13400</b>	<b>360</b>	<b>1.60</b>	<b>5.30</b>	<b>0.09</b>	<b>44</b>

WF=well flushing, P=produced water

Table 15 General water quality parameters and major anions measured in well COM337 water samples

Date	Production day	Water type	pH	Conductivity mS/cm	TSS mg/L	Alkalinity mg CaCO <sub>3</sub> /L	TOC mg/L	DOC mg/L	Chloride mg/L	Sulfate mg/L	Phosphate mg P/L	Nitrate mg N/L	Nitrite mg N/L	Total Ammonia mg N/L
12/10/2017	-8	WF	7.55	33.08	79	516	31	35	9300	42	0.017	0.54	0.009	0.026
12/10/2017	-8	WF	7.85	31.64	150	625	24	16	9500	45	0.017	0.024	<0.005	0.73
20/10/2017	0	P	8.42	33.12	183	463	27	21	9600	1400	0.014	6.0	<0.005	0.24
21/10/2017	1	P	7.49	13.39	915	1300	169	158	3900	<1	0.007	3.0	<0.005	5.0
22/10/2017	2	P	7.60	11.72	125	1330	155	142	2500	<1	0.011	5.1	<0.005	5.4
<b>Minimum</b>			<b>8.42</b>	<b>33.12</b>	<b>915</b>	<b>1330</b>	<b>169</b>	<b>158</b>	<b>9600</b>	<b>1400</b>	<b>0.017</b>	<b>6.0</b>	<b>0.009</b>	<b>5.4</b>
<b>Maximum</b>			<b>7.49</b>	<b>11.72</b>	<b>79</b>	<b>463</b>	<b>24</b>	<b>16</b>	<b>2500</b>	<b>&lt;1</b>	<b>0.007</b>	<b>0.024</b>	<b>&lt;0.005</b>	<b>0.03</b>

WF=well flushing, P=produced water



**Figure 16** The pH, conductivity, dissolved organic carbon (DOC) and dissolved boron concentrations measured in flowback and produced waters sampled from CSG wells. The vertical dotted lines (time zero) indicate the start of well production and flow of produced water.

Table 16 Dissolved boron and barium concentrations in well samples from Condabri

Well	Date	Production day	Water type	B mg/L	Ba mg/L
CNN218	19/07/2017	-13	F	30	0.81
	20/07/2017	-12	F	23	2.2
	20/07/2017	-12	F	20	2.3
	21/07/2017	-11	F	19	2.3
	22/07/2017	-10	F	22	3.1
	1/08/2017	0	P	7.4	2.5
	3/08/2017	2	P	7.3	6.1
	4/08/2017	3	P	8.3	7.7
	8/08/2017	7	P	9.7	18
	16/08/2017	15	P	5.7	11
	22/08/2017	21	P	5.4	6.9
	14/09/2017	44	P	3.1	3.1
	10/10/2017	70	P	2.3	2.1
	12/12/2017	133	P	1.3	1.3
	9/01/2018	161	P	1.2	1.2
	CON382	26/07/2017	-3	WF	15
26/07/2017		-3	WF	23	3.1
29/07/2017		0	P	8.8	6.1
30/07/2017		1	P	11	6.1
31/07/2017		2	P	9.9	6.3
1/08/2017		3	P	11	6.9
3/08/2017		5	P	11	6.6
4/08/2017		6	P	8.5	6.5
8/08/2017		10	P	8.9	5.9
16/08/2017		18	P	5.9	3.4
22/08/2017		24	P	4.8	2.8
22/08/2017		24	P	4.8	2.8
14/09/2017		47	P	3.0	1.7
10/10/2017		73	P	2.3	1.2
CNN204		12/08/2017	-2	WF	1.7
	12/08/2017	-2	WF	1.1	1.3
	14/08/2017	0	P	1.7	1.0
	15/08/2017	1	P	0.78	2.0
	16/08/2017	2	P	0.68	7.7
	22/08/2017	8	P	0.64	5.8
	29/08/2017	15	P	0.44	3.2
	5/09/2017	22	P	0.40	2.3
	13/09/2017	30	P	0.39	1.8
	10/10/2017	57	P	0.45	1.2
	15/11/2017	93	P	0.49	1.1
12/12/2017	120	P	0.49	1.1	
9/01/2018	148	P	0.49	1.1	
<b>ANZG DGV</b>				<b>0.37</b>	-

WF=well flushing, F=flowback, P=produced water  
 The concentrations marked in red exceed the ANZG default guideline value

Table 17 Dissolved boron and barium concentrations in well samples from Combabula

Well	Date	Production day	Water type	B mg/L	Ba mg/L
COM313	10/10/2017	-9	WF	0.08	1.3
	10/10/2017	-9	WF	0.45	1.1
	19/10/2017	0	P	0.67	0.39
	20/10/2017	1	P	8.7	7.3
	21/10/2017	2	P	6.7	5.7
	26/10/2017	7	P	4.0	4.3
	31/10/2017	12	P	2.7	3.3
	8/11/2017	20	P	2.0	2.6
	14/11/2017	26	P	1.6	2.0
	12/12/2017	54	P	0.98	1.8
	9/01/2018	82	P	0.84	1.8
	12/02/2018	116	P	0.78	1.3
	12/03/2018	144	P	0.82	1.9
	12/03/2018	144	P	0.78	1.9
	3/04/2018	166	P	0.77	1.9
	3/04/2018	166	P	0.84	2.0
	COM337	12/10/2017	-8	WF	0.35
12/10/2017		-8	WF	2.1	0.77
20/10/2017		0	P	0.43	0.39
21/10/2017		1	P	2.9	3.0
22/10/2017		2	P	2.8	3.0
COM359R	19/10/2017	-5	WF	43	0.75
	19/10/2017	-5	WF	7.4	1.4
	24/10/2017	0	P	0.39	0.28
	25/10/2017	1	P	17	13
	26/10/2017	2	P	14	12
	1/11/2017	8	P	6.4	8.6
	8/11/2017	15	P	4.5	6.1
	14/11/2017	21	P	2.9	5.1
	12/12/2017	49	P	1.6	4.0
	9/01/2018	77	P	1.3	3.6
	12/02/2018	111	P	0.96	3.1
	12/03/2018	139	P	0.93	3.6
	12/03/2018	139	P	0.94	3.7
	3/04/2018	161	P	0.92	3.7
3/04/2018	161	P	0.97	3.9	
ANZ DGV				0.37	-

WF=well flushing, F=flowback, P=produced water  
 The concentrations marked in red exceed the ANZG DGV

### 5.3.2 Trace element concentrations

A total of 63 and 69 trace elements were determined in the water and soil samples respectively. The complete data sets are available in the data report. This report focusses on the behaviour of the most common trace elements found in waters and soils and elements of regulatory concern (e.g. potentially toxic metals).

Owing to their significance in terms of bioavailability and toxicity, this section focuses on the dissolved elemental data. Total element concentration data for the well samples may be found in the data report (Apte et al. 2018b). The difference between total and dissolved elemental concentrations indicates the concentration of the element present in particulate form (i.e. associated with suspended solids). Highly soluble elements measured included boron, calcium, lithium, manganese, potassium, sodium and sulfur. Elements found predominantly in the particulate phase were aluminium, lead, chromium and iron. Elements displaying an intermediate behaviour included arsenic, copper, nickel and zinc.

To analyse the relationships between elements, a correlation matrix was constructed for the dissolved trace element data in all well samples. As expected with a large data set, a number of statistically significant correlations were observed between a range of elements. However, only correlations of potential geochemical significance are noted here. Highly significant correlations ( $r > 0.9$ ,  $P < 0.05$ ) were observed between chloride and the following elements: lithium, potassium, rubidium and sulfur. Boron and DOC also displayed a strong positive correlation.

The concentrations of dissolved major cations Ca, K, Mg, and Na, and trace metals and metalloids of significance: Ag, As, Cd, Cr, Cu, Fe, Hg (total), Mn, Ni, Pb, U and Zn measured in wells CNN218, CON382, CNN204, COM313 and COM359R are shown in Table 18 through to Table 23. Dissolved barium concentrations are presented in Table 16 and Table 17. The trends in major cation concentration with time are shown in Figure 17 and the trends in trace metals concentrations with time are shown in Figure 18.

Most elements exhibited a concentration peak a few days into the flowback or early produced water phase followed by a decrease. For wells COM313 and COM359R about half the metals and metalloids exhibited a concentration peak a few days into the flowback or early produced phase followed by a decrease while the other half exhibited a steady decrease. The trends observed for the more common metals are discussed in more detail below.

The concentration of dissolved potassium ranged from 29 to 8710 mg/L, except for one very high value of 70900 mg/L measured on the first day of produced water in well CNN218 (note: this point is not plotted in Figure 17). The high initial concentrations of potassium are not surprising given the presence of potassium chloride (KCl) in the HF fluids used at all well sites (Table 9). The lowest concentrations of dissolved potassium were measured at the end of the sampling period, with wells CNN204, COM313 and COM359R exhibiting steady decreases over time, while wells CNN218 and CON382 exhibited a peak in concentration in the first week of produced water, after which, concentrations decreased. Potassium was predominantly in the dissolved phase, with an average 98% of the total concentration being comprised of dissolved potassium.

The concentration of dissolved sodium ranged from 285 to 6230 mg/L and peaked in the first few days of produced water. The concentration of dissolved sodium was higher at the end of the sampling period than the start for wells CNN204 and COM313, was similar for well COM359R, and

was lower at the end of the sampling period for wells CNN218 and CON382. Sodium was predominantly in the dissolved phase, with an average 95% of the total concentration being comprised of dissolved calcium.

Total mercury concentrations were in the low parts per trillion range, ranging from <0.1 to 12 ng/L, except for two samples on days 24 and 47 of the produced water phase of well CON382, which had concentrations of 23.9 and 46.5 ng/L, respectively. All mercury concentrations were below the mercury DGV of 600 ng/L. The concentrations of total mercury were generally highest in the flow back water phase and early produced water phase, after which, they decreased over time.

For the purpose of assessing the risk of the metal and metalloids in the flowback and produced water, the concentrations were compared to the Australian and New Zealand DGVs for 95% species protection in freshwater (ANZG 2018) in Table 18 through to Table 22. The concentrations of seven metals were measured above the guideline values in selected samples: chromium, copper, manganese, lead, nickel, silver and zinc. None of these metals are constituents of HF fluids. Many of the exceedances were marginal and were mainly confined to the early stages of well production. Copper was the metal showing the greatest exceedance of the guideline values with concentrations up to 812 µg/L. This compares to the guideline value of 1.4 µg/L. Clearly any treatment processes applied to CSG waters need to reduce the concentrations of these chemicals to below acceptable levels.

### 5.3.3 Radionuclides

Information on the radionuclides determined, their origins and half-lives are provided in Table 24. Radionuclides are not constituents of the HF fluids and are of geogenic origin. Gross alpha and beta activities were unable to be measured on the well and soil samples owing to interference problems caused by the sample matrices. The primordial radionuclides (U-238 and Th-232) and their decay products provide information on the background radioactivity of the samples. Radium isotopes are of particular interest as they are relatively mobile in groundwaters with Ra-226 being the parent radionuclide for the gas radon-222 (Apte et al. 2017c).

Radionuclide activities measured in the well samples are shown in Table 25 through to Table 30. The well samples had the highest radionuclide activities of all sample types analysed. Out of the seven radionuclides quantified, Ra-226 had the highest activities measured. Ra-228, Th-230 activities were close to or below the limit of reporting in the water samples. Radionuclide activity data for Ra-226, U-238, U-234 and Th-230 are plotted against well production time in Figure 19. Similar to the major ions and trace elements, a general feature of these profiles is a maximum around the start of well production followed by a decrease in activity over the ensuing 40 days of production. Occasional spikes in radionuclide activity were observed in some of the wells throughout the remaining monitoring period (Figure 19).

Only limited radiological guidelines for surface waters are currently available in Australia. The existing guidelines cover irrigation and livestock watering (ANZG 2018). No radionuclides exceeded the ANZG guideline values for irrigation and livestock watering. In order to provide some additional effects-based benchmark, the well radionuclide data are also compared to the available international drinking water GVs for the respective radionuclides where available (Table 25 to

Table 30). Ra-226 activities marginally exceeded the USEPA maximum concentration level (MCL) for drinking water in eleven out of 65 well samples analysed. Clearly, the production bore water is not intended for human consumption, these comparisons to very stringent benchmarks give some indication to the low level of risks posed by the levels of radioactivity encountered.

An extensive literature search failed to identify any peer reviewed studies detailing radionuclide activities in flowback/produced waters from other coal seam gas operations either within Australia or overseas. Radionuclide data are available for some shale gas operations. However, given the differences in geological settings comparisons between data from the current study and shale gas studies are inappropriate.

Table 18 The concentrations of dissolved metals in well CNN218

Date	Production day	Water type	Ca	K	Mg	Na	Fe	Ag	As	Cd	Cr	Cu	Total Hg	Mn	Ni	Pb	U	Zn
			mg/L	mg/L	mg/L	mg/L	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	ng/L	µg/L	µg/L	µg/L	µg/L	µg/L
19/07/2017	-13	F	196	562	35	2640	3.6	0.06	2.1	<0.2	3.5	3.2	11.3	242	9.7	4.9	0.55	8.1
20/07/2017	-12	F	153	434	26	2750	6.9	<0.04	2.8	<0.2	2.9	1.6	5.7	254	6.3	1.0	0.35	5.4
20/07/2017	-12	F	134	397	24	2802	4.5	0.06	1.3	<0.2	2.3	<1	6.4	305	6.0	0.1	0.28	<4
21/07/2017	-11	F	121	298	21	2360	22	<0.04	5.5	<0.2	2.8	<1	5.5	474	6.9	<0.1	0.22	8.3
22/07/2017	-10	F	162	361	25	3120	13	<0.04	0.6	<0.2	1.9	<1	4.5	940	9.4	0.2	0.24	<4
1/08/2017	0	P	393	70900	79	2500	1.1	0.07	3.9	<0.2	<1	332		1980	19.5	0.1	0.02	51.1
3/08/2017	2	P	733	5630	187	6230	16	0.04	6.0	<0.2	2.8	18.1	3.7	1370	9.1	0.1	<0.01	11.1
4/08/2017	3	P	671	4570	146	5800	39	0.09	7.0	<0.2	<1	15.1	3.3	1220	7.5	0.1	0.02	137
8/08/2017	7	P	303	1980	62	4630	11	0.08	6.1	<0.2	3.5	4.2	3.9	652	4.9	<0.1	<0.01	22.6
16/08/2017	15	P	113	1490	32	3320	11	<0.04	3.9	<0.2	3.0	2.1	9.9	514	3.5	0.2	0.03	10.0
22/08/2017	21	P	65	632	20	2880	0.14	<0.04	2.4	<0.2	1.8	3.5	2.4	335	3.0	0.3	<0.01	17.9
14/09/2017	44	P	26	300	9.3	2120	2.6	<0.04	2.4	<0.2	1.8	<1	1.6	139	1.8	<0.1	<0.01	7.2
10/10/2017	70	P	16	172	6.5	1710	0.09	<0.04	2.1	<0.2	1.2	1.2	0.6	66	1.8	<0.1	<0.01	<4
12/12/2017	133	P	12	97	4.4	1570	0.02	<0.04	1.1	<0.2	<1	<1	0.3	86	<1	<0.1	<0.01	<4
9/01/2018	161	P	11	78	4.2	1590	0.05	<0.04	0.8	<0.2	1.5	<1	0.6	82	1.5	<0.1	<0.01	<4
<b>ANZG DGV</b>			-	-	-	-	-	0.05	13	0.20	1	1.4	600	1900	11	3.4	-	8
Minimum			11	78	4.2	1570	0.02	<0.04	0.6	<0.2	<1	<1	0.3	66.1	<1	<0.1	<0.01	<4
Maximum			733	70900	187	6230	39	0.09	7.0	<0.2	3.5	332	11.3	1980	19.5	4.9	0.55	137

F=flowback, P=produced water

The concentrations marked in red exceed the ANZG DGV

Table 19 The concentrations of dissolved metals in well CON382

Date	Production day	Water type	Ca	K	Mg	Na	Fe	Ag	As	Cd	Cr	Cu	Total Hg	Mn	Ni	Pb	U	Zn
			mg/L	mg/L	mg/L	mg/L	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	ng/L	µg/L	µg/L	µg/L	µg/L	µg/L
26/07/2017	-3	WF	143	317	18	3510	5.2	<0.04	1.3	<0.2	3.3	16.8	7.3	1930	32.7	<0.1	0.12	11.1
26/07/2017	-3	WF	240	948	27	3640	41	<0.04	1.7	<0.2	2.7	3.8	11.5	2410	18.2	1.3	0.16	57.1
29/07/2017	0	P	83	737	18	3190	5.6	0.08	0.9	<0.2	6.4	11.1	2.3	769	8.3	1.1	<0.01	63.9
30/07/2017	1	P	82	724	18	3210	2.5	<0.04	0.4	<0.2	6.6	11.3	1.7	728	8.5	1.1	<0.01	65.2
31/07/2017	2	P	82	731	17	3160	0.91	<0.04	0.4	<0.2	4.2	10.1	1.5	666	9.1	1.1	0.01	63.2
1/08/2017	3	P	80	636	17	3060	0.18	<0.04	0.6	<0.2	6.9	10.7	---	540	9.1	1.1	<0.01	65.1
3/08/2017	5	P	73	511	16	3000	2.0	<0.04	0.7	<0.2	4.3	10.0	1.7	524	9.1	0.9	<0.01	71.8
4/08/2017	6	P	66	477	15	2960	4.1	<0.04	1.0	<0.2	<1	1.3	3.6	449	2.9	0.3	0.01	13.6
8/08/2017	10	P	62	540	10	2650	0.084	<0.04	0.7	<0.2	<1	<1	---	481	11.1	<0.1	<0.01	4.7
16/08/2017	18	P	29	249	7.8	2410	0.17	<0.04	0.6	<0.2	1.8	1.2	4.6	118	2.4	0.3	0.01	24.5
22/08/2017	24	P	22	153	6.1	2160	0.028	<0.04	0.9	0.26	1.4	2.5	23.9	77	2.1	0.2	<0.01	8.7
22/08/2017	24	P	22	152	6.1	2150	0.040	<0.04	0.7	<0.2	<1	2.5	7.4	79	2.5	0.2	<0.01	9.8
14/09/2017	47	P	12	100	3.5	1710	0.074	<0.04	1.7	<0.2	<1	<1	46.5	46	<1	<0.1	<0.01	<4
10/10/2017	73	P	10	55	2.6	1350	0.037	<0.04	0.9	<0.2	1.9	<1	4.1	59	<1	<0.1	0.02	<4
<b>ANZG DGV</b>			-	-	-		-	0.05	13	0.20	1	1.4	600	1900	11	3.4	-	8
<b>Minimum</b>			10	55	2.6	1350	0.028	<0.04	0.4	<0.2	<1	<1	1.5	46	<1	<0.1	<0.01	<4
<b>Maximum</b>			240	948	27	3640	41	0.08	1.7	<0.2	6.9	17	46.5	2410	32.7	1.3	0.16	71.8

WF= well flushing, P=produced water

The concentrations marked in red exceed the ANZG DGV

Table 20 The concentrations of dissolved metals in well CNN204

Date	Production day	Water type	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Fe mg/L	Ag µg/L	As µg/L	Cd µg/L	Cr µg/L	Cu µg/L	Total Hg ng/L	Mn µg/L	Ni µg/L	Pb µg/L	U µg/L	Zn µg/L
12/08/2017	-2	WF	30	6850	8.2	459	0.038	<0.04	9.0	<0.2	<1	374	3.2	317	19.3	<0.1	0.04	<4
12/08/2017	-2	WF	67	5900	7.0	913	1.7	<0.04	12.7	<0.2	<1	812	5.4	3	60.0	0.4	0.13	<4
14/08/2017	0	P	154	---	34	895	0.017	<0.04	2.5	<0.2	1.2	228	7.3	1127	11.3	<0.1	<0.01	<4
15/08/2017	1	P	351	5000	80	884	22	<0.04	1.7	<0.2	<1	6.8	2.3	1202	9.1	<0.1	<0.01	5.5
16/08/2017	2	P	235	3040	55	3850	52	<0.04	3.4	<0.2	1.7	3.9	6.7	1073	7.9	0.2	<0.01	15.5
22/08/2017	8	P	77	894	20	2820	2.1	0.13	0.7	<0.2	3.7	3.0	2.8	424	5.2	0.2	0.01	12.2
29/08/2017	15	P	37	409	10	2090	0.55	<0.04	0.6	<0.2	1.8	<1	1.5	306	3.0	<0.1	<0.01	<4
5/09/2017	22	P	24	310	7.6	1850	2.5	<0.04	<0.1	<0.2	1.2	<1	2.7	423	1.6	<0.1	<0.01	4.4
13/09/2017	30	P	14	232	5.9	1690	0.22	<0.04	0.2	<0.2	1.6	<1	1.0	59	1.5	<0.1	<0.01	<4
10/10/2017	57	P	11	115	4.2	1390	0.070	<0.04	<0.1	<0.2	1.3	<1	0.6	78	1.4	<0.1	0.01	<4
15/11/2017	93	P	9.9	64	3.7	1380	0.012	<0.04	0.1	<0.2	<1	1.4	0.9	59	<1	<0.1	<0.01	<4
12/12/2017	120	P	9.5	56	3.5	1450	0.019	<0.04	1.0	<0.2	<1	<1	0.4	92	1.9	0.1	<0.01	<4
9/01/2018	148	P	9.3	43	3.5	1490	0.017	<0.04	1.1	<0.2	1.7	<1	0.2	56	<1	<0.1	<0.01	<4
<b>ANZG DGV</b>			-	-	-		-	0.05	13	0.20	1	1.4	600	1900	11.3	3.4	-	8
Minimum			9.3	43	3.5	459	0.012	<0.04	<0.1	<0.2	<1	<1	0.2	3	<1	<0.1	<0.01	<4
Maximum			351	6850	80	3850	52	0.13	12.7	<0.2	3.7	812	7.3	1900	60.0	0.42	0.13	15.5

WF=well flushing, P=produced water

The concentrations marked in red exceed the ANZG DGV

Table 21 The concentrations of dissolved metals in well COM313

Date	Production day	Water type	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Fe mg/L	Ag µg/L	As µg/L	Cd µg/L	Cr µg/L	Cu µg/L	Total Hg ng/L	Mn µg/L	Ni µg/L	Pb µg/L	U µg/L	Zn µg/L
10/10/2017	-9	WF	9.0	5770	6.0	285	0.12	<0.04	6.3	<0.2	<1	273	0.8	223	13.8	<0.1	0.17	<4
10/10/2017	-9	WF	12	6360	6.8	371	0.10	0.04	3.4	<0.2	<1	183	1.3	275	9.4	<0.1	0.05	5.3
19/10/2017	0	P	5.9	7200	3.8	346	0.013	<0.04	1.7	<0.2	1.6	<1	1.3	12	1.6	<0.1	<0.01	<4
20/10/2017	1	P	95	560	20	3070	1.84	<0.04	1.5	<0.2	1.6	1.1	7.6	652	6.2	<0.1	0.03	18.5
21/10/2017	2	P	67	256	14	2670	0.31	<0.04	1.1	<0.2	1.7	1.4	3.2	335	4.6	<0.1	0.03	71.2
26/10/2017	7	P	46	186	11	2330	0.069	<0.04	1.1	<0.2	7.4	1.2	1.0	159	1.7	0.1	0.01	6.4
31/10/2017	12	P	33	129	8.6	2050	0.071	<0.04	1.3	<0.2	4.1	1.3	1.2	119	11.9	<0.1	0.02	18.7
8/11/2017	20	P	29	89	8.4	2110	0.035	<0.04	0.8	<0.2	3.2	<1	2.8	186	2.4	<0.1	0.01	<4
14/11/2017	26	P	23	76	7.0	1840	0.041	<0.04	0.8	<0.2	<1	1.1	0.5	214	2.6	<0.1	<0.01	<4
12/12/2017	54	P	18	48	6.1	1730	0.023	<0.04	2.2	<0.2	<1	<1	0.7	121	11.5	<0.1	<0.01	<4
9/01/2018	82	P	18	45	6.2	1760	0.031	<0.04	1.6	<0.2	2.4	1.8	0.4	98	4.3	<0.1	<0.01	7.9
12/02/2018	116	P	18	34	6.2	1820	0.090	<0.04	3.8	<0.2	<1	<1	3.6	138	9.2	<0.1	0.19	<4
12/03/2018	144	P	18	31	6.0	1650	0.019	<0.04	1.3	<0.2	1.1	<1	<0.1	65	<1	<0.1	<0.01	<4
12/03/2018	144	P	18	30	6.1	1630	0.022	<0.04	1.1	<0.2	<1	<1	0.1	66	<1	<0.1	<0.01	<4
3/04/2018	166	P	14	29	6.0	1690	0.018	<0.04	1.7	<0.2	<1	<1	<0.1	37	<1	0.16	<0.01	---
3/04/2018	166	P	15	30	6.4	1760	0.025	<0.04	1.6	<0.2	<1	<1	<0.1	39	<1	<0.1	<0.01	<4
<b>ANZG DGV</b>			-	-	-	-	-	0.05	13	0.20	1	1.4	600	1900	11	3.4	-	8
<b>Minimum</b>			5.9	29	3.8	285	0.013	<0.04	0.8	<0.2	<1	<1	<0.1	12	<1	<0.1	<0.01	<4
<b>Maximum</b>			95	7200	20	3070	1.84	0.04	6.3	<0.2	7.4	273	7.6	652	13.8	0.16	0.19	71.2

