Water and Soil Quality Field Sampling Report

W12 Milestone 4 report
April 2018

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Document control

Milestone report
April 2018

Version	Date	Description	Author	Approved
1	11/04/18	First draft	SA	
2	22/04/18	Author reviewed report	SA	
3	30/4/18	CSIRO Peer reviewed report	SA	

ISBN (print): 978-1-4863-1010-4

ISBN (online): 978-1-4863-1011-1

Citation

Apte, S.C., Craig, A., King, J.J., Angel, B.M., Williams, M. and Kookana, R.S. (2018). Water and Soil Quality field sampling report, Project W12 Milestone 4 Report to the Gas Industry Social and Environmental Research Alliance (GISERA). CSIRO, Canberra.

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Cover Photo

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

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Acknowledgements

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 for more information about GISERA's governance structure, projects and research findings.

The authors thank Origin Energy, Queensland, for their logistical support throughout this project and access to their gas field operations in Central Queensland, and the field operations team at Origin Energy's Reedy Creek gas processing facility. We also gratefully acknowledge assistance from the frac teams at Origin and Schlumberger, Savanna rig crews, the team at the Reedy Creek Wastewater facility, SGS Chinchilla laboratory staff, HSE staff, and teams providing additional assistance with groundwater and soil sampling.

Executive summary

CSIRO is currently undertaking a detailed study of the impacts of hydraulic fracturing (HF) on air, soil and water quality at two locations in the Surat Basin, QLD. The air component of the study is being conducted by CSIRO Oceans & Atmosphere and the water/soil component is being conducted by CSIRO Land & Water.

The aims of the water and soil study are as follows:

(i) To quantify the impacts of HF operations on the concentrations of contaminants in nearby surface waters, groundwater and soils.

(ii) To assess the concentrations of HF chemicals and geogenic contaminants in flowback and produced waters resulting from CSG HF operations.

(iii) To check compliance of contaminant concentrations in the collected water and soil samples with relevant Australian water and soil quality guideline values.

(iv) To conduct a laboratory assessment of various spill scenarios involving spillage of hydraulic fracturing fluid and produced waters onto various soils types representative of the Surat Basin.

During the planning phase of the study, two sites were selected in the Surat Basin at Condabri and Combabula. Both gas fields are operated by Origin Energy. A sampling and monitoring plan for waters and soils was subsequently developed (Apte et al., 2017).

This report documents the sample collection phase of the project and includes details of sampling methodologies employed, field observations and number of samples collected. A comprehensive report describing the outcomes of chemical analyses conducted on the collected samples will be published by December 2018. The spills study on various soil types, which involves extensive laboratory experimentation, is being conducted as a parallel investigation.

The water and soil sampling campaign was carried out successfully over a period of 9 months (July 2017 to April 2018). The samples collected at the Condabri and Combabula sites comprised creek waters, groundwater, produced water, flow-back water, samples of hydraulic fracturing fluid, and soil cores from well pads. Some modifications to the original sampling plan were necessary owing to delays caused by bad weather and some operational issues (e.g. hydraulic fracturing 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. Soil sampling sample numbers were close to the planned number (36 samples collected compared to 40 planned). The samples collected are summarised in the table below.

The samples are now undergoing extensive laboratory analysis. The results will be reported in a future GISERA report later in 2018.

Summary of the water and soil sampling program

Sample type		Proposed number of samples	Actual no. samples taken	Notes
Surface waters				
Dogwood Creek	Surface water	16	10	Samples collected upstream and downstream of the Condabri study area. Five sampling events: 3 during and 2 after HF operations.
Farm dams	Surface water	12	0	Samples not taken owing to lack of suitable sampling sites
Water bores	Groundwater	12	12	Three registered bores at the Combabula study site sampled on four occasions. The first two sampling events were during hydraulic fracturing operations and the last two after operations had ceased.
Hydraulic fracturing	HF fluid samples	6	46	Frac zone samples (between 8 to 10 per well) used at 5 wells (typically between 8 and 10 zones) were obtained
Stimulation, flow-back and production waters	Flushing, produced & flowback waters	68	76	Six wells were monitored over a period of 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.
Wastewater treatment facility (WTF)	Incoming water	3	4	Samples taken at the Reedy Creek WTF on 3 occasions over a four month period
Post-treatment	RO treated water	3	3	Samples taken at the Reedy Creek WTF on 3 occasions over a four month period
Membrane rejects	Brine	3	3	Samples taken at the Reedy Creek WTF on 3 occasions over a four-month period
TOTAL		**123**	**154**	

Sample type		Proposed number of samples	Actual no. samples taken	Notes
Soils	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 has 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 contamination is detected).

1 Introduction

CSIRO is currently undertaking a detailed study of the impacts of hydraulic fracturing (HF) on air, soil and water quality at two locations in the Surat Basin, QLD. The air component of the study is being conducted by CSIRO Oceans & Atmosphere and the water/soil component is being conducted by CSIRO Land & Water.

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(i) To quantify the impacts of HF operations on the concentrations of contaminants in nearby surface waters, groundwater and soils.

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(iii) To assess contaminant concentrations in the collected water and soil samples with relevant Australian water and soil quality guideline values.

(iv) To 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.

During the planning phase of the study, two sites were selected in the Surat Basin at Condabri and Combabula. Both gas fields are operated by Origin Energy. A sampling and monitoring plan for waters and soils was subsequently developed (Apte et al., 2017).

This report documents the sample collection phase of the project and includes details of sampling methodologies employed, field observations and number of samples collected. A comprehensive report describing the outcomes of chemical analyses conducted on the collected samples will be published by the end of 2018. The spills study, which involves extensive laboratory experimentation, is being conducted as a parallel investigation.

2 Details of the field campaign

As foreshadowed in the sampling and monitoring plan (Apte et al., 2017), field activities were focussed around two rural sites (Condabri and Combabula) in Central Queensland which were scheduled to undergo hydraulic fracturing operations in the second half of 2017. Both sites were grazing properties.

The field sampling campaign was conducted between July 2017 and April 2018. Initial efforts were around the Condabri site (July to October) and were then gradually shifted to the other study area at Combabula. Background details on each of the study sites are given below.

The sampling operations were initially based out of Origin Energy's Condabri Integrated Operations Centre (IOC) and then Reedy Creek IOC which is in close proximity to the Combabula field site. CSIRO equipment and sample bottles were shipped to these sites and set up in the laboratories. Storage facilities for CSIRO equipment were provided by Origin Energy at both sites. CSIRO staff made regular visits to the site to coordinate field work and take samples. Urgent sample processing operations (e.g. filtration, preservation and extractions) were carried out by CSIRO staff at the Origin laboratories at Condabri and Reedy Creek.

2.1 Study site 1: Condabri

Site 1 (WAP2) is a farmland property of approximately 1030 ha located between Miles and Condamine (26°45’21’’ S, 150°10’49’’E). The property is predominantly flat, semi-arid open grassland with stands of native tree vegetation (Figure 1). Dogwood Creek, an ephemeral surface waterway, borders the western boundary of the property and the Leichhardt Highway borders the eastern boundary.

A total of six soil types were noted to be present across the project area. These included Dermosol, Sodosol, Hydrosol, Kandosol, Rudosol and Vertosol (Figure 2). The majority of soils present in the project area have formed from quaternary alluvium containing sand, silt mud and gravel.

The property contains 19 CSG wells, grid spaced at ~ 600 – 700 m intervals. Rig release dates provided by Origin Energy indicated that the wells were drilled and constructed between August and September 2015, with an additional well constructed in August 2016 (Source: Qld Globe). Well depths range from 740 – 860 m and target the Walloon Coal Measures. The wells were scheduled to undergo some form of wellbore stimulation in June and July 2017 after which they were brought on-line and connected to the gas and water pipeline network. Twelve of the wells will undergo HF.

Dogwood Creek runs along the western boundary of the property. The area to the west of Dogwood Creek is dominated by farmland with ~ 5 CSG wells within a 5 km radius of the boundary. In contrast, the area to the east of the property, bounded by the Leichhardt Highway, is dominated by farmland with a high density of CSG wells (grid spaced ~ 600 – 700 m) (Figure 1). 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.

A site familiarisation visit to this site was undertaken by CSIRO staff on 12 April 2017 in order to inspect the study area, make contact with key Origin Energy staff and organise field logistics.

