Design of a study to assess the potential impacts of hydraulic fracturing on air quality in the vicinity of well sites in the Surat Basin, Queensland (Draft 3 – Revised study design for Combabula site)

Task 4 Report for Air, Water and Soil Impacts of Hydraulic Fracturing (W.11)

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GISERA was co-founded by CSIRO and Australia Pacific LNG in July 2011. For further information visit gisera.csiro.au.

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Glossary

Units of measurement

Mm^3 – million cubic metres

$mg\ m^{-3}$ – milligrams per cubic metre (1 milligram = one thousandth of a gram)

$\mu g\ m^{-3}$ – 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

LPM – litres per minute

$mL\ min^{-1}$ – millilitres per minute

$m\ s^{-1}$ – meters per second

Bqm^{-3} – becquerels per cubic metre, a unit of radioactivity

Nomenclature

Aldehyde – a class of oxygenated volatile organic compounds

Ambient air – outdoor air

Anthropogenic – originating from human activities (man-made)

Biogenic – of biological origin

BTEX –benzene, toluene, ethylbenzene, xylenes (a subset of VOCs)

CSG – coal seam gas; a type of natural gas extracted from coal seams

Detection limit – the lowest measurable concentration of a pollutant for a particular analytical technique

pH – a scale used to assess the acidity or alkalinity of a solution

Gas processing facility (GPF) – facility which compresses and dries gas

Gathering networks – network of pipes which carry gas and water to treatment and processing facilities

Geogenic – of geological origin

PAH – Polycyclic aromatic hydrocarbon

PUF – polyurethane foam

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

VOC – volatile organic compound

Wellhead gas and water – gas and water sampled from the separator at an individual CSG wellhead

Abbreviations

APLNG – Australia Pacific Liquefied Natural Gas

AQMS – Air Quality Monitoring Station

BTEX – a subset of VOCs including benzene, toluene, ethylbenzene and xylenes

CO – carbon monoxide

CO_2 – carbon dioxide

CH_4 – methane

EIS – Environmental Impact Statement

GISERA – Gas Industry Social and Environmental Research Alliance

HF – Hydraulic Fracturing

H_2S – hydrogen sulfide

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

SBAAQ Study – Surat Basin Ambient Air Quality Study

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

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Important Note

This report is Draft 3 of the report of *Design of a study to assess the potential impacts of hydraulic fracturing on air quality in the vicinity of well sites in the Surat Basin, Queensland*. Draft 1 was externally peer reviewed and review comments were incorporated into Draft 2 of the report. Also included in the Draft 2 report was Appendix D which lists the peer reviewer's comments and the authors' responses to the comments.

The location for the proposed study described in Draft 1 and 2 of the report became unavailable due to a lack of access to mains power at the site to operate monitoring equipment, and delivery and suitability of instrumentation. An alternative site was selected, and the methodology described in Draft 2 was adapted for the new site and is presented here as Draft 3: *Design of a study to assess the potential impacts of hydraulic fracturing on air quality in the vicinity of well sites in the Surat Basin, Queensland (Draft 3 - Revised Study Design for Combabula Site)*. In terms of its approach and methodology, the revised report deviates as little as possible from the previous draft incorporating the response to peer-review. In addition to the change in location of the field measurement program some measurement systems have also been changed.

The present Draft 3 report includes a list of the differences between Draft 2 and Draft 3 Reports in Appendix D.

Executive summary

This report presents a methodology for an air quality study to investigate the impacts of hydraulic fracturing (HF) activities on local air quality in the vicinity of HF operations. The methodology comprises a suite of measurements of atmospheric gaseous and particle species to be undertaken before, during and after HF at a selected site in the Surat Basin. The aim of the proposed methodology is to satisfy the overall study objectives:

- **Objective 1**: Quantify enhancements 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.

The study location is a farmland property of approximately 600 ha. Roma, the largest nearby population centre is located approximately 80 km to the SSW. 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 are scheduled to undergo HF sometime between August and October 2017. Note that subject to health and safety requirements, the project team has complete autonomy to operate in the gas production field and to make measurements of any aspect of the operations.

The measurement methodology is presented as two parts: two fixed air quality monitoring stations (AQMS) located within the HF field, and five battery-powered perimeter monitoring stations located around the boundary of the property (perimeter monitoring sites). A three-tier hierarchy of air quality monitoring methods was established. If an air quality monitoring method was not available from the first tier, a subsequent tier was used.

- **Tier 1***:* Australian Standard methods as outlined in Schedule 3 of the Ambient Air Quality and Air Toxics NEPMs (NEPM 2011, 2015).
- **Tier 2:** Appropriate internationally recognised methods or standard techniques.
- **Tier 3***:* Non-standard methods with appropriate calibration and validation procedures to assess their accuracy and precision. Validation of Tier 3 measurements against Tier 1 and 2 methods will be undertaken where possible.

The proposed sampling and analysis methodologies provide a measurement of all air pollutants listed in the National Environment Protection Ambient Air Quality (NEPM 2015) and Air Toxics (NEPM 2011) Measures as well as mercury and hydrogen sulphide listed in the Queensland Government EPP air objectives (EPP 2008), and radon listed in the ARPANSA (2002) recommendations. Additional species were included if the species was detected in measurements of air at the proposed study site; and/or the species may have a potentially negative impact on air quality; and/or the species can be used as a tracer providing information on the sources of other potential air pollutants at the study site; and/or the species was reported or detected as present in HF chemicals, flow-back fluids, CSG at the proposed study site.

The report provides details of the sampling and analysis methodologies, the sampling plan and how the data collected will be used to address the objectives of the study and has been peer reviewed by experts from outside of CSIRO.

The outcomes of the project will be communicated to stakeholders (including industry, government and community) utilising the GISERA (Gas Industry Social and Environmental Research Alliance) communication and outreach facilities. Accompanying on-line report publication, communication of the results of this study is likely to include media interviews, information videos and fact sheets available on the GISERA website (gisera.org.au), and the sharing of this content on social media platforms.

Preface

CSIRO Climate Science Centre is leading a project within the Gas Industry Social and Environmental Research Alliance (GISERA) on the impact of hydraulic fracturing (HF) on air, soil and water quality. The project was initiated in 2016 and an initial phase (Phase 1) proposal was approved by the GISERA Queensland Regional Research Advisory Committee (RRAC) in late 2016. Phase 1 of the project involves conducting a review of the state of knowledge of impacts of HF on air, soil and water quality and the design of a study to measure these impacts in the vicinity of wells before, during and after HF (GISERA 2017). The outputs of Phase 1 include:

- *Task 1* – Establishment of external peer review by a panel of internationally recognised experts.
- *Task 2* – Report, including state of the knowledge about the potential sources of air pollutants associated with CSG extraction using HF.
- *Task 3* – Combabula site familiarisation visit.

The research presented in reports from Tasks 2 and 3 will be used to inform the remaining tasks:

- *Task 4* – Peer-reviewed report describing a suitable measurement program to provide enhanced information of the impacts of HF on air quality.
- *Task 5* – Peer-reviewed report describing a suitable measurement program to provide enhanced information of the impacts of HF on surface water, groundwater and soil.
- *Task 6* – Report on measurements of air made before HF commenced in October 2016.
- *Task 7* – Report on the collection of baseline soil and water samples at Combabula and a reference stream location.