WF=well flushing, P=produced water

The concentrations marked in red exceed the ANZG DGV

Table 22 The concentrations of dissolved metals in well COM359R

Date	Production day	Water type	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Fe mg/L	Ag µg/L	As µg/L	Cd µg/L	Cr µg/L	Cu µg/L	Total Hg ng/L	Mn µg/L	Ni µg/L	Pb µg/L	U µg/L	Zn µg/L
19/10/2017	-5	WF	432	4030	47	2980	295	<0.04	9.4	<0.2	50.7	28.5	6.7	7020	60.5	15.0	0.41	230
19/10/2017	-5	WF	79	7460	14	940	1.5	<0.04	3.1	<0.2	1.2	198	0.3	1631	22.7	<0.1	0.19	75.1
24/10/2017	0	P	7.7	8710	8.5	370	0.75	<0.04	5.6	<0.2	5.9	231	0.4	124	23.7	<0.1	<0.01	5.3
25/10/2017	1	P	196	591	37	4350	10	<0.04	2.9	<0.2	3.9	1.4	1.6	848	5.4	<0.1	0.01	23.8
26/10/2017	2	P	149	461	34	4000	0.19	<0.04	2.4	<0.2	3.8	1.2	1.3	524	4.7	<0.1	0.01	8.3
1/11/2017	8	P	86	261	23	3320	0.13	<0.04	1.1	<0.2	3.5	<1	0.6	252	5.2	<0.1	0.01	17.6
8/11/2017	15	P	67	182	19	3210	0.65	<0.04	1.4	<0.2	3.0	1.0	4.3	396	3.8	<0.1	0.05	<4
14/11/2017	21	P	54	211	16	2950	0.037	<0.04	0.6	<0.2	<1	16.6	2.4	355	3.5	<0.1	<0.01	14.7
12/12/2017	49	P	37	78	13	2620	0.37	<0.04	1.1	<0.2	2.4	1.4	0.5	217	12.1	<0.1	<0.01	5.0
9/01/2018	77	P	30	67	12	2650	0.01	<0.04	0.8	<0.2	2.3	1.2	2.9	180	10.0	<0.1	<0.01	<4
12/02/2018	111	P	27	45	12	2560	0.11	<0.04	7.1	<0.2	<1	<1	3.9	366	33.6	<0.1	0.13	<4
12/03/2018	139	P	28	36	11	2400	0.015	<0.04	2.4	<0.2	<1	<1	0.2	81	1.8	<0.1	0.01	<4
12/03/2018	139	P	28	36	11	2350	0.021	<0.04	2.2	<0.2	<1	<1	0.4	77	<1	<0.1	0.01	<4
3/04/2018	161	P	28	35	11	2520	0.015	0.06	1.4	<0.2	1.2	<1	0.1	67	1.1	0.1	<0.01	---
3/04/2018	161	P	30	37	12	2690	0.022	<0.04	1.6	<0.2	<1	<1	<0.1	78	10.8	<0.1	<0.01	<4
ANZG DGV			-	-	-	-	-	0.05	13	0.20	1	1.4	600	1900	11	3.4	-	8
Minimum			7.7	35	8.5	370	0.01	<0.04	0.6	<0.2	<1	<1	0.10	67	<1	<0.1	<0.01	<4
Maximum			432	8710	47	4350	295	0.06	9.4	<0.2	50.7	231	6.7	7020	60.5	15	0.41	230

WF=well flushing, P=produced water

The concentrations marked in red exceed the ANZG DGV

**Table 23**The concentrations of dissolved metals in well COM337

Date	Production Day	Water type	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Fe mg/L	Ag µg/L	As µg/L	Cd µg/L	Cr µg/L	Cu µg/L	Total Hg ng/L	Mn µg/L	Ni µg/L	Pb µg/L	U µg/L	Zn mg/L
12/10/2017	-8	WF	15	6850	7.8	333	0.073	<0.04	4.8	<0.2	<1	599	3.0	512	16	<0.1	0.26	<4
12/10/2017	-8	WF	22	6410	7.2	502	0.11	<0.04	3.6	<0.2	<1	195	1.6	65	10	<0.1	0.21	<4
20/10/2017	0	P	8.5	7550	3.1	396	0.13	<0.04	4.3	<0.2	3	198	4.4	23	13	<0.1	0.01	<4
21/10/2017	1	P	39	388	12	2100	0.22	<0.04	0.8	<0.2	3	4.1	4.4	408	5	<0.1	0.02	80
22/10/2017	2	P	35	208	11	2010	0.23	<0.04	1.2	<0.2	3	1.6	1.4	155	4	<0.1	0.02	26
<b>ANZG DGV</b>				-	-	-	-	<b>0.05</b>	<b>13</b>	<b>0.20</b>	<b>1</b>	<b>1.4</b>	<b>600</b>	<b>1900</b>	<b>11</b>	<b>3.4</b>	-	<b>8</b>
Maximum			39	7550	12	2100	0.23	<0.04	5	<0.2	<1	599	4	512	16	<0.1	0.26	<4
Minimum			9	208	3	333	0.073	<0.04	1	<0.2	3	2	1	23	4	<0.1	0.01	80

WF=well flushing, P=produced water

The concentrations marked in red exceed the ANZG DGV

**Table 24** Radionuclides determined and their properties

Radionuclide	Half-life (y)	Origin
U-238	4.5x10 <sup>9</sup>	Primordial radionuclide
Th-232	1.4x10 <sup>10</sup>	Primordial radionuclide
U-234	246,000	Part of U-238 decay series
Th-230	83,000	Part of U-238 decay series
Ra-226	1600	Part of U-238 decay series
Th-228	1.9	Part of Th-232 decay series
Ra-228	5.8	Part of Th-232 decay series

Table 25 Radionuclide activities in well CNN218 samples

Sampling Date	Production day	Water type	<sup>238</sup> U activity	<sup>234</sup> U activity	<sup>226</sup> Ra activity	<sup>228</sup> Ra activity	<sup>232</sup> Th activity	<sup>230</sup> Th activity	<sup>228</sup> Th activity
			mBq/kg	mBq/kg	mBq/kg	Bq/kg	mBq/kg	mBq/kg	mBq/kg
19/07/2017	-13	F	8.9	40.8	11.9	<0.2	<2	<6	5.1
20/07/2017	-12	F	3.2	22.4	15.3	<0.3	<2	<6	<5
20/07/2017	-12	F	3.6	25.0	132	<0.3	<2	<6	<5
21/07/2017	-11	F	2.9	17.3	18.7	<0.3	<2	<6	<5
22/07/2017	-10	F	1.8	8.4	114	0.2	<2	<6	<5
1/08/2017	0	P	0.9	1.8	126	<0.6	<2	<6	8.4
3/08/2017	2	P	0.8	2.6	98	<0.6	<2	<6	5.2
4/08/2017	3	P	2.6	1.6	315	<0.9	<2	<6	15.1
16/08/2017	15	P	<2.2	6.5	374	<0.6	<2	<6	8.8
22/08/2017	21	P	<1	<1	160	0.5	<1	<5	23.1
14/09/2017	44	P	13.2	18.2	130	0.4	<1	<5	15.6
10/10/2017	70	P	6.6	16.8	110	0.3	<1	<5	8.2
12/12/2017	133	P	<1	1.8	39	<0.3	<1	<5	4.1
9/01/2018	161	P	3.1	17.3	50	<0.4	<1	<5	4.3
<sup>a</sup> WHO GV			10,000	1000	1000	0.1	1000	1000	1000
<sup>b</sup> ANZG (2018)			200		5000	2000			
<sup>c</sup> USEPA MCL					185	185			

<sup>a</sup>WHO (2017) Guideline value for drinking water

<sup>b</sup>ANZG guidelines for livestock drinking/irrigation

<sup>c</sup>USEPA maximum concentration level (MCL) for drinking water

The activities in red exceed the USEPA MCL

F=flowback, P=produced water

Table 26 Radionuclide activities in well CNN382 samples

Sampling Date	Production day	Water type	<sup>238</sup> U activity mBq/kg	<sup>234</sup> U activity mBq/kg	<sup>226</sup> Ra activity mBq/kg	<sup>228</sup> Ra activity Bq/kg	<sup>232</sup> Th activity mBq/kg	<sup>230</sup> Th activity mBq/kg	<sup>228</sup> Th activity mBq/kg
26/07/2017	-3	WF	6.9	7.2	148	<0.6	<2	<6	7.1
26/07/2017	-3	WF	<2.8	5.4	267	<1	<2	<6	<5
29/07/2017	0	P	<1.4	1.0	202	<0.5	<2	<6	<5
30/07/2017	1	P	<1.7	1.9	185	<0.5	<2	<6	<5
31/07/2017	2	P	<1.0	1.1	208	<0.5	<2	<6	5.2
1/08/2017	3	P	<0.6	0.7	220	0.5	<2	<6	<5
3/08/2017	5	P	<1	<1	221	<0.5	<1	<5	27.8
4/08/2017	6	P	1.2	1.3	186	<0.8	<1	<5	27.4
8/08/2017	10	P	3.0	1.0	160	<0.5	3.6	<5	20.0
16/08/2017	18	P	<1	<1	72	<0.5	<1	<5	1.8
22/08/2017	24	P	<1	<1	74	<0.3	<1	<5	7.5
14/09/2017	47	P	<1	<1	35	<0.3	<1	<5	9.2
10/10/2017	73	P	<1	<1	22	<0.4	<1	<5	3.6
<sup>a</sup> WHO GV			10,000	1000	1000	0.1	1000	1000	1000
<sup>b</sup> ANZG (2018)			200		5000	2000			
<sup>c</sup> USEPA MCL					185	185			

<sup>a</sup>WHO (2017) Guideline value for drinking water

<sup>b</sup>ANZG guidelines for livestock drinking/irrigation

<sup>c</sup>USEPA maximum concentration level for drinking water

The activities in red exceed the USEPA MCL

WF=well flushing, P=produced water

Table 27 Radionuclide activities in well CNN204 samples

Sampling Date	Production day	Water type	<sup>238</sup> U activity mBq/kg	<sup>234</sup> U activity mBq/kg	<sup>226</sup> Ra activity mBq/kg	<sup>228</sup> Ra activity Bq/kg	<sup>232</sup> Th activity mBq/kg	<sup>230</sup> Th activity mBq/kg	<sup>228</sup> Th activity mBq/kg
12/08/2017	-2	WF	3.7	5.6	53	<0.3	2.0	<5	7.2
12/08/2017	-2	WF	26.6	29.3	133	0.7	23.6	20	48.3
14/08/2017	0	P	1.3	<0.9	91.2	<0.5	<2	<6	<5
15/08/2017	1	P	<1.3	1.8	80.3	<0.5	<2	<6	13.0
16/08/2017	2	P	<0.9	1.0	87.0	<0.7	<2	<6	7.0
22/08/2017	8	P	<1	1	240	0.6	<1	<5	30.1
29/08/2017	15	P	<1	<1	95	<0.3	<1	<5	8.7
5/09/2017	22	P	<1	<1	81	<0.3	<1	<5	17.8
13/09/2017	30	P	1.6	3.8	67	<0.2	<1	<5	10.0
10/10/2017	57	P	<1	<1	55	<0.4	<1	<5	8.2
15/11/2017	93	P	<1	2.2	44	<0.1	<1	<5	5.5
12/12/2017	120	P	<1	4.2	39	<0.3	<1	<5	4.3
9/01/2018	148	P	1.5	11.0	37	<0.3	<1	<5	3.0
<sup>a</sup> WHO GV			10,000	1000	1000	0.1	1000	1000	1000
<sup>b</sup> ANZG (2018)			200		5000	2000			
<sup>c</sup> USEPA MCL					185	185			

<sup>a</sup>WHO (2017) Guideline value for drinking water

<sup>b</sup>ANZG guidelines for livestock drinking/irrigation

<sup>c</sup>USEPA maximum concentration level for drinking water

The activities in red exceed the USEPA MCL

WF=well flushing, P=produced water

Table 28 Radionuclide activities in well COM313 samples

Sampling Date	Production day	Water type	<sup>238</sup> U activity mBq/kg	<sup>234</sup> U activity mBq/kg	<sup>226</sup> Ra activity mBq/kg	<sup>228</sup> Ra activity Bq/kg	<sup>232</sup> Th activity mBq/kg	<sup>230</sup> Th activity mBq/kg	<sup>228</sup> Th activity mBq/kg
10/10/2017	-9	WF	19	58	34	0.4	5.7	<5	25
10/10/2017	0	P	2.8	6.8	90	<0.3	<1	<5	5.4
19/10/2017	1	P	<1	<1	37	<0.3	<1	7.6	<1
20/10/2017	2	P	<1	5.4	252	<0.3	1	7.9	7.2
21/10/2017	7	P	1.2	1.9	182	<0.2	<1	<5	7.8
26/10/2017	12	P	<1	1.5	87	<0.2	<1	<5	4.0
31/10/2017	26	P	<1	<1	94	<0.36	<1	<5	4.5
14/11/2017	54	P	<1	<1	53	<0.2	<1	11	3.4
9/01/2018	82	P	<1	2.3	40	0.4	1.3	<5	5.2
12/03/2018	144	P	<1	<1	48	<0.4	<1	<5	2.3
<sup>a</sup> WHO GV			10,000	1000	1000	0.1	1000	1000	1000
<sup>b</sup> ANZG (2018)			200		5000	2000			
<sup>c</sup> USEPA MCL					185	185			

<sup>a</sup>WHO (2017) Guideline value for drinking water

<sup>b</sup>ANZG guidelines for livestock drinking/irrigation

<sup>c</sup>USEPA maximum concentration level for drinking water

The activities in red exceed the USEPA MCL

WF=well flushing, P=produced water

Table 29 Radionuclide activities in well COM337 samples

Sampling Date	Production day	Water type	<sup>238</sup> U activity mBq/kg	<sup>234</sup> U activity mBq/kg	<sup>226</sup> Ra activity mBq/kg	<sup>228</sup> Ra activity Bq/kg	<sup>232</sup> Th activity mBq/kg	<sup>230</sup> Th activity mBq/kg	<sup>228</sup> Th activity mBq/kg
12/10/2017	-8	WF	5.9	20	37	<0.2	1.6	<5	5.2
12/10/2017	-8	WF	8.0	15	83	<0.4	<1	<5	2.5
20/10/2017	0	P	<1	3.3	16	<0.3	<1	<5	<1
21/10/2017	1	P	3.5	4.7	135	<0.3	<1	<5	6.3
<sup>a</sup> WHO GV			10,000	1000	1000	0.1	1000	1000	1000
<sup>b</sup> ANZG (2018)			200		5000	2000			
<sup>c</sup> USEPA MCL					185	185			

<sup>a</sup>WHO (2017) Guideline value for drinking water

<sup>b</sup>ANZG guidelines for livestock drinking/irrigation

<sup>c</sup>USEPA maximum concentration level for drinking water

The activities in red exceed the USEPA MCL

WF=well flushing, P=produced water

Table 30 Radionuclide activities in well CNN359R samples

Sampling Date	Production day	Water type	<sup>238</sup> U activity	<sup>234</sup> U activity	<sup>226</sup> Ra activity	<sup>228</sup> Ra activity	<sup>232</sup> Th activity	<sup>230</sup> Th activity	<sup>228</sup> Th activity
			mBq/kg	mBq/kg	mBq/kg	Bq/kg	mBq/kg	mBq/kg	mBq/kg
19/10/2017	-5	WF	16	37	115	<0.4	9.2	10	28
19/10/2017	-5	WF	5.2	12	45	<0.6	1.7	5	1.9
24/10/2017	0	P	<1	4.4	15	<0.2	<1	<5	<1
25/10/2017	1	P	<1	<1	442	0.7	<1	<5	25
26/10/2017	2	P	<1	<1	112	1.0	<1	<5	21
1/11/2017	8	P	1.6	2	151	0.5	<1	<5	7
14/11/2017	21	P	10.3	8.7	204	0.4	2.3	8.1	12
9/01/2018	77	P	2.0	5.7	134	0.6	<1	<5	13.7
12/03/2018	139	P	2.2	6.4	96	<0.6	<1	<5	7.5
3/04/2018	161	P	<1	<1	85	<0.3	<1	<5	4.9
<sup>a</sup> WHO GV			10,000	1000	1000	0.1	1000	1000	1000
<sup>b</sup> ANZG (2018)			200		5000	2000			
<sup>c</sup> USEPA MCL					185	185			

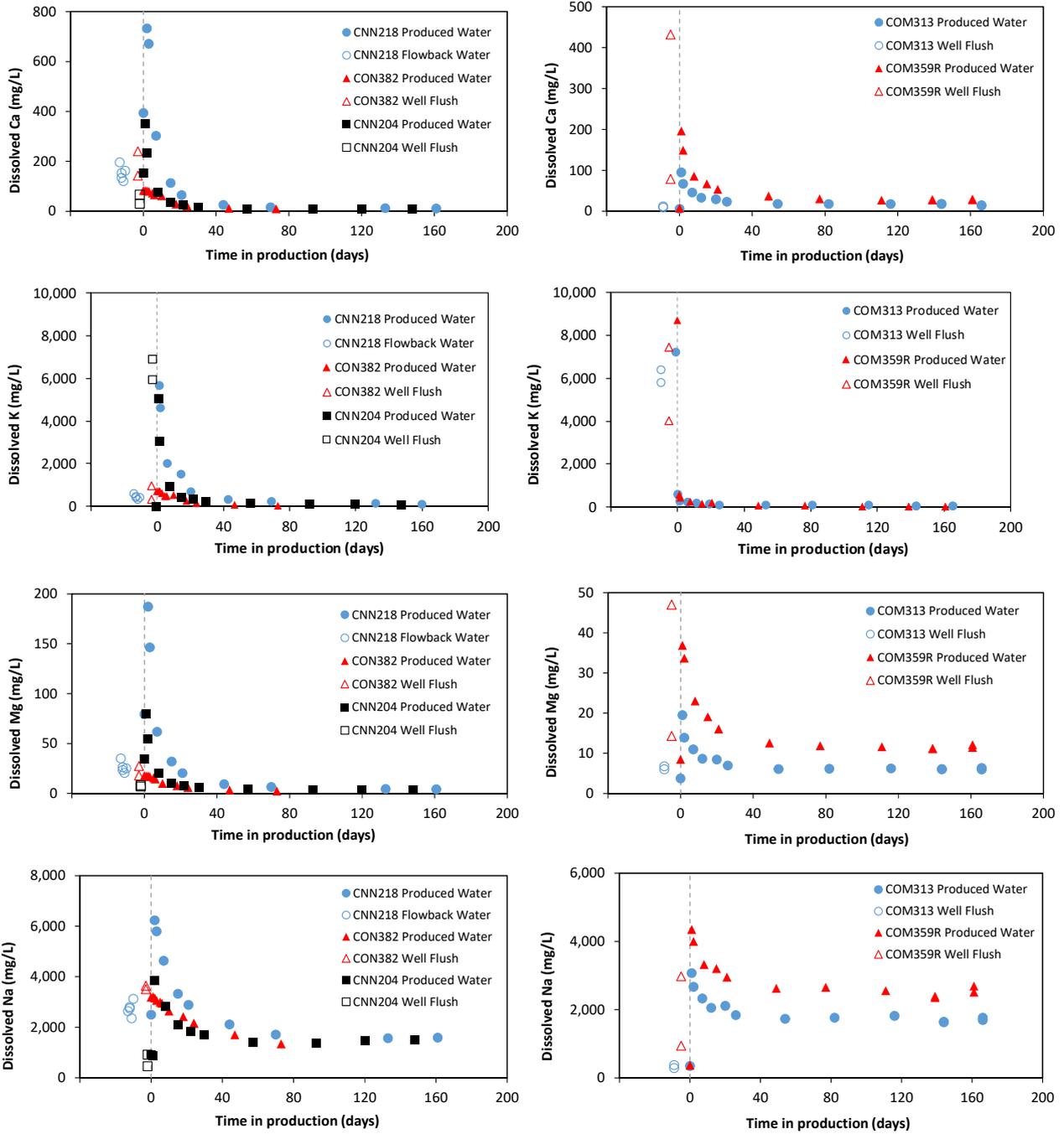
<sup>a</sup>WHO (2017) Guideline value for drinking water

<sup>b</sup>ANZG guidelines for livestock drinking/irrigation

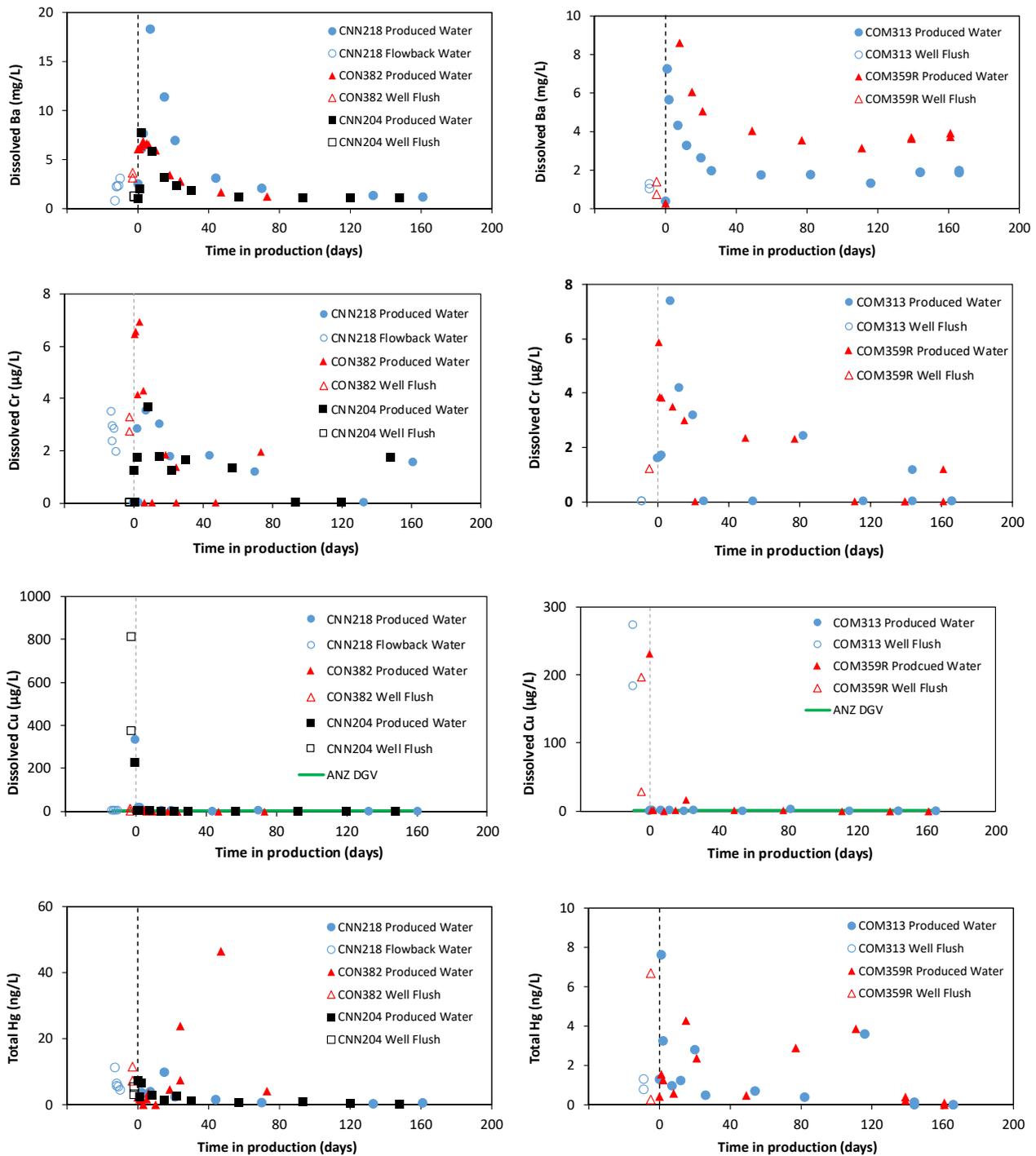
<sup>c</sup>USEPA maximum concentration level for drinking water

The activities in red exceed the USEPA MCL

WF=well flushing, P=produced water



**Figure 17** The concentration of dissolved major cations Ca, K, Mg and Na measured in flowback and produced waters sampled from CSG wells. The vertical dotted lines (time zero) indicate the start of well production and flow of produced water.



**Figure 18** The concentration of dissolved metals measured in flowback and produced waters sampled from CSG wells. The vertical dotted lines (time zero) indicate the start of well production and flow of produced water.