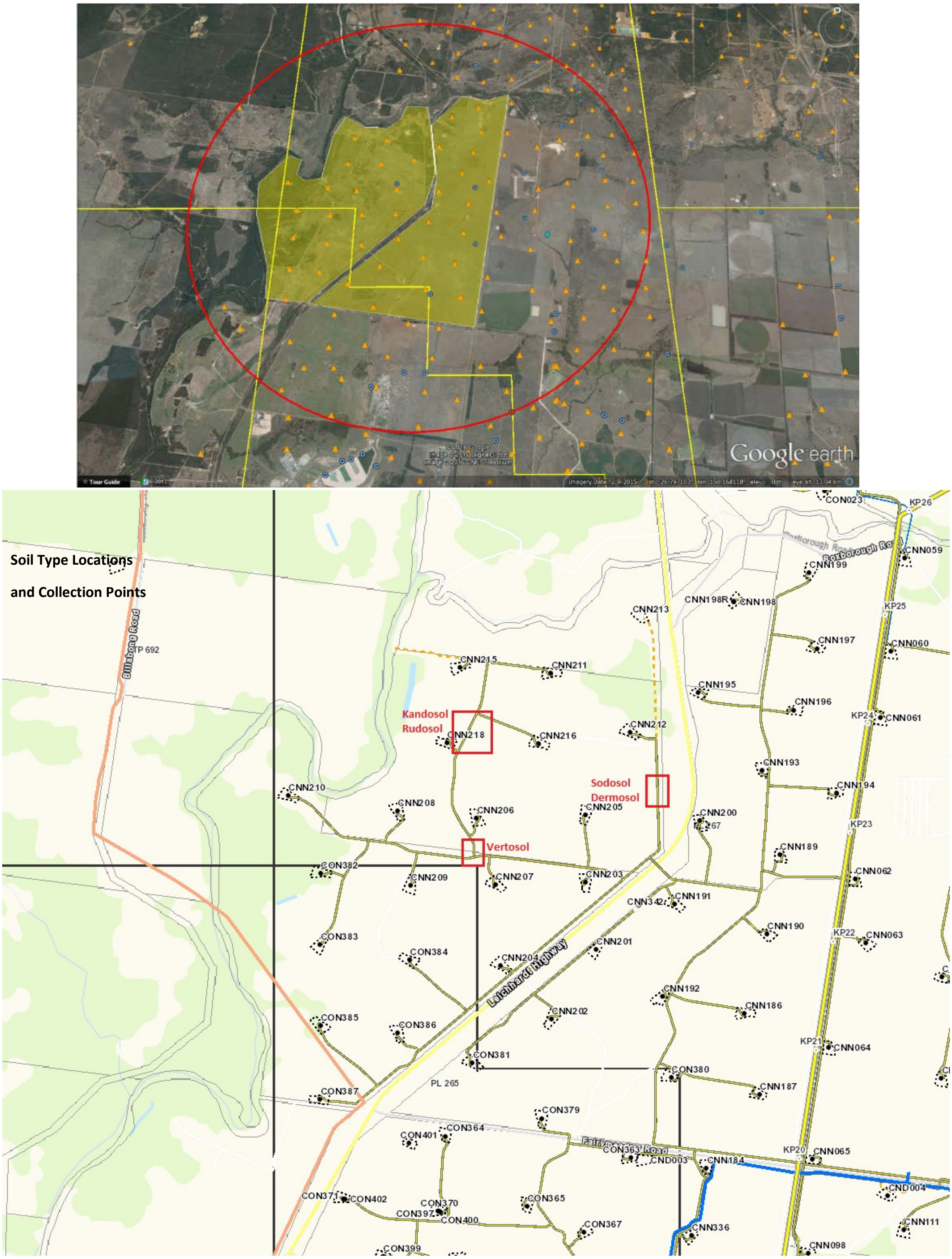

Figure 1. Google Earth image showing the location of the Condabri field site (WAP2); shaded in yellow. The orange triangles are the CSG wells and the blue dots denote registered water boreholes. The lower map shows the location of soil types in proximity of well bore locations including the ones sampled in this study.

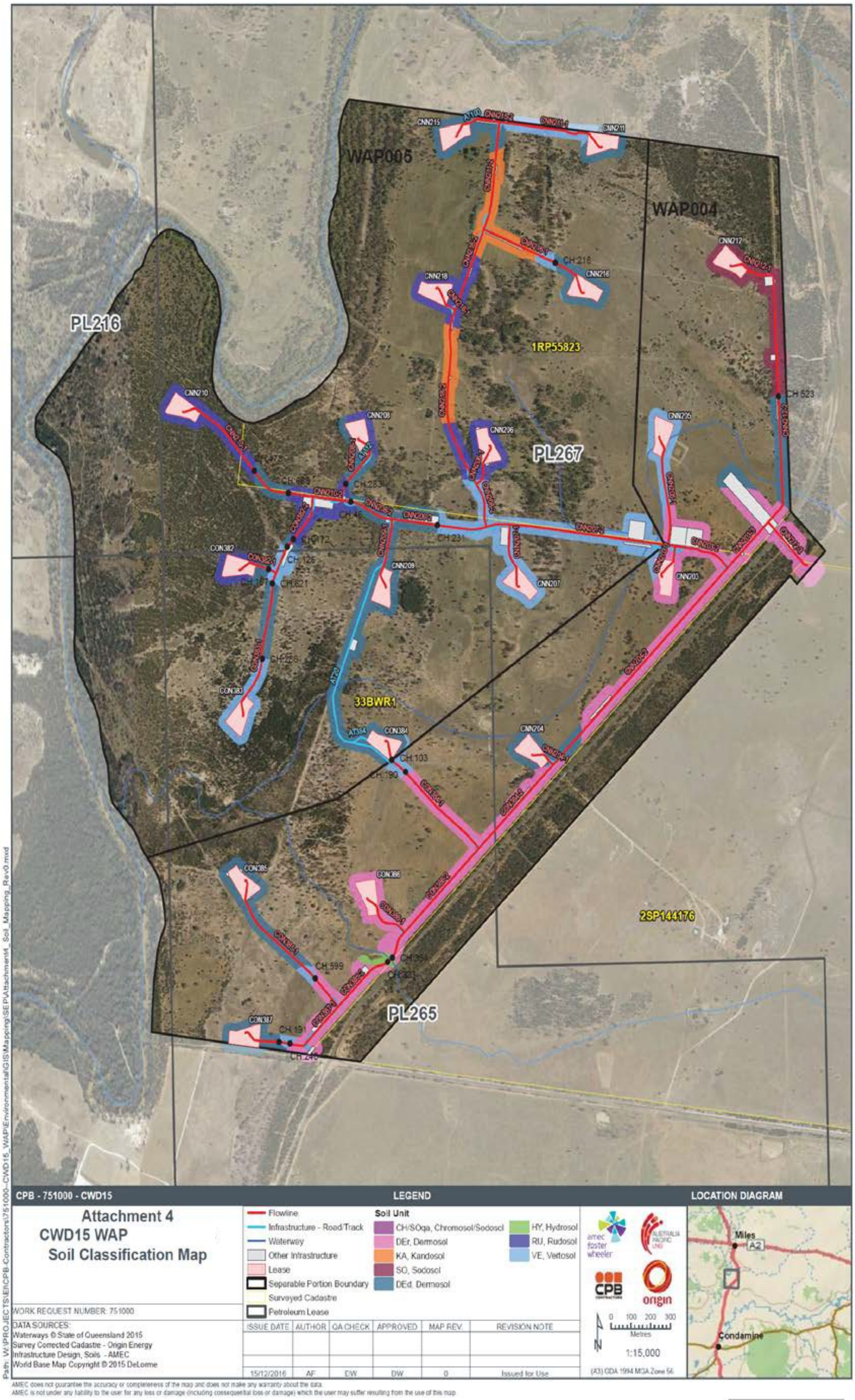

Figure 2. Soil classification map of the Condabri study area

2.2 Study site 2 - Combabula

Site 2 (Combabula) is a farmland property located approximately 100 km northwest of Miles (26°16’46’’ S, 149°33’22’’E) (Figure 3). Similar to Site 1, the property is predominantly semi-arid open grassland with stands of native tree vegetation (Figure 4). An ephemeral creek runs through the property.

The property has over 30 drilled wells, grid spaced at ~ 600 – 700 m intervals. Twenty-three of the wells were scheduled to undergo some form of well bore stimulation in the second half of 2017 after which they will be 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.

