Air Quality Measurement Report

Task 1 Report for Project W.12

Air, water and soil impacts of hydraulic fracturing: Phase 2

March 2018

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Document control

6 March 2018

Version	Date	Description	Author	Approved
1	28/02/2018	Draft report for CSIRO internal review	ED	MK
2	05/03/2018	Draft report incorporating review comments	ED	MK
3	14/3/18	Final Report	ED	MK PK

Report Title

ISBN (print): 978-1-4863-1008-1
ISBN (online): 978-1-4863-1009-8

The Gas Industry Social and Environmental Research Alliance (GISERA) undertakes publicly-reported research that addresses the socio-economic and environmental impacts of Australia's natural gas industries.
GISERA was co-founded by CSIRO and Australia Pacific LNG in July 2011. For further information visit gisera.csiro.au.

Citation

Dunne, E., Keywood, M., Selleck, P., Powell, J., Cheng, M., Desservettaz, M., Edwards, G., Harnwell, J., Henson, S., Molloy, S., , Sisoutham, O., Ward, J., Werczynski, S., Williams, A. (2018) Air Quality Measurement Report. Task 1 Report for Project W.12 to the Gas Industry Social and Environmental Research Alliance (GISERA). Feb 2018. CSIRO, Canberra.

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Photo of hydraulic fracturing activity in the Surat Basin. Photo credit to Erin Dunne

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Glossary

Units of measurement

ha	unit of area equal to 10 000 m^2, or approximately 2.47 acres or
$\mu g\ m^{-3}$	micrograms per cubic metre (1 microgram = one millionth of a gram)
$ng\ m^{-3}$	nanograms per cubic metre (1 nanogram = 1 billionth of a gram)
ppm	parts per million by volume
ppb	parts per billion by volume
$l\ min^{-1}$	litres per minute
$ml\ min^{-1}$	millilitres per minute
Bqm^{-3}	Becquerel per cubic metre, a unit of radioactivity
µm	micrometre (1 micrometre = 1 millionth of a metre)

Nomenclature

Aldehyde	**a class of oxygenated volatile organic compounds**
Ambient air	outdoor air
BTEX	benzene, toluene, ethylbenzene, xylenes (a subset of VOCs)
Coal Seam Gas (CSG)	a type of natural gas, composed primarily of methane, extracted from coal seams
Detection limit	the lowest reliably measurable concentration of a pollutant for a particular analytical technique
Flowback	Following HF, the target coal seams which have become pressurised, may be allowed to depressurise by opening a discharge valve on the wellhead, which allows the well to flow back fluid to surface.
Flowback fluids	Flowback fluids are fluids that are returned to the surface via the well directly after hydraulic fracturing during flowback. These fluids may contain HF fluids, groundwater from the coal seam, and coal seam gas.
Hydraulic Fracturing (HF)	a well stimulation process that is used to increase the flow of gas and water from a gas well. HF involves the high pressure injection of a large volume of fluids into a well in order to fracture targeted coal seams and open pathways for gas and fluids to flow into the well.
Hydraulic Fracturing Fluids	HF fluids are predominantly water and proppant (~ 97 - 98%) with a small amount of chemical additives

Isowipes	alcohol (isopropanol) wipes
Kimwipes	lint free tissues
pH	a scale used to assess the acidity or alkalinity of a solution
Proppants	Solids, usually sand, treated sand or manufactured ceramic material, added to hydraulic fracturing fluids in order to prop open the fractures in the target coal / shale seam induced by the hydraulic fracturing treatment.
Gas processing facility (GPF)	A facility which compresses and dries gas
Geogenic	of geological origin
Tracer	a gas or particle measurement used as a proxy for other atmospheric constituents not directly measured, or used to indicate the likely impact of a specific pollution source.

Abbreviations

ANSTO	Australian Nuclear Science and Technology Organisation
AQMS	Air Quality Monitoring Station
ARPANSA	Australian Radiation Protection and Nuclear Safety Agency
BTEX	a subset of VOCs including benzene, toluene, ethylbenzene and xylenes
CO	carbon monoxide
CO_2	carbon dioxide
CSG	Coal seam gas
CSIRO	Commonwealth Scientific and Industrial Research Organisation
DNPH	Dinitrophenylhydrazine
EPP	Environment Protection Policy- Queensland
CH_4	methane
GISERA	Gas Industry Social and Environmental Research Alliance
HF	Hydraulic Fracturing
H_2S	hydrogen sulphide
NEPM	National Environment Protection Measure
NO_x	oxides of nitrogen
NO_2	nitrogen dioxide
NPI	National Pollutant Inventory

O_3	ozone
PAH	polycyclic aromatic hydrocarbons
$PM_{2.5}$	particulate mass with an aerodynamic diameter of < 2.5 µm
PM_{10}	particulate mass with an aerodynamic diameter of < 10 µm
QAEHS	Queensland Alliance of Environmental Health Sciences
TSP	total suspended particles
VOC	volatile organic compounds

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.

We gratefully acknowledge the teams from the Queensland Alliance for Environmental Health Sciences (QAEHS) and the Australian Nuclear Science and technology Organisation (ANSTO) for their assistance in sample media preparation.

The field work component of this project would not have been possible without the cooperation of the landholders who hosted this study. We also gratefully acknowledge assistance from Origin Energy and the field operations team at Origin Energy's Reedy Creek gas processing facility for facilitating access to the study site.

Executive summary

Hydraulic fracturing (HF) is a well stimulation process that is used to increase the flow of gas and water from a gas well. HF involves the high pressure injection of a large volume of fluids into a well in order to fracture targeted coal seams and open pathways for gas and fluids to flow into the well. The potential impact on air, surface water, groundwater and soil of HF operations in coal seam gas production are of general concern to communities living in gas development regions.

The GISERA Air, Water and Soil Impacts of Hydraulic Fracturing: Phase 2 (W.12) project addresses some of these concerns by carrying out a comprehensive investigation of air, water and soil quality during hydraulic fracturing at a site in the Darling Downs. It continues on from the Phase 1 project (W.11) during which comprehensive peer-reviewed study designs were developed for air quality (Dunne et al., 2017) and water and soil quality (Apte et al., 2017) studies.

As part of Phase 2, CSIRO has undertaken a comprehensive measurement program to assess the impacts of HF on local air quality. The study design on which this project was based is detailed in Dunne et al. (2017).

The study location was a farmland property of approximately 600 ha containing 10 coal seam gas wells which underwent HF between September and October 2017. The measurement program ran from July – December 2017 covering periods prior to HF, during HF activity, and after HF had concluded. Measurements were conducted at six different sampling locations within the field, five of which were located adjacent to wells (within ~130 m).

Across the six sites, 16 different air quality variables were measured utilising a mixture of continuous measurement systems and integrated sampling of VOCs, aldehydes and particulates onto specialised sample cartridges or filters.

This report provides details of the measurement locations, the timeline of sampling and HF activities, measurement systems and sampling procedures, as well as data capture rates. Particular highlights of the measurement program undertaken by CSIRO and project partners for this study include:

- The most comprehensive suite of measurements of air quality undertaken in an Australian gas-field to date with over 50 individual measurement systems capable of detecting over 50 species including all air pollutants listed in the National Environment Protection Measures for Ambient Air Quality (NEPM 2015) and Air Toxics (NEPM 2011).
- High spatial resolution with measurements taken across 6 sites within a ~600 ha site containing 10 wells.
- High time resolution with the combination of continuous measurements and short duration integrated sampling (12-hour – 48-hour samples) which are in line with the duration of HF activities (~ 1 -2 days).

These observations will be used to address the following study objectives:

Objective 1: Quantify changes in air pollutant levels above background that occur during HF operations. The data acquired during the measurement program will be used to address Objective 1 by comparison of data from the HF site with:

- Measurements taken at the site before and after HF operations.
- Simultaneous measurements at other air monitoring sites as part of a separate GISERA project: The Surat Basin Ambient Air Quality (SBAAQ) Study (Lawson et al 2017).

Objective 2: Provide information on the contribution of HF and non-HF-related sources of air pollutants to local air quality at the selected study site. The data acquired during the measurement program will be used to address Objective 2 by:

- Comparison of temporal variations in pollutant levels observed by continuous measurement systems, with meteorological parameters (in particular, wind direction) and activities occurring upwind of the monitoring system on-site, and in the surrounding area.
- Investigation of the detailed composition measurements of particulate and gaseous pollutants and relationships between pollutants which can be used to estimate contribution of different sources to a given air pollutant load. For instance, the aluminium/silicon ratio in elemental composition analysis of particle samples collected on filters can be used to estimate the contribution of soil and sand including proppant to total particle load. Likewise, that ratio of the gases benzene to carbon monoxide differs between diesel exhaust and wood smoke emissions; levoglucosan in particle samples can also be used as a tracer for woodsmoke.
- Statistical analysis methods, which will be applied to the whole dataset to investigate pollutant sources. This may include analyses such as positive matrix factorisation (Dunne et al 2017).

Objective 3: Perform comparisons of the data with Australian federal and state air quality objectives, as well as data from other air quality studies undertaken in areas not directly impacted by HF operations both within the Surat Basin and in other locations in Australia. The measurement program described will be used to address Objective 3 by:

- using Australian Standard measurement techniques (see Table 3) and other properly validated techniques that will provide data that are directly comparable to NEPM and Queensland EPP ambient air quality guidelines
- providing compatible data from the HF site for comparison with measurements taken simultaneously at other monitoring sites in SBAAQ Study network.

1 Introduction

Hydraulic fracturing (HF) is a well stimulation process that is used to increase the flow of gas and water from a gas well. HF involves the high pressure injection of a large volume of fluids into a well in order to fracture targeted coal seams and open pathways for gas and fluids to flow into the well. The fractures created are kept open by solids called proppants, usually sand, which are added to the injected fluids, thus maintaining open pathways for gas and fluids to flow into the well.

The injected fluids are predominantly water and proppant (~ 97 - 98%) with a small amount of chemical additives used to optimise the HF fluid performance and enhance well production. HF can involve the injection of several hundred thousand to over a million litres of fluids per well (CSIRO , 2015), and while chemical additives are a small fraction (~2 – 3 %), there may be 5000 to >10 000 litres of chemicals additives stored, mixed and injected at each well pad.

Once the required volumes of fluid have been pumped into the well and fracturing has taken place, the coal seam is depressurised and the fluids are allowed to flow back to the surface via the well. Initially flow-back fluid will contain a mixture of HF fluids, proppant and groundwater from the coal seam. The flow-back fluids may also contain a number of contaminants mobilised from the coal seam during HF activities. These geogenic contaminants include trace elements (e.g. arsenic, manganese, barium, boron and zinc), radionuclides (e.g. isotopes of radium, thorium, and uranium) and organic compounds such as hydrocarbons, and phenols (Schinteie et al., 2015). When geogenic contaminants are mobilized in fluids or coal seam gas (CSG) there is a potential for an emission to the atmosphere (Field et al., 2014).

At the surface flow-back fluids are stored on site either in large (~30 000– 80 000 L) storage tanks, in on-site ponds, or captured directly at the wellhead and removed by a gathering network and transferred to a water treatment facility. Flow-back occurs over several hours to days and is ceased once the majority of solids have cleared from the fluids. Overall, the handling and storage of HF fluids, flowback fluids and CSG at the surface will determine the impact of HF activities on air quality.

In addition to air pollutants emitted from HF and flow-back fluids, emissions will also occur from equipment and vehicles on site including diesel exhaust emissions, evaporative fuel emissions, and road dust. At present, the levels of air pollutants and the contribution of each of these sources to air quality in the vicinity of HF operations in the Surat Basin is unknown.

The potential impact on air, surface water, groundwater and soil of HF operations in coal seam gas production are of general concern to communities living in gas development regions. Community concerns centre on disclosure of the nature and type of chemicals used in the HF operations; potential enhanced mobilization of geogenic contaminants (e.g. Rn, Hg, organics) from the coal seam; the environmental fate of HF chemicals and geogenic contaminants; and the potential for impacts on human health and the environment.

The GISERA Air, Water and Soil Impacts of Hydraulic Fracturing: Phase 2 (W.12) project addresses some of these concerns by carrying out a comprehensive investigation of air, water and soil quality during hydraulic fracturing at a site in the Darling Downs. It continues on from the Phase 1 project

(W.11) during which comprehensive peer-reviewed study designs were developed for air quality (Dunne et al., 2017) and water and soil quality (Apte et al., 2017) studies.

Presented here is the deliverable for Task 1; the report on the air quality measurement program.

The air quality measurement program was designed to achieve three main objectives

- Objective 1- Quantify changes in air pollutant levels above background that occur during HF operations.
- Objective 2- Provide information on the contribution of HF and non-HF related sources of air pollutants to local air quality at the selected study site.
- Objective 3- Provide comparisons of the air quality observed at a HF site with Australian federal and state air quality objectives, as well as data from other air quality studies undertaken in areas not directly impacted by HF operations both within the Surat Basin and in other locations in Australia.

This report provides details of the measurement locations, the timeline of sampling and HF activities, measurement systems and sampling procedures, as well as data capture rates. The study design on which this project was based is detailed in Dunne et al. (2017).

2 Target air pollutants

The study design developed for assessment of the impact of HF on air quality (Dunne et al. 2017) provided a list of key pollutants to be targeted as part of the sampling program and their potential HF related sources. The target air pollutants, their potential HF-related sources and associated air quality guidelines are listed in Table 1.