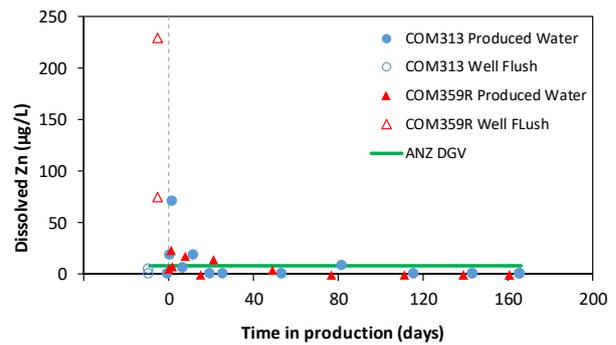
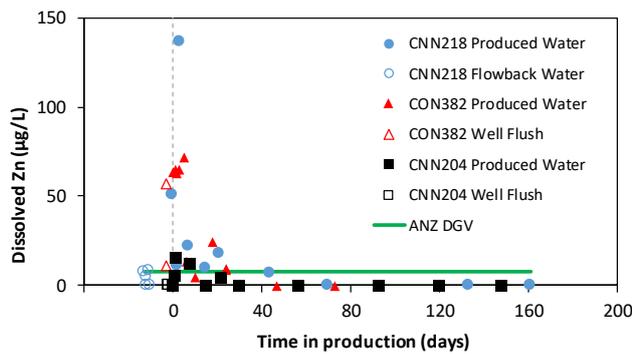
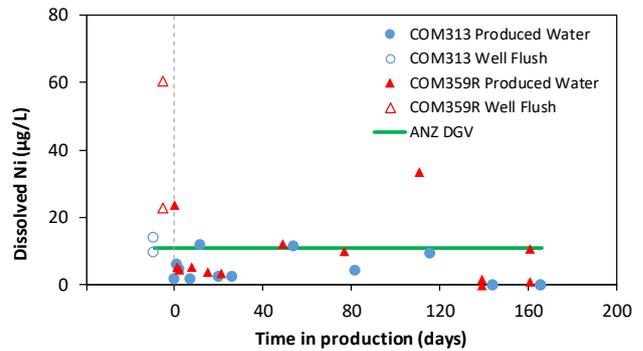
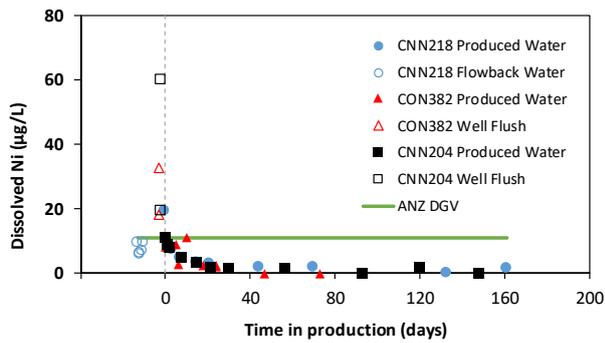
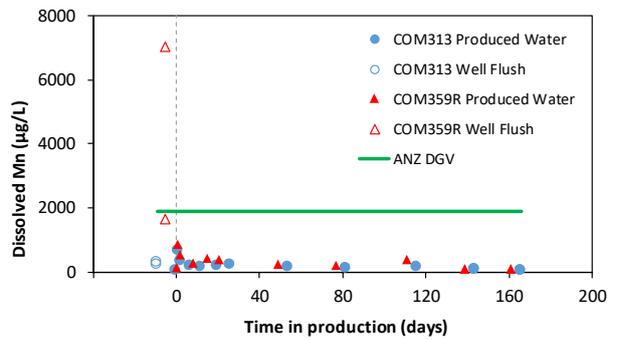
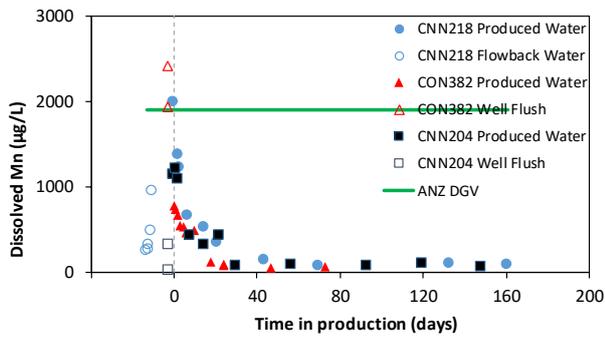


Figure 18 (continued) The concentrations of dissolved metals measured in flowback and produced waters sampled from CSG wells. The vertical dotted lines (time zero) indicate the start of well production and flow of produced water.

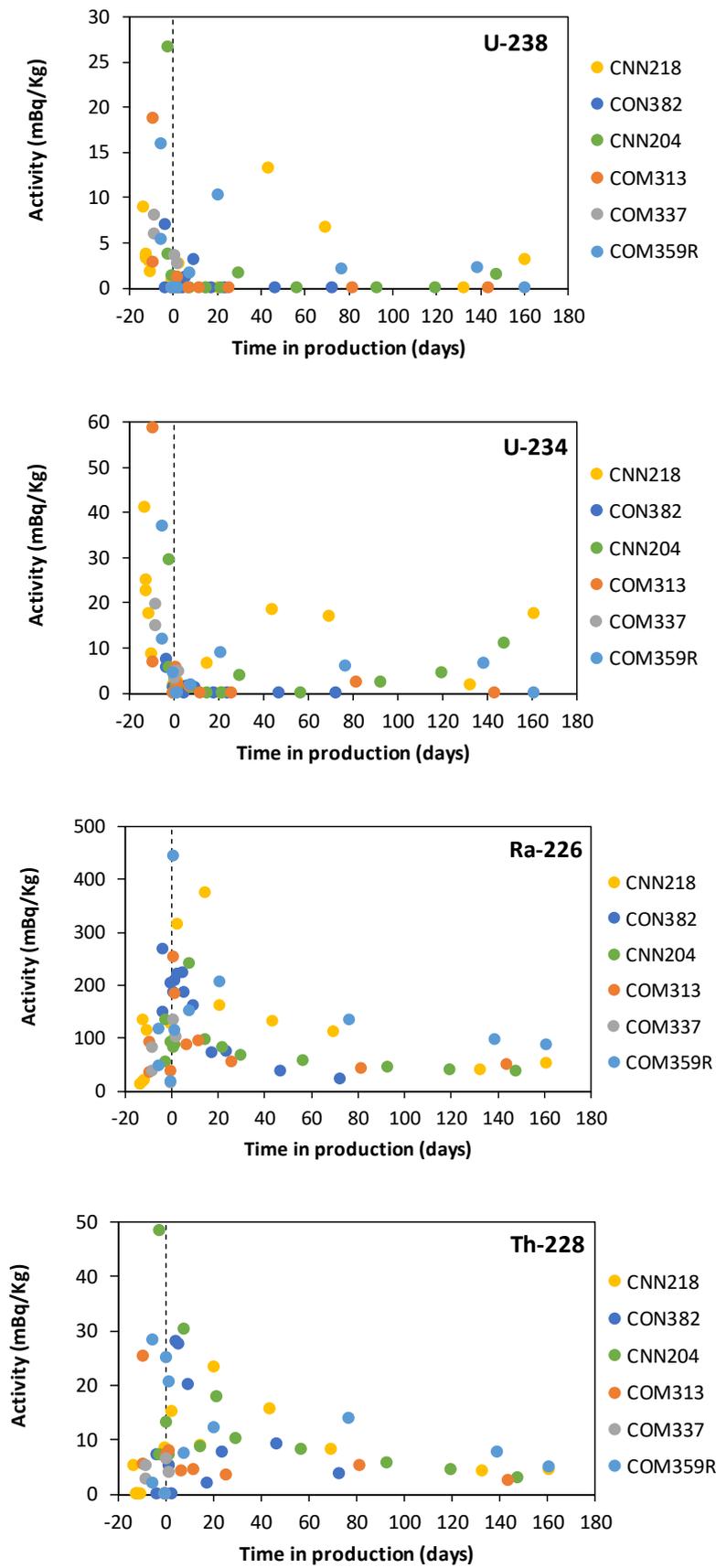


Figure 19 Radionuclide activities measured in flowback and produced waters sampled from the CSG wells. The vertical dotted lines (time zero) indicate the start of well production and flow of produced water.

### 5.3.3.1 Concentrations of HF organic chemicals

The chemical composition of the HF fluid used for the well stimulation was reasonably consistent across all of the wells studied (Table 9). Analyses conducted by CSIRO confirmed the presence of the key chemical components of the M275 biocide (MIT and CMIT) and the J318 breaker aid (triethanolamine) in the HF zone samples collected for each of the wells: CNN218, CNN204, CON382 and COM313. No zone samples were collected from COM359R.

Data for the HF-derived organic chemicals detected in well flushings, flowback and produced waters are summarised in Table 31 and Table 32. Apart from one sample, CMIT concentrations were below the limit of reporting in the produced waters (Table 31 and Table 32). MIT was not detected in water samples from Combabula and only sporadically at Condabri (Table 31 and Table 32, Figure 20). This would either suggest that these HF-derived organic chemicals were either breaking down within the coal seam, detained through sorption, or were sufficiently diluted in the produced water to be below their respective limits of reporting. Both MIT and CMIT have been reported to be readily degradable in water through hydrolytic, photochemical and biological actions (Krzeminski et al. 1975).

Triethanolamine (TEA) concentration versus time profiles for the wells at Condabri and Combabula are shown in Figure 21 and Figure 22. TEA was detected at wells from both sites with maximum concentrations generally occurring during well completion or the first twenty days of well production. After this period, TEA concentrations were below the limit of detection. A notable exception was well COM313 where TEA was detected in 4 out of the six samples taken after day 40. There is no clear explanation of why TEA was detected in these samples.

In the well samples from CNN 204 and CON 382, a number of fluorobenzoic acid (FBA) tracers were also quantified. FBAs are highly polar compounds and are used to represent the flow path of water injected for well stimulation. Ten tracers: 2-FBA, 3-FBA, 4-FBA, 2,3-DFBA, 2,4-DFBA, 2,5-DFBA, 2,6-DFBA, 3,4-DFBA, 3,5-DFBA, and 2,3,4,5-TTFBA were added to each well during well stimulation. However, quantification of only six of the tracers (3-FBA, 4-FBA, 2,4-DFBA, 2,5-DFBA, 2,6-DFBA, and 2,3,4,5-TTFBA) was possible due to lack of availability of analytical reference standards for 2-FBA, 2,3-DFBA, 3,4-DFBA and 3,5-DFBA.

In contrast to the HF organic chemicals, one or more of the FBA tracers were generally measurable in the produced water until the final collection date (Table 33, Figure 23). Peak FBA concentrations were observed during the first 20 days of production at both wells. Occasional spikes in FBA concentrations were observed at both wells over the remainder of the monitoring period (Table 33, Figure 23).

Table 31 TEA, MIT and CMIT concentrations measured in well samples from Condabri

Well	Date	Production Day	Water type	TEA µg/L	MIT µg/L	CMIT µg/L
<b>CNN218</b>	19/07/2017	-13	F	<10	<10	<10
	20/07/2017	-12	F	4720	59	<10
	20/07/2017	-12	F	<10	213	<10
	21/07/2017	-11	F	7470	352	<10
	22/07/2017	-10	F	1470	<10	<10
	1/08/2017	0	P	1890	<10	<10
	3/08/2017	2	P	<10	<10	<10
	4/08/2017	3	P	<10	<10	<10
	8/08/2017	7	P	2580	<10	<10
	16/08/2017	15	P	<10	<10	<10
	22/08/2017	21	P	<10	<10	<10
	14/09/2017	44	P	1740	177	67
	10/10/2017	70	P	<10	<10	<10
	12/12/2017	133	P	<10	<10	<10
	9/01/2018	161	P	<10	<10	<10
<b>CON382</b>	26/07/2017	-3	WF	2100	<10	<10
	26/07/2017	-3	WF	2160	<10	<10
	29/07/2017	0	P	2900	<10	<10
	30/07/2017	1	P	2770	<10	<10
	31/07/2017	2	P	3910	<10	<10
	1/08/2017	3	P	2480	<10	<10
	3/08/2017	5	P	1630	<10	<10
	4/08/2017	6	P	<10	<10	<10
	8/08/2017	10	P	<10	<10	<10
	16/08/2017	18	P	<10	<10	<10
	22/08/2017	24	P	<10	<10	<10
	22/08/2017	24	P	<10	<10	<10
	14/09/2017	47	P	<10	<10	<10
	10/10/2017	73	P	<10	<10	<10
	<b>CNN204</b>	12/08/2017	-2	WF	<10	<10
12/08/2017		-2	WF	<10	<10	<10
14/08/2017		0	P	<10	<10	<10
15/08/2017		1	P	<10	<10	<10
16/08/2017		2	P	<10	<10	<10
22/08/2017		8	P	2447	<10	<10
29/08/2017		15	P	113000	1986	<10
5/09/2017		22	P	91700	<10	<10
13/09/2017		30	P	422	<10	<10
10/10/2017		57	P	<10	<10	<10
15/11/2017		93	P	<10	<10	<10
12/12/2017		120	P	<10	<10	<10
9/01/2018	148	P	<10	<10	<10	

WF=well flushing, F=flowback, P=produced water

Table 32 TEA, MIT and CMIT concentrations measured in well samples from Combabula

Well	Date	Production Day	Water type	TEA µg/L	MIT µg/L	CMIT µg/L
<b>COM313</b>	10/10/2017	-9	WF	<10	<10	<10
	10/10/2017	-9	WF	447	<10	<10
	19/10/2017	0	P	<10	<10	<10
	20/10/2017	1	P	<10	<10	<10
	21/10/2017	2	P	<10	<10	<10
	26/10/2017	7	P	<10	<10	<10
	31/10/2017	12	P	<10	<10	<10
	8/11/2017	20	P	<10	<10	<10
	14/11/2017	26	P	<10	<10	<10
	12/12/2017	54	P	349	<10	<10
	9/01/2018	82	P	117	<10	<10
	12/02/2018	116	P	<10	<10	<10
	12/03/2018	144	P	<10	<10	<10
	12/03/2018	144	P	<10	<10	<10
	3/04/2018	166	P	177	<10	<10
3/04/2018	166	P	227	<10	<10	
<b>COM337</b>	12/10/2017	-8	WF	<10	<10	<10
	12/10/2017	-8	WF	<10	<10	<10
	20/10/2017	0	P	<10	<10	<10
	21/10/2017	1	P	<10	<10	<10
	22/10/2017	2	P	1390	<10	<10
<b>COM359R</b>	19/10/2017	-5	WF	<10	<10	<10
	19/10/2017	-5	WF	<10	<10	<10
	24/10/2017	0	P	<10	<10	<10
	25/10/2017	1	P	1760	<10	<10
	26/10/2017	2	P	<10	<10	<10
	1/11/2017	8	P	<10	<10	<10
	8/11/2017	15	P	<10	<10	<10
	14/11/2017	21	P	<10	<10	<10
	12/12/2017	49	P	<10	<10	<10
	9/01/2018	77	P	<10	<10	<10
	12/02/2018	111	P	<10	<10	<10
	12/03/2018	139	P	<10	<10	<10
	12/03/2018	139	P	<10	<10	<10
3/04/2018	161	P	<10	<10	<10	
3/04/2018	161	P	<10	<10	<10	

WF=well flushing, F=flowback, P=produced water

Table 33 Fluorobenzoic acid tracer concentrations measured in water samples from wells at Condabri

Well	Date	Production Day	Water type	3-FBA µg/L	4-FBA µg/L	2,4-DFBA µg/L	2,5-DFBA µg/L	2,6 DFBA µg/L	2,3,4,5-TFBA µg/L
CON382	26/07/2017	-3	WF	<10	<10	<10	<10	<10	<10
	26/07/2017	-3	WF	<10	<10	<10	<10	<10	<10
	29/07/2017	0	P	3229	943	710	75	3885	788
	30/07/2017	1	P	980	191	<10	<10	770	192
	31/07/2017	2	P	2445	832	693	207	4596	729
	1/08/2017	3	P	3110	3381	528	61	3291	559
	3/08/2017	5	P	328	386	218	<10	378	305
	4/08/2017	6	P	3034	4617	344	<10	1974	192
	8/08/2017	10	P	2353	5009	<10	<10	446	<10
	16/08/2017	18	P	1405	2305	53	<10	1725	580
	22/08/2017	24	P	1216	3603	<10	<10	107	<10
	22/08/2017	24	P	<10	<10	<10	<10	<10	<10
	14/09/2017	47	P	977	2982	<10	<10	<10	<10
	10/10/2017	73	P	<10	<10	<10	<10	<10	<10
CNN204	12/08/2017	-2	WF	233	257	<10	<10	<10	1062
	12/08/2017	-2	WF	<10	<10	<10	<10	211	63
	14/08/2017	0	P	<10	<10	<10	<10	434	222
	15/08/2017	1	P	<10	<10	496	1072	<10	<10
	16/08/2017	2	P	<10	<10	1548	313	1465	1804
	22/08/2017	8	P	<10	<10	2037	2086	2653	1044
	29/08/2017	15	P	<10	<10	1382	<10	2198	1113
	5/09/2017	22	P	<10	<10	<10	<10	625	493
	13/09/2017	30	P	<10	<10	<10	<10	2006	154
	10/10/2017	57	P	<10	<10	<10	<10	<10	<10
	15/11/2017	93	P	<10	<10	<10	<10	108	<10
	12/12/2017	120	P	59	37	<10	<10	<10	<10
	9/01/2018	148	P	588	623	<10	<10	546	<10

WF=well flushing, F=flowback, P=produced water



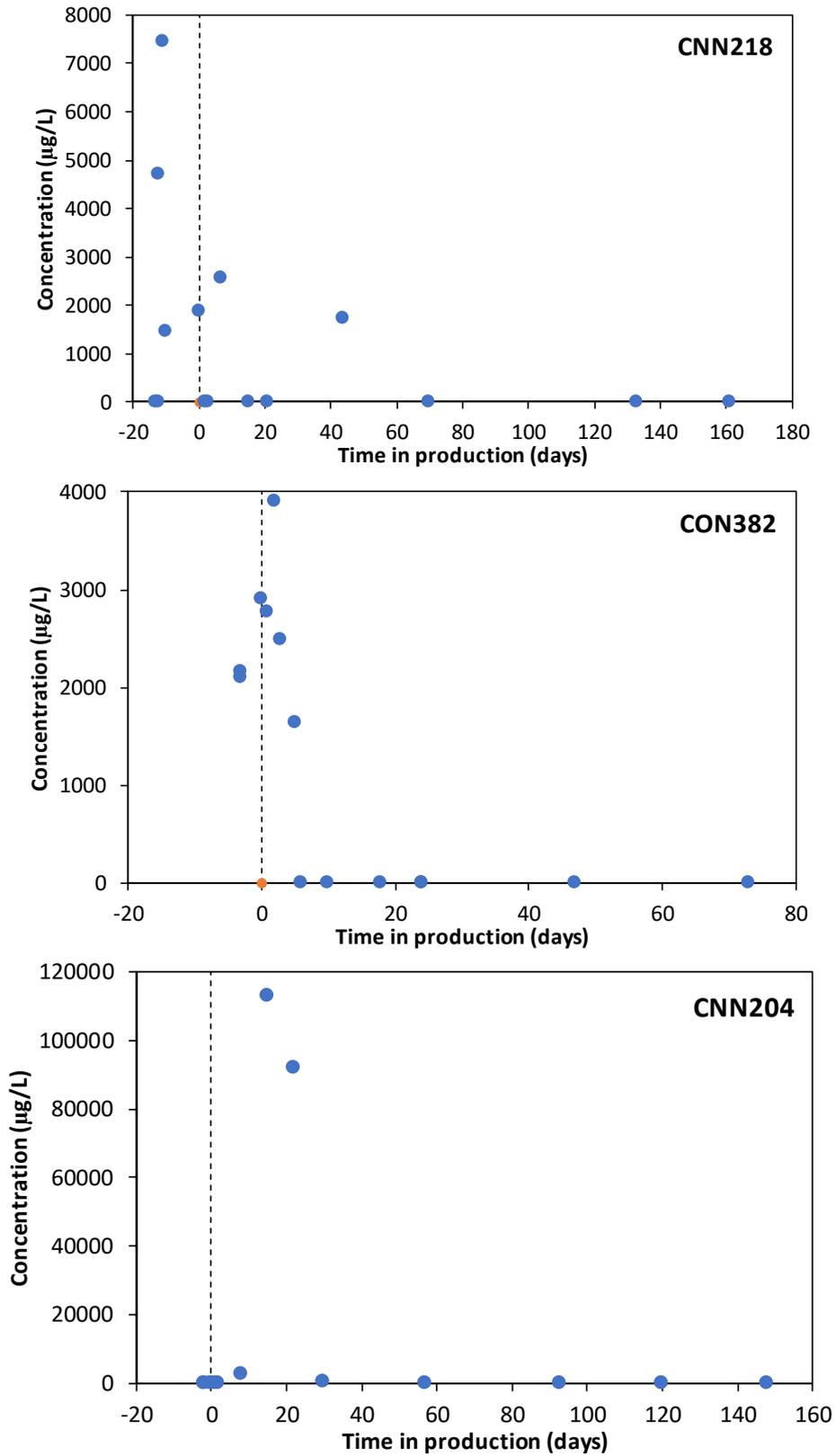


Figure 21 TEA concentrations in water samples from wells at Condabri. The vertical dotted lines (time zero) indicate the start of well production and flow of produced water.

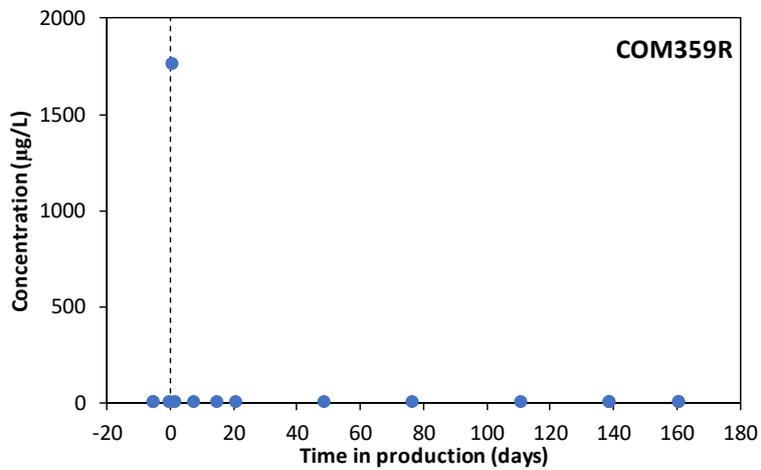
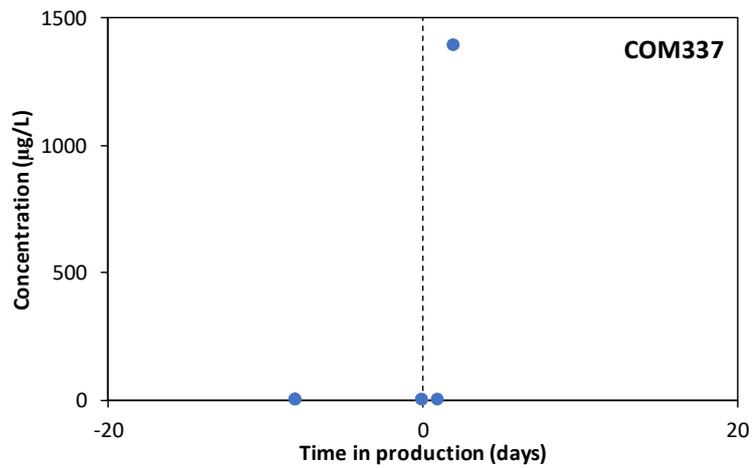
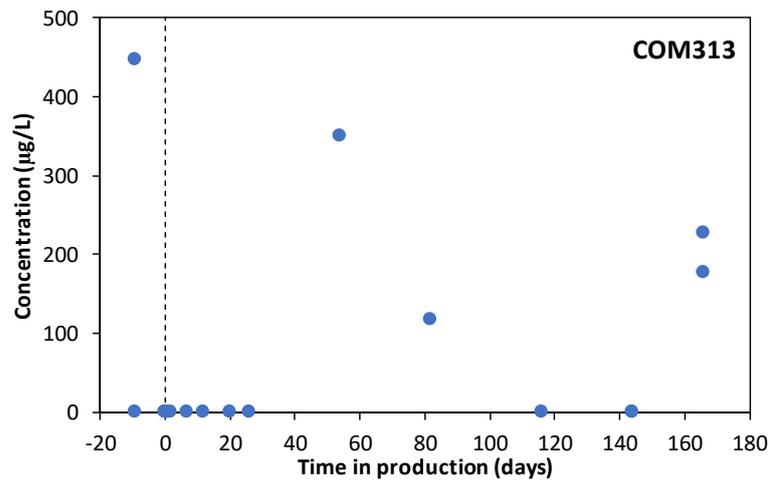


Figure 22 TEA concentrations in water samples from wells at Combabula. The vertical dotted lines (time zero) indicate the start of well production and flow of produced water.

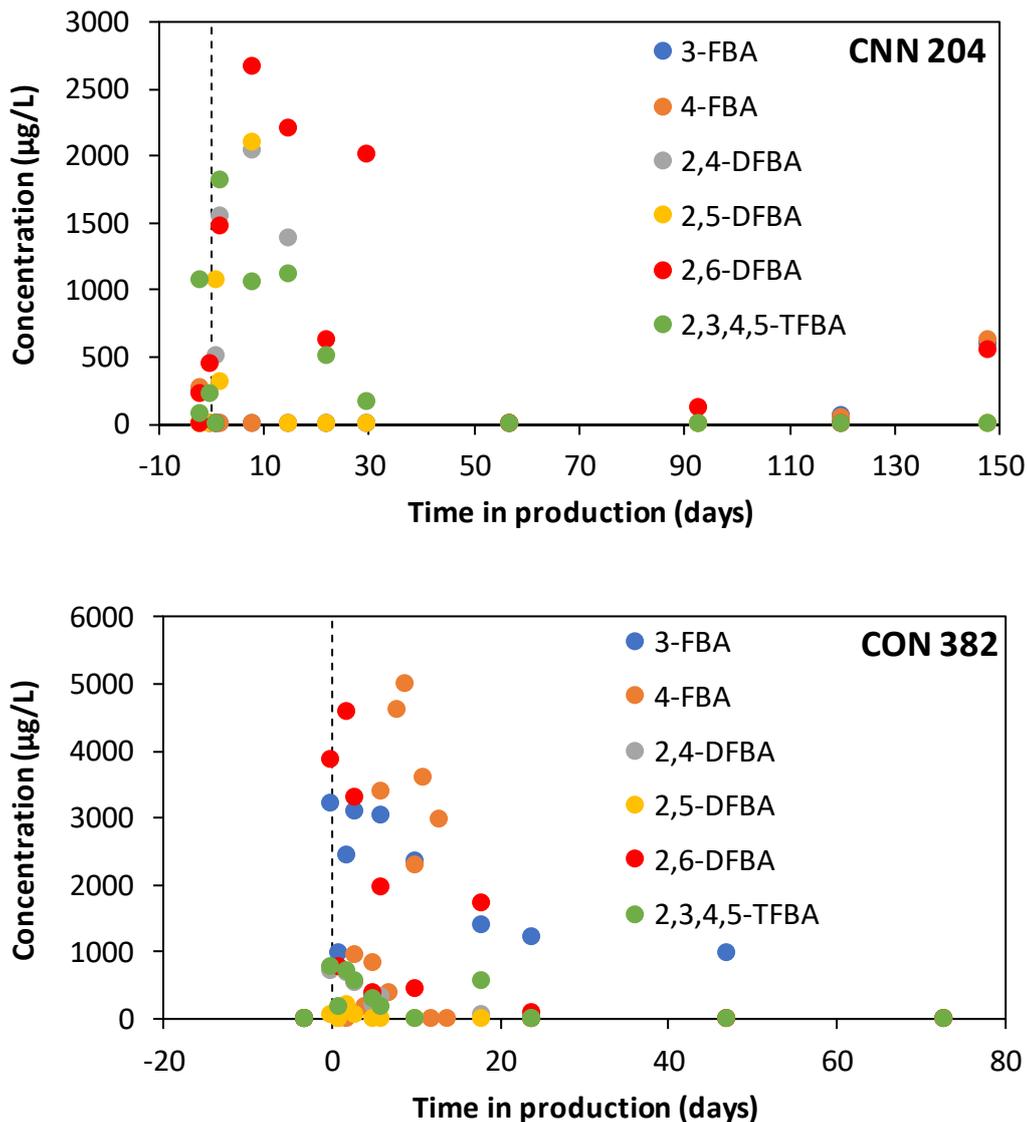


Figure 23 FBA tracer concentration measured in water samples from wells CNN 204 and CON 382. The vertical dotted lines (time zero) indicate the start of well production and flow of produced water.