The following report *Design of a study to assess the potential impacts of hydraulic fracturing on air quality in the vicinity of well sites in the Surat Basin, Queensland* is a product of *Task 4* of the GISERA project. The first draft of this report was submitted for peer review in April 2017 in accordance with the project order. A second draft incorporating the response to reviewer's comments was finalised in June 2017. The location for the proposed study described in Drafts 1 and 2 of the report became unavailable due to a lack of access to mains power to operate monitoring equipment at the site. Hence, an alternative site was selected and the study design was adapted for the new site. In terms of its approach and methodology, the revised study design deviates as little as possible from the previous draft incorporating the response to peer-review. The following report *Design of a study to assess the potential impacts of hydraulic fracturing on air quality in the vicinity of well sites in the Surat Basin, Queensland (Draft 3- Revised Study Design for Combabula Site)* is provided in its current form for CSIRO internal review. Appendix D of this report lists the major revisions to Draft 2 made in preparation of the current report.

Following review and subject to CSIRO and GISERA approval, the reports from research conducted as part of Tasks 2–5 were finalised in July 2017. The data and reports generated as part of this project will be made publicly available via the GISERA website for use by individuals, communities, research organisations, governments and industry.

1 Introduction

The Surat Basin is an area of intensive coal seam gas (CSG) extraction in Australia with annual CSG production rising from around 57 million cubic metres (Mm^3) in 2005 to over 21 000 Mm^3 in 2015 (Queensland Government 2017). As extraction from higher permeability coal seams reaches its peak, the use of stimulation techniques, such as hydraulic fracturing (HF), to access gas from lower permeability coal seams is likely to become more frequent. It is estimated that ~8% of the more than 5000 conventional and domestic petroleum and gas wells currently in Queensland have so far undergone HF (DEHP 2014). However, as the industry expands, 10– 40% of wells are likely to undergo HF (DEHP 2014). The potential health and environmental impacts of the CSG industry expansion and more frequent use of hydraulic fracturing are issues of particular concern to people living nearby these developments (Cham & Stone 2013).

Multiple public inquiries, reviews, roundtables and government reports on HF have been undertaken at both state and federal level in Australia within the last five years (ACOLA 2013; IESC 2014; CSE 2014; NTG 2014, 2017; NRC 2016; DPIPWE 2015; Victorian Auditor General 2015; EPC 2015; Legislative Council of WA 2015). Overall these reviews have concluded that the risks posed to human health and the environment by HF operations are manageable within acceptable limits with proper regulation and controls. However, as seen in the multiple public submissions to these inquiries, community acceptance of HF is mixed with many seeing the risks posed to human health and the environment as unmanageable and unacceptable. Notably lacking from the evidence considered in these inquiries is independent, robust monitoring of the impacts of the CSG industry in general as well as the impacts of HF on air quality in the Australian context, against which claims by industry, government and the community can be tested.

CSIRO is leading the currently underway GISERA Surat Basin Ambient Air Quality (SBAAQ) Study (Lawson et al. 2016) comprising a network of five ambient air quality monitoring stations (AQMS) and 10 sites at which air pollutants known as volatile organic compounds (VOCs) are being monitored. Of the five sites, two are used to measure regional levels of air pollutants and three are located closer to potential CSG emission sources such as gas field stations. Hourly air quality data are live-streamed on the DEHP website http://www.ehp.qld.gov.au/air/data/search.php. This report presents a proposed methodology for a study investigating the impacts of HF activities on local air quality at a site within the Surat Basin using an additional two AQMS and four VOC monitoring sites, and an extended suite of air quality measurement systems. Combined, the SBAAQ and the HF studies will represent a significant contribution to our understanding of the impact of CSG production and hydraulic fracturing on air quality in Australia's largest CSG production region.

This report begins with a discussion of the potential sources of air pollutants associated with HF as well as other non-HF air pollutant sources likely to be encountered in the Surat Basin (Sections 1.1 & 1.2). Based on this discussion a set of objectives for a proposed study of the impacts of HF on air quality are presented (Section 1.3) along with a list of relevant air quality standards (Section 1.4) and key air pollutants for incorporation into the proposed study design (Section 1.5). This is followed by a description of the proposed study site (Section 2) and the methodologies for measurement of key air pollutants (Section 3). Section 4 describes how the data from the proposed methodology will be used to address each study objective and provides a timeline for the monitoring period and reporting.

1.1 Potential sources of air pollutants associated with hydraulic fracturing

Hydraulic fracturing is a well stimulation process that involves the high-pressure injection of a large volume of fluids into a well to fracture targeted coal seams to increase gas production. The fractures created are propped open by solids called proppants, usually sand, which are added to the injected fluids, 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 chemical additives stored, mixed and injected at each well pad.

Some commonly used HF chemicals and their application include (CSIRO 2015):

- acids and alkalis, such as hydrochloric acid and sodium carbonate, to control the pH of HF fluids
- biocides, such as sodium hypochlorite and sodium hydroxide, used to prevent contamination and blockages due to the presence of bacteria
- guar gum used to increase fluid viscosity to form a gel that improves proppant transport into the coal seam fractures
- 'gel breakers', such as ammonium persulfate, used to breakdown HF gels prior to flushing the well; surfactants, such as alcohol, reduce surface tension in fluids improving fluid recovery from the fracture.

Coal seam gas companies operating in Queensland are required to submit a complete list of chemicals for approval to state regulators before gaining approval for HF (DEHP 2014). Details of the HF chemicals used by three CSG companies operating in the Surat and nearby Bowen Basin are publicly available online at:

- Origin Energy – APLNG: https://www.originenergy.com.au/content/dam/origin/about/our-approach/docs/OurApproach-2016-Hydraulic-Fracture-Stimulation.pdf
- Santos: https://www.santos.com/what-we-do/production/hydraulic-fracturing/material-data-safety-sheets/
- QGC – BG Group: http://www.bg-group.com/793/qgc/sustainability/environment/environmental-operations/hydraulic-fracturing-and-chemicals-used/

A fourth CSG company, Arrow Energy, does not currently undertake HF operations in the Surat Basin (Arrow Energy 2012).

The rate and pressure of injection, the volume of fluid, and proppant concentration are monitored in real-time during each injection to determine the progress of the fracturing and, where necessary, adjust the fluid composition and injection pressures. Consequently, the exact volume and mixture of HF chemicals differs for each well in response to operational requirements.

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. The concentration of these geogenic contaminants may be enhanced in flow-back water from hydraulicly fractured wells due to the chemicals used in HF (e.g. chelating agents, acids, surfactants and solvents) which may act to increase the potential for release contaminants from the coal seam. 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 mobilised in fluids or 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 or 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.