The methodology employed for measuring each of these key pollutants will be outlined in Section 5. It is important to note that the techniques used for measuring these key pollutants are also capable of screening for a much larger suite of atmospheric species. For instance, the techniques for measuring the air toxics BTEX (benzene, toluene, ethylbenzene, xylenes) and formaldehyde described in Section 5 are capable of measuring perhaps 30 other volatile organic compounds (VOC) and carbonyl species. Likewise, the particulate matter (PM) analysis techniques will provide detailed information on the composition of the particles collected during sampling. Therefore, the key pollutants listed here represent the minimum that will be reported.

Table 1 Target air pollutants, their potential HF-related sources and associated air quality guidelines. See Glossary for definition of acronyms

Pollutant	Ambient Air Quality Standard			Potential HF Activity Sources
	Averaging Period	**Max Concentration**	**Relevant Standard**	
Nitrogen dioxide	1 h 1 year	0.12 ppm 0.03 ppm		Exhaust from diesel powered equipment & vehicles
Sulphur dioxide	1 h 1 day 1 year	0.20 ppm 0.08 ppm 0.02 ppm	NEPM Qld EPP	Exhaust from diesel powered equipment & vehicles
Carbon Monoxide	8 h	9 ppm	NEPM Qld EPP	Exhaust from diesel powered equipment & vehicles
Ozone	1 h 4 h	0.10 ppm 0.08 ppm	NEPM Qld EPP	Secondary pollutant- No direct emissions. Product of reactive processes in air between VOCs and oxides of nitrogen (NO$_x$)
Particles <10 µm PM$_{10}$	1 day 1 year	50 µg m^{-3} 25 µg m^{-3}	NEPM Qld EPP	Windborne soil, sand, road dust. Mechanical generation of PM during mixing and storage of HF fluids and flowback. Vehicle exhaust and other combustion emissions. Secondary pollutant- No direct emissions. Product of reactive processes in air between gases or between gases and other particles. No specific HF source identified Roads, vehicles, dust, oil & gas extraction (NPI 2016).
Particles <2.5 µm PM$_{2.5}$	1 day 1 year	25 µg m^{-3} 8 µg m^{-3}	NEPM	
Lead	1 year	0.50 µg m^{-3}	NEPM	
Benzene	1 year	0.003 ppm	NEPM Qld EPP	Exhaust and Evaporative emissions from vehicles and equipment CSG & Flowback Fluids (Day et al., 2016)
Toluene	24 h 1 year	1 ppm 0.1 ppm		
Xylenes	24 h 1 year	0.25 0.2		
Formaldehyde	24 h	0.04 ppm	NEPM Qld EPP	Exhaust from diesel powered equipment & vehicles Secondary pollutant -Product of reactive processes in atmosphere between VOCs and NOx Minor components or secondary product of CSG and Flowback Fluids
Methane	na	na	na	Major component of CSG used as tracer for fugitive emissions
Poly aromatic hydrocarbons (PAHs) as benzo(a)pyrene	1 year	0.3 ng m^{-3}	NEPM Qld EPP	Exhaust from diesel powered equipment & vehicles Minor components of CSG and Flowback Fluids
Mercury	1 year	1.1 µg m^{-3}	Qld EPP	Minor components of CSG and Flowback Fluids
Radon		Households: 200 Bq m^{-3} Workplaces: 1000 Bq m^{-3}	ARPANSA	Minor components of CSG and Flowback Fluids
Hydrogen sulphide	24 h	0.11 ppm	EPP	Minor component of CSG

3 Measurement sites

The study location was a farmland property of approximately 600 ha. Roma, the largest nearby population centre is located approximately 80 km to the SSW. The property is predominantly flat, semi-arid open grassland with stands of native tree vegetation. Linked by Horse Creek Road, the township of Yuleba (population <200) lies approximately 35 km to the SSW of the proposed study site (Figure 1).

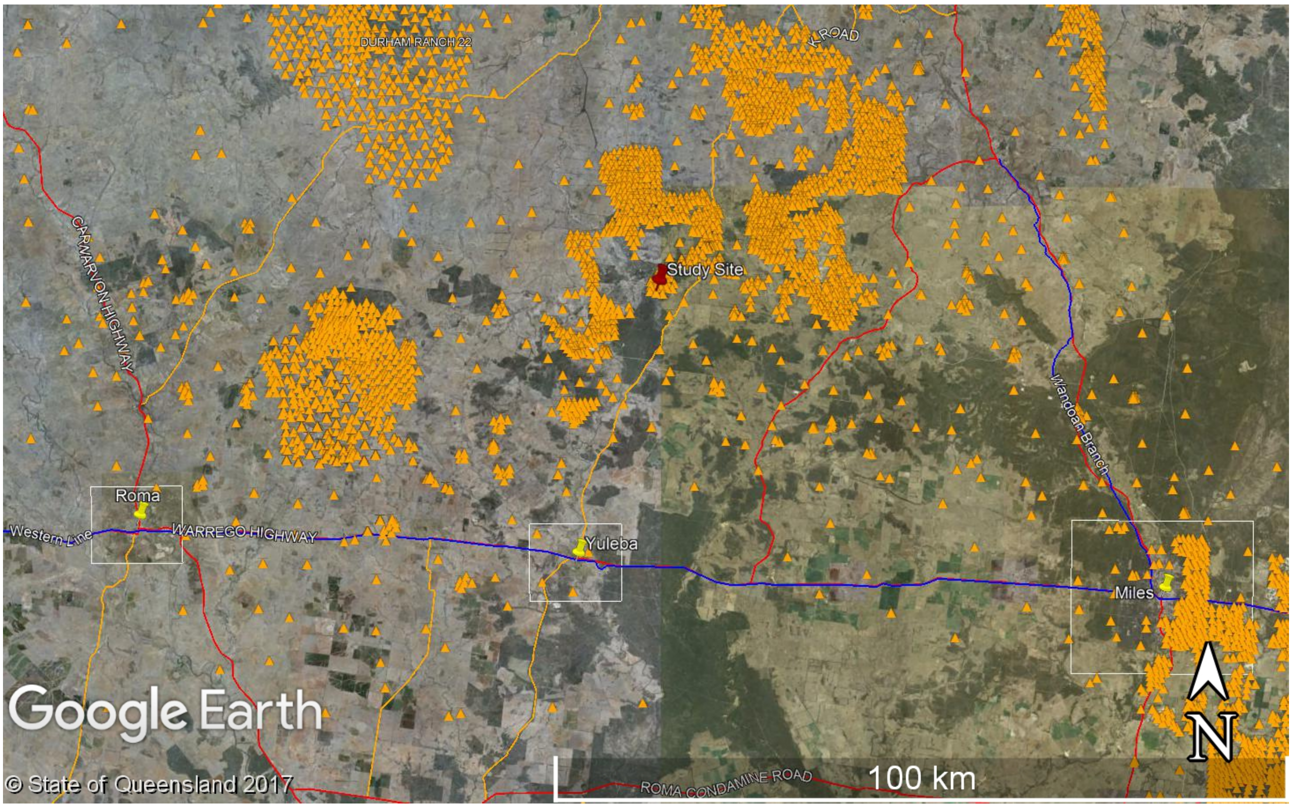

Figure 1 The study site within the Roma–Yuleba region of the Surat Basin. The orange triangles represent CSG wells.

The property contains 10 coal seam gas wells, grid spaced at ~600 – 800 m intervals. The wells are operated by Origin Energy Resources Pty Ltd and were drilled and constructed in 2017 targeting the Walloon Coal Measures. All 10 wells underwent HF between September and October 2017. The location of the wells and the sampling locations are shown in Figure 2.

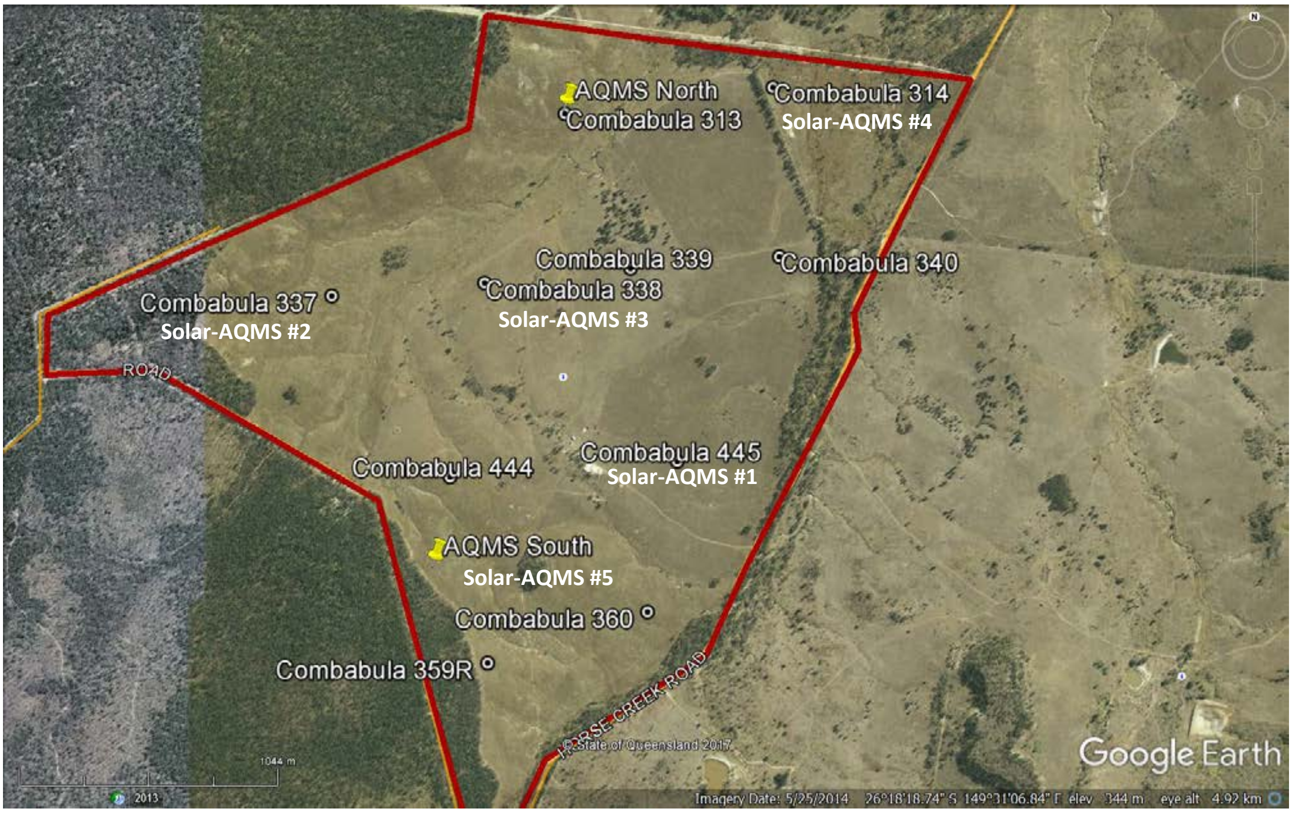

Figure 2 Map showing locations of wells that underwent HF (labelled by Well ID" Combabula ###), and the location of the North and South-AQMS (yellow pins) and the well sites where the five solar powered air monitoring stations were also located.

Two different types of air measurement systems were deployed in this study: two fixed air quality monitoring stations (AQMS) located at the North and South of the HF field, and five solar-powered air quality monitoring stations (Solar-AQMS) four of which were located adjacent to wells and one co-located with the South-AQMS. The North- and South-AQMS were located alongside two electricity sub-stations which provided the only available access to mains power necessary for the monitoring equipment within each of these enclosures. The North-AQMS was located adjacent to well COM 313 (Figure 3). The South-AQMS was located adjacent to a cleared area which contained a large above ground water tank used to store groundwater for HF sourced from a nearby bore. This area also served as a laydown area for diesel storage and refuelling tanks, trailers holding HF chemicals and proppant, trucks and equipment and experienced frequent truck traffic (Figure 4).

Figure 3 North-AQMS with hydraulic fracturing spread present at adjacent well (COM 313) in the foreground.

Figure 4 South-AQMS (right) with water storage tank and truck/equipment laydown area in the background.

The locations of the five Solar-AQMS, as shown in Figure 2, were determined with consideration given to:

- Locating sites on the eastern and western side of the property to provide measurements upwind and downwind of HF operations when ENE winds prevail.
- Locating sites on the northern and southern ends of the property to provide measurements upwind and downwind of HF operations when southerly/northerly winds prevail.
- Locating one site adjacent to the AQMS in the southern end of the field to provide validation of the Solar-AQMS instrumentation against high-quality AQMS instrumentation.
- Locating sites in proximity to wells (within ~ 100 m of well pad boundary) in order to enhance the probability of capturing impacts on air quality of HF operations which normally occurred over ~1 - 2 days per well.
- Compliance with AS/NZ S 3580.1.1:2016- Method for sampling and analysis of ambient air Part 1.1 Guide to siting air monitoring equipment.
- Site access, local terrain and vegetation.

4 HF activity and Sampling Timelines

The primary aim of the sampling program was to provide measurements to assess the impact of HF on air quality, however other well site activities also occurred during the measurement period. The range of activities that occurred at the study site during sampling, included:

- **Drilling and well construction** – Nine out of ten of the wells were drilled and constructed in 2017 with depths of 826 – 876 m, targeting the Walloon Coal Measures. Typically takes 1- 3 days.
- **Well integrity testing** – down-hole survey of the well. Typically takes 1 day.
- **Well casing perforation** – the well is perforated at target intervals using specialised explosive charges to create connection of the coal seam to the well. Typically takes 1 day.
- **Well head changeover** – installation of specialised HF well head. Typically takes 1 day.
- **Site set-up** – Hydraulic fracturing operations require a number of pieces of equipment including above ground water storage ponds, mixing units, high pressure pumps, coiled tubing unit to convey HF fluids down the well, crane, chemical and proppant storage trailers, flowback tanks, control vans. The set-up of the HF spread can take 2 – 3 days.
- **Hydraulic Fracturing** – the injection of HF fluids (water, sand, chemicals) into targeted intervals at high pressure via the coiled tubing unit. Typically takes 1 – 3 days.
- **Well Completion** – the well is flowed back, production equipment installed in the well and connected to surface production equipment (pumps, separators, and pipelines).