### 5.3.3.2 Geogenic organic chemicals

A range of geogenic organic chemicals, including phenols, total recoverable hydrocarbons (TRHs) and benzene, toluene, ethylbenzene and xylene (BTEX), were quantified in water samples collected from the six monitored wells (Table 34 to Table 42). These chemicals were assigned as being of geogenic origin as they are not constituents of the HF fluids used at the wells. Similar to the inorganics and radionuclides data, the concentrations of the measured chemicals were generally greatest in the first 20 days and tapered off to lower or non-detectable concentrations after additional weeks of sampling (Figure 24 through to Figure 29). The extent of the decrease in concentration was dependent on the chemical, with each well behaving differently.

Various TRH fractions (C6 – C10, >C10 – C16, >C16 – C30, >C30 – C34) were also detected sporadically in water samples. However, the concentrations did not follow a time-dependent pattern (Table 34 and Table 35). The highest TRH concentrations were found in samples from

CON382 which is not surprising as the well was decommissioned after ten weeks owing to oil production.

Phenol concentrations are summarised in Table 36 and Table 37. Phenol was only quantifiable for 16 to 21 days at the Combabula wells, while it was quantifiable for up to 48 to 68 days at the Condabri sites. Out of the phenols that were measured, the 3- and 4-methyl-substituted phenols (also known as 3&4-cresols) were present at the highest concentrations and consistently measured in samples for a longer period of time at all sites compared with phenol (Figure 24 and Figure 25). Peak phenol concentrations typically occurred within the first 10 days of production, however, at CON382 the maximum was observed after 24 days.

Naphthalene concentrations were below the limit of reporting (<0.5 µg/L) in all samples collected from COM 337 and COM 59R. However, naphthalene was detected at the other wells mainly at the start of well operations (Figure 27).

BTEX concentrations are summarised in Table 38 and Table 39. BTEX concentrations were below limit of reporting in CNN 218 and CON 382. The pattern of relatively consistent concentrations in collected produced water was also apparent for various BTEX components at sites COM 313 and COM 359R for up to 90 days (Figure 26). After this period, however, the BTEX became non-detectable, although toluene was still measurable for up to 180 days at COM 313. It is important to note that BTEX chemicals are not components of HF fluids or drilling muds used in CSG operations in Queensland. The detected compounds are therefore of geogenic origin. This suggests that longer term monitoring studies may be necessary to effectively quantify organic geogenic chemicals in produced waters for understanding their potential downstream risks.

Another notable geogenic organic chemical was acetone, which had a similar pattern of concentrations reducing over time (Table 40 and Table 41). The highest acetone concentrations (up to 49 µg/L) were detected during well flushing and flowback. However, acetone was also detected in three out of five field blank samples (27, 28 and 56 µg/L), which makes it difficult to reliably draw conclusions on its concentrations in CSG waters. The acetone data is included as it displayed a consistent pattern with the highest concentrations being detected at the start of well operations. The presence of acetone is consistent with other studies assessing organics in flowback water from unconventional gas extraction activities (Luek and Gonsior 2017, Hayes 2009).

At some sites, a number of geogenic organic chemicals were still detectable in the final produced water sample collected at the end of the study. For example, toluene and 3&4-cresols were still being measured in produced water 177 days after production began at COM 313 (Figure 25 and Figure 26). In contrast, naphthalene was only detected at low concentrations in samples collected on days 13, 65 and 127 (Figure 27).

Other chemicals that were sporadically detected in samples with no apparent concentration dependence over time included 2,4-dimethylphenol, dichloromethane, 4-methyl-2-pentanone (MIBK), 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, trichloroethene and tetrachloroethene (Table 42). Generally, these chemicals were measured at concentrations close to their respective limits of reporting (LORs) (Table 42).

DGVs for the protection of environmental waters currently exist in Australia for only a limited range of organic contaminants (ANZG 2018). All organic chemicals that have guideline values (Table 43), had concentrations well below the relevant DGV values.

TOC and DOC were measured at concentrations of up to hundreds of mg/L in produced water samples (Table 10 to Table 15) whereas the corresponding concentrations of organic compounds quantified were nearly all in the  $\mu\text{g/L}$  range (Table 34 to Table 42). It is clear that the organic compounds that comprised the fraction of measured DOC that were not quantified by the targeted analyses of the more than 100 different geogenic and HF fluid-associated organic chemicals. This highlights that our current understanding of organic chemicals in produced water is extremely limited and further investigations are needed to better understand what organic compounds contribute to the high TOC and DOC load in the samples. Of critical importance is understanding the contribution of guar gum breakdown products to TOC loadings in produced waters. It is highly likely that some proportion of TOC observed during the first few weeks of well production is derived from guar gum which is the gel forming component of HFF.

**Table 34 Concentration of total recoverable hydrocarbon (TRH) fractions measured in well samples at Condabri**

Well	Date	Production day	Water type	C6 - C10 µg/L	>C10 - C16 µg/L	>C16 - C34 µg/L	>C34 - C40 µg/L
<b>CNN218</b>	19/07/2017	-13	F	<25	<25	<100	<100
	20/07/2017	-12	F	<25	<25	<100	<100
	20/07/2017	-12	F	<25	<25	<100	<100
	21/07/2017	-11	F	<25	<25	<100	<100
	22/07/2017	-10	F	77	<25	<100	<100
	1/08/2017	0	P	<25	<25	<100	<100
	3/08/2017	2	P	<25	570	420	<100
	4/08/2017	3	P	<25	430	<100	<100
	8/08/2017	7	P	<25	1600	11000	3100
	16/08/2017	15	P	<25	<25	<100	<100
	22/08/2017	21	P	<25	<25	<100	<100
	14/09/2017	44	P	<25	<25	<100	<100
	10/10/2017	70	P	<25	<25	<100	<100
	12/12/2017	133	P	<25	<25	<100	<100
	9/01/2018	161	P	<25	<25	<100	<100
<b>CON382</b>	26/07/2017	-3	WF	<25	710	2600	<100
	26/07/2017	-3	WF	110	42	180	<100
	29/07/2017	0	P	<25	7600	28000	3000
	30/07/2017	1	P	<25	1100	2500	<100
	31/07/2017	2	P	<25	850	2400	<100
	1/08/2017	3	P	<25	<25	<100	<100
	3/08/2017	5	P	<25	3500	15000	1700
	4/08/2017	6	P	<25	12000	46000	6400
	8/08/2017	10	P	<25	390	2000	260
	16/08/2017	18	P	<25	<25	<100	<100
	22/08/2017	24	P	<25	<25	<100	<100
	22/08/2017	24	P	<25	<25	<100	<100
	14/09/2017	47	P	<25	1700	7100	840
	10/10/2017	73	P	<25	170000	720000	72000
	<b>CNN204</b>	12/08/2017	-2	WF	<25	<25	<100
12/08/2017		-2	WF	<25	<25	<100	<100
14/08/2017		0	P	<25	32	<100	<100
15/08/2017		1	P	<25	<25	<100	<100
16/08/2017		2	P	<25	<25	<100	<100
22/08/2017		8	P	<25	<25	<100	<100
29/08/2017		15	P	<25	<25	<100	<100
5/09/2017		22	P	<25	<25	<100	<100
13/09/2017		30	P	<25	<25	<100	<100
10/10/2017		57	P	<25	<25	<100	<100
15/11/2017		93	P	<25	<25	<100	<100
12/12/2017		120	P	<25	<25	<100	<100
9/01/2018	148	P	<25	<25	<100	<100	

WF=well flushing, F=flowback, P=produced water

Table 35 Concentration of total recoverable hydrocarbon (TRH) fractions measured in well samples at Combabula

Well	Date	Production day	Water type	C6 - C10 µg/L	>C10 - C16 µg/L	>C16 - C34 µg/L	>C34 - C40 µg/L
<b>COM313</b>	10/10/2017	-9	WF	<25	<25	<100	<100
	10/10/2017	-9	WF	<25	<25	<100	<100
	19/10/2017	0	P	38	1400	110	<100
	20/10/2017	1	P	91	<25	<100	<100
	21/10/2017	2	P	68	<25	<100	<100
	26/10/2017	7	P	<25	<25	<100	<100
	31/10/2017	12	P	61	<25	770	420
	8/11/2017	20	P	<25	<25	<100	<100
	14/11/2017	26	P	<25	<25	<100	<100
	12/12/2017	54	P	<25	<25	<100	<100
	9/01/2018	82	P	32	<25	<100	<100
	12/02/2018	116	P	<25	<25	<100	<100
	12/03/2018	144	P	<25	<25	<100	<100
	12/03/2018	144	P	<25	<25	<100	<100
	3/04/2018	166	P	<25	<25	<100	<100
	3/04/2018	166	P	<25	<25	<100	<100
<b>COM337</b>	12/10/2017	-8	WF	<25	<25	<100	<100
	12/10/2017	-8	WF	<25	<25	<100	<100
	20/10/2017	0	P	91	970	<100	<100
	21/10/2017	1	P	28	<25	<100	<100
	22/10/2017	2	P	<25	<25	<100	<100
<b>COM359R</b>	19/10/2017	-5	WF	<25	<25	<100	<100
	19/10/2017	-5	WF	<25	<25	<100	<100
	24/10/2017	0	P	76	380	<100	<100
	25/10/2017	1	P	65	<25	<100	<100
	26/10/2017	2	P	45	<25	<100	<100
	1/11/2017	8	P	90	<25	1000	530
	8/11/2017	15	P	<25	<25	<100	<100
	14/11/2017	21	P	<25	<25	<100	<100
	12/12/2017	49	P	<25	<25	<100	<100
	9/01/2018	77	P	<25	<25	<100	<100
	12/02/2018	111	P	<25	<25	<100	<100
	12/03/2018	139	P	<25	<25	<100	<100
	12/03/2018	139	P	<25	<25	<100	<100
3/04/2018	161	P	<25	<25	<100	<100	
3/04/2018	161	P	<25	<25	<100	<100	

WF=well flushing, F=flowback, P=produced water

Table 36 Concentrations of phenols measured in well samples from Condabri

Well	Date	Production day	Water type	Phenol µg/L	3-& 4- Methylphenols µg/L	2,4- Dimethylphenol µg/L	4-Chloro-3- methylphenol µg/L
<b>CNN218</b>	19/07/2017	-13	F	<1	<2	<1	<2
	20/07/2017	-12	F	<1	<2	<1	<2
	20/07/2017	-12	F	<1	<2	<1	<2
	21/07/2017	-11	F	<1	<2	<1	<2
	22/07/2017	-10	F	<1	<2	<1	<2
	1/08/2017	0	P	<1	<2	<1	<2
	3/08/2017	2	P	5.3	74	<1	9.4
	4/08/2017	3	P	5.8	89	<1	6.6
	8/08/2017	7	P	11	130	<1	<2
	16/08/2017	15	P	8.4	110	<1	<2
	22/08/2017	21	P	8	84	<1	<2
	14/09/2017	44	P	5.9	23	<1	<2
	10/10/2017	70	P	3.1	27	<1	<2
	12/12/2017	133	P	<1	13	<1	<2
	9/01/2018	161	P	<1	<2	<1	<2
<b>CON382</b>	26/07/2017	-3	WF	1.1	<2	<1	<2
	26/07/2017	-3	WF	1.9	6	<1	<2
	29/07/2017	0	P	1.7	6	<1	<2
	30/07/2017	1	P	6.5	14	<1	<2
	31/07/2017	2	P	9.7	28	<1	<2
	1/08/2017	3	P	<1	<2	<1	<2
	3/08/2017	5	P	5.7	18	<1	<2
	4/08/2017	6	P	3.9	25	<1	<2
	8/08/2017	10	P	12.0	86	<1	<2
	16/08/2017	18	P	13	51	<1	<2
	22/08/2017	24	P	9.8	95	<1	<2
	22/08/2017	24	P	9.8	79	<1	<2
	14/09/2017	47	P	4	17	<1	<2
	10/10/2017	73	P	<1	<2	<1	<2
	<b>CNN204</b>	12/08/2017	-2	WF	1.0	2	<1
12/08/2017		-2	WF	7.6	3	<1	<2
14/08/2017		0	P	14	2	1.6	<2
15/08/2017		1	P	6.7	27	<1	<2
16/08/2017		2	P	6.3	57	<1	<2
22/08/2017		8	P	5.4	95	<1	<2
29/08/2017		15	P	6.8	14	<1	<2
5/09/2017		22	P	4.4	9	<1	<2
13/09/2017		30	P	4.2	7	<1	<2
10/10/2017		57	P	3.8	14	<1	<2
15/11/2017		93	P	<1	<2	<1	<2
12/12/2017		120	P	<1	10	<1	<2
9/01/2018	148	P	<1	6	<1	<2	

WF=well flushing, F=flowback, P=produced water

Table 37 Concentration of phenols measured in well samples from Combabula

Well	Date	Production day	Water type	Phenol µg/L	3-& 4- Methylphenols µg/L	2,4- Dimethylphenol µg/L	4-Chloro-3- methylphenol µg/L
COM313	10/10/2017	-9	WF	<1	<2	<1	<2
	10/10/2017	-9	WF	<1	<2	<1	<2
	19/10/2017	0	P	5	<2	<1	<2
	20/10/2017	1	P	13	300	2.2	<2
	21/10/2017	2	P	12	270	1.6	<2
	26/10/2017	7	P	7	<2	<1	<2
	31/10/2017	12	P	5	110	2.0	<2
	8/11/2017	20	P	3	57	1.2	<2
	14/11/2017	26	P	<1	30	<1	<2
	12/12/2017	54	P	<1	39	<1	<2
	9/01/2018	82	P	<1	20	1.1	<2
	12/02/2018	116	P	<1	22	5.4	<2
	12/03/2018	144	P	<1	12	<1	<2
	12/03/2018	144	P	<1	13	<1	<2
	3/04/2018	166	P	<1	9	<1	<2
	3/04/2018	166	P	<1	8	<1	<2
COM337	12/10/2017	-8	WF	1.9	<2	<1	<2
	12/10/2017	-8	WF	1.4	<2	<1	<2
	20/10/2017	0	P	12	<2	<1	<2
	21/10/2017	1	P	3.8	72	<1	<2
	22/10/2017	2	P	2.9	60	<1	<2
COM359R	19/10/2017	-5	WF	1.3	<2	<1	<2
	19/10/2017	-5	WF	<1	<2	<1	<2
	24/10/2017	0	P	<1	<2	<1	<2
	25/10/2017	1	P	9.4	64	4	<2
	26/10/2017	2	P	7.7	70	3	<2
	1/11/2017	8	P	3.5	78	2	<2
	8/11/2017	15	P	3.3	76	1.2	<2
	14/11/2017	21	P	<1	30	<1	<2
	12/12/2017	49	P	<1	29	<1	<2
	9/01/2018	77	P	<1	13	<1	<2
	12/02/2018	111	P	<1	19	4.2	<2
	12/03/2018	139	P	<1	9.6	<1	<2
	12/03/2018	139	P	<1	8	<1	<2
	3/04/2018	161	P	<1	5.1	<1	<2
3/04/2018	161	P	<1	5	<1	<2	

WF=well flushing, F=flowback, P=produced water

Table 38 BTEX concentrations in well samples from Condabri

Well	Date	Production day	Water type	Benzene µg/L	Toluene µg/L	Ethylbenzene µg/L	m & p-Xylenes µg/L	o-Xylene µg/L
CNN218	19/07/2017	-13	F	<1	<1	<1	<2	<1
	20/07/2017	-12	F	<1	<1	<1	<2	<1
	20/07/2017	-12	F	<1	<1	<1	<2	<1
	21/07/2017	-11	F	<1	<1	<1	<2	<1
	22/07/2017	-10	F	<1	<1	<1	<2	<1
	1/08/2017	0	P	<1	<1	<1	<2	<1
	3/08/2017	2	P	<1	<1	<1	<2	1.1
	4/08/2017	3	P	<1	<1	<1	<2	<1
	8/08/2017	7	P	<1	<1	<1	<2	<1
	16/08/2017	15	P	<1	<1	<1	<1	<1
	22/08/2017	21	P	<1	<1	<1	<2	<1
	14/09/2017	44	P	<1	<1	<1	<2	<1
	10/10/2017	70	P	<1	<1	<1	<2	<1
	12/12/2017	133	P	<1	<1	<1	<2	<1
	9/01/2018	161	P	<1	<1	<1	<2	<1
CON382	26/07/2017	-3	WF	<1	<1	<1	<2	<1
	26/07/2017	-3	WF	<1	<1	<1	<2	<1
	29/07/2017	0	P	<1	<1	<1	<2	<1
	30/07/2017	1	P	<1	<1	<1	<2	<1
	31/07/2017	2	P	<1	<1	<1	<2	<1
	1/08/2017	3	P	<1	<1	<1	<2	<1
	3/08/2017	5	P	<1	<1	<1	<2	<1
	4/08/2017	6	P	<1	<1	<1	<2	<1
	8/08/2017	10	P	<1	<1	<1	<2	<1
	16/08/2017	18	P	<1	<1	<1	<1	<1
	22/08/2017	24	P	<1	<1	<1	<2	<1
	22/08/2017	24	P	<1	<1	<1	<2	<1
	14/09/2017	47	P	<1	<1	<1	<2	<1
	10/10/2017	73	P	<1	<1	<1	<2	<1
	CNN204	12/08/2017	-2	WF	2.5	2.3	<1	<2
12/08/2017		-2	WF	2.5	2.2	<1	<2	<1
14/08/2017		0	P	<1	<1	<1	5.3	2.4
15/08/2017		1	P	<1	<1	<1	2.1	<1
16/08/2017		2	P	<1	<1	<1	<1	<1
22/08/2017		8	P	<1	<1	<1	<2	<1
29/08/2017		15	P	<1	<1	<1	<2	<1
5/09/2017		22	P	<1	<1	<1	<2	<1
13/09/2017		30	P	<1	<1	<1	<2	<1
10/10/2017		57	P	<1	<1	<1	<2	<1
15/11/2017		93	P	<1	<1	<1	<2	<1
12/12/2017		120	P	<1	<1	<1	<2	<1
9/01/2018	148	P	<1	<1	<1	<2	<1	

WF=well flushing, F=flowback, P=produced water

Table 39 BTEX concentrations in well samples from Combabula

Well	Date	Production day	Water type	Benzene µg/L	Toluene µg/L	Ethylbenzene µg/L	m & p-Xylenes µg/L	o-Xylene µg/L
COM313	10/10/2017	-9	WF	<1	<1	<1	<2	<1
	10/10/2017	-9	WF	<1	<1	<1	<2	<1
	19/10/2017	0	P	<1	<1	3	22	6.3
	20/10/2017	1	P	1.8	5.8	<1	2.6	1.1
	21/10/2017	2	P	2.8	8.2	<1	5.2	2.1
	26/10/2017	7	P	1.6	4.7	<1	<2	<1
	31/10/2017	12	P	3.4	9.9	1.2	5.6	2.4
	8/11/2017	20	P	1.9	5.2	<1	2.3	1
	14/11/2017	26	P	1.9	6.5	<1	3.2	1.2
	12/12/2017	54	P	2.9	10	1.3	6.5	2.1
	9/01/2018	82	P	5.7	13	1.8	7	4.1
	12/02/2018	116	P	2	3.4	<1	1.6	1.1
	12/03/2018	144	P	<1	1.5	<1	<2	<1
	12/03/2018	144	P	<1	1.5	<1	<2	<1
	3/04/2018	166	P	<1	1.4	<1	<2	<1
	3/04/2018	166	P	<1	1.4	<1	<2	<1
COM337	12/10/2017	-8	WF	<1	<1	<1	<2	<1
	12/10/2017	-8	WF	<1	<1	<1	<2	<1
	20/10/2017	0	P	<1	<1	1.5	15	6.5
	21/10/2017	1	P	<1	1.7	<1	<2	<1
	22/10/2017	2	P	<1	<1	<1	<2	<1
COM359R	19/10/2017	-5	WF	3	3	<1	<2	<1
	19/10/2017	-5	WF	<1	<1	<1	<2	<1
	24/10/2017	0	P	<1	3.6	3.5	21	7
	25/10/2017	1	P	3	6	1	6	2
	26/10/2017	2	P	2	5	<1	4	1
	1/11/2017	8	P	2	6	4	29	8
	8/11/2017	15	P	1.3	3.1	<1	<2	<1
	14/11/2017	21	P	2	6	<1	5	1
	12/12/2017	49	P	2.5	7.3	1.2	6.9	2.1
	9/01/2018	77	P	4.1	6.1	1.4	6.9	3.5
	12/02/2018	111	P	1.6	1.5	<1	4.5	1.3
	12/03/2018	139	P	<1	<1	<1	<2	<1
	12/03/2018	139	P	<1	<1	<1	<2	<1
3/04/2018	161	P	<1	<1	<1	<2	<1	
3/04/2018	161	P	<1	<1	<1	<2	<1	

WF=well flushing, F=flowback, P=produced water

Table 40 Acetone and naphthalene concentrations in well samples from Condabri

Well	Date	Production day	Water type	Naphthalene µg/L	Acetone µg/L
CNN218	19/07/2017	-13	F	<0.5	29
	20/07/2017	-12	F	<0.5	39
	20/07/2017	-12	F	<0.5	49
	21/07/2017	-11	F	<0.5	49
	22/07/2017	-10	F	<0.5	44
	1/08/2017	0	P	1.3	<10
	3/08/2017	2	P	0.9	10
	4/08/2017	3	P	<0.5	<10
	8/08/2017	7	P	<0.5	14
	16/08/2017	15	P	<0.5	38
	22/08/2017	21	P	<0.5	13
	14/09/2017	44	P	<0.5	<10
	10/10/2017	70	P	<0.5	<10
	12/12/2017	133	P	<0.5	<10
	9/01/2018	161	P	<0.5	<10
CON382	26/07/2017	-3	WF	<0.5	30
	26/07/2017	-3	WF	2.2	45
	29/07/2017	0	P	0.5	15
	30/07/2017	1	P	<0.5	20
	31/07/2017	2	P	<0.5	16
	1/08/2017	3	P	<0.5	<10
	3/08/2017	5	P	<0.5	10
	4/08/2017	6	P	<0.5	13
	8/08/2017	10	P	<0.5	11
	16/08/2017	18	P	<0.5	<10
	22/08/2017	24	P	<0.5	13
	22/08/2017	24	P	<0.5	11
	14/09/2017	47	P	<0.5	<10
	10/10/2017	73	P	<0.5	15
	CNN204	12/08/2017	-2	WF	1.5
12/08/2017		-2	WF	0.5	11
14/08/2017		0	P	0.7	38
15/08/2017		1	P	1.3	15
16/08/2017		2	P	1.1	<10
22/08/2017		8	P	<0.5	12
29/08/2017		15	P	<0.5	<10
5/09/2017		22	P	<0.5	11
13/09/2017		30	P	<0.5	<10
10/10/2017		57	P	<0.5	<10
15/11/2017		93	P	<0.5	<10
12/12/2017		120	P	<0.5	<10
9/01/2018	148	P	<0.5	<10	

WF=well flushing, F=flowback, P=produced water

Table 41 Acetone and naphthalene concentrations in well samples from Combabula

Well	Date	Production day	Water type	Naphthalene µg/L	Acetone µg/L
<b>COM313</b>	10/10/2017	-9	WF	<0.5	14
	10/10/2017	-9	WF	<0.5	18
	19/10/2017	0	P	<0.5	17
	20/10/2017	1	P	<0.5	94
	21/10/2017	2	P	<0.5	70
	26/10/2017	7	P	<0.5	49
	31/10/2017	12	P	0.7	33
	8/11/2017	20	P	<0.5	41
	14/11/2017	26	P	<0.5	27
	12/12/2017	54	P	0.6	35
	9/01/2018	82	P	<0.5	15
	12/02/2018	116	P	0.6	24
	12/03/2018	144	P	<0.5	<10
	12/03/2018	144	P	<0.5	<10
	3/04/2018	166	P	<0.5	<10
3/04/2018	166	P	<0.5	<10	
<b>COM337</b>	12/10/2017	-8	WF	<0.5	<10
	12/10/2017	-8	WF	<0.5	22
	20/10/2017	0	P	<0.5	52
	21/10/2017	1	P	<0.5	41
	22/10/2017	2	P	<0.5	<10
<b>COM359R</b>	19/10/2017	-5	WF	<0.5	92
	19/10/2017	-5	WF	<0.5	42
	24/10/2017	0	P	<0.5	20
	25/10/2017	1	P	<0.5	66
	26/10/2017	2	P	<0.5	61
	1/11/2017	8	P	<0.5	38
	8/11/2017	15	P	<0.5	56
	14/11/2017	21	P	<0.5	26
	12/12/2017	49	P	<0.5	42
	9/01/2018	77	P	<0.5	20
	12/02/2018	111	P	<0.5	16
	12/03/2018	139	P	<0.5	<10
	12/03/2018	139	P	<0.5	<10
	3/04/2018	161	P	<0.5	10
3/04/2018	161	P	<0.5	13	