A site familiarisation visit to this site was undertaken by CSIRO staff on 20 July 2017 in order to inspect the study area, make contact with key Origin Energy staff and organise field logistics.

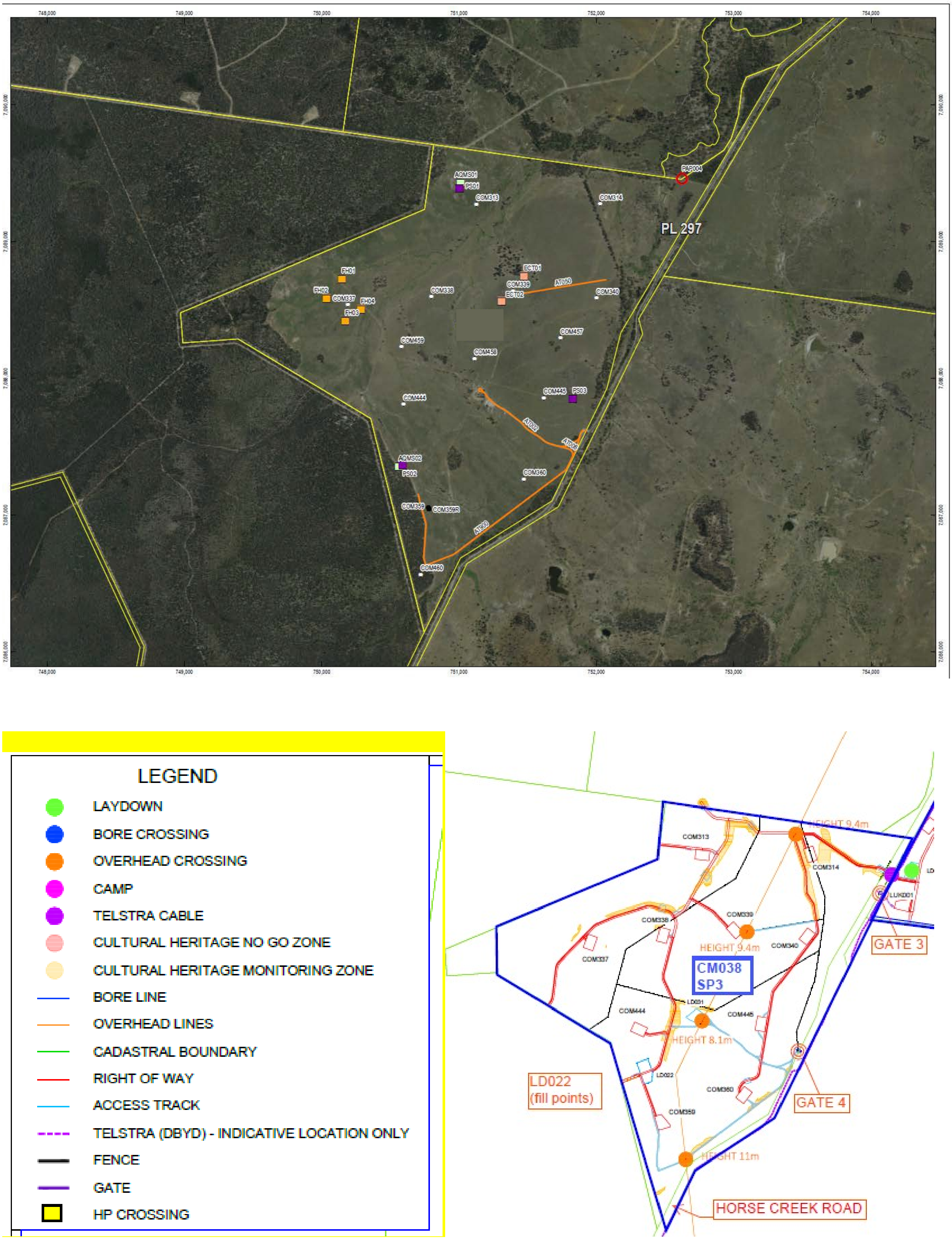

Figure 3. Google Earth image and map showing the location of the Combabula field site

Figure 4. Photographs of the Combabula property

2.3 Samples collected

2.3.1 Overview of activities

This section provides details of the samples collected during the sampling campaign. A log of the samples collected is presented in Table 1. Details of sample collection and processing procedures are provided in Section 3. Full details of the rationale underpinning the sampling plan and the chemical analyses to be conducted on the collected samples can be found in the sampling and monitoring plan (Apte et al., 2017).

2.3.2 Hydraulic fracturing fluid

Samples of HF fluids used at the five wells monitored during this study were provided by the Schlumberger HF teams (Table 1). Note that the fluid formulation is 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 were subjected to the same processing outlined in section 3.3 as other samples and then transferred to the CSIRO laboratory in Adelaide for subsequent analysis.

2.3.3 Flow-back 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 concerns, the well samples were taken by the Origin Pilots team with sample bottles and detailed sampling instructions supplied by CSIRO. A typical drill lease/well pad is shown in Figure 5.

Following HF (conducted by the Fracspread team), a separate rig was deployed (Savanna team) to flush the well. The well was then either immediately connected to the distribution system or flowed back into a holding pond for a period of time prior to connection. A nested sampling design was employed with 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.

Well flushing samples were obtained from all wells apart from CNN218 (Samples collected on behalf of CSIRO by the Savanna rig team). Only one well (CNN218) was flowed back, with water samples being obtained from the holding pond.

CON382 was taken off line after 10 weeks as the well started to produce crude oil. COM337 was suspended (pending maintenance) after 10 days of operation because of down-bore pump failure.

Further details of the samples taken may be found in the sample log (Table 1).

Figure 5. Well pad under construction at Combabula

2.3.4 Water-treatment facility (WTF) waters

Samples of raw water, post-treatment water and reject brines were taken by CSIRO staff at the Reedy Creek WTF on 3 occasions over the study period. Details of the samples collected may be found in the sample log (Table 1). Sampling locations in the treatment plant are shown in Figures 6 and 7. It should be noted that the WTF receives and treats water from CSG bores situated across the Reedy Creek and Combabula gas fields. The samples therefore provided an integrated view of water quality.

Figure 6. WTF plant input and output water sampling locations

Figure 7. WTF reject brine sampling location

2.3.5 Surface water samples

The major surface water feature within the Condabri study area is Dogwood Creek which borders the western side of the study area (Figure 8). Upstream of the study site, Dogwood Creek flows through the township of Miles and receives inputs from the town's sewage treatment works. Given concerns around 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 9) of the study area on the same day within one hour of each other. This sampling approach minimised the effects of variations in the upstream sample water quality caused by non-CSG related sources of contaminants. 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. All sampling was conducted by CSIRO staff using a clean plastic bucket attached to a nylon rope. Table 1 provides a full summary of the samples collected.

It was originally intended 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., 2017).