The handling and storage of HF fluids, flow-back fluids and CSG at the surface will determine the impact of HF activities on air quality (Field et al. 2014). Chemicals in HF fluids, flow-back fluids and CSG may enter the air by several pathways (CSE 2014):

- evaporation from spills and leaks from chemical storage tanks
- evaporation/formation of airborne particles from ponds, mechanical HF fluid mixing, injection pipelines and flow-back tanks
- dust from windblown/mechanical agitation of proppant
- fugitive emissions of CSG from flow-back fluids, well failure or connections between the coal seam and overlaying strata to surface via pathways created or expanded during HF.

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. Overall, 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 currently unknown.

1.2 Other air pollutant sources

As part of the SBAAQ Study, CSIRO is developing an air quality model to investigate the contribution of CSG industry emissions to air pollution levels across the Surat Basin (Lawson et al. 2016). The release or emission of pollutants from CSG and non-CSG sources will be represented in the model using an emission inventory. Emission sources were identified using a range of different information sources, including Queensland Government department and agency databases, Queensland Globe, the National Pollutant Inventory (NPI) database, industry environmental impact statements, and aerial photography.

In addition to emissions from the HF activity at the study site and CSG-related sources in the surrounding area, the CSIRO model inventory indicates emissions from non-CSG-related sources that may also impact the Surat Basin region include:

- natural sources such as soil, dust and emissions from vegetation
- traffic emissions
- agricultural and farming emissions including feedlots
- smoke from bushfires, prescribed burning and wood heaters
- industrial, commercial and domestic emissions
- other industry sources, such as quarries, mines, power stations, etc.

1.3 Study objectives

In the Surat Basin, coal seam gas wells are predominantly situated within rural agricultural properties. There are some important aspects of HF operations in this setting that need to be considered when designing an air quality study:

- In rural areas, the background concentrations of air pollutants are generally low, and are often close to the limit of detection for many measurement techniques.
- Air quality in the vicinity of HF operations may be influenced by a number of different HF activities occurring simultaneously including site set-ups, chemical storage, transport and mixing of chemicals, injection, flow-back and well completion activities. In addition, air quality within a CSG well field will be influenced by contributions from both CSG sources (including HF) and non-CSG-related sources
- HF activities occur on timescales of hours to days, so that air quality impacts are likely to be short term (hours to days) and transient.
- If air pollutants are emitted during HF activities, they will likely undergo significant dilution by mixing with cleaner background air as they are transported away from the source. The levels of pollutants emitted, meteorological factors, and the capacity of the airshed to dilute/remove the pollutants will determine the air quality experienced by nearby residents and communities.

Consequently, a study of the impacts of HF on air quality requires:

- measurements of a complex suite of compounds representative of the range of potential HF and non-HF sources of air pollutants
- sensitive instrumentation capable of detecting pollutants at low background concentrations
- high time resolution measurements that can capture peak events associated with different HF processes occurring on site
- spatially diverse measurements which capture air quality in the vicinity of wells undergoing HF as well as providing measurements of air quality that may be experienced by nearby residents and communities.

This report presents a proposed methodology for an air quality study to investigate the impacts of HF activities on local air quality in the vicinity of HF operations. The methodology comprises a suite of measurements of atmospheric gaseous and particle species to be undertaken before, during and after HF at a selected site in the Surat Basin. The aim of the proposed methodology is to satisfy the overall study objectives:

- **Objective 1**: Quantify enhancements 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.

1.4 Relevant air quality standards

Ambient air guidelines for a number of substances have been developed by Australian regulatory bodies to protect human health and the environment. Air quality criteria relevant to this report include:

- **National Environment Protection (Ambient Air Quality) Measure – 2016.** The pollutants to which this NEPM measure applies are nitrogen dioxide, carbon monoxide, ozone, sulphur dioxide, particulate matter (PM) with diameters less than 10 µm (PM_{10}) and 2.5 µm ($PM_{2.5}$), and lead.
- **National Environment Protection (Air Toxics) Measure – 2011.** The pollutants to which this NEPM measure applies are BTEX compounds (benzene, toluene, xylenes) as well as formaldehyde and poly aromatic hydrocarbons (PAHs) as benzo(a)pyrene.
- **Queensland Environmental Protection (Air) Policy (EPP) – 2008.** The EPP (2008) includes all air toxics prescribed in the NEPM along with 18 other organic and inorganic pollutants.
- **Australian Radiation Recommendations for Limiting Exposure to Ionizing Radiation (ARPANSA 2002)** (Guidance note [NOHSC:3022(1995)]). Provides recommended action levels for radon-222 concentration in air for households and workplaces.

Australian federal or state ambient air guidelines are not available for many of the VOCs expected to be measured in this study. In the absence of Australian guidelines, international guidelines that covered the range of VOCs measured in this study will be consulted, in particular the US EPA Regional Screening Levels for Chemical Contaminants at Superfund Sites –Resident Ambient Air (US EPA 2013).

The following section (1.5) lists the key air pollutants identified for incorporation into the proposed study design. Current state and federal Ambient Air Quality Standards that apply to pollutants identified in Section 1.5 are listed in Table 1.

1.5 Key air pollutants

The proposed sampling and analysis methodologies outlined in this report will provide a measurement of all air pollutants listed in the National Environment Protection Ambient Air Quality (NEPM 2015) and Air Toxics (NEPM 2011) Measures as well as mercury and hydrogen sulphide listed in the Queensland Government EPP air objectives (EPP 2008), and radon listed in the ARPANSA (2002) recommendations. These key pollutants are listed in **Error! Not a valid bookmark self-reference.** along with potential HF-related sources and relevant ambient air quality objectives.

The key pollutants listed here represent the minimum that would be reported as part of the proposed study design. The proposed methodology for measuring these key pollutants will be outlined in Section 3. The techniques for measuring the air toxics BTEX and formaldehyde described in Section 3 can measure many other VOC and carbonyl species. Likewise, the proposed particulate matter (PM_{10}) analysis techniques will provide detailed information on the composition of the particles captured during sampling.

Additional species will be considered for inclusion in analysis and reporting if:

1. The species was detected in measurements of air at the proposed study site. The species may be either only qualitatively identified (present/ not present) or its concentrations may be quantified depending on the suitability of the measurement technique applied; and
2. The species may have a potentially negative impact on air quality; and/or
3. The species can be used as a tracer providing information on the sources of other potential air pollutants at the study site; and/or
4. The species was reported or detected as present in HF chemicals, flow-back fluids, CSG at the proposed study site. Data will be sourced from the accompanying GISERA study on impact of HF on surface water, groundwater and soil quality and from industry stimulation impact monitoring data (see Section 3.6).