WF=well flushing, F=flowback, P=produced water

**Table 42 Organic compounds occasionally detected in well samples**

<b>Compound</b>	<b>Number of detects</b>	<b>% of total number of samples</b>	<b>Maximum concentration µg/L</b>	<b>Limit of reporting µg/L</b>
Tetrachloroethene	11	14	25	1
Ethylbenzene	10	13	4.3	1
1,2,4-Trimethylbenzene	5	6	5.9	1
4-Methyl-2-pentanone (MIBK)	5	6	30	10
Trichloroethene	4	5	2.7	1
1,3,5-Trimethylbenzene	3	4	2.4	1
Dichloromethane	3	4	2.8	1
4-Chloro-3-methylphenol	2	3	9.4	2
2,4-Dimethyphenol	12	15	5.4	1

**Table 43 Australia and New Zealand freshwater quality guideline values for the organic compounds detected in well samples**

<b>Compound</b>	<b>ANZG DGV µg/L</b>
Phenol	320
Benzene	950
m- and p-Xylenes	200
o-Xylene	350
Naphthalene	16

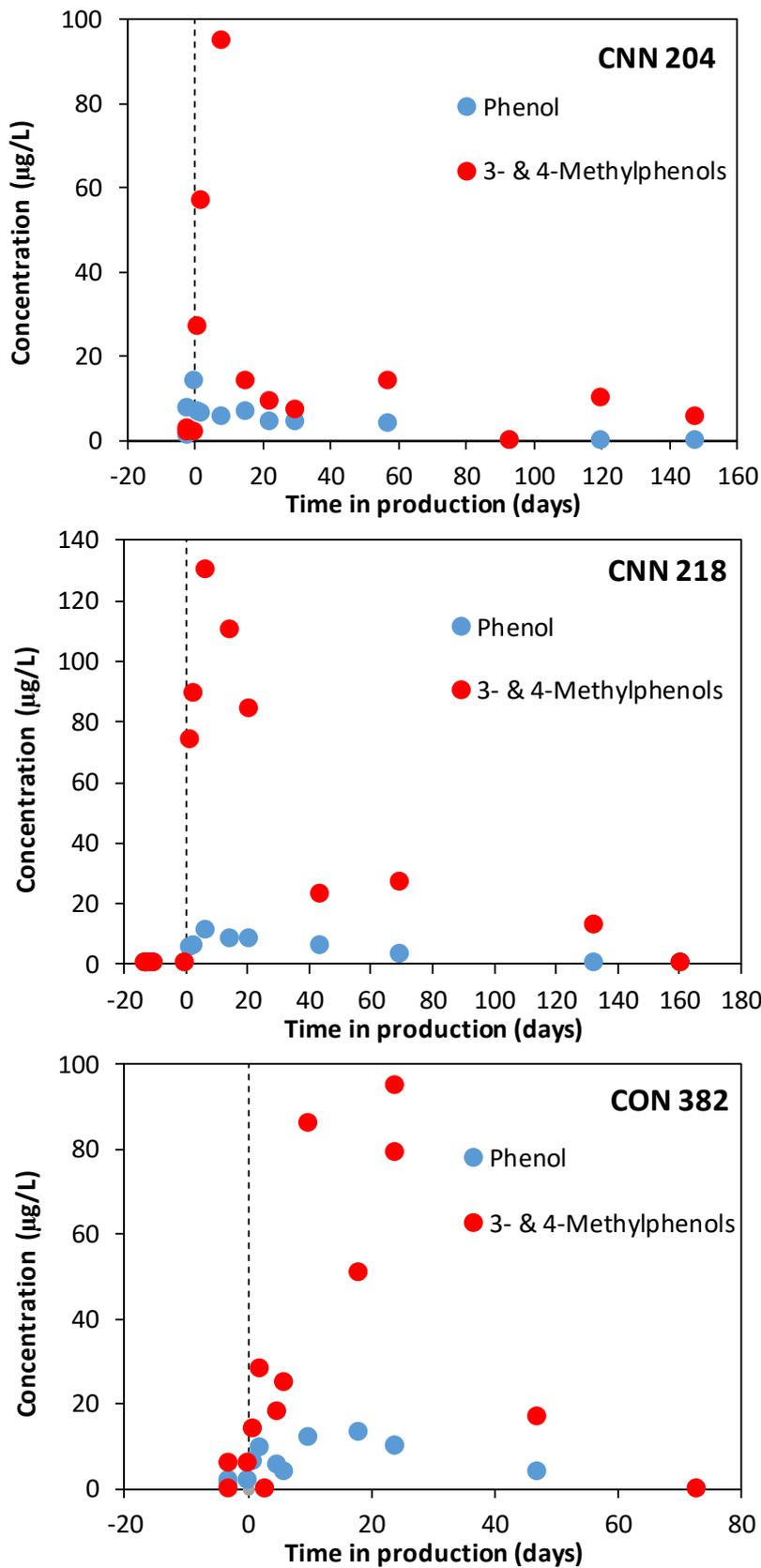


Figure 24 Phenol and 3&4-methylphenol concentrations measured in water samples from the CSG wells at Condabri. The vertical dotted lines (time zero) indicate the start of well production and flow of produced water.

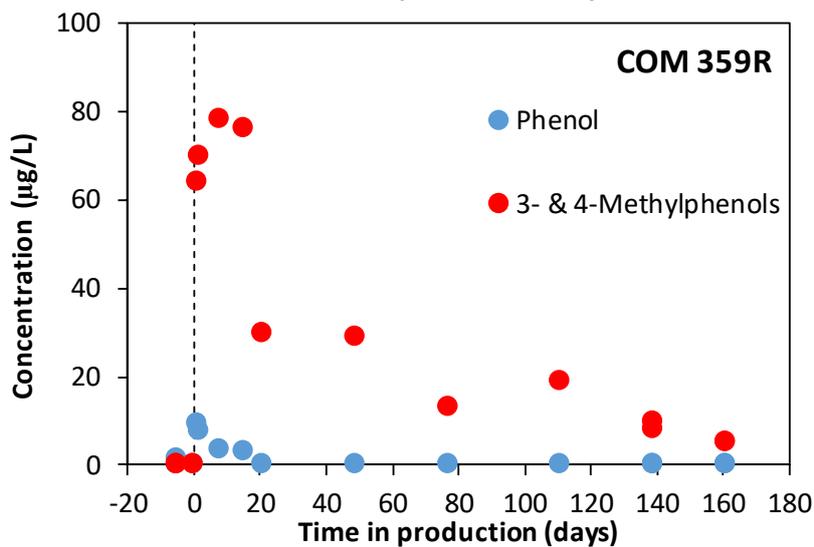
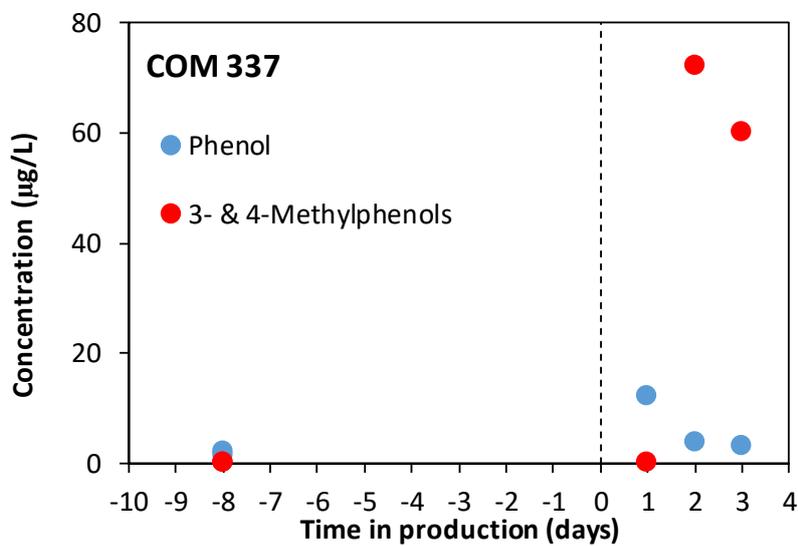
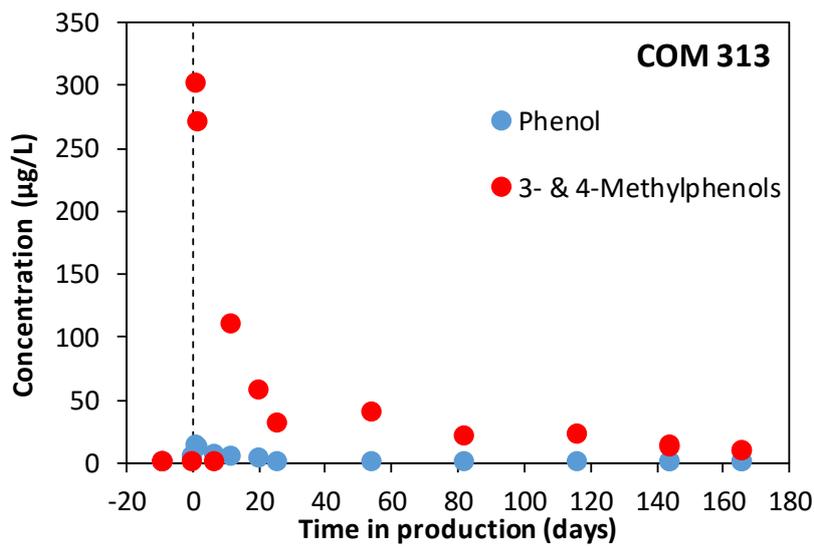


Figure 25 Phenol and 3&4-methylphenol concentrations measured in water samples from the CSG wells at Combabula. The vertical dotted lines (time zero) indicate the start of well production and flow of produced water.

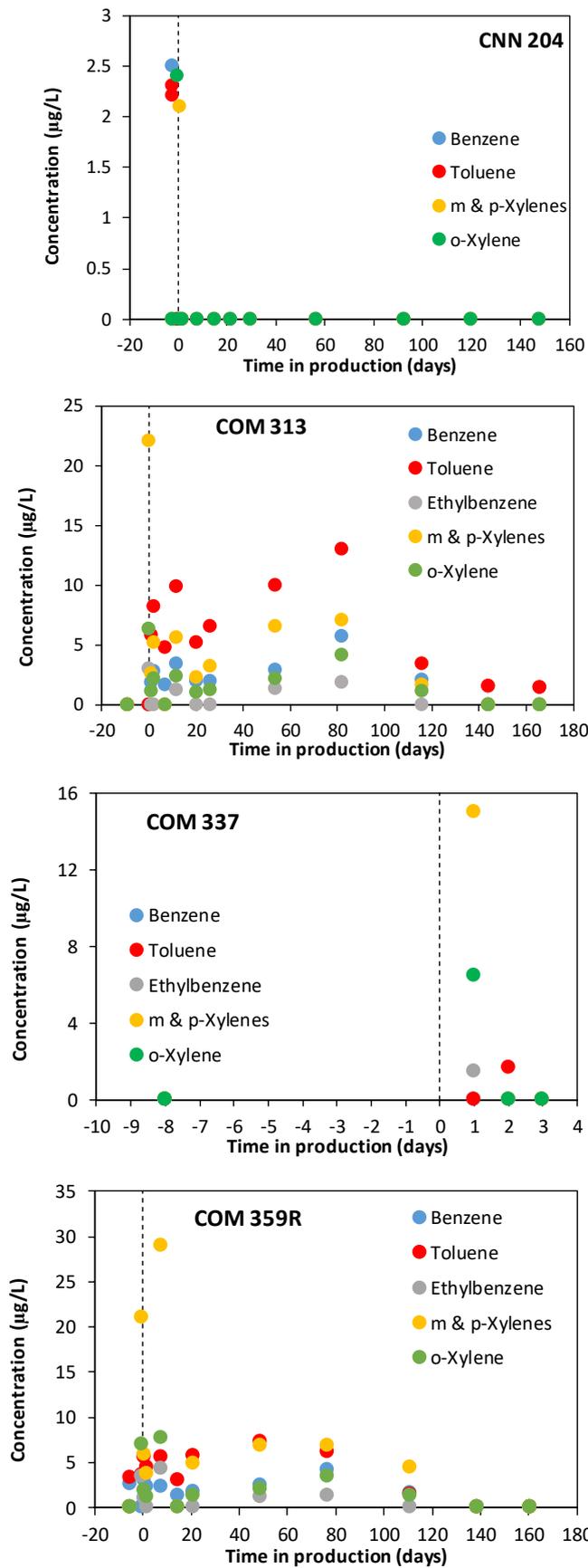
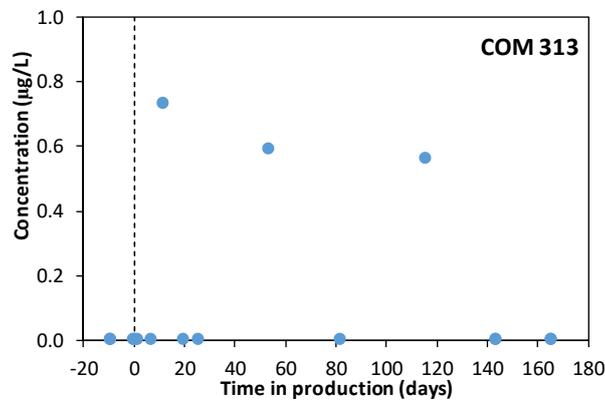
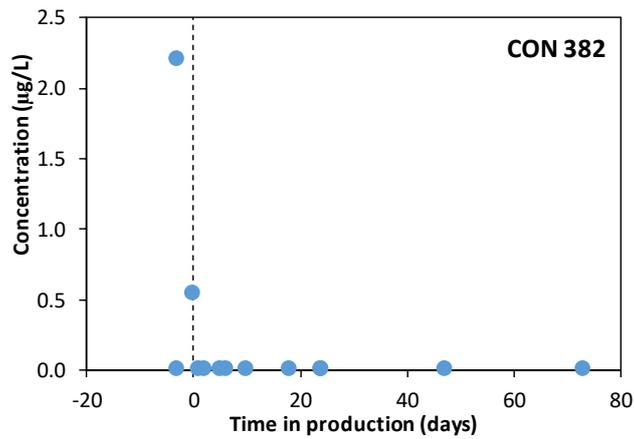
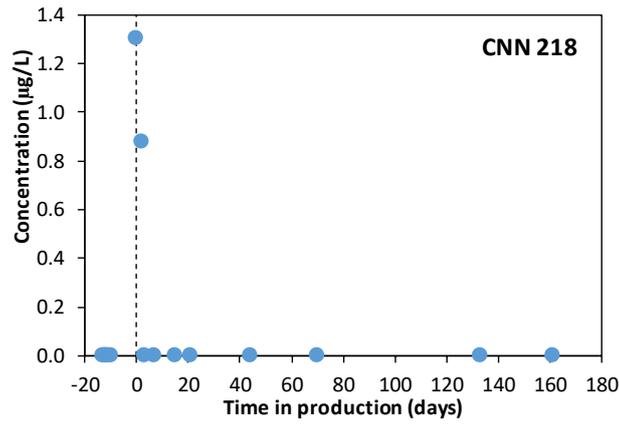
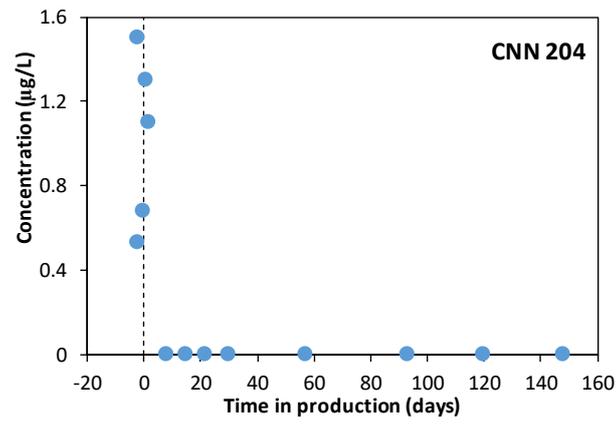


Figure 26 Summary of concentrations of benzene, toluene, ethylbenzene and xylenes (BTEX) concentrations in CNN 204, COM 313, COM 337 and COM 359R. The vertical dotted lines (time zero) indicate the start of well production and flow of produced water.



**Figure 27 Summary of concentrations of naphthalene measured in four wells: CNN 204, CNN 218, CON 382 and COM 313. The vertical dotted lines (time zero) indicate the start of well production and flow of produced water.**

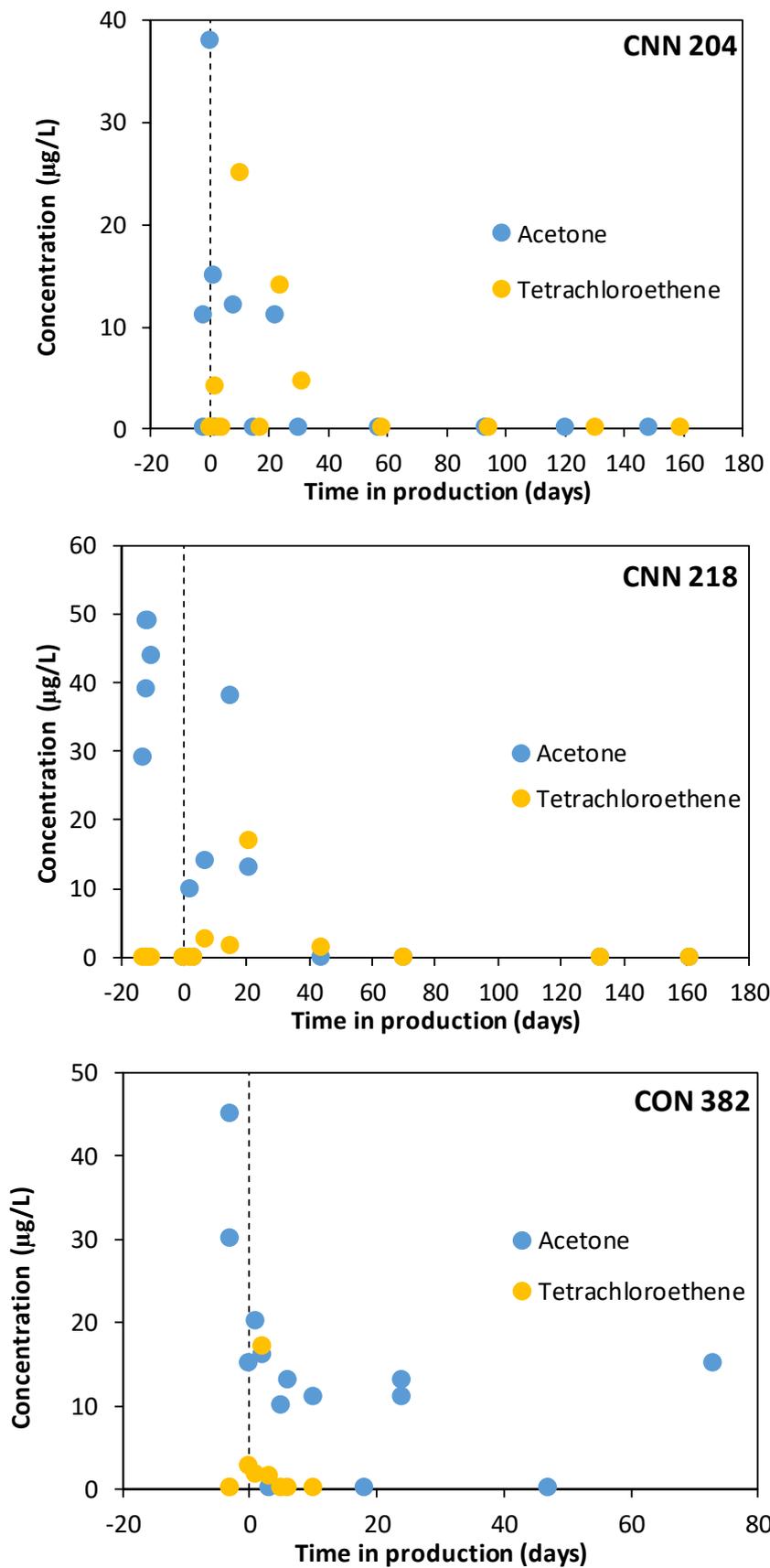


Figure 28 Acetone and tetrachloroethene concentrations in the CSG well samples from Condabri. The vertical dotted lines (time zero) indicate the start of well production and flow of produced water.

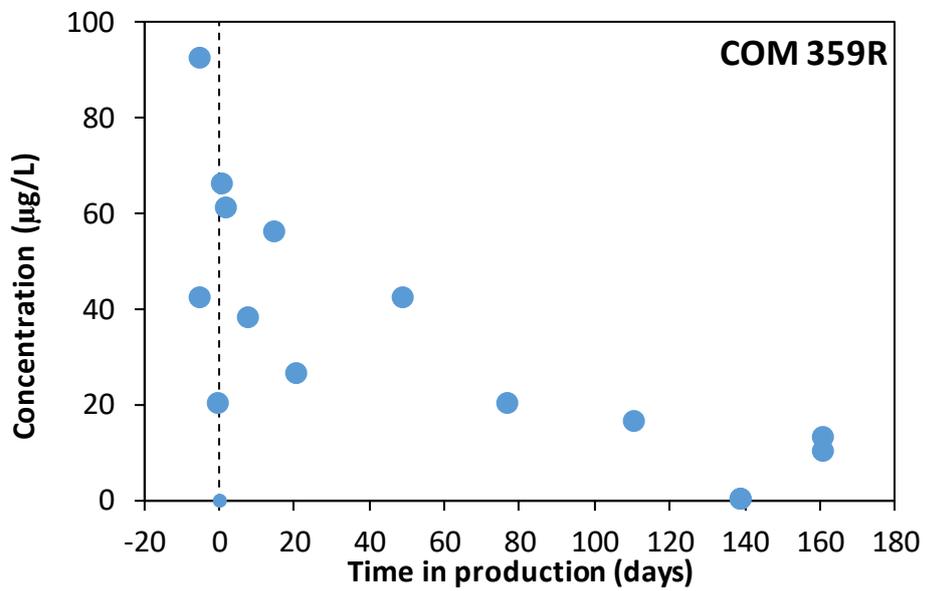
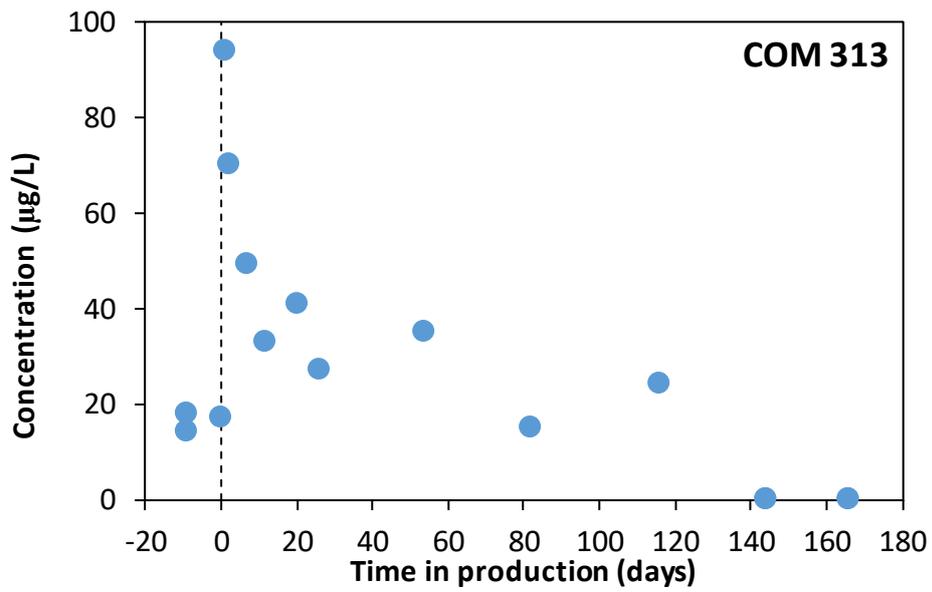


Figure 29 Acetone concentrations in the CSG well samples from Combabula. The vertical dotted lines (time zero) indicate the start of well production and flow of produced water.

## 5.4 Groundwater bore samples

General water quality parameters measured in groundwater samples are summarised in Table 44. The groundwaters were alkaline (mean pH  $\pm$  S.D. of  $8.81 \pm 0.18$ ) with a sample conductivity (mean  $\pm$  S.D. of  $1.64 \pm 0.18$  mS/cm) typically an order of magnitude higher than Dogwood Creek.

The concentrations of dissolved metals, metalloids and major cations measured in the groundwater samples are shown in Table 45. The concentrations of major cations, metals and metalloids were generally similar between the different bores and with time. The major cations concentrations were generally low (mean hardness (5 mg CaCO<sub>3</sub>/L) other than sodium that had concentrations in the range 260-380 mg/L. All samples generally contained low concentrations of trace metals and metalloids, with most being below the limit of detection. There were a couple of elevated concentrations such as 15 mg/L of potassium measured in GW1 on 19/10/2017.