Each of these activities required specialised rigs/equipment and during the measurement period it was not uncommon to observe several different activities occurring at different well pads at the same time. Consequently, the ambient air quality across the study site was likely to be impacted by multiple activities and not exclusively HF.

The sampling program consisted of two overlapping phases:

- **Continuous monitoring** at the North and South AQMS sites which began in July 2017 and concluded in November 2017 with a subset of measurement ongoing until February 2018.
- **Intensive monitoring** phase which occurred over periods before, during and after HF activities involving both the North and South AQMS and the five Solar-AQMS. The intensive monitoring phase comprised 56 days in which CSIRO scientists and technicians visited all six sampling locations daily to perform sample collection of gases and particles on specialised sample media (filters, adsorbent tubes, cartridges), to undertake daily checks on continuous monitoring equipment, and to observe HF operations.

A timeline of sampling and the timing of some key well site activities for the study period (Drilling, HF, and Well Completion) is shown in Table 2.

Table 2 Timeline of sampling and well site activities for the measurement period July – December 2017.

	July 2017	August 2017	September 2017	October 2017	November 2017	December 2017
Site Activity						
Well ID (Sampling Site)	**Drilling**		**Hydraulic Fracturing (HF) & Well Completion (WC)**			
COM 360	26/7 – 31/7		HF 21/9 – 22/9 WC 22/9 – 24/9			
COM 445 (Solar-AQMS 1)	31/ 7 – 31/8		HF 23/9 – 24/9 WC 27/9 – 29/9			
COM 340	3/8 – 6/8		HF 27/9 WC 29/9 – 30/9			
COM 313 (North-AQMS)	10/8 – 14/8		HF 6/10 – 7/10 WC 9/10 – 11/10			
COM 337 (Solar-AQMS 2)	14/8 – 18/8		HF 9/10 – 10/10 WC 11/10 – 13/10			
COM 338 (Solar-AQMS 3)	18/8 – 22/8		HF 11/10 WC 13/10 -15/10			
COM 444	25/8 – 28/8		HF 12/10 – 13/10 WC 15/10 – 16/10			
COM 359R	*drilled 17/3 – 21/3 2016*		HF 14/10 WC 16/10 – 20/10			
COM 339	22/8 – 25/8		HF 16/10 – 19/10 WC 20/10 – 23/10			
COM 314 (Solar-AQMS 4)	6/8 – 10/8		HF 26/10 WC 1/11 – 2/11			
Note: South-AQMS and Solar-AQMS 5 were co-deployed at a location adjacent to laydown yard and HF water storage tank, not directly adjacent to any wells						
Sampling Activity						
Continuous sampling	19/7 – 24/11					subset of measurements ongoing at AQMS
Intensive sampling		7/8 – 19/8	15/9 – 28/10		subset of measurements until 21/11	

5 Measurement systems

The sampling and analysis methods employed in this study provided measurements of all air pollutants listed in the National Environment Protection Measures for Ambient Air Quality (NEPM 2015) and Air Toxics (NEPM 2011), as well as mercury listed in the Queensland Government Environment Protection (Air) Policy (EPP 2008), and radon listed in the Australian Radiation and Nuclear Safety Agency recommendations (ARPANSA , 2002). The suite of instruments enabled the measurement of a significant number of additional species including over 30 VOCs and particle composition measurements for over 30 component species. Instruments were operated continuously and samples were collected, over defined periods, on sample media that will be analysed for their chemical composition in an analytical laboratory as the study progresses.

In this section we describe the instrumentation deployed at the North- and South-AQMS as well as the five Solar-AQMS sites. The large suite of instrumentation deployed in this study were operated by CSIRO along with partner research organisations including the Australian Nuclear Science and Technology Organisation (ANSTO), Macquarie University, and external contractors Ecotech (Brisbane, Queensland, Australia) and SGS-Leeder (Chinchilla, Qld).

This section provides a summary of the instrumentation, measurement locations, responsible organisations as well as the sampling phase (continuous/intensive) these measurements were operated in. Details of the sampling and measurement procedures that were employed in the field are provided in Section 6.

5.1 AQMS

The AQMS were air-conditioned mobile laboratories provided by Ecotech Pty Ltd. These enclosures are purpose-built for housing high-quality, sensitive measurement systems and come complete with masts and inlets, and require mains 240V power supply.

The instruments installed in the AQMS at both the northern and southern sites are summarised in Table 3 and Table 4.

The North-AQMS was comprised of two separate but co-located enclosures (Figure 5). One enclosure housed a suite of Ecotech operated instrumentation to measure carbon monoxide (CO), oxides of nitrogen (as NO_2, NO and NO_x), ozone (O_3), sulphur dioxide (SO_2), methane (CH_4), carbon dioxide (CO_2), particulate matter (TSP, PM_{10}, PM_4, $PM_{2.5}$ and PM_1), $PM_{2.5}$ black carbon and meteorology including wind speed, wind direction, 10-metre and 2-metre temperature, humidity, solar radiation, rainfall and barometric pressure.

For measurements of gas phase species at the two Ecotech AQMS, ambient air was drawn through a glass inlet ~3.5 m in length, into a common manifold via an inlet fan that provides ~20 l m^{-3} of constant flow at low pressure, from which instruments draw their sampling flows via Teflon tubing by way of individual vacuum pumps. For measurement of particles, there was a separate inlet which contained a drying system designed to remove the influence of moisture on particle size while preserving semi-volatile particles. The dryer used real-time ambient temperature and humidity measurements to dynamically adjust heating of the inlet tube to keep the relative humidity of the sampled air to less than 60% (the setting on the dryer used in this study was "remove volatile / moisture compensation").

A second enclosure located at the North-AQMS housed CSIRO instrumentation including a proton transfer reaction mass spectrometer (PTR-MS) for continuous VOC measurements, and a sampling system that collected two 12-hour samples per day of VOCs on specialised sample media for analysis offline at CSIRO's laboratories in Aspendale, Victoria.

Also located outside at this site were two particulate samplers, one collected PM_{10} samples (particles with diameter ≤ 10 µm) from midnight to midday and the second collected samples from midday to midnight. These filter samples will undergo analyses for elemental composition at ANSTO's laboratories at Lucas Heights, NSW and subsequent analyses for ionic composition and carbohydrates at CSIRO's laboratories in Aspendale, Victoria.

Figure 5 Two enclosures at North-AQMS located adjacent to a well pad undergoing drilling.

The South-AQMS was comprised of a single AQMS enclosure housing a matching suite of Ecotech operated instrumentation to measure carbon monoxide (CO), oxides of nitrogen (as NO_2, NO and NO_x), ozone (O_3), methane (CH_4), carbon dioxide (CO_2) particulates (TSP, PM_{10}, PM_4, $PM_{2.5}$ and PM_1) and meteorology including wind speed, wind direction, 10-metre and 2-metre temperature, humidity, solar radiation, rainfall and barometric pressure. Instrumentation for the measurement of gaseous elemental mercury (operated by Macquarie University) was also located in the South-AQMS enclosure. Located outside at this site was a radon monitor operated by the Australian Nuclear Science and Technology Organisation (ANSTO) and a CSIRO sampler for the collection of polycyclic aromatic hydrocarbons (PAHs).

5.2 Solar-AQMS

Five solar-powered air quality monitoring stations (Solar-AQMS) custom built by CSIRO were deployed in this project (Figure 6). All instruments in the Solar-AQMS' were operated by CSIRO.

Each Solar-AQMS included a Ecotech Microvol PM_{10} sampler for weekly integrated mass and chemical composition analysis, and a Met-One E-sampler for continuous $PM_{2.5}$ concentration measurement and weekly integrated mass and chemical composition analysis. The Solar-AQMS sites also contained sampling equipment for integrated 12-hour sampling of VOCs onto adsorbent tubes (US EPA Compendium method TO-17, US EPA 1999a) and 24-hour sampling of aldehydes onto DNPH (Dinitrophenylhydrazine) cartridges (US EPA Method TO-11A, US EPA 1999b) and Lufft WS 500UMB Weather Sensor for the measurement of air temperature, humidity, air pressure, wind direction and wind speed.

Figure 6 Solar-AQMS located adjacent to a well pad (COM 314) undergoing well perforation.

6 Sampling Procedures and Data Capture

6.1 Ecotech continuous measurements at AQMS

Ecotech were responsible for the operation, maintenance and data reporting for the continuous measurements of NO_x, CO, O_3, CH_4, CO_2, and the measurement of particles (TSP, PM_{10}, PM_4, $PM_{2.5}$, PM_1) by fine dust aerosol spectrometer (FIDAS) at the North- and South- AQMS in this study. Analysers for continuous measurement of $PM_{2.5}$ black carbon and SO_2 were also operated by Ecotech at North-AQMS. Tables 3 and 4 show the instrument parameters, uncertainties and calibration frequency for each instrument at the North- and South-AQMS.

Table 3 Ecotech operated instruments located at North-AQMS

Parameter	Instrument: Measurement technique	Resolution	Uncertainty (K factor 2)	Range	Calibration frequency
NO, NO_x NO_2	Ecotech EC9841: gas phase chemiluminescence	1 ppb	±14 ppb NO, NO_x ±16 ppb NO_2	0 to 500 ppb	1 month
CO	Ecotech EC9830: NDIR gas filter correlation photometry	0.1 ppm	±1.1 ppm	0 to 50 ppm	1 month
O_3	Ecotech EC 9810: UV absorption photometry	1 ppb	±16 ppb at 0 – 125 ppb	0 to 500 ppb	1 month
SO_2	Ecotech EC9850: UV fluorescence	1 ppb	±14 ppb	0 to 500 ppb	1 month
Black carbon	Met One BC 1054: multi wavelength absorption	0.1 ng m^{-3}	Not specified	0.01 to 100 µg m^{-3}	1 month
CO_2, CH_4	Picarro G2301: cavity ring-down spectroscopy	0.1 ppm	Not specified	Not specified	3 month
TSP, PM_{10}, PM_4, $PM_{2.5}$, PM_1	Fidas 200: optical light scattering	0.1 µg m^{-3}	PM_{10}: 9.1% at 50 µg m^{-3}	0 to 10,000 µg m^{-3}	3 month
Vector wind speed, direction	RM Young 85000: ultrasonic (elevation 10 m)	0.1 m s^{-1}, 1°	greater of ±0.22 m s^{-1} or 3 %, ±4°	0 to 20 m s^{-1} 0 to 360°	2 year
Temperature	MetOne 062MP (elevation 2m and 10 m)	0.1 °C	±0.25°C	0 to 50°C	6 month
Relative humidity	Vaisala HMS 112 (elevation 2 m)	1%	±5%	0 to 100%	6 month
Rainfall	Hydrological Services TB6	0.2 mm	greater of ±0.60 mm or 7.5%	0 to 80 mm/hr	1 year
Solar Radiation	Middleton Solar Pyranometer SK-01-D2	1 W m^{-2}	greater of ±5% or ±32 W m^{-2}	0 to 1100 W m^{-2}	1 year

Table 4 Ecotech operated instruments located at South-AQMS

Parameter	Instrument: Measurement technique	Resolution	Uncertainty (K factor 2)	Range	Calibration frequency
NO, NO_x NO_2	Ecotech Serinus 40: gas phase chemiluminescence	1 ppb	±13 ppb NO, NO_x ±17 ppb NO_2	0 to 500ppb	1 month
CO	Ecotech Serinus 30: NDIR gas filter correlation photometry	0.1 ppm	greater of ±1 ppm or 10% reading	0 to 50 ppm	1 month
O_3	Ecotech Serinus 10: UV absorption photometry	1 ppb	±16 ppb at 0 – 125 ppb	0 to 500 ppb	3 month
CO_2, CH_4	LGR GGA: cavity ring-down spectroscopy	0.1 ppm	not specified	not specified	3 month
TSP, PM_{10}, PM_4, $PM_{2.5}$, PM_1	Fidas 200: optical light scattering	0.1 µg m^{-3}	PM_{10}: 7.2, $PM_{2.5}$: 10.2%	0 to 10,000 µg m^{-3}	1 year
Vector wind speed, direction	RM Young 85000: ultrasonic (elevation 10 m)	0.1 m s^{-1}, 1°	greater of ±0.4 m/s or 2.0%, ±4°	0 to 20 m s^{-1}, 0 to 360°	2 year
Temperature	MetOne 062MP (elevation 2m and 10 m)	0.1 °C	±0.6°C	0 to 50°C	6 month
Relative humidity	Vaisala HMS 155 (elevation 2 m)	1%	±6%	1 to 100%	6 month
Rainfall	Hydrological Services TB6	0.2 mm	greater of ±0.60 mm or 7.5%	0 to 80 mm/hr	1 year
Solar Radiation	Middleton Solar Pyranometer SK-01-D2	1 W m^{-2}	greater of ±5% or ±32 W m^{-2}	0 to 1100 W m^{-2}	1 year

Data was logged at both Ecotech AQMS sites using PC based WinAQMS loggers. A second logger (Congrego) was used at the North-AQMS to log CO_2 and CH_4 from an additional cavity ring down instrument (LGR GGA: cavity ring-down greenhouse gas analyser) and a black carbon instrument. Overnight span and zero checks were performed for the gaseous criteria pollutants (NO, CO, O_3 and SO_2). Calibrations were performed by Ecotech at frequencies outlined by the relevant Australian Standard or in the absences of these, according to Manufacturer specifications (calibration frequencies are in Table 3 and 4).