Table 1 Key pollutants to be measured as part of the proposed HF air quality study

Pollutant	**Ambient Air Quality Standard**			**Potential HF Activity Sources**
	Averaging Period	**Max Concentration**	**Relevant Standard**	
Nitrogen dioxide	1 hour 1 year	0.12 ppm 0.03 ppm	NEPM Qld EPP	Exhaust from diesel powered equipment and vehicles
Sulphur dioxide	1 hour 1 day 1 year	0.20 ppm 0.08 ppm 0.02 ppm	NEPM Qld EPP	Exhaust from diesel powered equipment and vehicles
Carbon monoxide	8 hour	9 ppm	NEPM Qld EPP	Exhaust from diesel powered equipment and vehicles
Ozone	1 hour 4 hour	0.10 ppm 0.08 ppm	NEPM Qld EPP	Secondary pollutant – no direct emissions. Product of reactive processes in air between gases.
PM_{10}	24 hour 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 flow-back.
$PM_{2.5}$	1 day 1 year	25 µg m^{-3} 8 µg m^{-3}	NEPM	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.
Lead	1 year	0.50 µg m^{-3}	NEPM	No specific HF source identified. Roads, vehicles, dust, oil & gas extraction (NPI 2016).
Benzene	1 year	0.003 ppm	NEPM Qld EPP	Exhaust and evaporative emissions from vehicles and equipment CSG and flow-back fluids (Day et al. 2016)
Toluene	24 hour 1 year	1 ppm 0.1 ppm		
Xylenes	24 hour 1 year	0.25 ppm 0.2 ppm		
Formaldehyde	24 hour	0.04 ppm	NEPM Qld EPP	Exhaust from diesel powered equipment and vehicle. Secondary pollutant – product of reactive processes in atmosphere between gases. Minor components or secondary product of CSG and flow-back fluids.
Methane	na	na	na	Major component of CSG. Used as tracer for fugitive CSG emissions.
Poly aromatic hydrocarbons (PAHs) as benzo(a)pyrene	1 year	0.3 ng m^{-3}	NEPM Qld EPP	Exhaust from diesel powered equipment and vehicles. Minor components of CSG and flow-back fluids.
Mercury	1 year	1.1 µg m^{-3}	Qld EPP	Minor components of CSG and flow-back fluids.
Radon		Households: 200 Bq m^{-3} Workplaces: 1000 Bq m^{-3}	ARPANSA	Minor components of CSG and flow-back fluids.
Hydrogen sulphide	24 hour	0.11 ppm	EPP	Minor component of CSG.

2 Study area

The Surat Basin (Figure 1) is the largest CSG production region in Australia (Geoscience Australia 2016). As the industry there continues to expand, extraction from higher permeability coal seams is likely to peak necessitating the use of stimulation techniques, such as HF, to access gas from lower permeability coal seams. Currently there are over 4000 producing CSG wells in the Surat Basin (Queensland Government 2017).

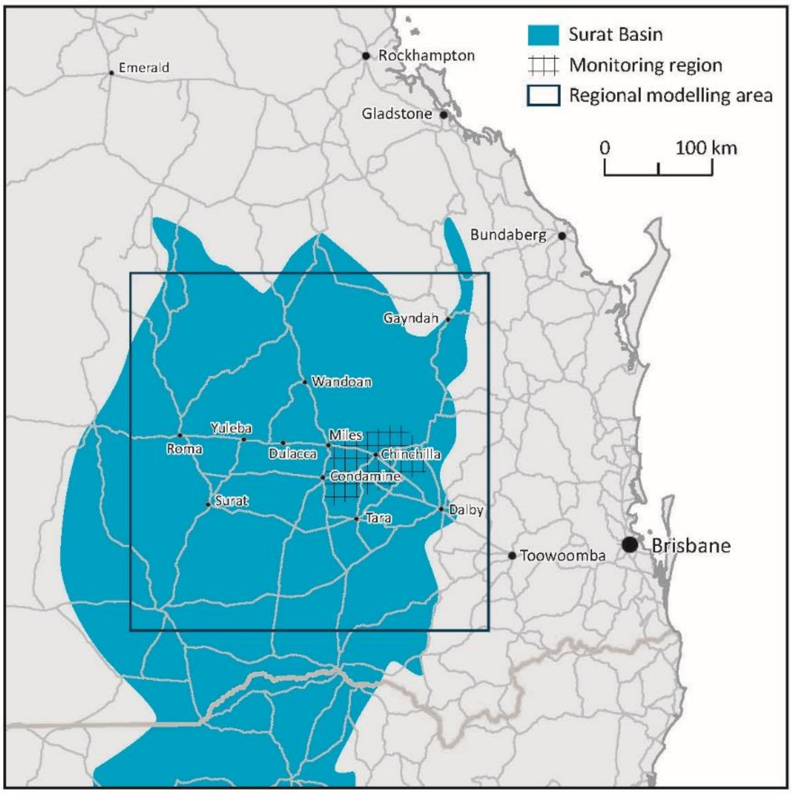

Figure 1 Map showing the Surat Basin (shaded in blue), the areas covered by the current Surat Basin Ambient Air Quality Study air monitoring network, and regional monitoring area (see Section 2.1) (Source: Lawson et al. 2016).

2.1 Proposed study location

Origin Energy has granted CSIRO access to development areas addressed in the approved Origin Energy–APLNG Hydraulic Fracturing Risk Assessment (AECOM 2016). The proposed study site is within the Roma—Yuleba region in the Combabula project area in which Origin Energy has approval to perform HF operations on 545 wells between 2016 and 2020. Descriptions of previous HF treatments were provided by Origin Energy on request from the CSIRO project team and this document is provided in Appendix B. Details of the planned HF treatments at the study site will be provided by Origin Energy and are likely to include the treatment types listed for previous HF activities.

The proposed study site was deemed appropriate for the purposes of this study based on:

- The scope of HF operations planned – injection volumes, pressures and the number of chemical additives - are representative of processes to be employed in future Origin Energy well stimulation activities based on the information provided by Origin Energy and presented in Appendix B and the APLNG Hydraulic Fracturing risk assessment (AECOM 2016).
- The timing of the planned operations is compatible with the timeframes proposed for the Phase 2 study.
- Availability of mains power for operation of monitoring equipment.

The proposed study location is 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. The Combabula State Forest borders the western boundary of the property and Horse Creek Road borders the eastern boundary. Linked by Horse Creek Road, the township of Yuleba (population <200) lies approximately 35 km to the SSW of the proposed study site.

The area to the north of the property is dominated by farmland with a high density of CSG wells (grid spaced ~600–800 m) (**Error! Reference source not found.**). The wells in this area are serviced by a gathering network connecting to the Reedy Creek Gas Processing Facility (GPF) which is approximately 12 km to the WSW. The areas to the east, west and south of the property are dominated by state forest and open farmland with a low density (<5) CSG wells.