All chemicals measured in the groundwater samples were below the available Australian drinking water quality guidelines (NRMMC 2011). There were four marginal exceedances of ANZG DGVs for freshwater at GW2; cadmium on 13/2/2018, copper and zinc on 17/08/2017, and mercury on 14/12/2017. The source of these metals is uncertain, but unlikely to be a signature of CSG-related contamination as other CSG-related elements such as boron and barium were not present at elevated concentrations.

Dissolved boron is a useful tracer of CSG inputs into water bodies as it is found at elevated concentrations in CSG well waters compared to surface waters and shallow groundwater. For instance, the mean concentration in the GW bores was 0.08 mg/L. Monitoring of groundwater bores by Origin Energy in April 2017 prior to the commencement of HF operations indicated a slightly higher concentration of 0.11 mg/L (Apte et al. 2018c). These values compare to typically 10 to 30 mg/L of boron in CSG well water samples collected during well commissioning and the early stages of well operation. There is therefore little evidence to suggest that groundwater bore boron concentrations have increased during HF operations at Combabula thereby inferring that the wells have not received any inputs of CSG related waters.

The concentration of all organic compounds measured in the groundwater samples were below the limits of reporting. This included the geogenic organic chemicals detected in the CSG well samples. This indicated that the bores were free of any significant contamination by organic chemicals derived from CSG activities or other sources.

Radionuclide activities in groundwater samples are presented in Table 46. Activities were generally very low, with Ra-226 and U-234 being the only two radionuclides consistently detected in samples. The measured activities in all samples analysed were well below the available guideline values for irrigation, livestock watering and human consumption (Table 46).

## 5.5 Surface water samples from Dogwood Creek

The general water quality parameters for the creek samples are summarised in Table 47. It is noteworthy that the Dogwood Creek samples had the lowest conductivity of all samples collected in this study (mean  $\pm$  S.D. of  $0.114 \pm 0.08$  mS/cm). The creek water pH was neutral to slightly acidic ranging from 6.34 to 7.40. The mean hardness was 14 CaCO<sub>3</sub>/L. Visually, the Creek waters from

both sampling sites were consistently very turbid. The presence of fine particulate matter was also indicated by the difficulties encountered filtering the samples (i.e. clogging of filters) in the laboratory.

Inorganic chemical data including trace metals are summarised in Table 48. Copper, chromium and zinc concentrations exceeded the ANZ DGVs for freshwaters in several samples at both upstream and downstream locations. As noted earlier, Dogwood Creek is a disturbed system that receives anthropogenic inputs from the Miles region including waters from a sewage treatment facility and it is highly likely there are upstream sources of contaminants. There was no evidence of consistent elevation of trace element concentrations downstream of the Condabri study site that could be linked to CSG runoff such as increases in concentration of chemicals associated with drilling muds and HF fluids such as boron and barium. For instance, the mean concentration of dissolved boron in the Dogwood Creek water samples was 0.07 mg/L which compares far higher concentrations of typically 10 to 30 mg/L of boron in CSG well water samples collected during well commissioning and the early stages of well operation.

The concentrations of most organic compounds analysed were below the limits of reporting. The only organic compounds detected were some hydrocarbon fractions (>C10-C34) (Table 50) which were sporadically detected at low concentrations at both the upstream and downstream sites. As with the metal contaminants, this pattern of behaviour is consistent with upstream inputs of hydrocarbons rather than CSG-related inputs.

Radionuclide activity data are presented in Table 49. Activities were generally very low. The measured activities in all samples analysed were well below the available guideline values for irrigation, livestock watering and human consumption (Table 49).

Overall the data did not indicate inputs of contaminants that could be associated with CSG-related activities at the study site.

Table 44 General water quality parameters, major anions and boron measured in groundwater samples

Sample	Date	pH	Conductivity mS/cm	TSS mg/L	Alkalinity mg CaCO <sub>3</sub> /L	TOC	DOC	Chloride	Sulfate	Phosphate mg P/L	Nitrate mg N/L	Nitrite mg N/L	Ammonia mg N/L	Boron mg/L
GW1	17/08/2017	8.81	1.49	<1	431	<1	1	150	16	0.095	0.01	<0.005	0.50	0.08
GW1	19/10/2017	9.33	1.78	32	550	1	2	290	34	0.012	0.01	<0.005	0.015	<0.05
GW1	14/12/2017	8.80	1.52	3	611	<1	<1	330	48	0.26	0.012	<0.005	0.56	0.05
GW1	14/12/2017	8.80	1.57	3	614	<1	<1	270	35	0.19	0.009	<0.005	0.56	0.09
GW1	13/02/2018	8.85	1.52	1	611	<1	<1	250	29	0.17	<0.005	<0.005	0.62	0.07
GW2	17/08/2017	8.73	1.64	2	419	<1	<1	110	7.3	0.062	0.10	0.014	0.12	0.06
GW2	19/10/2017	8.79	1.58	5	554	<1	<1	310	23	0.29	0.011	0.006	0.82	0.07
GW2	14/12/2017	8.70	1.58	5	580	<1	<1	280	27	0.17	0.006	<0.005	0.55	0.05
GW2	13/02/2018	8.77	1.35	3	586	<1	<1	250	21	0.18	<0.005	<0.005	0.55	0.14
GW3	17/08/2017	8.72	1.92	1	426	<1	<1	190	15	0.071	0.62	<0.005	0.16	0.09
GW3	19/10/2017	8.88	1.73	<1	567	<1	<1	390	36	0.22	0.37	<0.005	0.013	0.08
Pine Dam Bore	13/02/2018	8.59	1.98	2	681	<1	<1	320	81	0.087	0.006	<0.005	0.62	0.07
<b>ADWG</b>												3		4
<b>Mean</b>		<b>8.81</b>	<b>1.64</b>	<b>5.68</b>	<b>552</b>	<b>&lt;1</b>	<b>&lt;1</b>	<b>262</b>	<b>31.0</b>	<b>0.15</b>	<b>0.12</b>	<b>0.01</b>	<b>0.42</b>	<b>0.08</b>
<b>Minimum</b>		<b>8.59</b>	<b>1.35</b>	<b>&lt;1</b>	<b>419</b>	<b>&lt;1</b>	<b>&lt;1</b>	<b>110</b>	<b>7.30</b>	<b>0.01</b>	<b>&lt;0.005</b>	<b>&lt;0.005</b>	<b>0.01</b>	<b>0.05</b>
<b>Maximum</b>		<b>9.33</b>	<b>1.98</b>	<b>32.3</b>	<b>681</b>	<b>1.20</b>	<b>1.82</b>	<b>390</b>	<b>81.0</b>	<b>0.29</b>	<b>0.62</b>	<b>0.01</b>	<b>0.82</b>	<b>0.14</b>

ADWG = Australian drinking water guideline value (ADWG 2011)

Table 45 The concentrations of dissolved metals, metalloids and major cations in groundwater samples

Sample	Date	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Fe mg/L	Ag µg/L	As µg/L	Cd µg/L	Cr µg/L	Cu µg/L	Hg ng/L	Mn µg/L	Ni µg/L	Pb µg/L	U µg/L	Zn µg/L
GW1	17/08/2017	1.6	1.1	0.11	292	0.008	<0.04	0.22	<0.2	<1	<1	<0.1	5.5	<1	<0.1	<0.01	<4
GW1	19/10/2017	1.5	15	0.10	277	0.002	<0.04	<0.1	<0.2	<1	<1	0.55	1.0	<1	<0.1	0.01	<4
GW1	14/12/2017	1.6	0.9	0.14	365	0.008	<0.04	<0.1	<0.2	<1	<1	0.10	5.3	<1	<0.1	<0.01	<4
GW1	14/12/2017	1.6	0.7	0.15	283	0.008	<0.04	<0.1	<0.2	<1	<1	0.14	5.4	<1	<0.1	<0.01	<4
GW1	13/02/2018	1.6	0.8	0.12	305	0.008	<0.04	<0.1	<0.2	<1	<1	0.11	5.2	<1	<0.1	<0.01	<4
GW2	17/08/2017	1.5	0.9	0.14	299	0.004	<0.04	<0.1	<0.2	<1	1.6	<0.1	1.0	<1	0.2	0.01	9.3
GW2	19/10/2017	1.5	1.0	0.16	262	0.079	<0.04	<0.1	<0.2	<1	<1	<0.1	24	<1	<0.1	0.01	<4
GW2	14/12/2017	1.6	0.8	0.19	310	0.031	<0.04	<0.1	<0.2	<1	<1	0.72	5.0	<1	<0.1	<0.01	<4
GW2	13/02/2018	1.7	0.7	0.16	284	0.031	<0.04	<0.1	0.21	<1	<1	<0.1	5.8	<1	<0.1	<0.01	<4
GW3	17/08/2017	1.7	1.0	0.14	328	<0.002	<0.04	0.2	<0.2	<1	1.3	<0.1	<0.5	<1	<0.1	0.01	5.6
GW3	19/10/2017	1.5	1.2	0.15	286	<0.002	<0.04	0.2	<0.2	<1	<1	0.18	<0.5	<1	<0.1	0.02	<4
Pine Dam Bore	13/02/2018	3.3	1.2	0.50	378	0.13	<0.04	<0.1	<0.2	<1	<1	0.10	8.7	<1	<0.1	0.02	<4
<b>ADWG</b>						-	100	10	2	50	2000	1000	500	20	10	6	-
<b>ANZG DGV</b>		-	-	-	-	-	0.05	13	0.20	1	1.4	600	1900	11	3.4	-	8
<b>Mean</b>		1.72	2.08	0.17	306	0.03	<0.04	0.20	<0.2	<1	<1	0.18	6.70	<1	<0.1	<0.01	<4
<b>Minimum</b>		1.45	0.70	0.10	262	<0.002	<0.04	<0.1	<0.2	<1	<1	0.10	<0.5	<1	<0.1	<0.01	<4
<b>Maximum</b>		3.27	14.7	0.50	378	0.13	<0.04	0.22	0.21	<1	1.56	0.72	24.2	<1	0.21	0.02	9.3

ADWG = Australian drinking water guideline value (ADWG 2011)  
 The concentrations marked in red exceed the ANZG DGV for freshwaters

Table 46 Radionuclide activities in the groundwater samples

Sample	Date	<sup>238</sup> U activity mBq/kg	<sup>234</sup> U activity mBq/kg	<sup>226</sup> Ra activity mBq/kg	<sup>228</sup> Ra activity Bq/kg	<sup>232</sup> Th activity mBq/kg	<sup>230</sup> Th activity mBq/kg	<sup>228</sup> Th activity mBq/kg	Gross Alpha Bq/L	Gross Beta Bq/L
GW1 (West Supply Bore)	17/08/2017	<1	1.5	58	<0.2	<1	<5	<1	---	---
GW1 (West Supply Bore)	14/12/2017	<1	6.0	<1	<0.2	<1	<5	<1	<0.18	<0.09
GW2	17/08/2017	<1	1.3	60	<0.2	<1	<5	<1	---	---
GW3	17/08/2017	<1	1.3	63	<0.2	<1	<5	<1	---	---
Pine Dam bore	13/02/2018	3.1	7.8	2.8	<0.2	<1	8.0	<1	<0.07	<0.07
<sup>a</sup> WHO GV		10,000	1000	1000	0.1	1000	1000	1000		
<sup>b</sup> ANZG (2018)		200		5000	2000				0.5	0.5
<sup>c</sup> USEPA MCL				185	185					

<sup>a</sup>WHO (2017) Guideline value for drinking water

<sup>b</sup>ANZG guidelines for livestock drinking/irrigation

<sup>c</sup>USEPA maximum concentration level for drinking water

Table 47 Dogwood Creek general water quality data

Site	Date	pH	Conductivity	TSS	Alkalinity	TOC	DOC	Chloride	Sulfate	Phosphate	Nitrate	Nitrite	Ammonia	Boron
			mS/cm	mg/L	mg CaCO <sub>3</sub> /L	mg/L	mg/L	mg/L	mg/L	mg P/L	mg N/L	mg N/L	mg N/L	mg/L
Upstream	27/07/2017	7.04	0.113	267	22	14	9	14	6.1	0.006	0.41	0.008	0.016	<0.05
Upstream	3/08/2017	6.35	0.105	286	22	15	10	14	7.2	<0.005	0.37	<0.005	0.005	0.11
Upstream	18/08/2017	7.40	0.119	301	25	15	9	13	5.2	<0.005	0.48	<0.005	0.020	0.08
Upstream	13/09/2017	7.27	0.116	351	23	16	10	13	15	<0.005	0.20	<0.005	<0.001	0.06
Upstream	1/11/2017	7.20	0.111	304	32	15	10	15	6.7	<0.005	5.2	<0.005	0.026	0.12
Downstream	27/07/2017	6.95	0.114	323	23	16	11	16	1.2	0.006	0.23	0.009	0.005	<0.05
Downstream	3/08/2017	6.34	0.108	300	22	17	11	18	2.9	<0.005	1.3	<0.005	0.030	0.08
Downstream	18/08/2017	7.30	0.120	242	30	16	11	13	3.0	0.018	0.24	<0.005	0.010	<0.05
Downstream	13/09/2017	7.34	0.101	356	24	17	11	16	3.2	<0.005	0.14	<0.005	<0.001	<0.05
Downstream	1/11/2017	7.24	0.130	259	38	17	12	17	<1	<0.005	4.8	<0.005	0.024	<0.05
<b>LOD</b>			---	<b>1</b>	<b>10</b>	<b>1</b>	<b>1</b>	<b>0.1</b>	<b>0.1</b>	<b>0.005</b>	<b>0.005</b>	<b>0.005</b>	<b>0.001</b>	<b>0.05</b>

Table 48 Dogwood Creek dissolved metals data

Site	Date	Ca	K	Mg	Na	Fe	Ag	Al	As	Ba	Cd	Cr	Cu	Total Hg	Mn	Ni	Pb	U	V	Zn
		mg/L	mg/L	mg/L	mg/L	mg/L	µg/L	µg/L	µg/L	mg/L	µg/L	µg/L	µg/L	ng/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Upstream	27/07/2017	2.1	2.4	1.6	12	0.50	<0.04	701	0.4	0.034	<0.2	2	1.1	7.8	36	2	0.2	0.08	1.5	5
Upstream	3/08/2017	1.9	2.2	1.7	14	2.7	<0.04	1921	0.9	0.15	<0.2	1	2.1	7.5	28	2	1.1	0.12	6.7	<4
Upstream	18/08/2017	1.7	2.8	1.5	15	1.1	<0.04	594	0.2	0.12	<0.2	2	3.2	8.2	10	2	0.6	0.09	4.1	---
Upstream	13/09/2017	1.7	3.0	1.5	15	0.38	<0.04	148	0.6	0.039	<0.2	<1	1.5	8.3	5.8	1	<0.1	0.06	2.1	<4
Upstream	1/11/2017	1.9	2.2	1.8	10	5.4	<0.04	3673	1.2	0.059	<0.2	5	1.5	9.0	26	3	1.9	0.14	15	17
Downstream	27/07/2017	2.1	2.3	1.7	13	0.52	<0.04	872	0.7	0.045	<0.2	2	1.1	8.5	4.6	2	0.1	0.10	1.7	9
Downstream	3/08/2017	2.1	2.4	1.8	12	2.5	<0.04	1948	0.6	0.12	<0.2	2	1.9	8.1	13	2	0.9	0.15	5.9	<4
Downstream	18/08/2017	2.7	3.4	2.5	15	8.2	<0.04	4729	1.5	0.21	<0.2	7	5.0	9.4	32	4	3.4	0.27	20	<4
Downstream	13/09/2017	1.9	2.8	1.7	15	0.54	<0.04	302	0.6	0.044	<0.2	1	1.6	9.7	4.5	1	0.2	0.08	3.4	<4
Downstream	1/11/2017	2.8	2.3	2.7	11	10	<0.04	6960	1.8	0.11	<0.2	9	3.9	---	83	4	3.3	0.25	22	14
<b>LOD</b>		<b>0.01</b>	<b>0.1</b>	<b>0.01</b>	<b>1</b>	<b>0.002</b>	<b>0.04</b>	<b>6</b>	<b>0.1</b>	<b>0.0002</b>	<b>0.2</b>	<b>1</b>	<b>1</b>	<b>0.1</b>	<b>0.5</b>	<b>1</b>	<b>0.1</b>	<b>0.01</b>	<b>0.4</b>	<b>4</b>
<b>ANZG DGV</b>		-	-	-	-	-	<b>0.05</b>	-	<b>13</b>	-	<b>0.2</b>	<b>1</b>	<b>1.4</b>	<b>600</b>	<b>1900</b>	<b>11</b>	<b>3.4</b>	-	-	<b>8</b>

The concentrations marked in red exceed the ANZG DGV for freshwaters

Table 49 Dogwood Creek radionuclides data

Site	Date	<sup>238</sup> U activity	<sup>234</sup> U activity	<sup>226</sup> Ra activity	<sup>228</sup> Ra activity	<sup>232</sup> Th activity	<sup>230</sup> Th activity	<sup>228</sup> Th activity	Gross Alpha	Gross Beta
		mBq/kg	mBq/kg	mBq/kg	Bq/kg	mBq/kg	mBq/kg	mBq/kg	Bq/L	Bq/L
Upstream	27/07/2017	2.2	4.2	4.1	<0.2	<2	<6	<5	0.07	0.14
Upstream	1/11/2017	3.6	4.0	6.1	<0.2	<1	<5	<1	0.15	0.12
Downstream	27/07/2017	2.6	4.1	6.2	<0.1	<2	<6	<5	0.15	0.11
Downstream	1/11/2017	5.0	5.6	7.3	<0.3	<1	<5	<1	0.14	0.14
<sup>a</sup> WHO GV		10,000	1000	1000	0.1	1000	1000	1000		
<sup>b</sup> ANZG (2018)		200		5000	200				0.5	0.5
<sup>c</sup> USEPA MCL				185	185					

<sup>a</sup>WHO (2017) GV for drinking water (mBq/L)

<sup>b</sup>Guideline for livestock drinking/irrigation

<sup>c</sup>USEPA maximum concentration level for drinking water

Table 50 Dogwood Creek total recoverable hydrocarbons (TRH) data

Sample Description	Date	TRH C6 - C10 µg/L	TRH>C10 - C16 µg/L	TRH>C16 - C34 µg/L	TRH>C34 - C40 µg/L
Upstream	27/07/2017	<25	<25	<100	<100
Upstream	3/08/2017	<25	<25	310	<100
Upstream	13/09/2017	<25	<25	<100	<100
Upstream	1/11/2017	<25	<25	<100	<100
Downstream	27/07/2017	<25	<25	<100	<100
Downstream	3/08/2017	<25	31	610	<100
Downstream	13/09/2017	<25	<25	<100	<100
Downstream	1/11/2017	<25	71	100	<100

## 5.6 Water treatment facility

### 5.6.1 WTF inorganics

Samples of inflow, outflow (permeate) and membrane reject (brine) waters were collected by CSIRO staff from the Reedy Creek WTF on three occasions over the study period. A summary of measured physico-chemical parameters, dissolved major ions, and chemicals for which water quality GVs exist are presented in Table 51 and Table 52. The concentrations of less commonly measured elements are provided in the data report (Apte et al. 2018b) and in the online data repository.

Water pH was slightly alkaline and conductivities decreased (as expected) in the sequence: Brine > WTF inflow > WTF outflow indicating removal of ions from the inflow sample and their concentration in the membrane reject solution.

The concentrations of trace elements in the inflow water entering the WTF were generally less than those measured in the produced waters collected from the Combabula wells sampled throughout this study (COM313, COM337 and COM359R). This was likely because the WTF inflow water was sampled on entry to the RO plant and had already undergone some preliminary treatment (i.e. settling in a collection pond and coarse screening), as well dilution by produced waters from older wells containing lower concentrations of trace elements. Given the very low TSS in the outflow water, the majority of trace elements were found in the dissolved phase.

Measured concentrations of key chemical constituents such as chloride, sodium, boron, organic carbon and alkalinity were comparable to values obtained from another study of 150 individual wells within the Surat Basin (Rebello et al. 2017). The measured inflow concentrations were also quite consistent over the course of the three sampling events (4 months). The inflow waters are typically characterised by alkaline pH (8.6 – 8.8), high alkalinity (1200 – 1300 mg/L CaCO<sub>3</sub>) and high salt content (chloride and sodium). The Combabula CSG Water Management Plan (APLNG, 2010b) identified these parameters, along with boron, suspended solids, temperature and adjusting

dissolved oxygen concentrations to those of the receiving waters as the key issues limiting the re-use of untreated CSG water.

Comparing concentrations of dissolved chemical constituents in the WTF inflow samples to ANZG water quality GVs (Table 51 and Table 52), it can be seen that while most concentrations are low, ammonia exceeds the pH corrected ANZG 95% protection DGV for slightly to moderately disturbed systems, while boron also exceeds the ANZG 95% DGV, as well as the ANZG Irrigation long-term (100-year) trigger value (LTV). There was also one exceedance of the copper DGV (inflow sample 9/11/2017: 1.8 µg Cu /L). The concentration of total suspended solids (TSS) in the WTF inflow water was lower than those measured directly from the wells. This is likely due to the pre-treatment which the produced water undergoes (settling, filtration) prior to entry into the RO plant.

In addition to the discrete ANZG trigger values, the Combabula CSG Water Management Plan (APLNG 2010a) sets out water quality objectives for sodium and chloride based on the ANZG irrigation guidelines. Ranges for sodium and chloride are 115 – 460 mg/L and 175 – 700 mg/L, respectively. To facilitate comparisons, the lowest value in the given ranges was used as a guideline value (i.e. 115 mg/L sodium and 175 mg/L chloride). Sodium and chloride concentrations were above these values in the inflow water received at the WTF (Table 51).

There were no exceedances of guideline WQ values for the treated outflow water (permeate) (Table 51 and Table 52), with measured concentrations of many chemicals below detection limits. Electrical conductivity of the permeate was also very low (0.47 – 0.68 mS/cm), a further indication of the low inorganic salt content of the permeate.

Removal efficiencies of >90% (difference of inflow and permeate concentrations as a percentage of inflow concentrations) were observed for most chemical constituents, apart from boron (67%) and ammonia (69%). Difficulties in boron and ammonia removal are a well-known problem in RO treatment (Öztürk et al. 2008, Awadalla et al. 1994). Due to the pH at which RO plants generally operate, boron is present as the neutral boric acid compound which, due to its lack of charge, it is able to diffuse through RO membranes (Öztürk et al. 2008; Hou et al. 2013). Similar issues also apply to ammonia owing to the ability of unionised ammonia (present in waters having an alkaline pH) to diffuse through RO membranes (Awadalla et al. 1994). Figure 30 shows the removal efficiencies for chemicals which were detectable in both the inflow and permeate waters of the WTF. The concentrations of selected chemical constituents in inflow, permeate and brine waters are compared in Figure 31 and Figure 32 in order to illustrate the efficacy of the water treatment process. All of the inorganic chemicals in the CSG well waters that exceeded guideline values were removed or reduced to acceptable levels by the treatment process.

The chemical constituents removed from inflow water during the RO process are contained in the brine waste product which is stored in large evaporation ponds adjacent to the RO facility. As expected and shown in Table 51 and Figure 31 and Figure 32, concentrations of chemical constituents in the brine rejects are much higher than those measured in the inflow waters. The concentrations of dissolved copper, boron, sodium, chloride and ammonia were all above ANZG ecosystem protection DGVs (irrigation TV in the case of sodium and chloride). There was little variation in the concentrations of the chemicals quantified across the three sampling time points. As brine composition is predominantly controlled by feed-water composition (Rioyo et al. 2017),

this is to be expected given that the composition of the inflow was also quite consistent across the three samples events.

Radionuclide activities in WTF samples are shown in Table 53. The measured activities in all of the inflow and outflow samples analysed were well below the available guideline values for irrigation, livestock watering and human consumption (Table 49). The samples with the highest activities were the two brine samples analysed with Ra-226 activity in one sample slightly exceeding the very stringent USEPA MCL for drinking water. The activities of radionuclides in both brine samples were below the ANZG (2018) GVs for livestock watering and irrigation (Table 53).

The current management of brine reject from the Reedy Creek WTF involves transferring brine solution into specially constructed brine ponds, allowing residual liquid to evaporate, while remaining salts precipitate. The majority of this salt would likely be in the form of sodium chloride, as these are the predominant ions in the brine samples. However, there would also be smaller quantities of salts and precipitates from other major ions such as magnesium and calcium, as well as trace elements (e.g. boron, copper), rare earth elements (e.g. cerium) and radionuclides (e.g. radium).