The logged data was monitored remotely using *Airodis* data management software (Ecotech). The software package downloads data each day and also sends error reports to field engineers if instruments fall out of operating tolerance. Weekly Summary Reports (csv and pdf) of raw concentration data as scatter plots and time series plots were sent to CSIRO each week for review. The raw data was also sent.

In addition, CSIRO had independent access to the data loggers at both sites. Data was downloaded each day and reviewed using control charting of logged data these included ambient, zero and span concentrations, flow rates, instrument parameters and communication and meteorology. If deviations from defined ranges of tolerance were detected, CSIRO contacted Ecotech field engineers to investigate the cause. This daily process by CSIRO meant that issues were identified before the data was reviewed by Ecotech analysts, which only occurred once per month.

Validation of data by Ecotech analysts occurred on the 15th day of the following month. Raw data was validated according to ISO17025 and Australian Standards or other established methods. Raw and validated data as a percentage of total data for each month for the North- and South-AQMS instruments is provided in Table 5 and Table 6 below.

The Ecotech validated data was provided as a report of concentrations, whether they met air quality objectives and any measurement issues that occurred for that month. Hourly data and 24-hourly data were calculated from 5-minute averages. The minimum 5-minute data capture allowed for the validated averages was 75%.

The final check performed by CSIRO was to control chart the 5-minute and hourly average data independently downloaded by CSIRO and the 5-minute and hourly average validated data provided by Ecotech. Periods of invalid data were reviewed as well as periods where calibration data was used to apply a linear offset or multiplier being applied to raw data. Deviations in data between North- and South-AQMS were also reviewed.

Table 5 North-AQMS percent data capture (12th July – 31 December 2018), 5-minute observations per month raw, valid.

	Jul	Aug	Sep	Oct	Nov	Dec
CO	0, 0	82, 10	95, 95	96, 76	96, 94	95, 93
$NO_x/NO/NO_2$	0, 0	82, 11	96, 96	97, 84	97, 97	97, 97
O_3	0, 0	11, 11	97, 85	97, 96	97, 97	97, 97
SO_2	0, 0	81, 11	95, 95	96, 84	96, 96	96, 96
CO_2	39, 39	91, 91	97, 97	96, 98	99, 98	86, 93
CH_4	39, 39	91, 91	97, 97	96, 98	99, 98	86, 93
PM	40, 39	100, 100	100, 100	100, 100	97, 93	100, 100
BC	39, 39	95, 95	98, 35	95, 0	57, 0	86, 99
10m Temp	41, 39	100, 100	98, 99	100, 100	98, 98	99, 99
2m Temp	41, 39	100, 100	99, 100	100, 100	100, 100	99, 100
RH	41, 39	100, 100	99, 99	100, 100	99, 99	99, 99
SR	41, 39	100, 99	99, 99	100, 94	99, 92	99, 93
WS, WD	40, 39	100, 100	99, 100	100, 100	100, 100	100, 100
RF	41, 39	100, 100	100, 100	100, 100	100, 100	100, 100
BP	41, nr	100, nr	100, nr	100, nr	100, nr	100, nr

Table 6 South-AQMS Percent data capture (12th July – 31 December 2018), for 5-minute observations per month: raw, valid.

	Jul	Aug	Sep	Oct	Nov	Dec
CO	16, 14	96, 89	95, 74	96, 96	72, 10	0, 0
$NO_x/NO/NO_2$	24, 12	97, 95	97, 75	97, 97	97, 97	97, 97
O_3	0, 0	4, 0	96, 94	96, 94	96, 94	96, 95
CO_2	16, 0	99, 99	99, 99	99, 79	99, 99	99, 98
CH_4	16, 14	99, 99	99, 98	99, 79	99, 99	99, 98
PM	37, 32	100, 98	71, 70	100, 98	98, 96	100, 98
10m temp	39, 32	100, 100	100, 100	100, 100	100, 100	100, 100
2m temp	39, 32	100, 100	100, 100	100, 100	100, 100	100, 100
RH	39, 32	100, 100	100, 100	100, 100	100, 100	100, 100
SR	39, 32	100, 99	100, 99	100, 99	100, 99	100, 97
WS, WD	38, 32	100, 100	100, 97	100, 100	100, 100	100, 100
RF	39, 32	100, 100	100, 100	100, 100	100, 100	100, 100
BP	39, nr	100, nr	100, nr	100, nr	100, nr	100, nr

Nr not reported

6.2 ANSTO - gaseous radon measurements

ANSTO deployed a dual flow loop, two-filter radon detector at the South-AQMS for the continuous monitoring of radon in ambient air. A report of the radon measurement program from ANSTO is provided in the Appendix -Section 8.1

6.3 Macquarie University - gaseous mercury measurements

Mercury was measured continuously at the South-AQMS by Macquarie University using a Tekran® 2537 unit for total gaseous mercury and gaseous elemental mercury (TGM/GEM) measurement. The manufacturer stated detection limits are 0.1 µg m^{-3} and the unit is capable of autonomous calibration using an in-built permeation source. Ambient air was drawn via the inlet tubing (¼” PTFE (Teflon)) with a 2 µm Teflon 47 mm filter at intake height of 10 m.

Reactive mercury filters were installed at 3 m height. The Cation Exchange Membranes used have been proven to capture oxidized forms of mercury from ambient air with no interference from elemental forms of mercury thereby representing the reactive mercury (RM) component of the atmosphere. The RM measurement will provide insights into the cycling of mercury locally.

Zeros and spans were performed every 23 hours taking 25 minutes per calibration. The period of 23 hours was used so that the same half hour was not lost each day. Data recovery during the period 16 August to 6 December 2017 was 93%. The 7% data loss was due to power outages and instrumental issues.

The Tekran gaseous elemental mercury data is currently undergoing data processing and analysis by Macquarie University. The processing and analysis procedures will be reported alongside the results in a subsequent report for this project.

6.4 CSIRO - PM_{10} and $PM_{2.5}$ Sampling

During the intensive phase of the measurement program CSIRO collected particle samples on filters using three different types of particle sampling instruments– two (Derenda and Microvol) for collecting samples ≤ 10 µm in diameter (PM_{10}) and one (E-Sampler) for collecting particles ≤ 2.5 µm in diameter ($PM_{2.5}$). This section provides details of the particle sampling procedures used for each of the three instrument types and the filter preparation and handling.

The sampled filters are currently undergoing analysis for total gravimetric mass determination, and ion beam analysis for elemental composition by ANSTO, and ion chromatography analysis for major soluble ions by CSIRO (see Dunne et al., 2017). Details of the analysis procedures and results will be described in the final report for this project.

6.4.1 Filter preparation and handling

Pall 47 mm Teflo 2 µm pore size filters, part no R2PJ047, were used for all three integrated particle sample collection in this study (Derenda, Microvol, E-Sampler). Teflo filters are made of Teflon membranes stretched across a polymethyl-pentene support ring. Two hundred and twenty-five Teflo filters were sent to ANSTO for pre-gravimetric mass determination and light transmittance for black carbon determination. Each filter was placed in a Millipore filter tray and assigned a unique filter ID that was recorded on the filter tray, 1-11138 to 225-11138. The sample site, sampler type and sampling start and stop date and times were also recorded on the filter tray during sampling. Five laboratory blanks were also collected during study and kept at the CSIRO Aspendale laboratories for the duration of the field study and sent back to ANSTO for analysis along with the samples and field blanks.

Filters were stored in the field laboratory at room temperature prior to sampling and then refrigerated at the field laboratory and at CSIRO Aspendale laboratories after sampling and prior to being sent to ANSTO for analysis. Filters were loaded into and unloaded from their instrument filter holders in the field laboratory and transported approximately 30 km to and from the field site in sealed containers. The filter holders were cleaned with Isowipes and dried with Kimwipes between each sample.

6.4.2 Derenda low volume particle sampler

PM_{10} samples were collected on 47mm Teflo filters (Pall Teflo 2µm 47mm p/n R2PJ047) using Comde-Derenda low volume samplers. These instruments are a reference sampling method in compliance with the European standard for the measurement of particulate mass (EN12341:2014.-BS EN 2014).

Two of these low volume samplers were located at the North-AQMS site spaced approximately 2m apart (Figure 5). Two 12-hour samples were collected each day, one on each sampler. The PM_{10} impactor inlets were ~1.7 m above the ground and the samplers were operated at a set flow rate of 2.3 m^{3} h^{-1}. The PM_{10} inlet and filter holders were cleaned using Isowipes and 18.2 mΩ deionised water and the inlet impactor plate was sprayed with silicon grease before use. The volumetric flow rate was monitored by a measuring orifice and the flow was regulated to an accuracy of better than 2%. The samplers were also equipped with their own ambient temperature, pressure and humidity sensors.

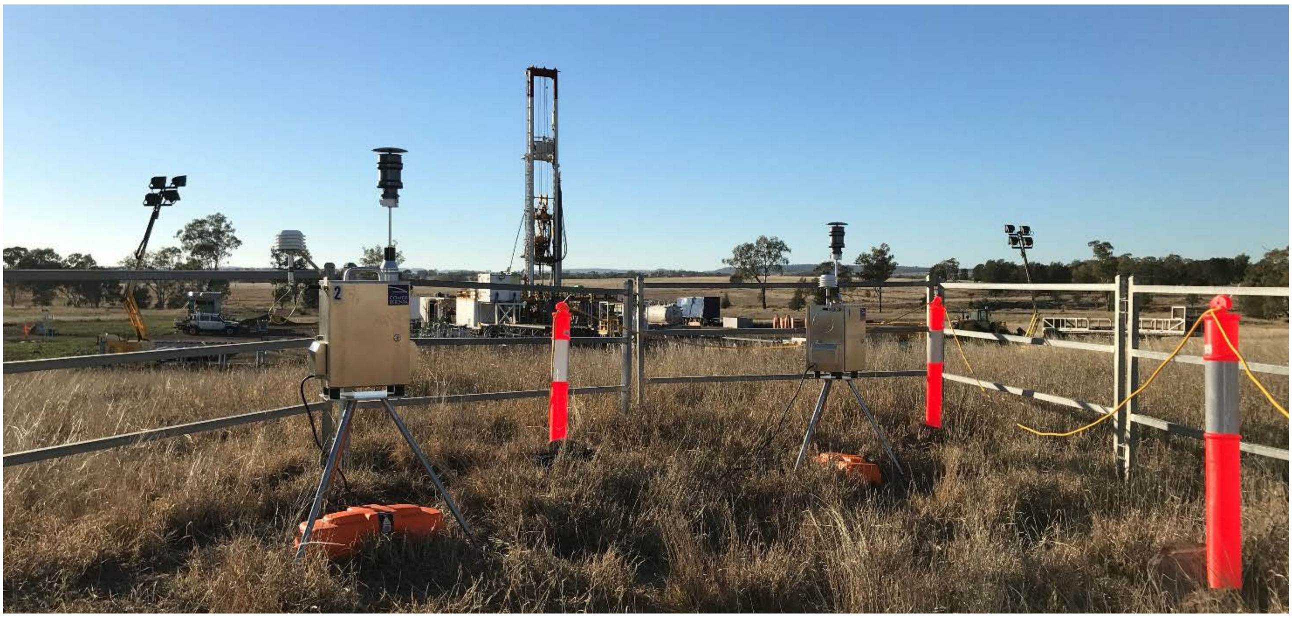

Figure 5 The two Comde-Derenda PM_{10} sampling systems at the North-AQMS with a drill rig at the adjacent well pad (COM 313) in the background.

Each Derenda sampler was leak checked and flow audited before deployment. Both samplers passed the leak checks but the flow rates for both samplers were more than 5% below the set flow rate of 38.33 l min^{-1}. Both samplers were recalibrated using a TSI 4040 thermal mass flowmeter configured to display volumetric flow rate. The samplers were then flow audited again and Derenda # 1 (s/n w11340) was within 0.7% of the set flow rate and Deranda #2 (s/n w11348) was within 1.4%. Weekly flow audits by the same method were performed in the field during sampling and the results recorded in an instrument log-sheet. The Derenda samplers operated for the entire study without breakdowns or faults.

In total, 96 Derenda filter samples were collected during the campaign, however two filters were damaged so will not be analysed. Nineteen filters were collected in the pre-HF period, and 77 were collected during HF activity. The filter ID, sampler ID, sampling start /stop times, as well the sample volume and average temperature and pressure were recorded in the instrument log sheets. With the exception of filter ID this information was also recorded by the instrument and stored in the internal data logger which was downloaded and backed-up periodically over the study period. This information will be used to determine the sample volume each filter was exposed to and subsequently used to calculate the average airborne concentration of the PM_{10} ($\mu g\ m^{-3}$) over the sample period from the mass on the filter and concentrations of elemental and soluble ions from the chemical analyses carried out on the filters.

A total of 48 days of filter samples were collected which equates to a data coverage of ~ 86% over the intensive measurement phase of the field campaign. Due to wet weather no access was allowed on to the sampling sites from 1st October to the 4th October, 7th October to 8th October and the 17th October to 18th October so that filter samples were not collected on these dates.

Seven field blanks were collected during the study. Field blanks were stored, transported and handled identically to the samples. Field blanks were loaded into the sampler with the sample pump turned off, then immediately retrieved and returned to the field laboratory at the end of the day.

No duplicate samples were collected during the field measurement campaign as the two Derenda samplers were not run simultaneously. Typically a duplicate should be collected for every ten samples. Duplicate samples will be collected at CSIRO Aspendale Laboratories (Victoria) as part of a follow-up instrument characterisation in March 2018. The duplicate samples will be subject to gravimetric mass determination to assess the measurement precision.