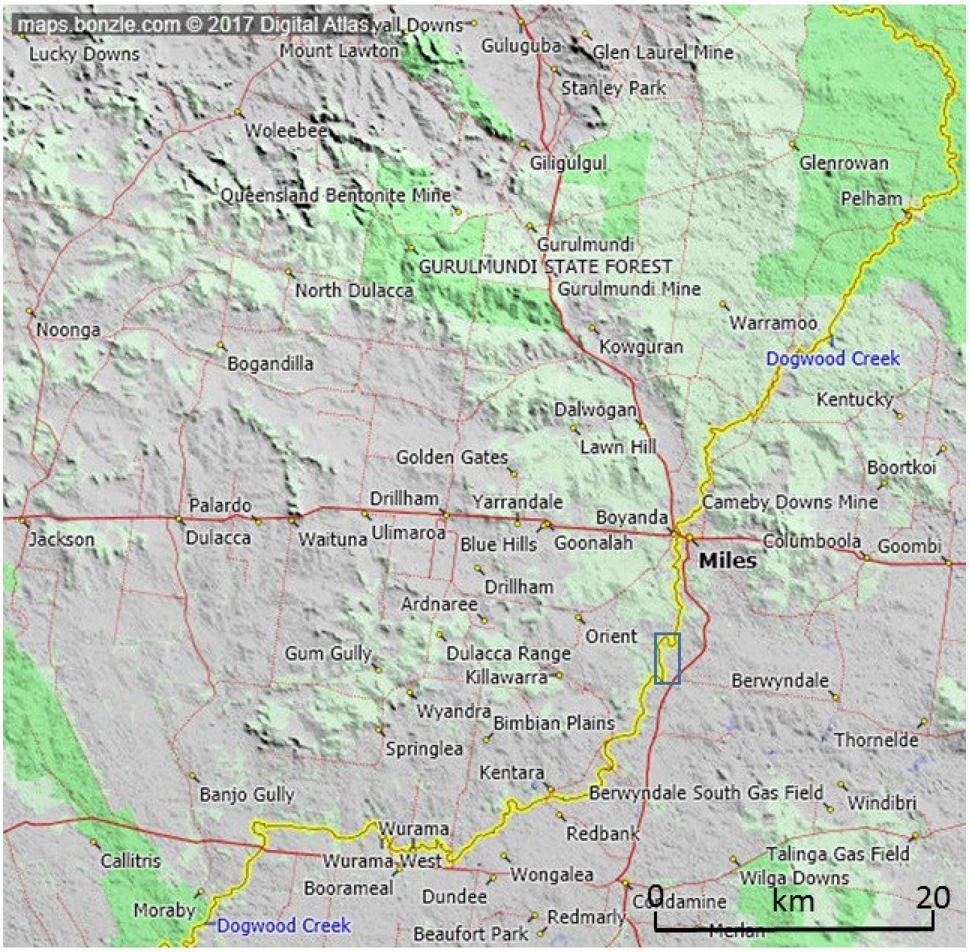

Figure 8. Map of the Condabri region showing Dogwood Creek (in yellow). The approximate location of the study area is indicated by the blue rectangle.

Figure 9. Dogwood Creek upstream and downstream sampling locations

2.3.6 Groundwater bore samples

Two registered bores at the Combabula study site were sampled on four occasions (Table 1). The location of the bores is shown in Figure 10. The first two sampling events were during HF operations and the last two after operations had ceased. Pre-HF baseline data for these bores have been provided by Origin Energy and will be reported in a forthcoming report which summarises pre-HF water and soil quality data. Sampling was conducted by CSIRO staff with assistance from Origin Energy staff. Sampling of the western supply bore, Combabula is depicted in Figure 11.

During the groundwater bore sampling events, the Eastern Supply Bore was inaccessible due to pump failure. In the last groundwater sampling campaign (February 2018), Pine Dam Bore was included.

Figure 10. Map showing the location of groundwater bores sampled during the study

Figure 11. Sampling from the western supply bore, Combabula

2.3.7 Soil sampling at Condabri (WAP2)

A common practice in the industry when preparing the well-pad is to scrape the surface soils (generally to a depth of 20-30 cm) and store them for later rehabilitation of the soil. Therefore, the subsoil on the well-pad has a greater exposure to any spills during HF operations and that of the flowback water. Soil samples were taken once the site was fully rehabilitated and was ready to be handed over 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.

Three wells: CON382, CNN218 and CNN204, at the Condabri site were selected for sampling (analysed immediately after collection). Another three wells (CNN207, CNN209 and CNN210) were sampled and archived (frozen) for future analysis if needed. The locations of the well pads/drill leases are shown in Figure 1. On the same day, samples from reference soils, i.e. adjacent areas to drill lease site but untouched by well activities (e.g. drilling, fracking, commissioning) were taken and are referred to as Background samples.

Soil cores were collected at six points around the well pad within the drill lease, excluding areas containing gas and/or water pipelines and also from a nearby reference site (Figure 12) which was deemed to be undisturbed by the HF and associated operations. The cores were sectioned into depths of 0-20 cm, 20-40 cm and 40-60 cm. Due to extensive clearing of trees at CON382 reference site, access was unable to be gained. Hence no background samples were taken for this site.

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 at CNN210.

The following sampling protocol was used:

1. Determine the location of an undisturbed site, as discussed above. The size of the sampled area will be approximately similar to drill lease sampling area. Match the soil type between the well pad and the undisturbed site.
2. With the corer, collect a core 0-60 cm and divide by measuring into 0-20, 20-40 and 40-60 cm layers. Place each layer in a respectively labelled polyphenylene ether, (PPE) sealable bag. Repeat at 5 more sample locations within the undisturbed site and create composite samples of each layer.
3. Cover sampling holes with surrounding soil as sampling takes place.
4. Complete all undisturbed areas first before starting sampling inside drill lease. Wipe/wash corer to limit potential contamination between sites.
5. At the corresponding Well Pad site, with the corer, collect a core 0-60 cm and divide by measuring into 0-20, 20-40 and 40-60 cm layers. Each. Place each layer in a respectively labelled PPE sealable bag. Repeat at 5 more sample locations within the drill lease. Samples collected will form a composite sample.
6. Cover sampling holes with surrounding soil as sampling takes place.
7. Wipe/wash the auger down and move on to next drill lease.
8. Repeat the process at all remaining drill leases.

A total of 36 composite soil samples were collected. A log of the samples collected is presented in Table 2.

The samples were subsequently shipped to the CSIRO laboratory in Adelaide for analysis. Soil samples will be subjected to chemical analysis following suitable sample preparation and extraction of the soil. Chemicals targeted will be based on the results from the chemical characterisation of the water samples. No physical or microbial characterisation will be carried out on these samples.

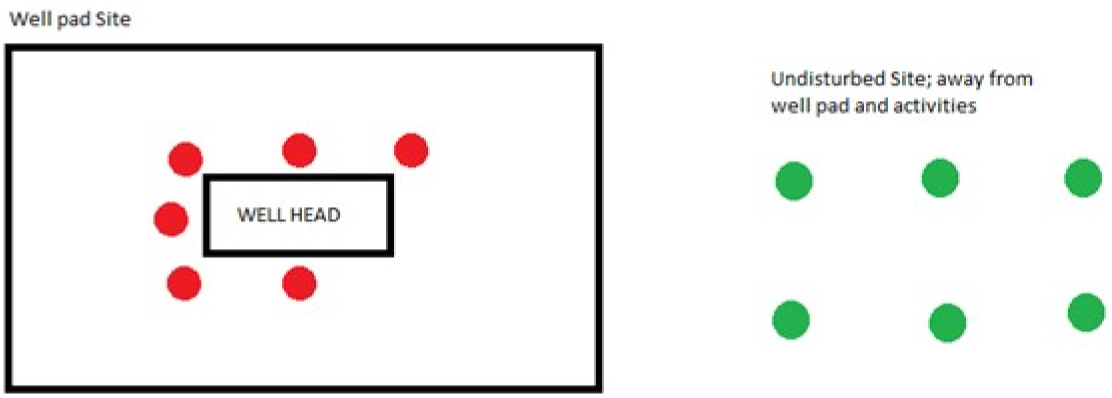

Figure 12. Example of soil sample collection locations within well pad site (red dots) and undisturbed site (green dots) with same soil type

3 Sample collection and processing procedures

3.1 Water sample collection

A number of sample bottles were filled at each sampling point.

For inorganic chemicals analysis, there were three sample bottles:

- 1 x 5 L carboy for radionuclides
- 1 x 500 mL fluorinated ethylene propylene (FEP) or fluorinated high density polyethylene (FLPE) bottle for total mercury. The bottle contained a pre-dispensed preservative - 50 mL of 0.01M bromine monochloride (BrCl). This results in a final concentration of 0.5% BrCl once the bottle is completely filled.
- 1 x 1 L acid-washed Nalgene bottle for metals and other analytes

Bottles for trace metals and total mercury were acid washed prior to shipment/use using established CSIRO procedures.

For organics analysis, five amber glass bottles were filled (Figure 13):

- 1 x 200 mL glass bottle for PAHs and phenols (supplied by CSIRO)
- 2x 40 mL glass bottles for TPH and BTEX (supplied by Australian Laboratory Services (ALS), both pre-acidified)
- 2 x 500 mL bottles for other organics including geogenic compounds (supplied by CSIRO, pre-acidified by adding 250 μL of concentrated sulfuric acid to each bottle)

The 200 mL and 500 mL bottles supplied by CSIRO were solvent washed and baked prior to use using established CSIRO procedures. At each sample collection time the bottles were filled with water to the top, ensuring zero headspace and capped with a polytetrafluoroethylene (PTFE) lined cap. The bottles were placed in an Esky (cooled with ice packs) and kept in the dark. The samples were transferred to the field laboratory as soon as possible and stored in a refrigerator.

Field blanks were prepared at regular intervals by filling a set of bottles with ultra-high purity (MQ) deionisedMilli-Q) water. Duplicate samples and field spiked blanks were also taken at selected locations.