Table 51 Physical chemistry parameters and dissolved elemental concentrations in Water Treatment Facility (WTF) samples

Sample	Date	pH	TSS mg/L	Conductivity mS/cm	Chloride mg/L	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	Al µg/L	B µg/L	Cu µg/L	Pb µg/L	Mn µg/L	Ni µg/L	Se µg/L	Zn µg/L
WTF In	9/11/2017	8.8	15	6.41	1500	7.8	9.7	3.3	1100	<6	600	1.8	<0.1	<0.5	<1	<5	<4
	11/01/2018	8.7	23	6.76	1800	8.6	14	3.6	1200	<6	540	<1	<0.1	<0.5	<1	<5	<4
	7/03/2018	8.6	16	6.55	1700	7.6	7.9	3.3	1100	7	430	<1	<0.1	1.0	<1	<5	<4
WTF Out	9/11/2017	8.1	5	0.68	170	0.72	0.9	0.35	110	<6	170	<1	0.1	<0.5	<1	<5	<4
	11/01/2018	7.8	2	0.51	120	0.55	0.8	0.27	92	<6	190	<1	<0.1	<0.5	<1	<5	<4
	7/03/2018	7.7	2	0.47	110	0.48	0.5	0.22	77	8	160	<1	<0.1	<0.5	<1	<5	4
WTF Brine	9/11/2017	8.5	75	35.6	12100	49	74	20	7600	9	2350	3.0	<0.1	3.6	3	<5	<4
	11/01/2018	8.5	12	35.0	12000	53	95	21	9100	8	2300	2.5	0.1	4.7	2	<5	<4
	7/03/2018	8.4	3	37.6	12000	46	59	19	7600	52	1990	2.3	<0.1	33	4	<5	9
ANZG 95% DGV	---	---	---	---	---	---	---	---	---	55	370	1.4	3.4	1900	11	11	8
ANZG Irrigation LTV	---	---	---	---	175	---	---	---	115	5000	500	200	2000	200	200	20	2000
ANZG Livestock TV	---	---	---	---	---	---	---	---	---	5000	5000	400	100	---	1000	20	20000

**Values in red indicate exceedances of DGV or TV**

ANZG 2018 95% DGV for slightly to moderately disturbed systems

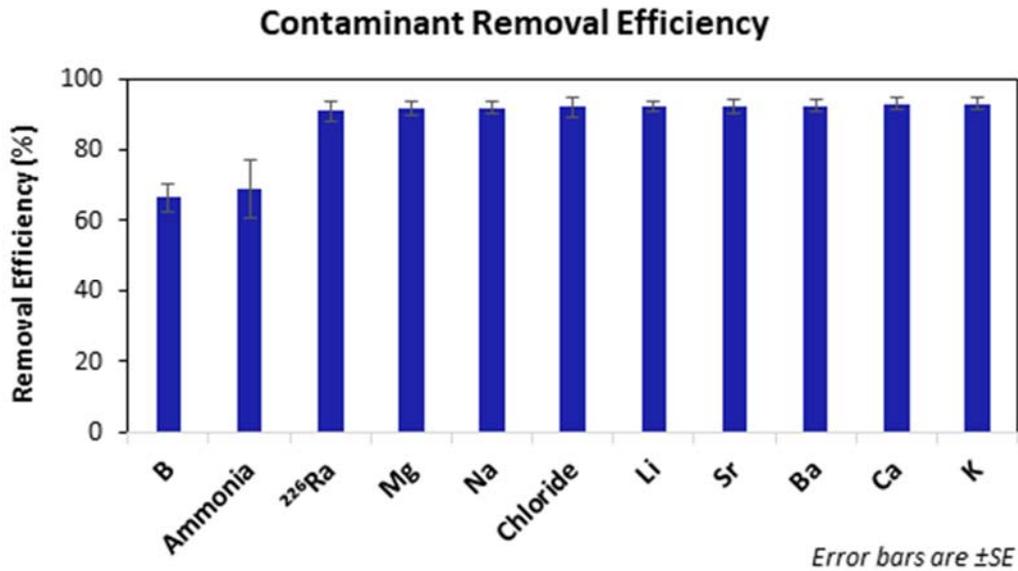
ANZG Irrigation LTV: Long-term trigger value for irrigation water

ANZG Livestock TV: recommended trigger value for livestock drinking water

**Table 52 Ammonia concentrations and pH corrected ANZG (2018) Default Guideline Values in Water Treatment Facility samples**

Sample	Date:	pH	Ammonia-N mg/L	ANZ DGV at sample pH
WTF In	09/11/2017	8.8	<b>0.52</b>	0.24
	11/01/2018	8.7	<b>0.58</b>	0.29
	07/03/2018	8.6	<b>0.41</b>	0.34
WTF Out	09/11/2017	8.1	0.13	0.78
	11/01/2018	7.8	<0.001	1.2
	07/03/2018	7.7	0.15	1.3
WTF Brine	09/11/2017	8.5	<b>3.1</b>	0.40
	11/01/2018	8.5	<b>3.6</b>	0.40
	07/03/2018	8.4	<b>4.1</b>	0.48

*Values in bold indicate exceedances of DGV  
ANZG (2018) DGV for slightly to moderately disturbed systems, corrected for sample pH*



**Figure 30 Removal efficiencies for chemicals detectable in both WTF inflow and permeate samples**

Table 53 Radionuclide concentrations in the WTF samples

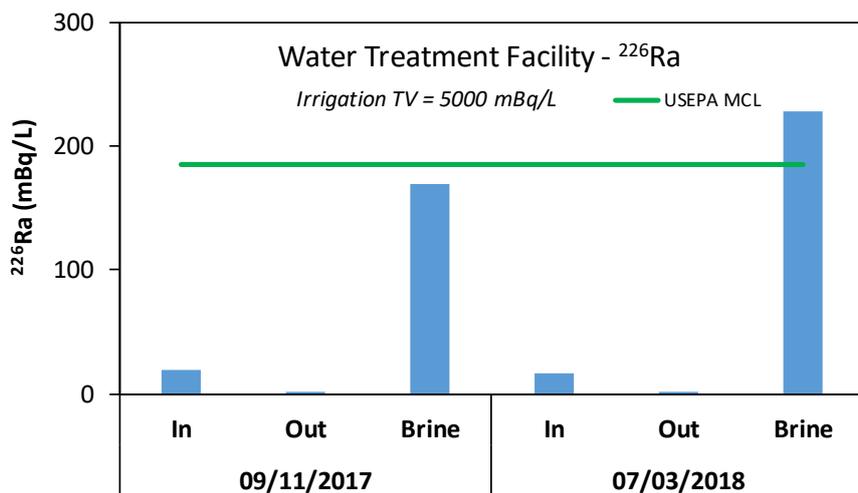
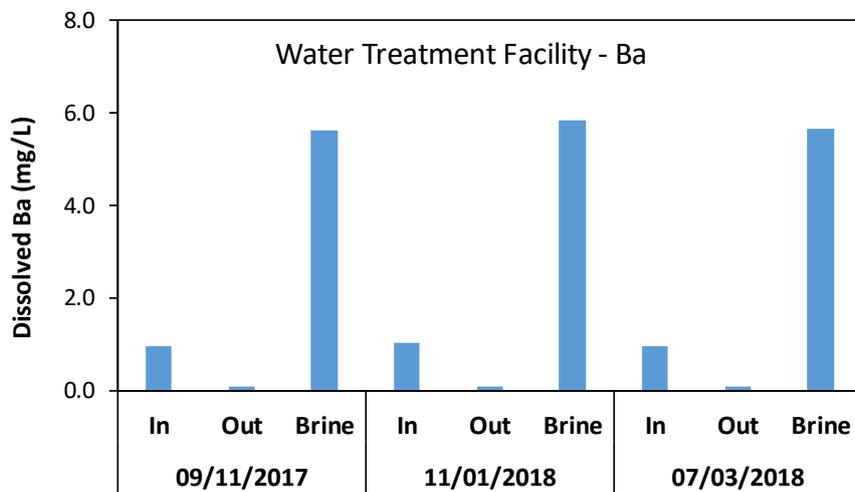
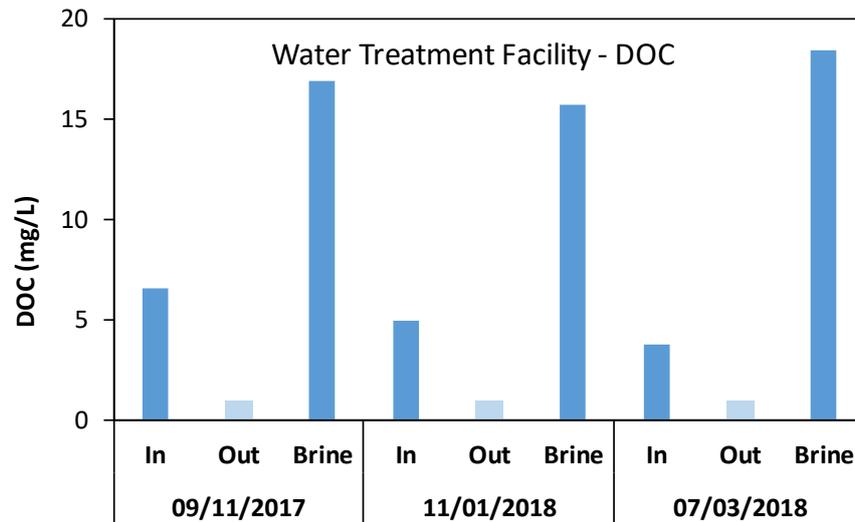
Sample	Date	<sup>238</sup> U activity mBq/kg	<sup>234</sup> U activity mBq/kg	<sup>226</sup> Ra activity mBq/kg	<sup>228</sup> Ra activity Bq/kg	<sup>232</sup> Th activity mBq/kg	<sup>230</sup> Th activity mBq/kg	<sup>228</sup> Th activity mBq/kg	Gross Alpha Bq/L	Gross Beta Bq/L
WTF Influent	9/11/2017	<1	<1	19	<0.2	2.0	<5	6.3	---	---
WTF Influent	7/03/2018	<1	<1	17	<0.1	1.9	10.6	3.5	---	---
WTF Out	9/11/2017	<1	<1	1.4	<0.5	3.5	<5	14.6	0.04	0.02
WTF Out	7/03/2018	<1	<1	1.9	<0.1	<1	<5	1.5	<0.03	<0.03
WTF Brine	9/11/2017	<1	4.9	169	<0.3	1.6	6.2	32.4	---	---
WTF Brine	7/03/2018	<1	3.2	228	<0.7	1.6	7.3	18.8	---	---
<sup>a</sup> WHO GV		10,000	1000	1000	0.1	1000	1000	1000		
<sup>b</sup> ANZG (2018)		200		5000	2000				0.5	0.5
<sup>c</sup> USEPA MCL				185	185					

<sup>a</sup>WHO (2017) GV for drinking water (mBq/L)

<sup>b</sup>ANZG Guideline for livestock drinking and irrigation

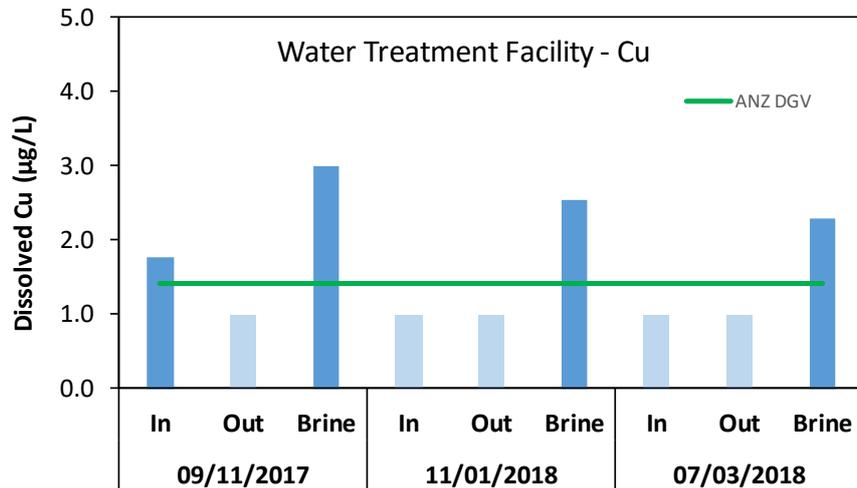
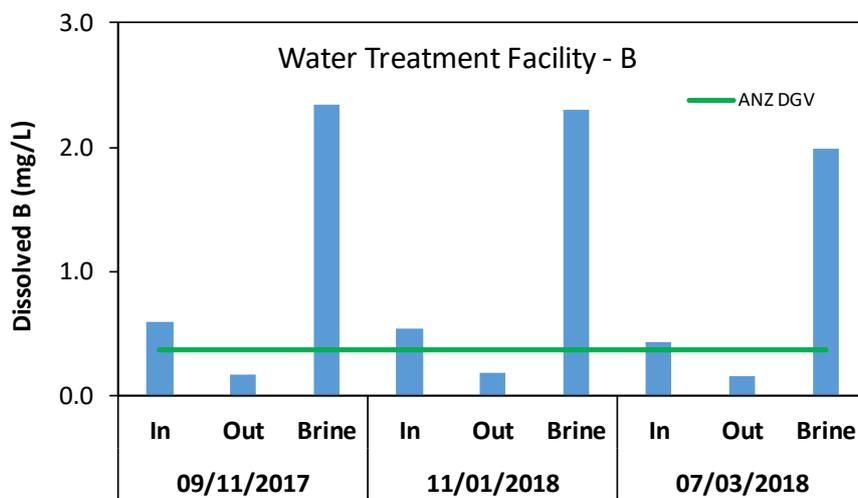
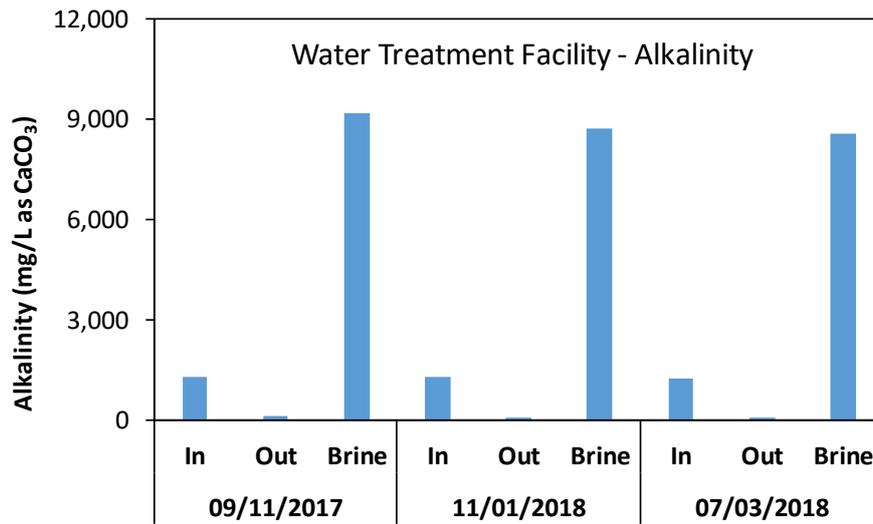
<sup>c</sup>USEPA maximum concentration level for drinking water

The activities marked in red exceed the USEPA MCL



Light blue shaded box indicated value <LOD (LOD value plotted)

Figure 31 Concentrations of selected inorganic constituents in inflow, permeate and brine waters



*Light blue shaded box indicated value <LOD (LOD value plotted)*

**Figure 32 Concentrations of chemicals in inflow, permeate and brine waters**

### 5.6.2 WTF organics

The number of organic chemicals quantified in the WTF samples was low in comparison to produced water samples. The majority of target organic chemicals were present at concentrations below their limits of reporting. The only exceptions were selected trihalomethanes (THMs) and acetone (Table 54, Figure 33). However, given that acetone was detected in three out of five field blanks at concentrations higher than observed in the WTF samples it is highly likely that the acetone concentrations measured in the WTF samples are a consequence of sample contamination. The source of the acetone in the blanks is likely to be organic solvents used during sample processing at the field laboratory. Consequently, acetone data is reported, but not discussed any further.

As noted earlier, the WTF receives inputs from many established production wells across the Reedy Creek area and the newly commissioned wells represent only a small proportion of the total. It is therefore expected that the composition of the organic chemicals detected in the WTF will be different from the produced water samples collected from the CSG wells that were monitored over their first 6 months of operation. For instance, FBA tracers which are only added to a small number of selected wells during HF are unlikely to be detected at the WTF owing to dilution by produced waters from other CSG wells.

The THMs detected were chloroform (trichloromethane), bromodichloromethane, dibromochloromethane and bromoform. THMs concentrations were consistently highest in the RO reject brines indicating rejection by the RO process. Chloroform was detected in three out of the four influent samples and bromoform in only one influent sample. The concentrations of the chlorinated and brominated THMs were all below Australian Drinking Water Guideline values (250 µg/L) (NRMMC 2011).

The most likely source of the measured THMs is due to disinfection, via chloramination of the produced water during treatment at the WTF. THMs are often identified as by-products of chlorine disinfection of water containing organic matter (Agus et al. 2009, Farré and Knight 2012, Richardson 2003, Sadiq and Rodriguez 2004). The presence of the THMs may also indicate the presence of other halogenated by-products, which were not targeted in this study.

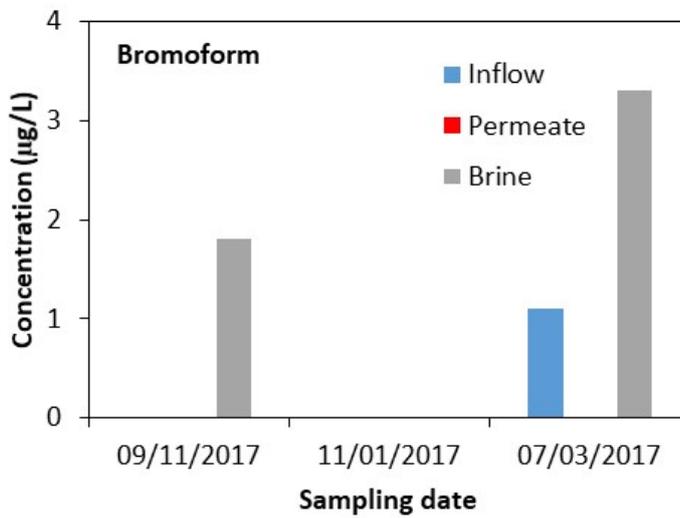
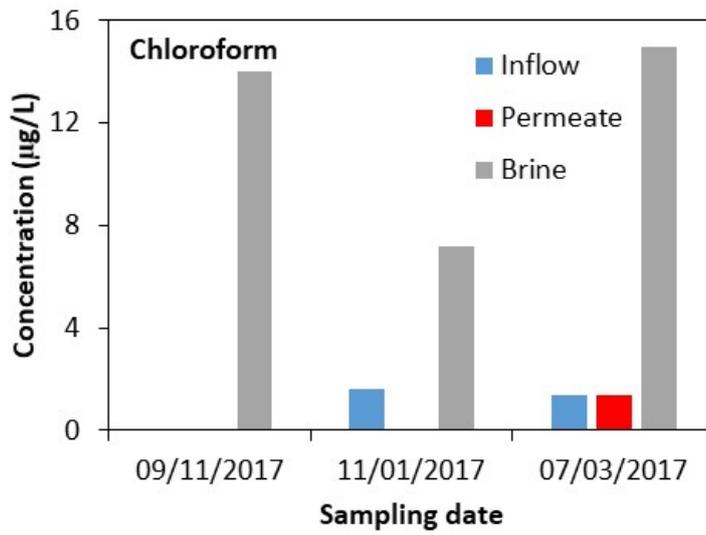


Figure 33 Concentrations of chloroform and bromoform measured in samples collected at different stages of water treatment in the Combabula WTF

Table 54 Target organic chemical concentrations in the WTF samples

Sample Description	Date	Chloroform µg/L	Bromodichloromethane µg/L	Dibromochloromethane µg/L	Bromoform µg/L	Acetone µg/L
Field Blank	18/08/2017	<1	<1	<1	<1	<10
Field Blank	17/10/2017	<1	<1	<1	<1	27
Field Blank	14/12/2017	<1	<1	<1	<1	56
Field Blank	7/03/2018	<1	<1	<1	<1	<10
Field Blank	3/04/2018	1.5	<1	<1	<1	28
WTF Influent November 2017	9/11/2017	<1	<1	<1	<1	<10
WTF Influent January 2018	11/01/2018	1.6	<1	<1	<1	<10
WTF Influent January 2018 duplicate	11/01/2018	1.7	<1	<1	<1	<10
WTF Influent March 2018	7/03/2018	1.4	<1	<1	1.1	<10
WTF Out November 2017	9/11/2017	<1	<1	<1	<1	<10
WTF Out January 2018	11/01/2018	<1	<1	<1	<1	<10
WTF Out March 2018	7/03/2018	1.4	<1	<1	<1	12
WTF Brine November 2017	9/11/2017	14	5.4	2.4	1.8	19
WTF Brine January 2018	11/01/2018	7.2	2.8	1.1	<1	15
WTF Brine March 2018	7/03/2018	15	5.7	3.2	3.3	<10

## 5.7 Soil quality

Detailed results for the soil cores are provided in the data report (Apte et al. 2018b) and in the on-line data repository. The concentrations of key trace elements are summarised in Table 55. The elements in this compilation includes ones that may be associated with CSG activities such as boron (geogenic chemical)/HF fluid additive, potassium (present in HF fluid) and barium (used in drilling muds).

The results are compared to the available soil guidelines that apply in Australia for human health protection (NEPM 2011) in Table 55. None of the elements measured in the soil samples from both the drill leases and background sites exceeded the guideline values.

The data were characterised by significant variability in metal concentrations at both the drill lease and background sites. There were no consistent trends in trace element concentrations with depth. Statistical analysis (paired t-test) of concentration data for 26 elements measured at both the background and drill lease sites indicated only 12 instances where elemental concentrations were significantly greater ( $P < 0.05$ ) at the drill lease site compared to background sites (CNN204: Na; CNN207: Ag, Co, Mn, U; CNN209: Mo, Sb; CNN210: Ag, Ca, Co, K; CNN218: Cr). The elevated concentrations at the drill lease sites are unlikely to be associated with inputs from CSG related activities as they include elements such as silver, and antimony which are not normally associated with CSG chemicals or produced waters.

Soil radionuclides data are summarised in Table 56. All seven measured radionuclides were detectable in the soil samples and had similar activities. Statistical analysis of the data (t-test) indicated no significant difference ( $P < 0.05$ ) between the background and drill pad mean activities for each radionuclide.

Kleinschmidt (2017) calculated mean activities for U-238 and Th-232 in soils for the whole of Australia and for the individual States. The mean data for Queensland were: U-238:  $30 \pm 28$  Bq/kg, Th-232:  $37 \pm 18$  Bq/kg. The mean  $\pm$  S.D. soil activities measured for U-238 and Th-232 (all data) from this study were:  $21.3 \pm 3.8$  Bq/Kg and  $31.6 \pm 9.3$  Bq/Kg respectively. These values lie well within the ranges reported by Kleinschmidt (2017).

The soils in the well-lease areas showed no measurable contamination due to organic chemicals including polycyclic aromatic hydrocarbons (PAHs), phenols, cresols, benzene, xylenes and total residual hydrocarbons (Table 57). Toluene was detected at one site. However, the concentrations were just above the limit of reporting and similar concentrations were detected in background soils. Overall, the data show that the activities on the site during HF did not cause any measurable organic chemical contamination of the soils in the well lease area.