6.4.3 Ecotech Microvol 1100 low volume particle sampler

Weekly PM_{10} samples were collected on 47 mm Teflon filters (described in section 6.4.1) at each Solar-AQMS using a Microvol 1100 low volume sampler (Ecotech, Knoxfield Victoria). The PM_{10} impactor inlets sat at ~2.2 m above the ground. Prior to sampling the PM_{10} inlet and filter holders were cleaned using Isowipes and 18.2 mΩ deionised water and silicon grease was applied to the impaction surface on the inlet impactor plate before use to ensure no larger particles (≥ 10 µm) were collected.

The instruments are microprocessor controlled and maintain a constant volumetric flow rate of 3.0 l min^{-1} using a mass flow sensor and ambient temperature and pressure sensors. Each Microvol was flow audited before deployment and all were within 5% of the set flow rate and all met the Australian standard for the measurement of particulate mass by low volume samplers (AS/NZS 3580.9.9:2006). Daily flow checks were performed in the field using a Bios Defender flowmeter (Bios International Corp, NJ) and the results recorded in an instrument log-sheet.

A total of 44 weekly PM_{10} filter samples were collected across the five Solar-AQMS (9 per site) during the whole campaign. At each site 2 filters were collected before HF activity started, 6 were collected during HF and 1 collected after HF (Excl. Solar AQMS #4, no filter collected after HF). This amounted to a total of 76 days sampling at each Solar-AQMS site which equates to ~90 -100% data coverage for the intensive sampling phase of the measurement campaign which comprised 56 days of sampling. The Microvol samplers at the five Solar-AQMS were part of a subset of measurements from the intensive measurement phase (7 August to 28 October 2017) that continued to collect samples until the 21st November 2017.

The filter ID, sampling site, sampler ID, sampling start / stop date and time, sample volume, average temperature and pressure and daily flow checks were recorded in the instrument log-sheets for each sample. This information will be used to determine the sample volume each filter was exposed to and subsequently used to calculate the average airborne concentration of the PM_{10} ($\mu g\ m^{-3}$) over the sample period from the mass on the filter.

Seven field blanks were collected during the sampling campaign and this involved following the same handling and transport procedures as the samples and loading them into the sampler but not turning the sampler on. Impactor heads containing the field blanks were connected to the sampler with the sample pump turned off, then immediately retrieved and returned to the field laboratory at the end of the day.

No replicate samples were collected during the field measurement campaign as the five Solar-AQMS could only accommodate one Microvol per unit. Typically one replicate should be collected for every ten samples. Replicate samples will be collected by operating the five Microvols from the Solar-AQMS side by side at CSIRO Aspendale Laboratories (Victoria) as part of a follow-up instrument characterisation in March 2018. The replicate samples will be subject to gravimetric mass determination to assess the measurement precision.

6.4.4 Met-One E-Sampler

Each Solar-AQMS was fitted with an E-Sampler (Met-One Instruments Inc. Oregon, USA) which continuously measured $PM_{2.5}$ concentration through near-forward light scattering as well as collecting weekly filter samples of $PM_{2.5}$ particles in ambient air on 47 mm Teflon Filters. In this instrument, a visible laser light source scatters particles in proportion to the particulate load. Validation of the performance of the light scattering measurement will occur by utilizing the E-

Samplers ability to collect a sample on a filter simultaneously which is used to determine the sample-period specific mass scattering coefficient.

Each sampler was equipped with a $PM_{2.5}$ cyclone inlet with an inlet sampling height of ~2m. Prior to sampling the $PM_{2.5}$ inlets were cleaned using Isowipes and 18.2 mΩ deionised water. The inlets were inspected and cleaned using Isowipes ~ every 2 weeks during sampling.

The E-sampler is microprocessor controlled and maintains a constant volumetric flow rate of 2.0 l min^{-1} using a mass flow sensor and ambient temperature and pressure sensors. Air is drawn through the $PM_{2.5}$ size-selective inlet and onto a 47 mm Teflo filter. Each E-Sampler was flow audited before deployment and all were within ± 5% of the set flow rate flow. Daily flow checks were performed in the field using a Bios Defender flowmeter (Bios International Corp, NJ) and the results recorded in an instrument log-sheet.

The averaging time for the data logging of the continuous (light-scattering) $PM_{2.5}$ measurements was set at 1-minute during the intensive phase of the measurement program when CSIRO personnel were in the field daily. At this averaging time the internal logger had 3 days capacity and the data was downloaded onto a field PC every 1 to 3 days. Outside of the intensive monitoring phase the E-sampler was set to 15-minute averaging time allowing up to 3 weeks of data to be recorded by the internal logger and periodically downloaded when were CSIRO personnel not in the field on daily basis.

The E-samplers made continuous measurements of $PM_{2.5}$ for over 100 days. Removing the ~15 minutes per day when the data were downloaded and the samplers were not measuring equates to a data coverage of ~ 99%. Accounting for occasional instrument or technical failures that occurred during sampling resulted in an estimated 90% or better data coverage for each site.

A total number of 40 filter samples of $PM_{2.5}$ were collected at the perimeter sites during the whole campaign; 8 at each of the 5 Solar-AQMS sites. At each Solar-AQMS sites, 3 samples were collected before HF started, 4 were collected during HF and 1 collected after HF. This amounted to over a 100 days sampling at each Solar-AQMS site which equates to 100% data coverage for the intensive sampling phase of the measurement campaign which comprised 56 days of sampling. The E-samplers at the five Solar-AQMS were part of a subset of measurements from the intensive measurement phase (7/8 - 28/10/2017) that continued to collect samples until the 21st November 2017.

The filter ID, sampling site, sampler ID, sampling start / stop date and time, and details and daily flow checks were recorded in the instrument log-sheets for each sample. This information will be used to determine the sample volume each filter was exposed to and subsequently used to calculate the average airborne concentration of the $PM_{2.5}$ (μg m^{-3}) over the sample period from the mass on the filter.

Four field blanks were collected during the sampling campaign and this involved following the same handling procedures as the samples. Filter holders containing the field blank were inserted into the sampler with the sample pump turned off, then immediately retrieved and returned to the field laboratory at the end of the day.

No replicate samples were collected during the field measurement campaign as the 5 Solar-AQMS could only accommodate one E-Sampler per unit. Typically one replicate should be collected for every ten samples. Replicate samples will be collected by operating the five E-samplers from the Solar-AQMS side by side at CSIRO Aspendale Laboratories (Victoria) as part of a follow-up instrument characterisation in March 2018. The replicate samples will be subject to gravimetric mass determination to assess the measurement precision.

6.5 Sampling of Volatile Organic Compounds (VOCs)

During the measurement program four different VOC sampling methods were employed - one continuous method, two active sampling methods and one passive sampling method that all involve extractive sampling of VOCs onto specialised sample media. This section provides details of the VOC sampling procedures used for each of the four methods.

The data from the continuous measurements is currently being processed and analysed. The VOC samples are currently undergoing analysis at the CSIRO Aspendale laboratories in Victoria. Details of the analysis procedures and results will be described in a subsequent report for this project.

6.5.1 Continuous measurement of VOCs by Proton Transfer Reaction Mass Spectrometry

Proton transfer reaction mass spectrometry (PTR-MS) is an online mass spectrometry method capable of detecting a range of VOCs at sub- parts per billion (ppb) levels in near real-time. A commercially built PTR-MS instrument (Ionicon Analytik GmbH, Innsbruck, Austria) was operated by CSIRO continuously in an enclosure at the North-AQMS site from July – November 2017.

The sampling inlet was located ~ 6m above ground attached to a mast on the Ecotech North-AQMS. A flow of 5-6 l min^{-1} of ambient air was drawn through the inlet into the CSIRO AQMS enclosure via ~ 12 m of 3/8 inch O.D. Teflon tubing inlet by a sampling pump. A flow of 1.5 l min^{-1} of air sampled via the inlet was drawn through the PTR-MS auxiliary system via a constant flow sampling pump and the PTR-MS sampled 300 ml min^{-1} from the auxiliary system.

In the PTR-MS, the sample air is pumped through the instrument where VOCs are selectively ionized (i.e. become positively charged), and sorted according to their mass by a quadrupole mass spectrometer. The ion current at each mass is measured by an ion detection system in pulse counting mode. The raw data output is in counts per second for each mass. In the present study, the PTR-MS continuously scanned 157 masses between 21 and 180 amu with a dwell time for a single mass of 1 second, generating a full mass scan approximately every 3 minutes. This is roughly equivalent to 20 data points per hour for each mass.

The PTR-MS operates with the aid of custom built auxiliary equipment that regulates the flow of air in the sample inlet and controls whether the PTR-MS is sampling ambient or zero air or calibration gas. Zero air readings are made by diverting ambient air through a zero furnace (350° C) with a platinum wool catalyst that destroy VOCs in the air before entering the PTR-MS. Zero air readings were made twice per day (00:00 – 01:00 and 17:30 – 18:00). All PTR-MS ion signals from calibration and ambient air measurements will be background corrected by subtracting the zero air measurements from the ambient data.

The PTR-MS was calibrated daily. For each calibration measurement a set flow of 10 – 20 ml min^{-1} of a ~1 ppm calibration standard was diluted in a flow 1500 ml min^{-1} of ambient air that had been passed through the zero furnace. Calibrations occurred once per day from 01:20 – 02:40. Two calibration gases were measured for 40 minutes each during each calibration measurement with the remaining time used to pre-flush calibration gas lines. Five different certified gas calibration standards were used on rotation during the measurement period. In total 20 VOCs were present in these standards, though each individual standard contained only a subset of these. The VOCs present in the calibration standards are listed in Table 7. These certified gas standards were supplied by Apel-Reimer Environmental Inc (Broomfield CO, USA). The stated accuracy for each component in the standards was ± 5%.

Table 7 Compounds present in certified gaseous standards used to calibrate the PTR-MS during the field campaign.

Compounds present in PTR-MS calibration standards		
Methanol	m-Xylene	Chlorobenzne
Acetonitrile	Trimethylbenzene	Dichlorobenzene
Formaldehyde	Phenol	Trichlorobenzene
Acetaldehyde	o-Cresol	Dimethyl sulphide
Acetone	Naphthalene	
Methacrolein	Isoprene	
Methyl ethyl ketone	a-Pinene	
Benzene	1,8-Cineole	
Toluene		

Daily checks were performed on the PTR-MS instruments throughout the measurement period either in person when CSIRO technicians were in the field, or via remote connection to the instrument's PC. These daily checks were entered into an instrument log-sheet that also included flow checks on inlet sample pumps and checks that instrument operating parameters where within a normal range, checks of the calibration and zero data and a record that back-up of the data to an external data storage had occurred.

Overall the PTR-MS operated for 128 days over the continuous phase of the study period. When the time taken for calibration and zero measurements (~3 hours per day) is subtracted this equates to ~ 87.5 % data coverage for that period. The PTR-MS raw data is yet to undergo detailed QA/QC checking, data processing and analysis. However, we estimate that ~ 0.5 days per week were lost due to the instrument parameters being outside of normal operating conditions and the time required to re-tune the instrument. Removing this time, we estimate that the PTR-MS measurements provided ~ 80% data coverage for the study period.

The PTR-MS raw data will undergo detailed QA/QC checking, and data processing and analysis. During data processing the raw data will be converted to airborne concentrations (ppbv) using CSIRO custom software by applying the zero readings and calibration factors from the measurements of certified gas standards to the raw data. The processing and analysis procedures will be reported alongside the results in a subsequent report for this project.

6.5.2 CSIRO- Active sampling of VOCs onto adsorbent tubes

Two systems were used in this study for the sampling of VOCs onto adsorbent tubes- one method was deployed at the North-AQMS and the other was installed in the Solar-AQMS. Both systems involved the collection of VOC samples onto adsorbent tubes (AT-VOC). Subsequent analysis of the absorbent tubes was compatible with ISO 16017-1:2000 and USEPA Compendium method TO-17 Determination of Volatile Organic Compounds in Ambient Air using active sampling onto sorbent tubes (USEPA 1999).

All sample tubes were conditioned and cleaned in a Markes TC-20™ tube conditioner according to manufacturing's specifications and were analysed to obtain clean blank profiles of tubes prior to sampling.

Before and after sampling, the VOC adsorbent tubes were refrigerated and stored in clean sealed metal containers at the CSIRO Aspendale laboratories and in the field laboratory. Before and after sampling VOC adsorbent tubes were transported ~30 km to and from the field laboratory to the study site unrefrigerated in their containers.

North-AQMS- Sampling of VOCS using the CSIRO automated sampler

At the North-AQMS, ambient air was actively drawn through a ~ 12 m length of 3/8 inch O.D. PTFE tubing inlet (inlet height ~ 6 m) into a CSIRO custom designed automated sampler. The automated sampler is a programmable continuous air sampler with two channels allowing for simultaneous active sampling onto VOC adsorbent tubes and DNPH cartridges (Section 6.5.3). With 16 sampling ports per channel. Two 12-hour samples per day were collected by the automated sampler (00:00 – 12:00 and 12:00 – 0:00) which actively drew air onto a multi-adsorbent VOC tubes (Markes Markes Carbograph 1TD/ Carbopack X) using a constant flow air sampling pump (SKC Model 222-4) at a set flow rate of 20 ml min^{-1} with a sample volume ~14.4 litres for each VOC sample.