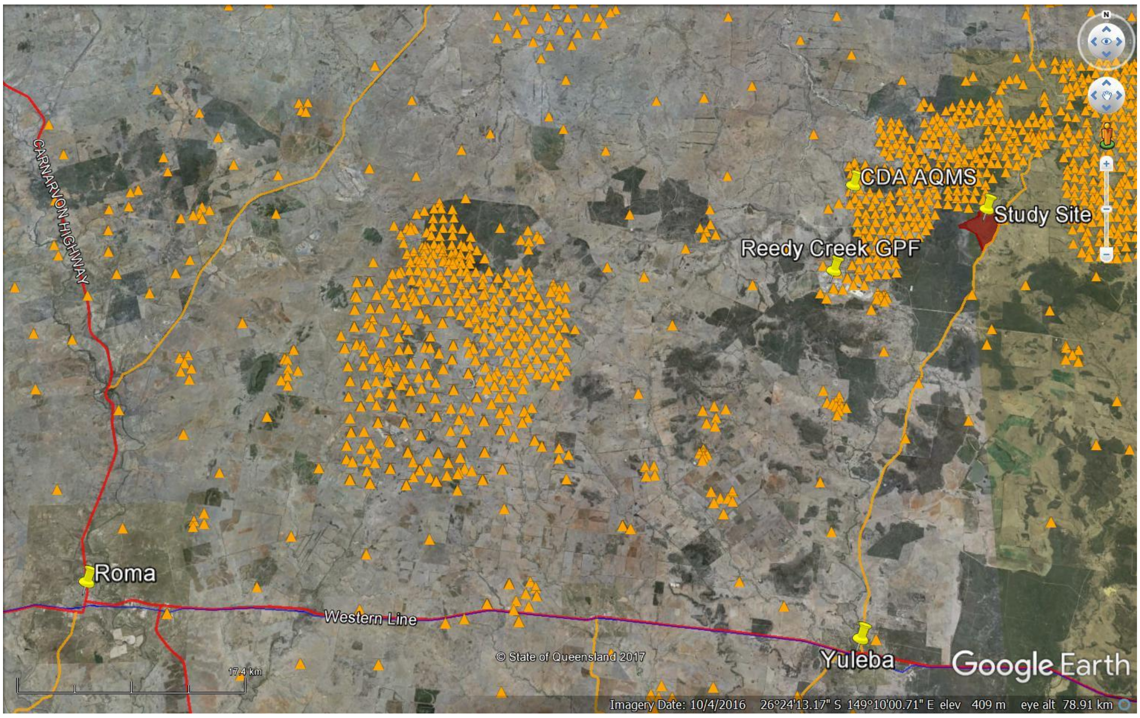

Figure 2 The proposed study site within the Roma–Yuleba region of the Surat Basin. The orange triangles represent CSG wells. The locations of the proposed study site, the Reedy Creek Gas Processing Facility (GPF) and the Combabula Development Area (CDA) Air Quality Monitoring Station (AQMS) (see Sections 3.1 & 3.2) are indicated.

The property contains 10 CSG 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 are scheduled to undergo HF sometime between August and September 2017 after which they will be brought online and gathering system (AECOM 2016).

2.2 Meteorology

The Surat Basin is characterised as sub-tropical with winter months (April to September) predominantly cool and dry, and summer months (November to February) mostly hot with higher rainfall. As part of an investigation to identify potential locations for air monitoring stations in the Surat Basin, Day et al. (2015) used the TAPM meteorological model to approximate annual wind rose data for Miles for the period 2011–2013 (Figure 3). The results of this analysis indicate predominant winds during the scheduled period for HF activities at the site in August to October are likely to be south-westerly with an equivalent east/north-easterly component.

In 2015 Origin Energy commissioned Katestone Environmental Pty Ltd to review the results of an ambient air monitoring program, including meteorological data, that was undertaken in July–November 2015 in the Combabula Development Area (CDA) (Katestone Environmental 2016). The scope of this study is discussed further in Section 2.3.3. Meteorological observations were undertaken at an air quality monitoring station (AQMS) in the CDA, located ~12 km to the WSW of the site proposed for the study presented here (Figure 2).

A wind rose of the observed 1-hour average wind speed and direction at the CDA AQMS is presented in Figure 3 alongside the outputs of the TAPM modelling by Day et al. (2015). Winds measured at the CDA monitoring station were predominantly north-easterly, with an equivalent proportion of southerly winds.

The frequency of observed wind speeds at the CDA AQMS by time of day is shown in **Error! Reference source not found.**. Moderate winds (2–4 m s^{-1}) were measured for approximately 58% of the monitoring period with ~20% light winds (<2 m s^{-1}), ~20% moderate to strong winds (4–6 m s^{-1}) and <5% strong winds (>6 m s^{-1}) were observed.

Table 2 Measured wind speed frequency at the CDA ambient air monitoring station (% of total for period) Source: Katestone Environmental (2016).

Time of day	Observed wind speed frequency (%)			
	< 2 m s^{-1}	2–4 m s^{-1}	4–6 m s^{-1}	6–10 m s^{-1}
Midnight – 6 am	16	66	16	2
6am - Midday	17	55	25	3
Midday – 6 pm	17	50	30	3
6 pm – midnight	22	62	15	1
All periods	18	58	21	3