Table 55 Trace element concentrations in the soils core samples

Well	Sample Type	Depth cm	B µg/g	Ba µg/g	Ca µg/g	Cr µg/g	Cu µg/g	K µg/g	Mn µg/g	Na µg/g	Ni µg/g	Pb µg/g	Zn µg/g
CNN207	BG	0-20	<2	112	794	25	4.8	340	552	680	9.5	11	11
	BG	20-40	<2	165	862	20	4.6	337	301	1430	14	8.5	11
	BG	40-60	<2	143	860	16	4.5	392	166	1710	11	7.2	8.9
	DL	0-20	6	267	1030	33	6.1	510	1830	881	20	13	13
	DL	20-40	5	174	1220	21	5.2	366	1230	1850	20	8.8	8.6
	DL	40-60	6	205	3060	19	6.0	545	1430	1950	28	9.9	12
CNN204	BG	0-20	<2	107	1220	36	9.6	512	1280	665	18	10	17
	BG	20-40	11	256	4120	44	10	402	1210	2780	32	11	21
	BG	40-60	11	286	3220	43	11	494	1000	3040	27	10	25
	DL	0-20	<2	91	2040	28	8.5	314	1420	1600	22	12	10
	DL	20-40	12	252	5010	48	11	505	1130	3290	42	12	25
	DL	40-60	7	208	8300	32	8.9	380	1080	3540	32	10	16
CNN209	BG	0-20	<2	93	1090	11	3.6	207	437	695	6.1	8.5	5.3
	BG	20-40	3	136	1870	24	6.0	422	375	1880	15	9.4	17
	BG	40-60	<2	207	5140	20	5.5	370	287	2290	14	9.7	13
	DL	0-20	4	143	1260	18	4.9	435	426	934	8.3	10	11
	DL	20-40	7	201	2050	23	5.4	465	381	1710	17	11	16
	DL	40-60	5	177	1980	13	4.7	353	367	1890	14	9.3	8.2
CNN210	BG	0-20	<2	34	310	4.3	2.0	252	140	<50	1.4	3.2	4.1
	BG	20-40	<2	31	88	2.8	1.0	167	75	<50	0.96	2.7	1.5
	BG	40-60	<2	37	158	3.9	1.2	172	48	<50	1.3	3.0	2.9
	DL	0-20	3	37	475	3.7	1.8	279	174	<50	<0.03	3.1	3.7
	DL	20-40	2	32	280	3.8	1.3	222	101	<50	<0.03	3.1	2.8
	DL	40-60	3	35	248	4.0	1.4	231	60	<50	<0.03	3.3	3.8
CNN218	BG	0-20	<2	54	494	6.6	2.5	475	320	<50	3.6	4.5	4.5
	BG	20-40	<2	42	472	6.1	1.7	340	144	<50	3.1	4.2	3.0
	BG	40-60	<2	52	634	8.0	1.8	322	80	<50	3.9	4.8	5.1
	DL	0-20	3	54	385	4.3	2.0	434	341	<50	2.9	3.7	4.8
	DL	20-40	2	56	427	4.7	1.5	361	205	<50	3.4	3.7	5.1
	DL	40-60	2	73	696	5.6	1.4	275	61	<50	2.4	4.3	4.4
CON382	DL	0-20	3	47	763	5.7	2.7	439	356	81	1.5	4.1	6.0
	DL	20-40	3	46	238	7.1	2.5	419	181	54	2.0	4.5	6.9
	DL	40-60	2	43	336	6.7	2.0	285	114	60	1.4	4.3	5.1
NEPM (2011)			5000			100	7000		3000		400	300	8000

DL = Drill lease

BG = Background

NEPM (2011): Health investigation level A

Numbers in red: mean drill lease concentration significantly > mean background concentration (paired t-test, P<0.05)

Table 56 Soil radioactivity data

Well	Sample type	Depth (cm)	<sup>238</sup> U activity Bq/kg	<sup>234</sup> U activity Bq/kg	<sup>232</sup> Th activity Bq/kg	<sup>230</sup> Th activity Bq/kg	<sup>228</sup> Th activity Bq/kg	<sup>226</sup> Ra activity Bq/kg	<sup>228</sup> Ra ( <sup>228</sup> Ac) activity Bq/kg
CNN204	Background	0-20	24.2	21.5	34.8	45.5	44.0	15.1	34.8
CNN204	Background	20-40	22.6	23.3	42.2	35.2	53.2	24.4	37.1
CNN204	Background	40-60	24.9	17.8	31.2	37.2	33.6	15.5	36.1
CNN204	Drill Lease	0-20	21.7	21.9	43.0	39.2	39.3	33.0	38.2
CNN204	Drill Lease	20-40	18.2	17.6	40.6	37.9	36.9	16.1	37.7
CNN204	Drill Lease	40-60	26.3	18.6	42.7	49.0	49.1	20.6	38.7
CNN207	Background	0-20	23.6	22.0	37.4	46.6	43.4	26.4	35.5
CNN207	Background	20-40	22.0	20.9	41.9	35.9	43.3	29.1	35.2
CNN207	Background	40-60	20.9	22.7	36.4	32.1	42.7	25.0	34.0
CNN207	Drill Lease	0-20	24.9	24.1	36.3	38.9	48.1	30.4	36.2
CNN207	Drill Lease	20-40	30.9	22.5	43.7	39.9	51.6	20.2	39.4
CNN207	Drill Lease	40-60	23.9	23.2	39.0	33.7	41.7	24.1	36.9
CNN209	Background	0-20	24.5	26.9	38.2	35.5	45.6	25.2	36.9
CNN209	Background	20-40	23.4	22.4	39.5	32.2	49.8	25.3	37.0
CNN209	Background	40-60	20.9	21.5	46.6	30.0	42.7	25.7	37.7
CNN209	Drill Lease	0-20	23.7	24.3	38.9	38.8	41.6	25.7	35.1
CNN209	Drill Lease	20-40	23.3	21.2	40.6	34.3	41.1	27.7	39.2
CNN209	Drill Lease	40-60	26.3	24.4	44.3	33.9	44.5	22.1	39.4
CNN210	Background	0-20	14.2	14.9	16.7	23.3	17.9	12.0	19.0
CNN210	Background	20-40	27.3	16.6	20.8	29.9	21.0	18.4	18.8
CNN210	Background	40-60	18.8	17.6	19.8	23.1	22.3	12.2	23.0
CNN210	Drill Lease	0-20	19.6	19.4	21.7	22.1	24.6	18.6	21.5
CNN210	Drill Lease	20-40	18.7	17.8	23.0	22.2	20.1	13.3	21.7
CNN210	Drill Lease	40-60	21.7	23.0	22.3	28.0	26.7	20.6	21.5
CNN218	Background	0-20	16.2	17.1	11.4	14.4	12.2	14.4	21.5
CNN218	Background	20-40	17.3	16.2	27.4	33.0	24.6	18.5	25.7
CNN218	Background	40-60	17.1	16.2	25.3	30.2	29.0	13.4	22.9
CNN218	Drill Lease	0-20	14.5	14.9	22.8	27.4	27.8	14.4	20.0
CNN218	Drill Lease	20-40	16.9	16.0	22.9	24.0	22.7	18.1	20.3
CNN218	Drill Lease	40-60	15.4	16.0	26.3	22.4	32.8	14.5	23.8
CON382	Drill Lease	0-20	18.4	18.1	24.9	22.7	27.0	17.9	25.9
CON382	Drill Lease	20-40	20.0	19.3	27.5	27.9	26.6	20.3	25.1
CON382	Drill Lease	40-60	20.3	19.9	28.6	43.1	33.1	11.1	25.4

**Table 57 The highest concentrations detected for various chemical contaminants in soils from well-lease areas subjected to HF activities in comparison with those in background soils**

<b>Chemical</b>	<b>Soil depth</b>	<b>Well-lease area soils (n = 18)</b>	<b>Background soils (n = 18)</b>
	cm	mg/kg	mg/kg
BTEX	0-20	0.58 (CNN207)	<0.50
(Only Toluene detected)	20-40	0.55 (CNN204)	0.53 (CNN204)
	40-60	<0.50	0.57 (CNN204)
PAHs (none detected)	0-20	<0.01-<0.02	<0.01-<0.02
	20-40	<0.01-<0.02	<0.01-<0.02
	40-60	<0.01-<0.02	<0.01-<0.02
Phenols and Cresols (none detected)	0-20	<0.1-<0.2	<0.1-<0.2
	20-40	<0.1-<0.2	<0.1-<0.2
	40-60	<0.1-<0.2	<0.1-<0.2
TRH C6-C9; C10-C14; C15-C28; and C29-C36 (none detected)	0-20	<25-<100	<25-<100
	20-40	<25-<100	<25-<100
	40-60	<25-<100	<25-<100

## 6 Discussion

### *Comparison with other studies*

Comparative data from relevant CSG operations in both Australia and the USA are summarised in Table 58. Despite the geographical differences and different geological timeframes over which the coal beds were formed, there are similarities in the concentration ranges of major components of waters associated with coal seam gas from the US and Australia. Comparisons with shale gas data where water quality is influenced by the geology of the shale formations and the very different operating conditions are not included.

Of the studies that have investigated water quality parameters associated with CSG waters, most have measured general WQ parameters and major ion concentrations, with less attention on concentrations of trace metals. For example, the waters associated with CSG extraction in New Zealand and the USA generally have high bicarbonate (402–435 mg/L), chloride (49.3–146 mg/L) and sodium (184–334 mg/L) concentrations, and low calcium (6–20 mg/L), magnesium (0.9–6.5 mg/L) and sulfate (0.7–27.6 mg/L) concentrations (Van Voast 2003; Taulis and Milke 2007, 2012).

The concentration of total dissolved solids (TDS) is commonly reported in CSG formation water and may vary considerably between different basins. For example, Dahm et al. (2011) described an extensive study of several thousand wells from the Rocky Mountain area of the central United States, and found a substantial range of TDS ranging from a few hundred mg/L to >35,000 mg/L. Kinnon et al. (2010) reported TDS concentrations in coal seam water from the Bowen Basin in Queensland, were generally less than 10,000 mg/L, comprised of mainly Na, Cl and HCO<sub>3</sub><sup>-</sup>, and minor concentrations of calcium and magnesium, K, F, Al and Fe.

Rebello et al. (2017) summarised water quality from 150 coal seam gas production wells from the Surat Basin, Queensland, and found that the coal seam gas water predominantly contained bicarbonate (<2030 mg/L), chloride (<5910 mg/L) and sodium (<3700 mg/L). Principal component analysis revealed three groups of water quality parameters which described the data. Iron, manganese and aluminium were in one group; bromide, magnesium, strontium, potassium, hardness, calcium, chloride, electrical conductivity, total dissolved solids and sodium appeared as a second group and a third group comprised of fluoride, bicarbonate alkalinity as CaCO<sub>3</sub>, sodium adsorption ratio, pH, boron, silica, total organic carbon, and sulfate.

HF fluid organic chemicals (TEA, CMIT and MIT) were largely absent in the well water samples and when detected were largely present during the early phases of well operation. One explanation for the low concentrations of biocides (CMIT and MIT) measured in the flowback waters is rapid degradation. This is consistent with the findings of Kookana et al. (2020) who demonstrated that 90% of both MIT and CMIT degraded in soils within 2 days.

Radionuclides showed similar trends to trace metals and organics with a concentration maximum in activity occurring during well flowback and early production stages. The activities of seven radionuclides were measured in water and soil samples. Radium-226 was the most abundant radionuclide in waters. In most samples Ra-226 activities were below the very stringent drinking water guideline levels aside from a small number of water samples taken at the early stages of well operation. Compared to shale gas operations the typical activities measured in flowback and

produced waters in the present study are much lower. For instance, Rosenblum et al. (2017) reported Ra-228 activities in shale gas produced waters of up to 3,100 mBq/L. This compares to a mean in our study of 115±88 mBq/L.

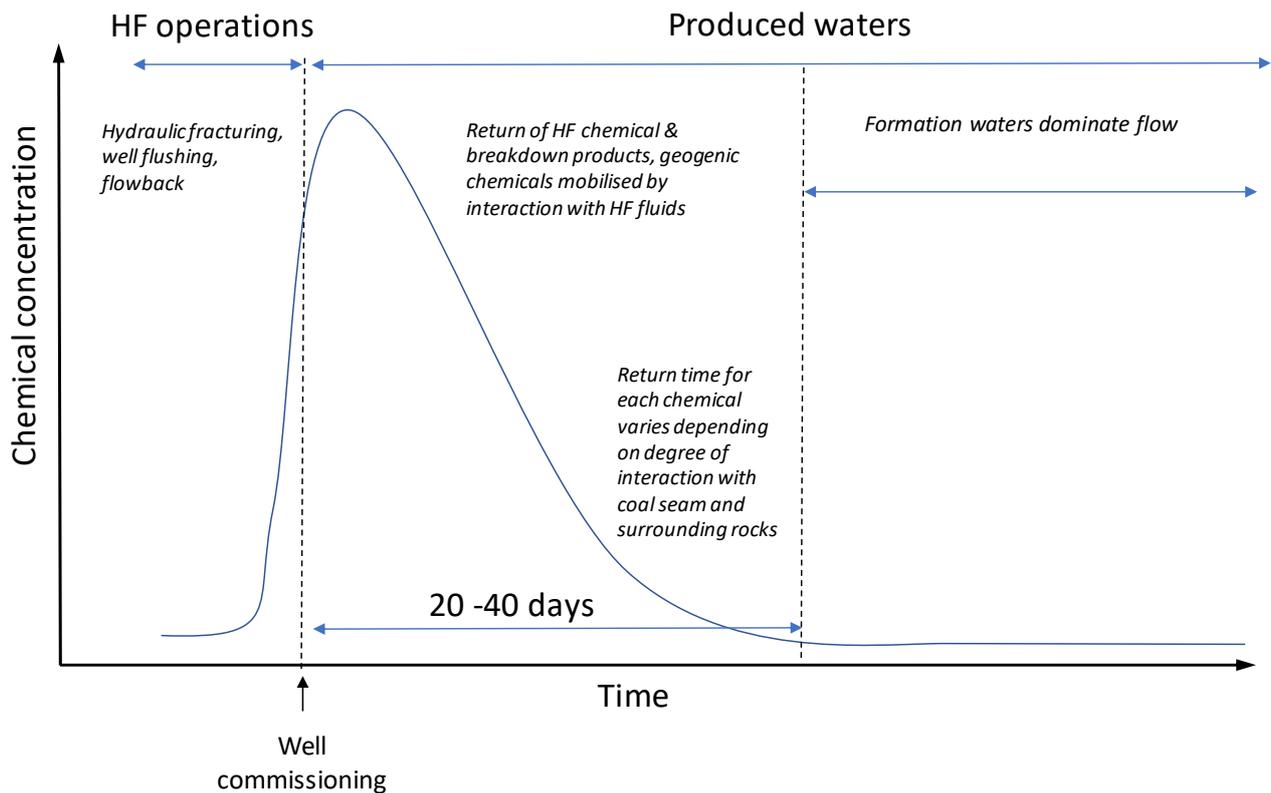
### ***Concentration versus time profiles for the CSG wells***

The peak concentrations of many chemicals were observed during the flowback/early produced waters stages at all wells.

Concentration versus time profiles for the wells showed similar trends for a range of HF fluid derived chemicals and geogenic chemicals with the maximum concentrations occurring during well flushing/flowback and typically the first 20 to 40 days of production which is the duration over which most of the waters injected during HF are returned to the surface. After this period, the concentrations of the chemicals typically declined rapidly (exponential decay) to a fairly constant 'baseline' concentration. Occasional spikes in concentrations were observed during the decay period. The concentrations of synthetic chemicals in HF fluids that are not present in nature should eventually drop to zero, whereas the concentration of geogenic chemicals and trace elements such as boron, will decline until they reach the concentration found in the formation waters from the area.

An element with one of the shortest retention profiles was potassium (added to HF fluid as potassium chloride and also naturally present at much lower concentrations in formation waters) which reached a maximum concentration within a couple of days of well operation whereas other chemicals show a longer return time. The time delays observed for the chemicals provides indication of the relative importance of various retention processes occurring in the coal seams (i.e. solution/solid interactions). A conceptual model which accounts for the general trends shown in the chemicals data is presented in Figure 34.

For the geogenic chemicals, the observed concentration maxima is assumed to result from the interaction of HF fluids with coal seams leading to mobilisation of geogenic chemicals. This hypothesis is supported by the findings of laboratory studies which demonstrate mobilisation of geogenic chemicals from coal samples on exposure to HF chemicals (Apte et al. 2017c). The large number and concentrations of geogenic chemicals detected is not unexpected and is consistent with laboratory studies (Apte et al. 2017c). The lower chemical concentrations observed after several months of production are more likely to reflect the formation water chemistry of the coal seams and adjacent rocks. An ideal way to confirm this conceptual model would be to monitor some CSG production wells from start-up that were not subjected to HF. In the absence of HF chemicals, the increase in geogenic chemical concentrations over the first 20-40 days should not be observed.



**Figure 34 Conceptual model of chemical concentrations observed in CSG well waters**

There are few studies that provide temporal data on chemical concentrations in CSG water. However, previous work on water quality profiles after HF for shale gas extraction also demonstrates time-dependent chemical signatures of organic chemicals (Oetjen and Thomas 2016, Orem et al. 2014, Luek and Gonsior 2017, Hayes 2009). For example, a study by Hayes (2009) monitored more than 170 volatile and semi-volatile organic chemicals in produced water collected in the Marcellus Shale region for up to 90 days after well production commenced at 19 well sites. Organic geogenic chemicals such as acetone, BTEX, naphthalene and other substituted benzene and naphthalene compounds, displayed a peak in their concentrations typically after five days followed by a substantial decline in concentrations over the following 90 days (Hayes 2009). This trend, however, was not consistent at all sites with concentration of acetone, pyridine, 3&4-cresols and phenol remaining relatively constant over time or being detected only in the final collected samples of the time series.

A longer-term study (up to 240 days) by Orem et al. (2014), reported that organic chemicals (analysed by GC-MS) in shale gas produced water decreased rapidly within three weeks. This study also compared signatures of organic chemicals present in produced water from both shale and coal seam gas extraction and noted that there were broad similarities between the signatures of extractable hydrocarbons (Orem et al. 2014). In the case of CSG produced waters, there was a higher amount of aromatic chemicals compared with shale, which is consistent with the more aromatic nature of coal relative to shale (Orem et al. 2014).

### ***Identification of key contaminants of concern***

HF chemicals were detected mainly in the first stages of well production. Based on their concentrations and their comparison with surface water quality guidelines, geogenic chemicals were the main potential contaminants identified. The chemicals measured at concentrations above Australian default guideline values (DGVs) for surface water quality were ammonia, boron and seven trace metals: chromium, copper, manganese, lead, nickel, silver and zinc. Many of the exceedances were marginal and were mainly confined to the early stages of well production, an exception being boron which was consistently present at concentrations above the Australian DGV of 0.37 mg/L. Clearly any treatment processes applied to CSG waters need to reduce the concentrations of these chemicals to below acceptable levels.

The activities of seven radionuclides were measured in water and soil samples. The highest activities were measured in Radium-226 was the most abundant radionuclide in waters. All radionuclides were below the existing levels of regulatory concern that apply in Australia. In many samples radionuclide activities were even below the most stringent international drinking water guideline values.

### ***Impacts on surface waters and groundwater***

Sampling of surface and groundwaters for an extensive range of chemical constituents did not indicate any significant impacts of CSG operations on water quality. As noted earlier, there was a significant depth separation between the extent of the groundwater bores and CSG wells at the study site. The maximum groundwater bore depth was 194 m compared to a depth of 443 m for the shallowest coal seam that was targeted for HF.

Surface water quality in the vicinity of CSG operations may potentially be impacted direct inputs of HF chemicals or flowback waters caused by spills or uncontained runoff from drill cuttings or exposed soils. Additionally, general land disturbance (e.g. well pad construction and creation of access tracks) may increase sediment runoff and dust generation. Water samples from Dogwood Creek adjacent to one of the study areas did not indicate any signs of contamination relating to CSG activities. This was consistent with the absence of any reported spills over the duration of HF operations over the study period. However, the Creek's water quality showed evidence of impacts such as hydrocarbon and trace metals contamination arising from other sources (e.g. sewage treatment works discharges) upstream of the CSG operations. In general, contamination events of surface waters are likely to be short term and event-related. Full recovery of water quality would be expected following the cessation of HF activities and rehabilitation of the initially disturbed area around the well pad.

### ***Efficacy of water treatment***

Water sampling of a CSG water treatment facility indicated the current treatment procedure which incorporates reverse osmosis was effective in treating most CSG-related chemicals from the wastewater stream which contains the produced waters collected from the production wells. This included the chemicals identified in this study as contaminants of concern in the CSG well waters. Consequently, the highest chemical concentrations were observed in the concentrated reject brine samples. Chlorinated and brominated organic chemicals were also detected in the brines which are a known by-product of wastewater chlorination.

### ***Organic carbon composition of CSG-derived waters***

Well samples were characterised by high concentrations of dissolved organic carbon which reached concentrations in excess of 100 mg C/L during the early stages of well production. The identified organic compounds (e.g. hydrocarbons, HF chemicals) typically only comprised a small fraction (<5%) of the DOC and the remaining pool of carbon is currently uncharacterised.

The geogenic organic chemicals within CSG produced waters are a complex mixture which presents significant analytical challenges in terms of their characterisation and quantification. They comprise organic chemicals originating from coal and also in the first phases of operation, the breakdown products of guar gum which is a component of HFF. Orem et al. (2007) identified over 170 separate organic compounds in produced waters from CSG wells in Powder River Basin, Wyoming, with concentrations ranging from 0.01 to 18 µg/L. A similar issue has been highlighted for carbon speciation in shale gas waters (Luek and Gonsior 2017). Over a thousand geogenic organic compounds have been identified in shale produced water samples, however quantification and, therefore, closure of the carbon mass balance is not yet possible (Luek and Gonsior 2017). Additional research is needed to develop new high resolution LC-MS and GC-MS analytical methods that can be used to further interrogate data collected from collected water samples for chemical identification and additional targeted quantification techniques. This work would preferably be done in conjunction with toxicological assays, which may highlight where this additional identification and quantification analysis should be prioritised. Tracer techniques for measuring the contributions to organic carbon concentrations made by guar gum are also needed.

**Table 58 Comparison of results in the current study with those in previous studies**

<b>Parameter</b>	<b>Our study</b>	<b>Rebello et al. 2017</b>	<b>Dahm et al. 2011</b>	<b>McBeth et al (2003)</b>	<b>Rice et al (2003)</b>
<b>pH</b>	6.23-8.94	7.83-8.89	6.86-9.31	6.99±0.01	7.0-8.2
<b>Conductivity</b> (mS/cm)	8.17-219	3630-17200	232-18066		
<b>Alkalinity</b> (mg/L)	117-1640	5-2030	51-11400		
<b>TSS</b> (mg/L)		2190-10200	1.0-580		
<b>TOC</b> (mg/L)	1.73-1100	1-138	0.25-13		
<b>Cl</b> (mg/L)	1700-24000	471-5910	4.5-20100		1190-24800
<b>SO<sub>4</sub></b> (mg/L)	0.10-540	1-48	0.45-1800		
<b>Ca</b> (mg/L)	5.87-733	2-137	0.81-5530		14-480
<b>K</b> (mg/L)	29-8710	3-20	1.7-970		15-100
<b>Mg</b> (mg/L)	2.56-187	1-34	0.010-2.0		7.7-290
<b>Na</b> (mg/L)	285-6230	786-3700	12-7834		2540-15300
<b>Al</b> (mg/L)	0.0056-4.50	0.01-40.9	0.014-2.90	0.0067±0.001	
<b>As</b> (mg/L)	0.00012-0.013		0.027-0.300		
<b>B</b> (mg/L)	0.08-42.9	0.17-0.68	0.21-4.70	0.051±0.006	1.6-9.3
<b>Ba</b> (mg/L)	0.28-18.3	0.38-9.38	0.05-74.0	0.386±0.14	7.5-190
<b>Cr</b> (mg/L)	0.0011-0.051		0.002-3.71	0.033 ±0.004	
<b>Cu</b> (mg/L)	0.0010-0.812		0.005-4.60	0.01±0.001	
<b>Fe</b> (mg/L)	0.01-51.7	0.09-45.1	0.03-258	0.154±0.032	0.26-220
<b>Mn</b> (mg/L)	0.0117-7.02	0-3.59	0.02-2.0	0.011±0.005	
<b>Ni</b> (mg/L)	0.0011-0.061		0.005-2.61		
<b>Sr</b> (mg/L)	0.53-73.6	0.7-20.2	0.01-27.0		
<b>V</b> (mg/L)	0.0005-0.018				
<b>Zn</b> (mg/L)	0.0047-0.230		0.014-3.90	5±1	

Rebello et al. 2017: Single sample from each of 150 CSG wells, Surat Basin, Queensland

Dahm et al. 2011: Various CSG wells, Rock Mountain basins, United States

Rice et al. (2003): CSG wells, Central Utah (n=28)

McBeth et al. (2003) Powder River Basin, Wyoming

## 7 Conclusions

The findings of the study were as follows:

1. Water sampling was conducted at six wells in the Surat Basin during hydraulic fracturing operations and periodically for up to 6 months post HF. The suite of HF chemicals used at the wells sites was relatively simple and comprised 9 chemicals plus guar gum and gelatine. The chemicals were ethylene glycol, sodium tetraborate, boric acid, hydrochloric acid, triethanolamine, potassium chloride, CMIT & MIT (both biocides) and diammonium peroxydisulfate. Additives (proppant plus chemicals) comprised typically 9% of the total injected volume. The water composition of well flowback and produced waters was found to be dominated mainly by geogenic chemicals with HF fluid-derived chemicals (e.g. triethanolamine and MIT, a biocide) only being detected during the early stages of well operations.
2. Chemical concentrations in the flowback and produced waters were dynamic and changed with time. Peak concentrations of many chemicals were observed during well commissioning and the first few days of produced water flow which is the duration over which most of the waters injected during HF are returned to the surface. After this period, the concentrations of the chemicals declined over a period of 20 to 40 days with occasional spikes in concentrations. The relatively stable concentrations observed toward the of the sampling program were assumed to represent formation water quality whereas the increased concentrations during flowback reflect the interaction of HF fluids with coal seam materials and subsequent release of geogenic contaminants. A conceptual model of chemical behaviour with time is presented in Figure 34. With time, the concentrations of synthetic chemicals in HF fluids that are not present in nature should eventually drop to zero, whereas the concentration of geogenic chemicals and trace elements such as boron, will decline until they reach the concentration found in the formation waters from the area.
3. Water quality data for the six wells was compared to Australian surface water quality guideline values (DGVs) in order to identify contaminants of potential concern. Based on their concentrations and their comparison with surface water quality guidelines, geogenic chemicals were the main potential contaminants identified. The chemicals measured at concentrations above Australian default guideline values (DGVs) for freshwaters were ammonia, boron and seven trace metals: chromium, copper, manganese, lead, nickel, silver and zinc. Many of the exceedances were marginal and were mainly confined to the early stages of well production, an exception being boron which was consistently present at concentrations above the Australian DGV of 0.37 mg/L. Any treatment processes applied to CSG well waters need to reduce the concentrations of these chemicals to below acceptable levels which are determined by the final use of the water. RO treatment was found to be effective in reducing the concentrations of the identified contaminants of concern to below the very stringent Australian guidelines for freshwaters.
4. The activities of seven radionuclides were measured in water and soil samples. All radionuclides were below the existing levels of regulatory concern that apply in Australia throughout the HF

process and beyond. Radium-226 was the most abundant radionuclide in water. Aside from selected water samples taken during the first 20 days of well operation, Ra-226 activities were very low, and were even below the very stringent international guideline levels for drinking water.

5. Concentrations of dissolved organic carbon (DOC) reached concentrations in excess of 100 mg C/L during the early stages of well production. However, the organic compounds that were able to be specifically identified (e.g. hydrocarbons, HF fluid chemicals) typically only comprised a small fraction (<5%) of the total DOC and the remaining pool of carbon is currently uncharacterised. It is likely that the breakdown products of guar gum contribute to DOC concentrations during the early phases of well operation.

6. Sampling of nearby groundwater bores for an extensive range of potential contaminants did not indicate any impacts of CSG operations on water quality.

7. Water samples from a local creek adjacent to one of the study areas did not indicate signs of contamination relating to CSG activities. However, the creek's water quality showed evidence of impacts from hydrocarbon and trace metals contamination arising from non-CSG related sources (e.g. sewage treatment works discharges) upstream of the CSG operations.

8. Water sampling of a CSG water treatment facility indicated the treatment procedures for produced waters which incorporate reverse osmosis were effective in removing or lowering the concentrations CSG-related chemicals to below acceptable regulatory levels from the wastewater stream. This included all of the chemicals of potential concern identified in the CSG well waters. As expected, the highest concentration of chemicals were observed in samples of the concentrated brines (the waste product of the treatment process) which are stored in ponds on site.

9. Soil sampling from across drill leases and nearby background sites did not reveal any contamination that could be associated with CSG activities during HF operations. This finding was expected as there were no spills of HF chemicals reported over the time of the study. Given that the probability of capturing a spill event in the field is low, a companion laboratory study was conducted where spills of HF fluid chemicals and produced waters were simulated in the laboratory and residues measured over time. Readers are referred to the final report by Kookana et al. (2020) for more information.

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