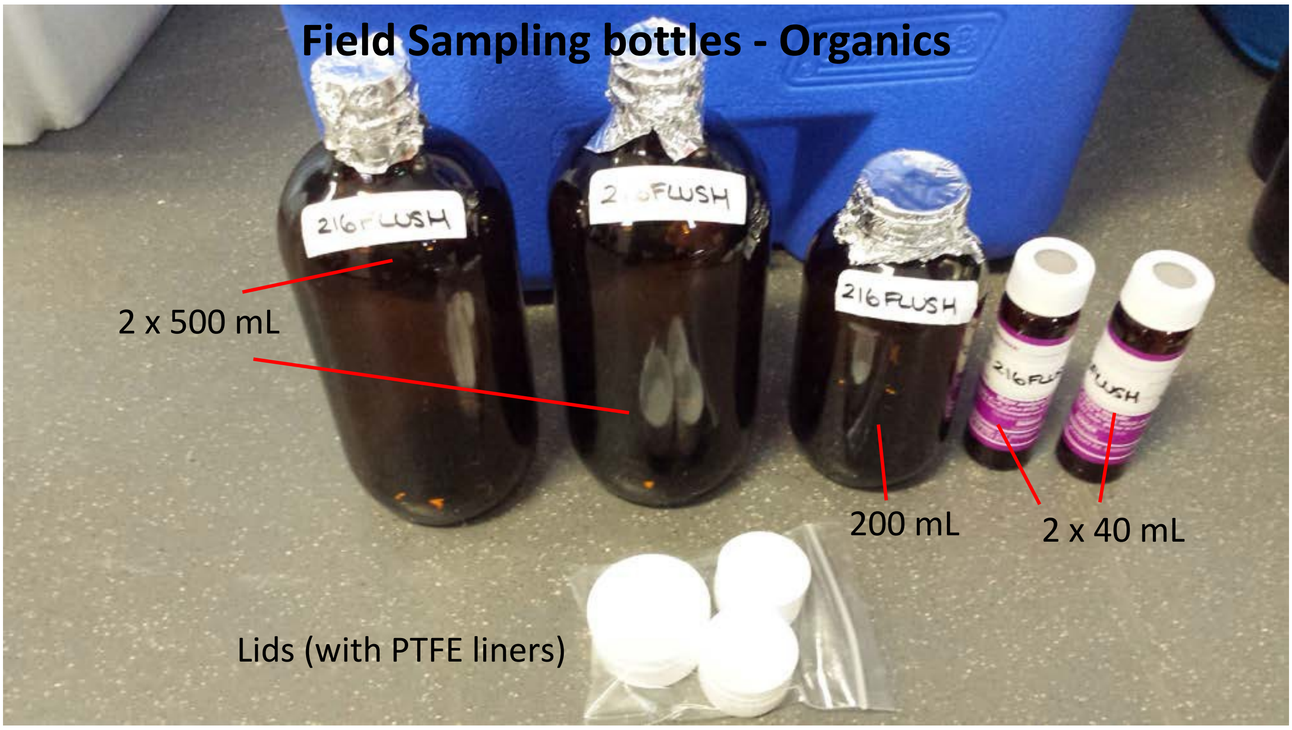

Figure 13. Sampling bottles for field collection of water samples for organics analysis

3.2 Sample processing - Inorganics

The collected samples were processed in the field laboratory as indicated below. The bottles used in the sample processing operations are shown in Figure 14.

Radionuclides (5 L carboy) - no further treatment was required. Samples were stored at room temperature and transferred to ANSTO, Lucas Heights, NSW for radiochemical analysis.

Total mercury (500 mL FEP bottle) - no further processing was required. The samples were stored refrigerated or at room temperature and transferred to CSIRO Land &Water, Lucas Heights for subsequent analysis.

The following sub-samples were taken from the 1 L Nalgene bottle:

Total metals A 100 mL sub-sample was decanted into an acid-washed polyethylene bottle (125 or 250 mL). The sub-sample was then acidified to 0.2% v/v nitric acid (0.2 mL concentrated nitric acid per 100 mL sample).

TSS/Alkalinity A sub-sample (200 to 300 mL) was decanted into a 500 mL polyethylene bottle and stored refrigerated.

Total Organic Carbon (TOC) A sub-sample was decanted into a 40 mL glass vial and stored refrigerated.

Sample filtration (dissolved metals)

Filtration was carried using an all plastic, acid-washed Sartorius filtration rig loaded with a 0.45 µm membrane filter. The filter was cleaned by filtering 50 mL of dilute nitric acid (10% v/v) followed by two 100 mL aliquots of ultrapure deionised water and a 50 mL aliquot of the sample.

Between 50 and 100 mL of the sample was then filtered, decanted into an acid-washed, 125 or 250 mL polyethylene bottle and then acidified to 0.2% v/v nitric acid (0.2 mL concentrated nitric acid per 100 mL sample). The bottle was stored at room temperature.

If samples were difficult to filter, pre-filtration was carried out using an acid-washed GF/C or GF/F glass fibre filter prior to filtration through a 0.45 µm membrane filter.

Nutrients and anions

Sub-samples for nutrients and anion analysis were first filtered using disposable syringes and 0.45 µm filter cartridges. For nutrient analysis, at least 40 mL of the filtrate was then transferred into a National Measurement Institute (NMI) ammonia bottle which contained a pre-dispensed sulfuric acid preservative. The bottle was then stored refrigerated.

Another 40 mL aliquot of filtrate for anions analysis at NMI was dispensed into a plastic bottle and stored frozen. Approximately 20 mL of filtrate was transferred into a 30 mL polycarbonate vial and stored frozen. This vial was for anions analysis to be carried out at CSIRO.

Sample transfer

All processed samples were subsequently transferred to CSIRO Land & Water, Lucas Heights, NSW. Samples for nutrients and radiochemical analyses were then delivered to the NMI and ANSTO respectively. Both laboratories are situated in Sydney, NSW.