The automated sampler is fitted with an electronic flow sensor that measures and logs the flow every minute during sampling. Before the start of the measurement period, the flow sensor was calibrated against the inlet flow using a Bios Defender flow meter. Prior to the start of the measurement period the inlet and outlet flow on each sampling channel was measured to ensure agreement within ± 5%. During the measurement period daily flow checks on the outlet of the automated sampler were performed to ensure it was 20 ± 3 ml min^{-1}. If the flow was outside of this range the pump was re-calibrated between samples.

Daily checks and calibrations were recorded in the instrument log-sheet which contained the sample tube ID, sample channel, sample start/stop times, flow rate measured by internal flow sensor and displayed in instrument software, and the flow rate measured in daily checks.

The automated sampler was run during the 56 days of the intensive measurement periods between the 7 August and the 28 October 2017. Due to instrument failure, samples were not collected from 12pm on 22 September to 12pm on 11 October. In total, 42 samples were discarded due to instrument failures or sample integrity issues (38 during HF, 4 after HF).

Overall 75 (excluding 42 of discarded) VOC adsorbent tube samples were successfully collected during the whole campaign. This includes 17 samples that were collected before HF started, 49 that were collected during HF and 9 (from 29 Oct to 4 Nov) that were collected after HF. In addition, 15 field blanks were collected during the sampling campaign and 20 analysis blanks were retained in the laboratory for analysis. This equates to 37.5 days of data giving a data coverage over the intensive sampling phase of ~ 67%. (= no. days sampled / 56 days)

Solar-AQMS- VOC sampling using SKC pocket pumps

Two identical VOC sampling systems were installed in each of the five Solar-AQMS sites to permit two samples to be collected per day. The sampling systems operated by actively drawing ambient air through a ~ 1.5 m length of 1/4 inch silco steel tubing (inlet height ~2 m) and onto a multi-adsorbent VOC tube using battery powered constant flow air sampling pumps (Pocket pump SKC) at a set flow rate of 20 ml min^{-1}. The sampling volume was ~14.4 L for each sample. The pumps were programmed to collect 2 x 12-hour samples per day using the SKC pocket pump software however the actual sample start/stop times were determined by the times when CSIRO technicians visited the sites to change the samples.

During sampling at the Solar-AQMS sites, the VOC adsorbent tube samples were housed in a fan ventilated instrument box and were collected daily to minimise their exposure to ambient temperatures (Figure 7).

Before each sample, the sample flow rate was measured in-line between the outlet of the adsorbent tube sample and the inlet of the pump with a Bios Defender flowmeter to ensure it was 20 ± 3 ml min^{-1}. If the flow was outside of this range the pump was re-calibrated. Following each sample the flow was rechecked to ensure it was within ± 10 % of the initial sample flow. Samples with post-sample flow rates measured outside of this range were flagged. The data from the pumps was downloaded for each sample and the sample tube ID, flow rates befoe and after sampling, flow test temperature and pressure, and sample start and stop times were recorded in sample log-sheets.

A total number of 472 12-hour samples were collected from across the five Solar-AQMS sites during the intensive phase of the measurement period. Of these, 21 were discarded due to instrument failures or sample integrity issues, leaving 451 VOC samples that were successfully collected from across the five Solar-AQMS sites:

- Solar-AQMS #1- 84 samples
- Solar-AQMS #2- 92 samples
- Solar-AQMS #3- 95 samples
- Solar-AQMS #4- 85 samples
- Solar-AQMS #5- 95 samples

This equates to between 75% and 85% data coverage for the 56 days of the intensive phase of the measurement period.

In addition, 52 field blanks were collected over the sampling period. Field blanks were deployed daily at Solar-AQMS #5 and the procedure involved leaving the VOC tube with the caps on inside the insulated cabinet alongside the sample. Also, 65 analysis blanks were collected over the sampling period. Analysis blanks were VOC adsorbent tubes prepared at the same time as sample tubes and retained at the CSIRO Aspendale laboratories and analysed alongside the samples.

The flow rate of 20 ml min^{-1} for a 12-hour sample, was assumed to be within the safe sample volumes for the target species. Exceedances of safe sample volumes can result in breakthrough of the VOCs and losses from the sample. To ensure breakthrough did not occur, 4 samples (8 tubes) were collected in which 2 VOC adsorbent tubes were connected in series for each sample. Detection of the target species (> 5%) on the back-up tubes will indicate if any breakthrough occurred at that sample volume.

No duplicate samples were collected during the field measurement campaign as the Solar-AQMS VOC sampling systems were not run simultaneously. Duplicate samples will be collected at CSIRO Aspendale Laboratories (Victoria), by programming the paired pumps in each Solar-AQMS VOC sampling system to run simultaneously, as part of a follow-up instrument characterisation in March 2018. The duplicate samples will be subject to the same analysis procedures as the study samples to assess the measurement precision. The automated sampler cannot be used to collect duplicates as it cannot collect two samples on the same channels simultaneously.

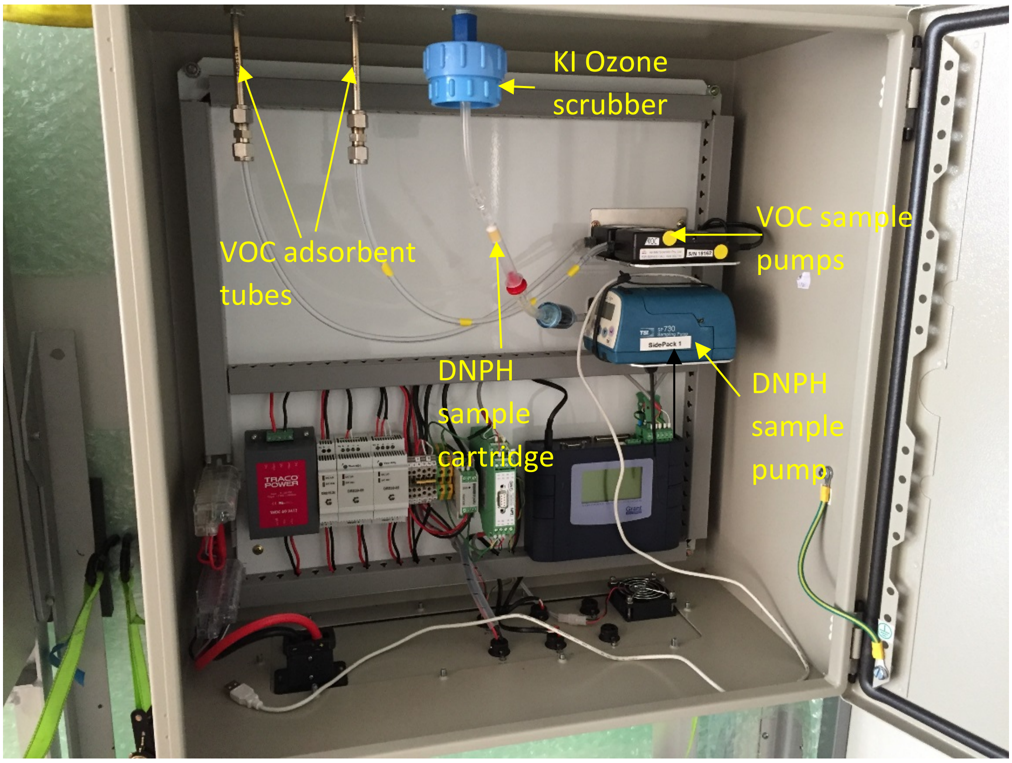

Figure 7 Inside the Solar-AQMS fan-ventilated instrument box which housed the VOC sample tubes, DNPH cartridges, sample pumps and ozone scrubber in the DNPH inlet line. This case also housed the electrical connections between the power input from the solar-battery pack and the power outputs for the instruments (bottom left) as well as a data logger for the meteorology sensor (bottom right).

6.5.3 CSIRO- Active sampling and derivatization of aldehydes and ketones onto DNPH cartridges

Two systems were used in this study for the sampling of aldehydes and ketones onto DNPH (dinitrophenylhydrazine) coated solid silica adsorbent cartridges (Supleco LpDNPH)- one system was deployed at the North-AQMS and the other was installed in the Solar-AQMS. Both systems of sampling for aldehydes and ketones used methods that were compatible with USEPA Compendium method TO-11A Determination of formaldehyde in ambient air using adsorbent cartridge followed by high performance liquid chromatography (HPLC) [Active sampling method] (USEPA 1999).

North-AQMS- Sampling of aldehydes and ketones using the CSIRO automated sampler

At the North-AQMS, ambient air was actively drawn through a ~ 10 m length of 3/8 inch O.D. PTFE tubing inlet (inlet height ~ 6 m) into the CSIRO custom designed automated sampler. The automated sampler is a programmable continuous air sampler with two channels allowing for simultaneous active sampling onto VOC adsorbent tubes and DNPH cartridges (Section 6.5.3) with 16 sampling ports per channel. Two 12-hour samples per day were collected by the automated sampler (00:00 – 12:00 and 12:00 – 0:00) which actively drew air onto DNPH cartridges using a constant flow air sampling pump at a set flow rate of 1 l min^{-1} with a sample volume 720 litres for each DNPH cartridge sample.

The automated sampler is fitted with an electronic flow sensor that measures and logs the flow every minute during sampling. Before the start of the measurement period, the flow sensor was calibrated against the inlet flow using a Bios Defender flow meter. Prior to the start of the measurement period the inlet and outlet flow on each sampling channel was measured to ensure agreement within ± 5%. During the measurement period daily flow checks on the outlet of the automated sampler were performed to ensure it was 20 ± 3 ml min^{-1}. If the flow was outside of this range the pump was re-calibrated between samples.

There is a known deterioration, over one or more days, of derivatized DNPH-carbonyl samples at room temperature. Because of this, the compartment housing the DNPH cartridges in the automated sampler was maintained at ~15° C. All cartridges were refrigerated before and after sampling. An ozone scrubber, consisting of a potassium iodide impregnated filter, was placed in front of all DNPH cartridges and replaced monthly during sampling to account for known artefact formation due to the presence of ozone.

Daily checks were recorded in the instrument log-sheet which contained the sample tube ID, sample channel, sample start/stop times, flow rate measured by internal flow sensor and displayed in instrument software, and the flow rate measured in daily checks.

The automated sampler was run during the 56 days of the intensive measurement periods between the 7 August and the 28 October 2017. Due to instrument failure samples were not collected from 12pm on the 22 September to 12pm on the 11 October. In total, 17 samples were collected before HF started, 49 were collected during HF and 9 collected after HF. In addition, 15 field blanks were collected during the sampling campaign. Overall 76 DNPH samples were successfully collected during the whole campaign. This equates to 37.5 days of data giving a data coverage over the intensive sampling phase of ~ 67%.

Solar-AQMS- Sampling of aldehydes and ketones using TSI Sidepak pumps

A the Solar-AQMS sites, ambient air was drawn through a DNPH coated solid silica adsorbent cartridges (Supleco LpDNPH) via a ~1.5 m length of 1/4 inch Teflon tubing (inlet height ~2 m) using a constant flow air sampling pump (TSI Sidepak) at a set flow rate of 1 l m^{-3}.

The pumps were programmed to collect 24-hour samples using the TSI pump software and the actual sample start/stop times were determined by the times when CSIRO technicians visited the sites to change the samples. Samples periods frequently occurred for 24 hours over two calendar days.

During sampling at the Solar-AQMS sites the DNPH cartridges were housed in a fan-ventilated instrument box (Figure 6) and were collected daily to minimise their exposure to high ambient temperatures. All cartridges were refrigerated before and after sampling. An ozone scrubber (potassium impregnated filter) was placed in front of all DNPH cartridges during sampling and replaced monthly to account for known artefact formation due to the presence of ozone.

All the TSI sidepak pumps were flow calibrated and audited before deployment into the field using a TSI 4140 thermal mass flowmeter. All of the pumps were within ± 1% of the set flow rate after the flow calibrations. The flow rate through the whole sampling setup was measured before and after every sample period with a Bios Defender flowmeter and recorded in the log-sheet for each site. The pump was recalibrated if the flow rate was more than ± 5% different to the set flow rate. The data from the pumps was downloaded for each sample and the sample tube ID, flowrates measured before and after sampling, flow test temperature and pressure, and sample start and stop times were recorded in sample log-sheets.

A total number of 236 DNPH samples were collected from across the five Solar-AQMS sites during the intensive phase of the measurement campaign:

- Solar-AQMS #1- 43 samples
- Solar-AQMS #2- 48 samples
- Solar-AQMS #3- 51 samples
- Solar-AQMS #4- 45 samples
- Solar-AQMS #5- 49 samples

This equates to between 77% and 91% data coverage for the 56 days of the intensive phase of the measurement period.

In addition, 24 field blanks were collected over the sampling period. The blanks were deployed daily at Solar-AQMS #5 and the procedure involved leaving the DNPH cartridge in its sealed package inside the insulated cabinet alongside the sample.

The flow rate of 1 l min^{-1} for a 24-hour sample, was within the safe sample volumes for the target species. Exceedances of safe sample volumes can result in breakthrough of the analyte and loss from the sample media. To ensure breakthrough did not occur 3 samples were collected in which two DNPH cartridges in series were sampled. Detection of the target species on the second cartridge will indicate if breakthrough occurred.

6.5.4 SGS Leeder- Passive sampling of VOCs, aldehydes, and hydrogen sulphide onto Radiello tubes

Measurements of VOCs, aldehydes, ketones and hydrogen sulphide by passive Radiello sampling was undertaken by external contractor SGS Leeder (Chinchilla), on behalf of GISERA. The Radiello sample cartridge is a passive sampler (i.e. air passively moves into the cartridge rather than being actively drawn in with a pump). In the Radiello passive sampler, samples gases pass through a diffusive surface on the cartridge at a known rate and the gases are trapped on an adsorbent surface. Different adsorbent surface materials are used to capture different species (Radiello Manual, 2006). In the present study three different cartridge types were employed: one for the collection of 46 VOCs including BTEX (benzene, toluene, ethylbenzene, sum of xylenes); another for the collection of 9 aldehydes) including formaldehyde; and one for the collection of hydrogen sulphide.