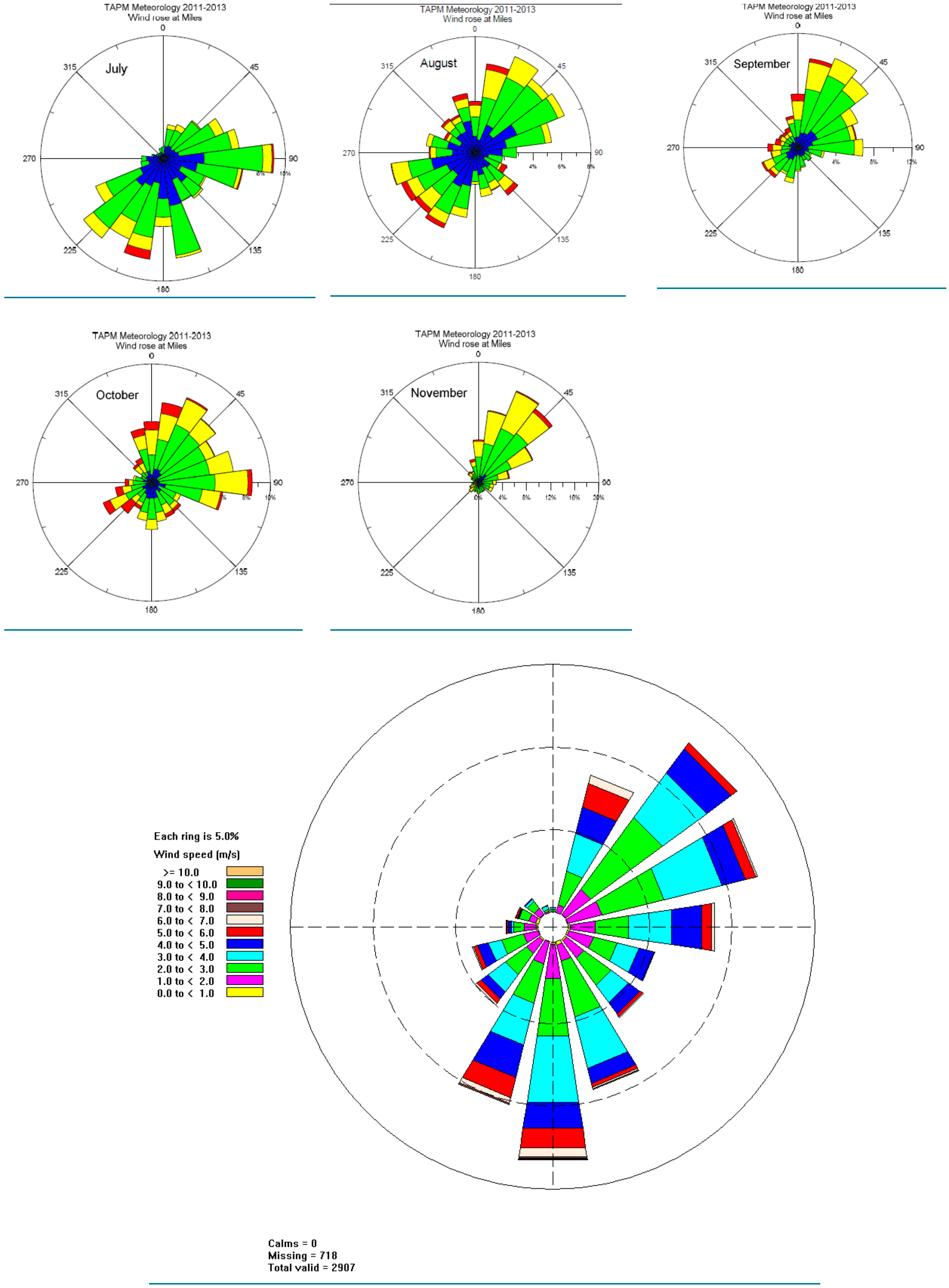

Figure 3 (Top) Monthly wind rose data derived from TAPM meteorological modelling for July–November 2011–2013 (Day et al. 2015). (Bottom) Hourly wind rose data from the Combabula Development Area Air Monitoring Site for July–November 2015 (Katestone Environmental 2016).

2.3 Existing air quality measurements

2.3.1 Surat Basin Ambient Air Quality Study

As discussed previously, CSIRO is leading the GISERA Surat Basin Ambient Air Quality (SBAAQ) Study (Lawson et al. 2016) which is currently underway in the Miles–Chinchilla–Condamine region of the Surat Basin, approximately 100 km to the ESE of the proposed study site (Figure 1).

The SBAAQ Study comprises a network of five ambient air quality monitoring stations and 10 sites at which volatile organic compounds (VOCs) are being monitored. This network includes two sites outside of areas of concentrated gas infrastructure and under appropriate wind conditions will provide regional background measurements of air pollutants.

Both the SBAAQ Study area and the area under consideration in this study share similar geography, intensity of CSG infrastructure (Queensland Globe 2016) and meteorology (see Section 2.2). Given the similarity, the data from the SBAAQ Study can reasonably be considered representative of the wider region, including the proposed study site, and the data can be used as a comparison of regional air pollutant levels against which local enhancements in air pollutants associated with HF activities can be assessed.

2.3.2 VOC monitoring

In June 2017, Origin Energy, with advice from CSIRO, initiated an additional program of VOC monitoring at three locations within the proposed study site, and at one location in a neighbouring field 7 km directly to the east. This location contains CSG infrastructure but will not be undergoing HF activities in the near future. This VOC monitoring is planned to end in late 2017 and the data will be incorporated into reporting for this HF study, providing critical longer term information on the levels of VOCs before, during and after HF activities in the proposed study site.

Additional VOC data will be reported from VOC monitoring that began in October 2015 at two properties in the Miles region of the Surat Basin. Over 20 wells on these properties were subject to HF treatments in November 2015 and June–July 2016. VOC monitoring was conducted at seven sites across the two properties and is planned to end in late 2017. The data will be incorporated into reporting for this HF study, providing a second set of long-term data on the levels of VOCs before, during and after HF activities.

2.3.3 Combabula Development Area Air Monitoring Program

As described in Section 2.2, Katestone Environmental Pty Ltd was engaged by Origin Energy in 2015 to review the results of an ambient air monitoring program that was undertaken in the Combabula Development Area (CDA) (Katestone Environmental 2016). The air monitoring program comprised an air quality monitoring station (AQMS) located ~12 km to the WSW of the site proposed for the for the present study, as shown in Figure 2. Air pollutants measured as part of the CDA program included carbon monoxide, oxides of nitrogen (NO, NO_2, NO_x) and ozone for the period July–November 2015. These observations will provide useful historical data from the Combabula region against which local air pollutant levels during HF activities can be compared.

3 Methodology

The proposed measurement methodology will be presented as two parts: fixed air quality monitoring stations (AQMS) located within the HF field, and five battery-powered perimeter monitoring stations located around the boundary of the property (perimeter monitoring sites).

3.1 Proposed measurement locations

The following provides a description of the proposed monitoring locations and the rationale for their selection. Due to site constraints (power, access) or other unforeseen factors, the final location of monitoring sites is subject to change during deployment.

AQMS

The proposed locations of the two AQMS are at the northern and southern ends of the HF field (Figure 4). The dominant factor considered in determining their location was access to power at the site, which was limited to locations near existing substations that form part of the CSG infrastructure within the property. The proposed location was determined following consultations between Origin and CSIRO with consideration given to:

- proximity to wells scheduled to undergo HF treatment: all 10 wells are within 1200 m of an AQMS (Figure 4)
- meteorology: as described in Section 2.2, winds from the south and east/north-east sectors are expected to dominate when HF operations are underway in August–September 2017.
- compliance with AS/NZS 3580.1.1:2007: Guide to siting air monitoring equipment (AS/NZS 2007) in terms of distance from trees, proximity to nearby roads and clear sky angle.

Perimeter monitoring sites

The proposed locations of the five solar-battery-powered perimeter monitoring sites will be determined in the field following similar criteria as outlined above. Likely areas in which perimeter sites will be located are shown in Figure 4. When determining these locations consideration will also be 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 winds prevail
- locating one site adjacent to the AQMS in the southern end of the field to provide validation of perimeter site instrumentation against high-quality AQMS instrumentation
- locating sites in proximity to wells where possible to enhance probability of capturing impacts on air quality of HF operations which normally occur over ~2–4 days per well.

The location of the AQMS and perimeter monitoring sites within the HF field is designed to capture the potentially complex, spatially and temporally dynamic mixture of air pollutants from multiple HF and non-HF-related sources across the site.