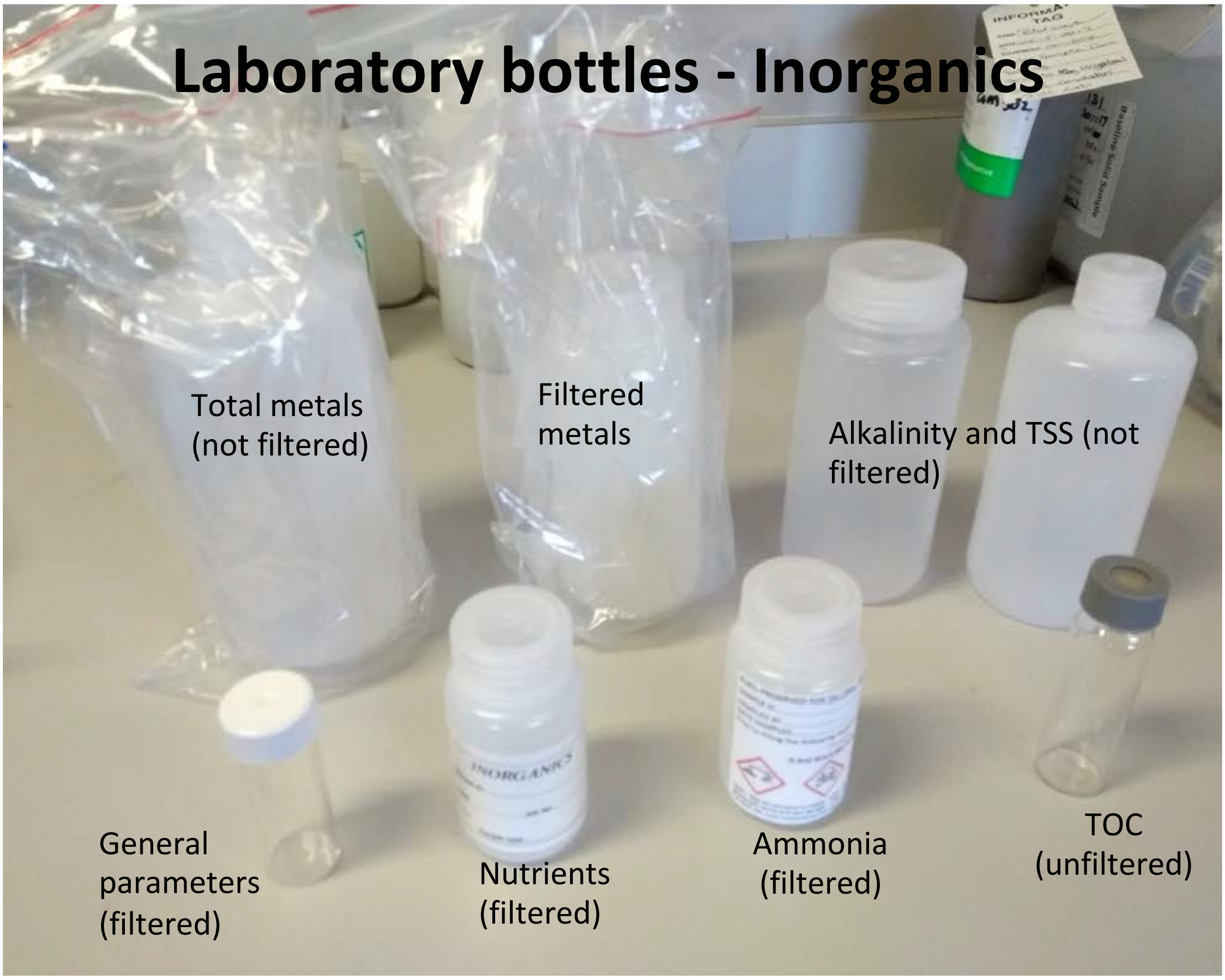

Figure 14. Sample bottles for inorganics samples processed in the field laboratory

3.3 Sample processing - Organics

Laboratory processing

On return to the laboratory, all samples were stored refrigerated (<4^{o}C). The 200 mL polyethylene bottle and 40 mL glass bottles did not require any further processing and were shipped to NMI, Sydney within 3 days of collection (within the advised holding time) for analysis. The 500 mL samples required extensive sample processing involving filtration, spiking with analytical and deuterated standards and solid phase extraction (Figure 15). Prior to the start of sample processing, one 500 mL bottle was labelled ‘a’ and the other labelled ‘s’.

Preparation of spikes, standards and dinitrophenylhydrazine (DNPH) solution

The sample spike additions and DNPH derivatisation solution were prepared in methanol as outlined below. Once prepared, solutions were stored at -18^{o}C and when required for sample spike additions were let to come to room temperature for use and then returned to the freezer.

Isotope 10 mg/L stock solution containing:

1 mL of 1 mg/mL triethanolamine d15

1 mL of 1 mg/mL fumaric Acid ^{13}C

10 mL of 0.454% (v/v) formaldehyde ^{13}C, d2

Final volume made up to 100 mL with methanol

Isotope Geogenic 10 mg/L stock solution containing:

1 mL of 1 mg/mL p-cresol d8

1 mL of 1 mg/mL naphthalene d8

1 mL of 1mg/mL anthracene d10

Final volume made up to 100 mL with methanol

Standard Addition (StdAdd)

10 mL of 1 mg/mL HMX (octogen)

10 mL of 1 mg/mL formaldehyde

10 mL of 1 mg/mL methylisothiazolinone

10 mL of 1 mg/mL fumaric acid

10 mL of 0.1% (v/v) butoxyethanol solution

10 mL of 1 mg/mL dimethylformamide

10 mL of 0.2% (v/v) glutaraldehyde solution

Final volume made up to 100 mL with methanol. The concentration of the standards in the StdAdd solution was 100mg/L aside from glutaraldehyde which was 200 mg/L.

Fluorobenzoic acid (FBA StdAdd1) 100 mg/L stock solution containing:

10 mL of 1 mg/mL 4-fluorobenzoic Acid

10 mL of 1 mg/mL 3-fluorobenzoic Acid

10 mL of 1 mg/mL 2-trifluoromethylbenzoic Acid

10 mL of 1 mg/mL 2,6-difluorobenzoic Acid

10 mL of 1 mg/mL 2,3,4-trifluorobenzoic Acid

Final volume made up to 100 mL with methanol

Fluorobenzoic acid (FBA StdAdd2) 100 mg/L stock solution containing:

10 mL of 1 mg/mL 2,3,4,5-tetrafluorobenzoic acid

10 mL of 1 mg/mL 2,4,5-Trifluorobenzoic Acid

10 mL of 1 mg/mL 2,4-difluoromethylbenzoic acid

10 mL of 1 mg/mL 2,5-difluorobenzoic acid

Final volume made up to 100 mL with methanol

BTEX (used only for Spike Blanks for NMI analysis) prepared as a 200 mg/L solution:

Using 1 mL of 2 mg/mL BTEX mixture and made up to 10 mL with methanol. No headspace present.

DNPH derivitising solution

Add 20 mL of 1 g/L DNPH solution in acetonitrile to a graduated vial. Blow solution down under N_2 until 2 mL remains. Add 10 mL Milli-Q water, transfer to an amber bottle and add 4 mL of concentrated hydrochloric acid.

Sample filtration and spiking

Samples were filtered using an all-glass manifold connected to vacuum pump and GF/F filter papers. The filters were replaced as required when water flow reduced markedly. Used filters were transferred to individual labelled zip-lock bags and stored in the dark at -18^{o}C.

Once filtration was completed, the original collection bottle was rinsed with Milli-Q water and the filtrate returned to the bottle. Each 500 mL bottle then had 8 mL of solution removed by pipette and transferred to small amber vial. These were labelled “UNKNOWNS”. Unknown samples were stored at <4^{o}C and analysed at CSIRO for HF chemicals using liquid chromatography-quad time of flight-mass spectrometry (LC-QTOF-MS).

To both 500 mL bottles, 100 µL of ISOTOPE and 100 µL of ISOTOPE GEOGENIC standards were then added. From bottle ‘a’ another 8 mL aliquot was removed and transferred to a small amber-glass vial, to which 400 µL of DNPH solution was added. This aliquot was labelled “ALDEHYDE ‘a’ ”.

To bottle ‘s’, 100 µL each of StdAdd, FBA StdAdd 1 and FBA Std 2 were added. The spiked solution was mixed thoroughly by gentle agitation and then another 8 mL portion was removed by pipette and transferred to an amber glass vial, to which 400 µL of DNPH solution was added. This aliquot was labelled “ALDEHYDE ‘s’ ”.

All prepared solutions were stored at <4^{o}C until required for the SPE step (see below).

Solid Phase Extraction (SPE)

The SPE extraction manifold which was set up in the field laboratory is shown in Figure 16. In order to isolate a wide range of organic compounds, three SPE cartridge types were used: 6 mL and 3 mL hydrophilic-lipophilic balance (HLB) copolymer, as well as C18 and activated carbon (AC2). The C18 and AC2 cartridges were connected together using adapters (C18/AC2). A 3 mL plastic syringe barrel was installed on top of the C18 cartridge to allow rinsing and connection to sample uptake lines.

All cartridges were pre-conditioned by passing successive aliquots of dichloromethane (DCM), methanol then two lots of Milli-Q water through the columns. For the 3 mL cartridges, 3 mL of each solvent was used, for the 6 mL cartridges, 6 mL of each solvent was used. Care was taken to ensure that the C18/AC2 cartridges did not run dry. Sample uptake lines were filled with Milli-Q water (using a pipette) and connected to the cartridges and a vacuum pump. The required flow rate was approximately 1 drop per second for all cartridges.

Both lots of 500 mL were split in half, one portion of which was passed through the conditioned C18/AC2 cartridges, the other half was passed through the 6 mL HLB cartridge. The masses of each portion loaded onto the cartridges were recorded. The 8 mL amber-glass vial 'ALDEHYDE' samples were loaded onto separate 3 mL HLB cartridges.

Once all solutions were drawn through the cartridges, the vacuum flow was continued for an additional 15 min to dry the SPE cartridge. Once dry, the cartridges were recovered and stored frozen.

The extraction manifold and uptake lines were cleaned between samples by passing approximately 100 mL of methanol and then 100 mL MQ water through the manifold. The apparatus was then left to drain. If sample was particularly dirty, the apparatus was cleaned with paper towel, rinsed with acetone and allowed to dry.

For each sample, there was a:

- 1x 6 mL HLB cartridge denoted "a"
- 1x 6 mL HLB cartridge denoted "s"
- 1x C18/AC2 cartridge denoted "a"
- 1x C18/AC2 cartridge denoted "s"
- 1x 3 mL HLB cartridge denoted ALDEHYDE "a"
- 1x 3 mL HLB cartridge denoted ALDEHYDE "s"

All cartridges were transferred to the CSIRO laboratory in Adelaide for subsequent sample elution and analysis for selected organic compounds by liquid chromatography tandem-mass spectrometry (LC-MS/MS).