Radiello samples were deployed at the study site for ~14 days / sample from 14 June 2017 to 1 December 2017 at three locations: one adjacent to the North-AQMS, one adjacent to the South-AQMS and one adjacent to Solar-AQMS #1 at well site COM 445.

Cartridges were deployed by SGS staff on purpose built poles ~2m in height, fitted with manufacturer supplied shelters to protect the Radiello samplers from weather. Each cartridge was exposed to air for approximately two weeks, and then packed in a sealed container and sent to SGS Leeder’s laboratories in Notting Hill, Victoria for analysis. In the laboratory, samples were chemically extracted from the Radiello cartridges and analysed by gas chromatography with flame ionisation detection for VOCs, High performance liquid chromatography for aldehydes, and spectrophotometric method for H_2S.

For each of the three sites 11 out of the 12 two-weekly samples were collected successfully, resulting in 92% data coverage for the continuous monitoring period. Blanks and duplicates were deployed at other sampling sites within the Surat Basin as part of a wider sampling program (Lawson et al., 2017) and the results from these blanks and duplicates will be used for QA/QC purposes for the present study. CSIRO received the analysis data from each round of sampling directly from SGS. The data will be incorporated into a data base where it will undergo QA/QC auditing by CSIRO. Data of sufficient quality will be analysed and the results communicated in a subsequent report for this project.

6.6 Sampling of Polycyclic aromatic hydrocarbons (PAHs)

Sampling for PAHs was performed at South AQMS using a Flowset High Volume Polyurethane Foam (PUF) Sampler (Lear Siegler, Caringbah, NSW). The sampler draws air at a constant rate through a quartz filter (102 mm diameter) and polyurethane foam (PUF) sorbent plug (75 mm long; 65 mm diameter) to collect both aerosol phase and gas phase PAHS. This instrument is compliant with USEPA Method TO-13A, Determination of Polycyclic Aromatic Hydrocarbons and AS/NZS 3580.16:2014 Methods for sampling and analysis of ambient air and USEPA. Method16: Determination of polycyclic aromatic hydrocarbons (PAH).

Before the campaign, 102 mm diameter quartz filters (Pall Tissuequartz, part 7202, pure quartz, no binder) were cleaned by baking at 850^{o}C for 2 hours. The baked filters were wrapped in foil that had been baked at 200^{o}c for 2 hours and stored in a freezer at CSIRO Aspendale laboratories. Pre-cleaned PUFs (65 mm x 125 mm glass sorbent tube with 75 mm PUF, SKC 226-131) were sent to University of Queensland's –Queensland Alliance for Environmental Health Sciences (QAEHS) for addition of deuterated PAH standards to be used to assess break-through. A mixture of 100 ng of D-Naphthalene, D-Acenaphthylene, D-Anthracene, D-Pyrene and D-Dibenzo (a,h) anthracene in isooctane was added to each PUF (deuterated spikes are required for checking breakthrough if sample volumes are greater than 350 m^{3}). The PUFs were stored in a freezer at QAEHS before the campaign then transported and stored in a freezer in the field laboratory during the campaign. Two pre-cleaned PUFs were retained by the laboratory to be used as analytical blanks.

Throughout the campaign, the sampling period was nominally 48 hours. The sampler was operated at the default volumetric flow rate of 225 l min^{-1}, yielding a nominal volume of 648 m^{3}. Volumetric flow was achieved by a mass flow sensor, PID control and ambient temperature and pressure compensation using in-built pressure and temperature sensors. The calibration of the temperature and pressure sensors was checked at the start and end of the sampling campaign. The volumetric flow rate was monitored by a measuring orifice and the flow was regulated to a precision of better than 1%.

On the day of sampling the filter sample cartridge housing was cleaned with Isowipes and dried with Kimwipes. An unexposed filter was removed from the freezer and installed in the filter sample cartridge which was wrapped in aluminium foil. The wrapped cartridge and a sealed unexposed PUF were both transported in a cooler to the site (about 30 km). At the site, the unexposed PUF was removed from its storage container and added to the cartridge which was then installed in the sampler.

For each sample, the filter ID, sampling site, sampler ID, sampling start/ stop date and time, and details of flow checks were recorded in the instrument log-sheets. This information will be used to determine the sample volume each sample was exposed to and subsequently used to calculate the average airborne concentration of the PAHs (µg m^{-3}) over the sample period from the mass on the samples.

Three field blanks were collected during the sampling campaign (before, during and after the HF period) meeting the requirement of one field blank for every 10 samples. To perform a field blank, a sample cassette containing the aerosol filter and PUF cartridge was inserted into the sampler with the sample pump turned off, then immediately retrieved and returned to the field laboratory at the end of the day where they were unloaded and stored in a freezer.

During the campaign, the volumetric flow rate was checked for 1 in 5 samples, using a calibrated orifice plate and a manometer. All flow checks met the requirement of 225 l min^{-1} ±10%. The mean flow variation was ± 3%.

A total number of 24 PAH filter samples and PUF cartridges were collected during the intensive sampling phase of the measurement campaign, which equates to 51 days of sampling and a data coverage of 92%.

At the end of the campaign, the 24 samples and 3 field blanks were sent to QAEHS where they are currently undergoing analysis by extraction in n-hexane and acetone then analysis for 13 PAH compounds including the NEPM listed pollutant, Benzo(a)pyrene, using a Thermo 1310 gas chromatograph coupled to a DFS Magnetic Sector high-resolution mass spectrometer (GC-HRMS).

7 Summary

CSIRO has undertaken a comprehensive measurement program to assess the impacts of HF on local air quality. The study location was a farmland property of approximately 600 ha containing 10 coal seam gas wells which underwent HF between September and October 2017. The measurement program ran from July – December 2017 covering periods prior to HF, during HF activity, and after HF had concluded.

Measurements were conducted at six different sampling locations within the field, five of which were located adjacent to wells (within ~130 m). Across the six sites, 16 different air quality variables were measured utilising a mixture of continuous measurement systems and integrated sampling of VOCs, aldehydes and particulates onto specialised sample cartridges or filters. Table 8 lists each of the target air pollutants, sampling locations, and a summary of the rate of data capture for the study period.

Particular highlights of the measurement program undertaken by CSIRO and project partners for this study include:

- The most comprehensive suite of measurements of air quality undertaken in an Australian gas-field to date with over 50 individual measurement systems capable of detecting over 50 species including all air pollutants listed in the National Environment Protection Measures for Ambient Air Quality (NEPM 2015) and Air Toxics (NEPM 2011).
- High spatial resolution with measurements taken across 6 sites within a ~600 ha site containing 10 wells
- High time resolution with the combination of continuous measurements and short duration integrated sampling (12-hour – 48-hour samples) which are in line with the duration of HF activities (~ 1 -2 days).

Table 8 Target air pollutants measured, measurement locations within the selected study site, and data coverage attained over the field work period.

Target Air Pollutants	Location	Data capture
NOx, O_3, CO, SO_2 – continuous	AQMS North & South	**Data coverage Aug – Dec 2017:** **O_3 ~ 75%** **CO 76 % (North), 54% (South)** **NOx 77% (North), 92% (South)** **SO_2: 76 % (North)**
Methane & CO_2 – continuous	AQMS North & South	**95% data coverage Aug – Dec**
VOCs by PTR-MS – continuous	AQMS North	**> 80% data coverage for period July – Nov** Continuous measurements of > 20 VOC compounds incl. BTEX & formaldehyde
VOCs by 12h samples on VOC adsorbent tubes	AQMS North 5 x Solar-AQMS	**~ 530 samples (12h) collected** Analysis for VOC compounds incl. BTEX underway
Aldehydes & ketones by 12h samples on DNPH cartridges	All sites	**Over 300 samples collected** Analysis for ~ 16 aldehydes & ketones incl. formaldehyde & acetone underway
VOCs, aldehydes, H_2S by fortnightly samples on radiello tubes	AQMS North & South Solar-AQMS #5	**33 fortnightly samples** Analysis of samples for 46 VOC species underway.
Particles (PM) – continuous Incl. PM 1, 2.5,4, 10 µm & TSP	All sites	**> 90% data coverage Aug – Dec**
PM 10 by Comde-Derenda sampler (12h)	AQMS North	**Over 90 filter samples collected** Particle mass & composition to be analysed by ANSTO & CSIRO
PM 10 by Microvol sampler (weekly)	5 x Solar-AQMS	**44 filter samples collected** Particle mass & composition to be analysed by ANSTO & CSIRO
PM 2.5 sampling by E-sampler continuous & weekly samples on filters	5 x Solar-AQMS	**> 90% data coverage (Jul – Nov) for continuous $PM_{2.5}$** **> 40 filter samples collected across 5 sites** Particle mass & composition to be analysed by ANSTO &CSIRO
Mercury – continuous	AQMS South	**> 90% data coverage for period Aug – Dec 2017**
Radon – continuous	AQMS South	**> 90% data coverage for period Aug – Nov 2017**
PAHs by sampling on PUF cartridges	AQMS South	**24 samples (48h) for period Sept – Oct** Analysis of samples for PAHs by QAEHS underway
Meteorology	All sites	**> 90% data coverage for period Aug – Nov**

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9 Appendices

9.1 ANSTO - gaseous radon measurements

The Australian Nuclear Science and Technology Organisation (ANSTO) deployed instrumentation for the continuous monitoring of ambient radon in air. The following is a report of the radon measurement program provided by ANSTO.

A SUMMARY REPORT ON RADON IN AIR AND SOIL MESUREMENTS AT A HYDRAULIC FRACTURING STUDY SITE IN THE SURAT BASIN, QLD

December, 2017

Sylvester Werczynski, Ot Sisoutham, Alistair Williams

Comprehensive radon measurements in ambient air and radon emanation from soil study have been undertaken a property in the Surat Basin (between the townships of Roma and Miles in Qld) from 8th August till 25th November 2017 (Figure A.1).

The purpose of the study was to investigate the influence of coal seam gas (CSG) activities and hydraulic fracturing (HF) on radon emissions in this region.

Measurement area

An ANSTO 1500 litre dual flow loop two-filter radon detector was installed at the South-AQMS (26.31108^{0}S, 149.50979^{0}E), together with the automatic radon flux chamber and radon in soil measurements. Another 100 litre radon detector was installed at the same time outside the area of interest between Barramornie and Tara at Greenlea property (27.135061˚S, 150.243761˚E), about 117 km SE of the study area (Figure A.2).

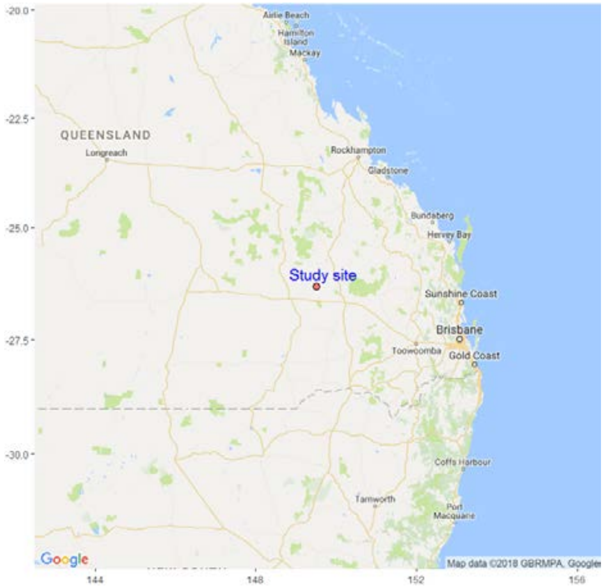

Figure A.1 Location of radon measurement area

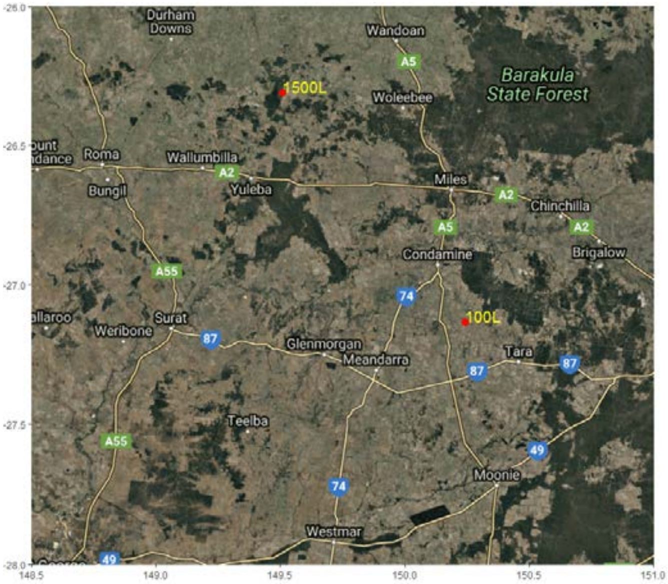

Figure A.2 Location of two radon detectors – 1500L at the Study site and 100L at Greenlea 'background' site.

Radon in air measurements

Measurements of ^{222}Rn concentrations in air were performed using ANSTO continuous radon-in-air detectors (1500 l and 100 l).

Air sampled from a 2m mast above the ground at the rate of 65 l min^{-1} (1500 l detector) and 15 l min^{-1} (100 l detector) first passes through an air filter to remove dust or other aerosol pollution, as well as the radon "progeny" (products of radon's radioactive decay process) in the sampled air stream.