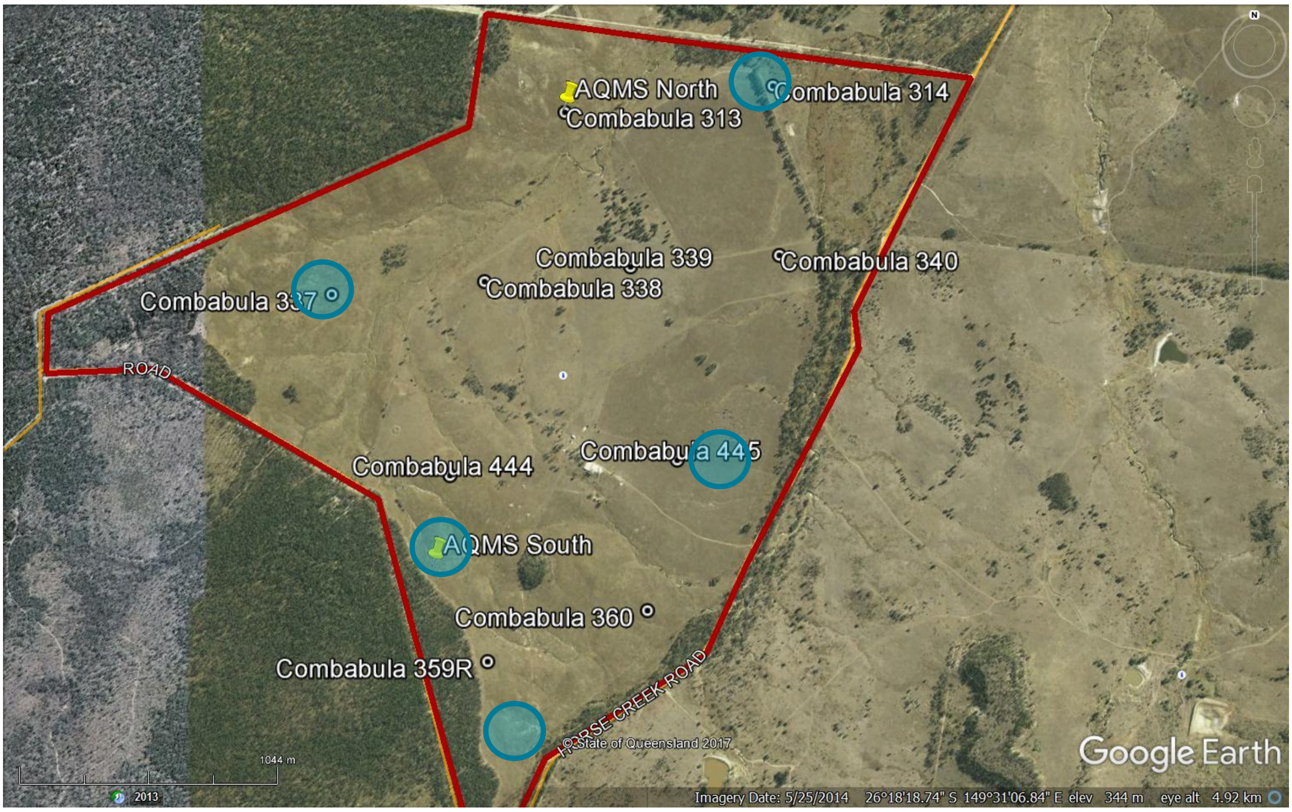

Figure 4 Map showing locations of wells to undergo HF (labelled by Well ID Combabula ###), and the proposed location of the AQMS (yellow pins) and perimeter monitoring stations (blue circles)

3.2 Measurement systems

A three-tier hierarchy of air quality monitoring methods for incorporation in the proposed study design was established. If an air quality monitoring method was not available from the first tier, a subsequent tier was used.

- **Tier 1***:* Australian Standard methods as outlined in Schedule 3 of the Ambient Air Quality and Air Toxics NEPMs (NEPM 2011, 2015).
- **Tier 2:** Appropriate internationally recognised methods or standard techniques.
- **Tier 3:** Non-standard methods with appropriate calibration and validation procedures to assess their accuracy and precision. Validation of Tier 3 measurements against Tier 1 and 2 methods will be undertaken where possible.

Appropriate operation, maintenance, calibration and validation procedures for each method will be followed during the course of the study. Deviations from the Australian and International Standard methods will be addressed alongside the relevant data in the reporting for this study.

The suitability of measurement techniques was also assessed in terms of the time resolution required to capture emissions from specific activities within the whole HF process (e.g. chemical mixing, injection and flow-back) which occur on time scales of hours to days. In addition, each measurement method was assessed in terms of the required method sample periods, detection limits and measurement uncertainty to provide robust and meaningful information about the concentration of an air pollutant. For instance, if the method detection limit is not significantly lower (i.e. ~10 × lower) than the relevant NEPM or EPP objective for the pollutant under consideration, the method was deemed inappropriate for this study. Likewise, methods were chosen that could determine pollutant concentrations over the same averaging periods as prescribed in NEPM or EPP air quality objectives. The remote location of the study site also provides limitations on suitable measurement techniques in terms of power, access and weatherproofing as well as labour and cost constraints.

The following sections provide a more detailed description of the proposed measurement methods for each target species to be deployed at the AQMS and perimeter sites.

3.2.1 AQMS

The AQMS are air-conditioned mobile laboratories (Figure 5) provided by Ecotech Pty Ltd (Brisbane, Queensland, Australia). 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 proposed instrumentation to be installed in the AQMS at both the northern and southern sites is summarised in Table 3. The AQMS in the south of the field (AQMS South) will be comprised of two separate but co-located enclosures.

One enclosure will house a suite of Ecotech owned and operated instrumentation to measure carbon monoxide (CO), Nitrogen dioxide (NO_2), ozone (O_3), methane (CH_4), particulate matter (TSP, PM_{10} & $PM_{2.5}$) and black carbon and meteorology (wind speed, temperature, humidity, pressure). The validated data from each instrument will be collected by Ecotech Pty Ltd, and the data will provided to CSIRO for Quality Assurance and reporting.

For measurements of gas phase species at this AQMS, ambient air will be drawn through a glass inlet height ~3.5 m into a common manifold via an inlet fan that provides ~20 LPM 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 is a separate inlet which contains a drying system to remove the influence of moisture on particle size whilst preserving semi-volatile particles. The dryer uses real-time ambient temperature and humidity measurements to adjust heating of inlet tube to keep the humidity of the sampled air to less than 60%.

A second enclosure located at the site will house CSIRO instrumentation including a proton transfer reaction mass spectrometer (PTR-MS) for continuous VOC measurements, systems for integrated sampling of VOCs onto adsorbent tubes and DNPH cartridges, and a collection of particulate samples onto filters.

The AQMS in the north of the field (AQMS North) will be comprised of a single AQMS enclosure housing a matching suite of Ecotech owned and operated instrumentation to measure carbon monoxide (CO), nitrogen dioxide (NO_2), ozone (O_3), methane (CH_4), particulates (TSP, PM_{10} &

$PM_{2.5}$) as well as instrumentation for measurements of gaseous elemental mercury, radon and PAHs provided by CSIRO and project partners Macquarie University and the Australian Nuclear Science and Technology Organisation (ANSTO).

Figure 5 Mobile AQMS (Ecotech Australia). Two similar enclosures will be located at the AQMS site for the HF Study.

A highlight of the proposed study will be the first deployment in an Australian unconventional gas field of a PTR-MS which is capable of high time resolution (<1 minute), high sensitivity (ppt – ppb) measurements of a range of VOCs, including NEPM Air Toxics BTEX and formaldehyde. This technique is ideal for tracking short duration HF events and has been successfully used in studies of unconventional oil and gas in the US and Canada (e.g. Warneke et al. 2015, Li et al. 2017). There is sufficient overlap between the species measured by the PTR-MS, a Tier 2 method, and the Tier 1 compendium methods TO-17 and TO-11A (US EPA 1999a, 1999b) to provide robust checks on the independent instrument calibrations.