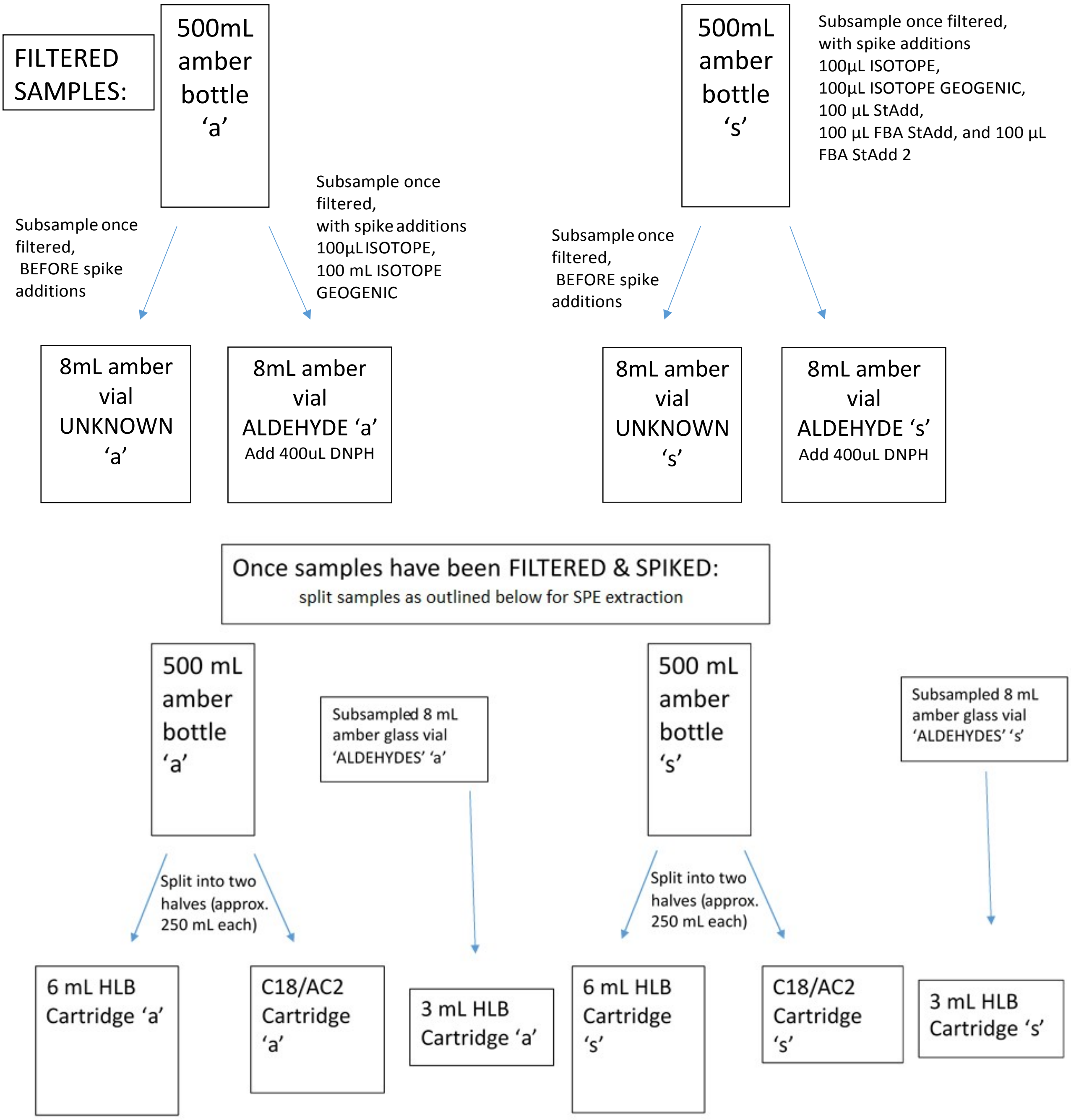

Figure 15. Organic analysis: sample preparation scheme and SPE extraction scheme

Figure 16. Views of the SPE apparatus set up at Reedy Creek

Table 1. Log of samples collected during the field study and pH/conductivity measurements

Sample Description	Sampling Date	pH	Conductivity (mS/cm)
Surface waters			
Dogwood Creek Upstream	27/07/2017	7.04	0.113
Dogwood Creek Upstream 11 am	3/08/2017	6.35	0.105
Dogwood creek upstream	18/08/2017	7.40	0.119
Dogwood Creek Upstream	13/09/2017	7.27	0.116
Dogwood Creek Upstream	1/11/2017	7.20	0.111
Dogwood Creek Downstream	27/07/2017	6.95	0.114
Dogwood Creek Downstream 11:30 am	3/08/2017	6.34	0.108
Dogwood creek downstream	18/08/2017	7.30	0.120
Dogwood Creek Downstream	13/09/2017	7.34	0.101
Dogwood Creek Downstream	1/11/2017	7.24	0.130
Groundwater			
GW1 (Western Supply Bore)	17/08/2017	8.81	1.490
GW1 (taken from holding pond)	19/10/2017	9.33	1.782
GW1	14/12/2017	8.80	1.524
GW1 duplicate	14/12/2017	8.80	1.567
GW1	13/02/2018	8.85	1.523
GW2	17/08/2017	8.73	1.635
GW2 (COM-LB037) 9:00 am	19/10/2017	8.79	1.578
GW2 (COM-LB037) 9:45am	14/12/2017	8.70	1.577
GW2	13/02/2018	8.77	1.353
GW3 (tank originally thought to be Eastern Supply Bore)	17/08/2017	8.72	1.923
GW3 9:30 am	19/10/2017	8.88	1.733
Pine Dam Bore Feb 2018	13/02/2018	8.59	1.976

Sample Description	Sampling Date	pH	Conductivity (mS/cm)
Wastewater treatment plant			
WTF In	9/11/2017	8.76	6.412
WTF In	11/01/2018	8.69	6.778
WTF In duplicate	11/01/2018	8.70	6.745
WTF In	7/3/2018	8.59	6.545
WTF Out	9/11/2017	8.14	0.682
WTF Out	11/01/2018	7.81	0.508
WTF Out	7/3/2018	7.73	0.473
WTF Brine	9/11/2017	8.53	35.62
WTF Brine	11/01/2018	8.49	34.96
WTF Brine	7/3/2018	8.38	37.56
Hydraulic fracturing fluids			
CNN218 Zones 1 to 8	19/07/2017	-	-
CNN204 Zones 1 to 10	12/08/2017	-	-
CON382 Zones 1 to 10	26/07/2017	-	-
COM313 Zones 1 to 10	10/10/2017	-	-
COM337 Zones 1 to 8	12/10/2017	-	-
Flowback and Produced Waters			
CNN218a-1 (flowback)	19/07/2017	6.81	26.54
CNN218a-2 (flowback)	20/07/2017	6.65	21.89
CNN218a-3 (flowback)	20/07/2017	6.60	20.71
CNN218a-4 (flowback)	21/07/2017	6.45	20.01
CNN218 (flowback)	22/07/2017	6.55	18.79
CNN218 (produced)	1/08/2017	7.04	219.4
CNN218 (produced)	3/08/2017	6.93	58.31
CNN218 (produced)	4/08/2017	7.05	49.00
CNN218a-8 (produced)	8/08/2017	7.11	32.75
CNN218 (produced)	16/08/2017	7.23	24.31
CNN218 (produced)	22/08/2017	7.56	18.29
CNN218 (produced)	14/09/2017	8.22	12.83
CNN218 (produced)	10/10/2017	8.56	10.54
CNN218 (produced)	12/12/2017	8.18	8.778
CNN218 (produced)	9/01/2018	8.19	8.171
CON382 flush 11am (Flush-1)	26/07/2017	6.86	20.14
CON382 end of flush 1330 (Flush-2)	26/07/2017	6.23	23.71
CON382	29/07/2017	6.89	19.72
CON382	30/07/2017	6.95	19.43
CON382	31/07/2017	6.99	19.45
CON382	1/08/2017	7.01	18.98
CON382	3/08/2017	7.14	18.00