The air then enters the "thoron delay volumes" (Figure A.3- the big blue drums). Thoron (^{220}Rn) is an isotope of radon (^{222}Rn) and can interfere with the measured radon signal. As the half-life of thoron is only 55.6 seconds, it can be almost completely removed by delaying the sampled air in these thoron delay volumes by 6 minutes.

The air then passes into the main "delay" volume, which allows the radon to decay under controlled conditions. From there the air passes through a screen, which collects the newly formed decay products. The screen sits close to a "zinc sulphide scintillator", which emits light when struck by radiation from radon decay. The scintillator is connected to a "photomultiplier tube" which detects this light. This detection is processed electronically and recorded as a count rate by a data logger.

The 100 l detector operates on the same principle, but it requires smaller "thoron delay volumes" due to the smaller volume of the tank and slower air flow rates (~15 l min^{-1}).

The 1500 l detector was set up at the South-AQMS, next to the substation COM358 and the Ecotech Air Quality Monitoring Station (AQMS).

The 100 l detector was set-up at Greenlea property, around 117km away from the Study site as a ‘background’ measurement not affected by the influence of CSG activities. The detector was setup with solar panels charging a 12V battery, which runs the instrument (Figure A.4). The datalogger in the 100 l radon detector was also set-up to continuously monitor the ambient air temperature, relative humidity, barometric pressure, and wind speed and wind direction.

Figure A.3 The 1500 litre radon detector at COM358 at the HF Study site

Figure A.4 The 100 litre radon detector located at Greenlea "background" site

Automatic radon flux measurement

An automatic system for measuring the radon flux at soil surface (AutoFlux) was set up next to the 1500 l radon detector at HF Study site (Figure A.5). By exposing the ground surface to the normal weather conditions between series of consecutive measurements, this method is used to study, in the long term, the effects of meteorological factors on the radon flux density at the soil-atmosphere interface.

The automatic chamber is controlled by the Campbell Scientific datalogger CR1000 and the radon is measured by a portable radon monitor AlphaGUARD 2000PRO model.

AlphaGUARD (Saphymo Company) is a portable monitor designed for instantaneous or continuous, hourly measurement of radon concentrations in air between 2–2,000,000 Bq m^{-3}. The instrument uses a pulse-counting ionization chamber (alpha spectroscopy) for its measurements, and offers a high detection efficiency, wide measurement range, fast response and permanent maintenance-free operation with a long-term stable calibration.

The datalogger CR1000 is programmed to close the lid of the accumulation chamber every 3 hours for 60 minutes duration (Figures A.6 – A.7). To obtain accurate measurements, conditions in the drum must closely match those outside and the air in the accumulation chamber is continuously replaced via inlet and outlet with a ventilation rate of approximately 1 l min^{-1}. Once closed, the rate of change of the measured radon concentration within the chamber is continuously monitored, and the surface radon flux can then be estimated from the integrated measurements. After opening the lid, the system runs for two hours in the background mode while flushing the portable monitor with ambient air at 1 l min^{-1}. This allows background measurements to be performed.

The AutoFlux measurement system includes additional sensors for selected atmospheric and soil parameters (soil moisture inside the chamber and outside, rain gauge, wind speed and wind direction, barometric pressure, air temperature and relative humidity). This allows getting a better understanding of processes and mechanisms controlling the release of radon from the soil.

All other parameters are recorded at 10 minutes intervals.

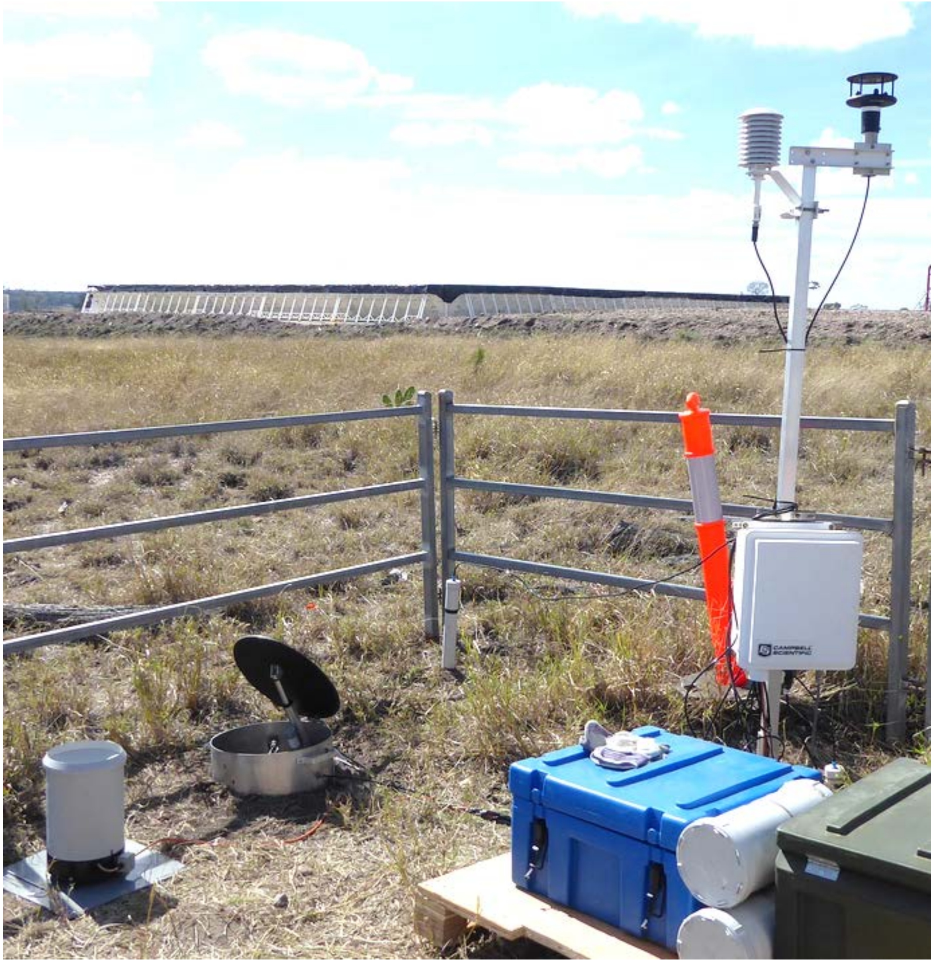

Figure A.5 View of automatic radon flux system AutoFlux

Figure A.6 View of AutoFlux accumulation chamber in background mode

Figure A.7. View of AutoFlux accumulation chamber in measurements mode

Radon in soil measurements

A purpose build radon in soil system was set-up in the vicinity of AutoFlux and 1500 l radon detectors. Soil radon gas concentration was measured at 2 close locations (about 1.5 meters apart) at different depths: 70 cm and 20 cm below the surface (Figures A.8 – A.9). The system uses 2 radon gas analysers AlphaGUARD 2000 PRQ including 2 small pumps. The air was drawn from the probe into the AlphaGuard at the rate of 1 l min^{-1} though a 6 l delay volume, in order to allow thoron (^{220}Rn) to be removed before the gas is analysed. The air is continuously drawn from these two sampling tubes and analysed for radon concentration at 10 minute intervals.

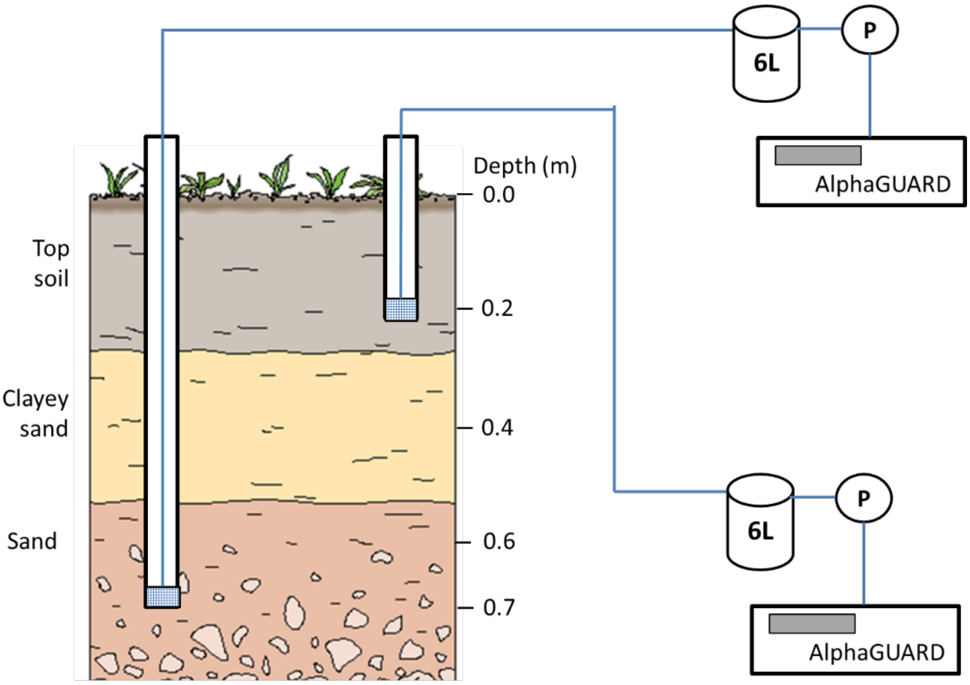

Figure A.8 Diagram of radon in soil measurements

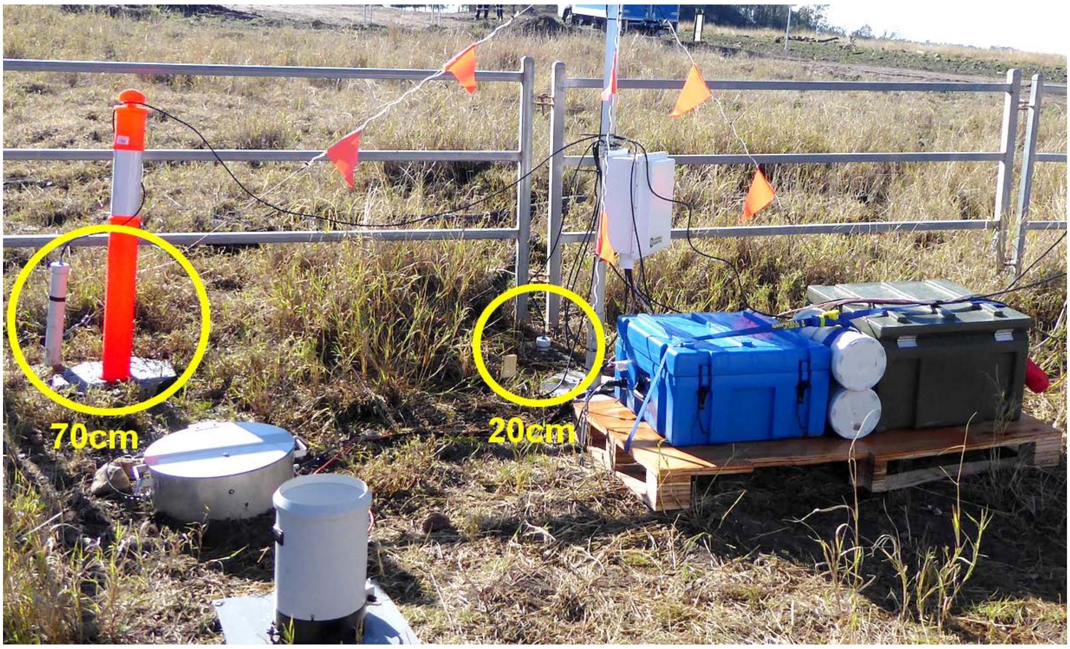

Figure A.9 Location of 70cm and 20cm radon in soil sampling tubes.

Radon flux survey

In order to characterise the surface radon emissions from soil at the area of interest, the ANSTO radon emanometer was used. Two sets of measurements were performed, one before the HF activity at the site and one at the end of the survey. The instrument is designed to simultaneously measure the radon and thoron flux densities from soil or rock surfaces. Radon and thoron flux estimates are made based on the flow-through accumulator method, with each sample taking approximately 24 minutes.

The strength of radon emissions from the land surface into the atmosphere depends on the soil mineralogy and porosity, and to a lesser extent also varies with changes in atmospheric pressure and soil moisture.

The ANSTO portable accumulation chamber allows radon to accumulate in a chamber placed over the soil (Figures A.10 – A.11). The evolution of the measured radon concentration within the chamber is continuously monitored, and the surface flux at that location can then be estimated after a given time period from the integrated measurements.

Figure A.10 View of ANSTO portable radon emanometer

Figure A.11 View of accumulation chamber during radon flux measurement

Radon data coverage

The radon measurements at the Study site and Greenlea properties started on 4th August and continued until 27th November 2017, but in the first and last week of the survey both detectors were calibrated and the background noise measured to ensure the integrity and quality of the data recorded.

As a result, only data from 8/08/2017 till 25/11/2017 was used and the percentage of valid data for the various methods is summarized in the table below:

Measurement method	Number of sampling days	Number of valid records	% Valid data
Radon in air concentration at the Study site property (1500 l radon detector) at 10 min intervals	110	14517	92
Radon in air concentration at Greenlea property (100 l radon detector) at 10 min intervals	110	15412	98
Automatic radon flux measurements at 3 hours intervals	110	868	99

Met parameters from automatic flux measurements at 10 min intervals	110	15778	100
Radon flux survey with portable emanometer	2	14	100
Radon in soil measurements (20 cm and 70 cm below surface)	110	8710	55

The poor data coverage of radon in soil measurements was affected by heavy rains at the site in October and November 2017. The unusually heavy rain caused the blockage of radon in soil system inlet's air filters by water and mud. As a result, the measurements from 7th October 2017 till the end of the survey are invalid.

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