Sample Description	Sampling Date	pH	Conductivity (mS/cm)
CON382	4/08/2017	7.23	17.74
CON382	8/08/2017	7.59	17.26
CON382	16/08/2017	8.11	14.10
CON382	22/08/2017	7.75	12.37
CON382 duplicate	22/08/2017	7.75	12.23
CON382	14/09/2017	8.19	9.415
CON382	10/10/2017	8.42	8.198
CNN204 clean (Flush-1)	12/08/2017	7.19	31.70
CNN204 dirty (Flush-2)	12/08/2017	8.82	31.67
CNN204	14/08/2017	7.28	109.3
CNN204	15/08/2017	7.24	41.94
CNN204	16/08/2017	6.70	34.35
CNN204	22/08/2017	7.12	18.05
CNN204	29/08/2017	7.36	13.71
CNN204	5/09/2017	7.57	11.48
CNN204	13/09/2017	8.05	10.39
CNN204	10/10/2017	8.94	8.148
CNN204	15/11/2017	8.00	7.870
CNN204	12/12/2017	8.38	7.943
CNN204	9/01/2018	8.30	7.913
COM313 Flush-1	10/10/2017	7.41	27.71
COM313 Flush-2	10/10/2017	7.52	29.63
COM313 Produced Day 1	19/10/2017	8.53	32.68
COM313 Produced Day 2	20/10/2017	7.45	19.12
COM313 Produced Day 3	21/10/2017	7.54	16.10
COM313 Produced Water Week 1	26/10/2017	7.80	13.72
COM313 Produced Water	31/10/2017	7.64	13.20
COM313 Produced Water	8/11/2017	8.14	11.43
COM313 Week 4	14/11/2017	7.83	11.32
COM313	12/12/2017	8.05	9.488
COM313	9/01/2018	8.26	9.642
COM313	12/02/2018	8.17	9.574
COM313	12/3/2018	8.12	10.38
COM313 April 2018	4/4/2018	Pending	Pending
COM313 (duplicate) April 2018	4/4/2018	Pending	Pending
COM337 Flush-1	12/10/2017	7.55	33.08
COM337 Flush-2	12/10/2017	7.85	31.64
COM337 Produced Day 1	20/10/2017	8.42	33.12
COM337 Produced Day 2	21/10/2017	7.49	13.39
COM337 Produced Day 3	22/10/2017	7.60	11.72

Sample Description	Sampling Date	pH	Conductivity (mS/cm)
COM359R Flush-1	19/10/2017	4.52	35.96
COM359R Flush-2	19/10/2017	6.62	34.39
COM359R Produced Water Day 1	24/10/2017	7.78	36.28
COM359R Produced Water Day 2	25/10/2017	7.05	25.98
COM359R Produced Water Day 3	26/10/2017	7.14	24.55
COM359R Produced Water	1/11/2017	7.14	20.70
COM359R Produced Water	8/11/2017	8.14	17.80
COM359R Week 4	12/12/2017	7.45	17.31
COM359	12/12/2017	8.25	14.80
COM359R	9/01/2018	7.96	14.16
COM359R	12/02/2018	8.07	13.25
COM359R March 2018	12/3/2018	8.04	14.52
COM359R April 2018	4/4/2018	Pending	Pending
COM359R (duplicate) April 2018	4/4/2018	Pending	Pending

Table 2. Soils samples collected from Condabri

	Well	Type	Depth (cm)	Date Collected
1	CNN204	Background	0-20	8/11/2017
2	CNN204	Background	20-40	8/11/2017
3	CNN204	Background	40-60	8/11/2017
4	CNN207	Background	0-20	8/11/2017
5	CNN207	Background	20-40	8/11/2017
6	CNN207	Background	40-60	8/11/2017
7	CNN209	Background	0-20	8/11/2017
8	CNN209	Background	20-40	8/11/2017
9	CNN209	Background	40-60	8/11/2017
10	CNN210	Background	0-20	8/11/2017
11	CNN210	Background	20-40	8/11/2017
12	CNN210	Background	40-60	8/11/2017
13	CNN218	Background	0-20	8/11/2017
14	CNN218	Background	20-40	8/11/2017
15	CNN218	Background	40-60	8/11/2017
16	CNN210	Hand Auger background	0-20	8/11/2017
17	CNN210	Hand Auger background	20-40	8/11/2017
18	CNN210	Hand Auger background	40-60	8/11/2017
19	CNN204	Drill lease	0-20	8/11/2017
20	CNN204	Drill lease	20-40	8/11/2017
21	CNN204	Drill lease	40-60	8/11/2017
22	CNN207	Drill lease	0-20	8/11/2017
23	CNN207	Drill lease	20-40	8/11/2017
24	CNN207	Drill lease	40-60	8/11/2017
25	CNN209	Drill lease	0-20	8/11/2017

	Well	Type	Depth (cm)	Date Collected
26	CNN209	Drill lease	20-40	8/11/2017
27	CNN209	Drill lease	40-60	8/11/2017
28	CNN210	Drill lease	0-20	8/11/2017
29	CNN210	Drill lease	20-40	8/11/2017
30	CNN210	Drill lease	40-60	8/11/2017
31	CNN218	Drill lease	0-20	8/11/2017
32	CNN218	Drill lease	20-40	8/11/2017
33	CNN218	Drill lease	40-60	8/11/2017
34	CON382	Drill lease	0-20	8/11/2017
35	CON382	Drill lease	20-40	8/11/2017
36	CON382	Drill lease	40-60	8/11/2017

Table 3. Summary of the water and soil sampling program

Sample type	Samples to be collected	Proposed number of samples	Actual no. samples taken	Notes
Dogwood Creek	Surface water	16	10	Samples collected upstream and downstream of the Condabri study area. Five sampling events: 3 during and 2 after HF operations.
Farm dams	Surface water	12	0	Samples not taken owing to lack of suitable sampling sites
Water bores	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.
Hydraulic fracturing	HF fluid samples	6	46	Frac zone samples (between 8 to 10 per well) used at 5 wells (typically between 8 and 10 zones) were obtained
Stimulation, flow back and production phases	Flushing, produced & flowback waters	68	76	Six wells were monitored over a period of 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.
Wastewater treatment facility	Incoming water	3	4	Samples taken at the Reedy Creek WTF on 3 occasions over a four month period
Post-treatment	RO-treated water	3	3	Samples taken at the Reedy Creek WTF on 3 occasions over a four month period
Membrane rejects	Brine	3	3	Samples taken at the Reedy Creek WTF on 3 occasions over a four month period

Sample type	Samples to be collected	Proposed number of samples	Actual no. samples taken	Notes
TOTAL		**123**	**154**	
Soils	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 has 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 contamination is detected).

4 Overview and observations

A summary of the number of water and soil samples collected compared to the planned numbers is presented in Table 3. Despite some changes to the sampling program owing to delays and some HF equipment breakdowns there was an increase in the number of samples collected (154) compared to planned (123).

Conductivity and pH data for the water samples collected are presented in Table 1. Detailed interpretation of the field data alongside the data generated during the laboratory analysis phase of the project will be presented in the final project report (due end of 2018). However, some preliminary observations can be drawn from the pH and conductivity data (Table 1):

- Dogwood Creek samples have the lowest conductivity of all samples collected (mean: 0.114 ± 0.08 mS/cm). The creek water pH is neutral to slightly acidic.
- Groundwater sample pH is alkaline (mean: 8.81±0.18). Sample conductivity (mean: 1.64 ± 0.18 mS/cm) is an order of magnitude higher than Dogwood Creek.
- WTF samples: water pH was alkaline and conductivities decease (as expected) in the sequence: Brine> WTF in > WTF out.
- Well waters have high variability in pH and conductivity across sites. The pH range is typically 6.5 to 8.5 and conductivity ranged typically from 10 to 50 mS/cm with some excursions to higher values. Note that coastal seawater has typical conductivity of approximately 50 mS/cm.

5 Conclusions

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

2. The samples comprised creek waters, groundwater, produced water flowback water, samples of HF fluid and soil cores from well pads.

3. A total of 154 water and HF fluid samples were collected compared to 123 planned. Soil sampling was conducted at selected drill leases at Condabri and the number of samples collected were close to the planned number (36 samples collected compared to 40 planned).

4. The samples are now undergoing extensive laboratory analysis. The results will be reported in a future GISERA report later in 2018.

6 Reference

Apte, S.C., Kookana, R.S. and Williams, M. (2017). 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. A task report to the Gas Industry Social and Environmental Research Alliance (GISERA), July 2017. CSIRO, Canberra, 28 pages.

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