US EPA Method TO-17 (1999a) is also capable of measuring alkanes > C_5 which cannot be detected by PTR-MS. Alkanes are expected to be a small but important emission from HF activities, reflecting the source gas composition of the CSG reservoir being produced which will be dominated by methane and the light alkanes (ethane, propane, butanes, etc.). These VOCs are relatively unreactive, and not listed as air toxics. However, due to their abundance in source gases there have been instances in oil and gas fields in the US where these compounds have been observed to act as significant precursors to ozone production (Gilman et al. 2013). Measurements of the light alkanes are not provided by either the PTR-MS or the TO-17 method applied here. In the absence of these measurements, source gas composition information from the wells under consideration will be sought from the operators (Origin Energy). Where source gas composition data is available, the light alkane composition of any emitted gas could be inferred from the observed methane concentrations and included in the study report.

An additional highlight of the proposed Combabula monitoring program will be the collection of a large number of particle samples on filters at the AQMS. The filters will undergo several analytical procedures to determine the mass and detailed composition of the particles. The PM_{10}

composition analysis includes ion beam analysis (IBA) on 12-hourly samples of PM_{10} collected on 47 mm Teflon filters and analysed non-destructively on the ANSTO STAR 2MV accelerator using simultaneous nuclear IBA techniques:

- Proton induced X-ray emission (PIXE) –analysis of elements from aluminium to lead
- Proton induced gamma-ray emission (PIGE) – analysis of light elements (e.g. fluorine and sodium)
- Proton elastic scattering analysis (PESA) – analysis of hydrogen.

The PM_{10} samples will also be analysed via ion chromatography for major water-soluble ions and anhydrous sugars including levoglucosan (a woodsmoke tracer) by two different ion chromatography methods. The species whose concentrations will be determined from the PM_{10} samples are listed in Appendix A.5.

The results of the IBA and IC analysis will be used to assess the potential contribution of HF and non-HF sources to total particle load. This methodology was recently successfully used to investigate the sources of airborne particles in a coal mining region in the Upper and Lower Hunter Particle Characterization Studies (Hibberd et al. 2013, 2015).

Table 3 Proposed instrumentation in AQMS North and South and performance characteristics of each.

#	Pollutant	Instrument/ method	Tier	Performance characteristics	AQMS North/ South
1	NO_2	AS/NZ 3580.5.1.2011 Ecotech EC 9841 analyser Direct reading Chemiluminescence method	1	Continuous sampling Detection limit 0.5 ppb Precision 0.5 ppb or 1% of reading Daily zero and span measurements	Both
2	CO	AS/NZ 3580.7.1.2011 Ecotech EC 9830 analyser Direct-reading non-dispersive infra-red photometer	1	Continuous sampling Detection limit 0.05 ppm or 0.2% of reading Precision 0.1 ppm or 1% of reading Daily zero and span measurements	Both
3	Ozone	AS/NZ 3580.6.1.2011 Ecotech EC 9810 analyser Direct-reading non-dispersive ultraviolet (UV) photometry method	1	Continuous sampling Detection limit 0.5 ppb or 0.2% of reading Precision 0.1 ppm or 1% of reading Daily zero and span measurements	Both
4	PM_{10} & $PM_{2.5}$	Palas Fidas 200 Optical light scattering aerosol spectrometer Compatible with: EN 12341, EN 14907	2	Continuous sampling Simultaneous measurement of concentrations of $PM_{2.5}$, PM_{10} and TSP Range 0–10 000 μg m^{-3} Sample flow 4.8 LPM ± 0.3 m^3 h^{-1} 3-monthly calibration by Ecotech	Both
5	$PM_{2.5}$ Black carbon	Met One Instruments BC 1054 Multispectrum Black Carbon analyser	3	Continuous sampling Sample flow 2 LPM Detection limit <8 ng m^{-3} for 1 min sample, 1 ng m^{-3} for 1 h sample	South
6	PM_{10} sampling	NEPM prescribed method-Sampling by Comde-Derenda low vol sampler Compatible with EN 12341:1998	2	Integrated sampling 2 × 12 h samples per day (12 am–12 pm–12 am)[1] 2.3 m^3 h^{-1} on 47 mm Teflon filter 10% field blanks	South
7	PM_{10} mass analysis	Gravimetric mass measurements of PM_{10} Compatible with EN 12341:1998	2	Integrated sampling (see #6 above) Repeat filter weighing before and after sampling, until three weights within 0.001 mg are obtained. Balance resolution 0.0001 mg.	South
8	PM_{10} elemental analysis	Ion beam analysis (IBA)	3	Integrated sampling (see #6 above) Simultaneous IBA techniques applied are: • Proton induced X-ray emission (PIXE) – analysis of elements from Al to Pb; detection limits a few ng m^{-3} • Proton induced gamma-ray emission (PIGE) – analysis of light elements (e.g. F and Na); detection limits ~100 ng m^{-3} • Proton elastic scattering analysis (PESA) – analysis of hydrogen; detection limits ~20 ng m^{-3}	South

#	Pollutant	Instrument/ method	Tier	Performance characteristics	AQMS North/ South
9	PM_{10} analysis for soluble ions & anhydrous sugars	Ion chromatography (IC) and anion exchange chromatography (HPAEC)	3	Integrated sampling (see #6 above) Analysis of major water soluble ions by IC and anhydrous sugars including levoglucosan by HPAEC	South
10	BTEX & other VOCs	Sampling by CSIRO custom-built automated sampler US EPA Compendium method TO15-Active sampling of VOCs onto adsorbent tubes analysed by GC-FID-MS.	2	Integrated sampling 2 × 12 h samples per day (12 am–12 pm–12 am)[1] 20 mL min^{-1} on Markes Carbograph 1TD/ Carbopack X sorbent tubes 10% field blanks GC-FID-MS calibration with certified gaseous standards Typical detection limits 0.005–0.010 ppb Typical uncertainties (2σ) ~10–15%	South
11	Formaldehyde & other carbonyls	Sampling by CSIRO custom-built automated sampler NEPM prescribed method- US EPA Compendium Method TO11A-Active sampling and derivatization of aldehydes and ketones onto DNPH cartridges analysed by HPLC	1	Integrated sampling 2 × 12 h samples per day (12 am–12 pm–12 am)[1] 1 LPM on Supelco LpDNPH S10 cartridges 10% field blanks Calibration of HPLC with certified liquid stds Typical detection limits 0.03–0.14 ppb Typical uncertainties (2σ) ~9–12%	South
12	BTEX, formaldehyde & other VOCs	Direct reading by Proton transfer reaction mass spectrometry (PTR-MS)	3	Continuous sampling Daily zero and calibration measurements with certified gas standards. Typical detection limits 0.003 –0.2 ppb Typical uncertainties (2σ) ~11–22%	South
13	BTEX Formaldehyde H_2S	Passive sampling onto Radiello tubes with chemical desorption and analysis by GC-FID (VOCs), HPLC (aldehydes), UV Spectrophotometer (HS)	3	Integrated sampling 1 sample per fortnight Typical detection limits 0.01–0.24 ppb Stated uncertainty (2σ) 2.5–14.5% Blanks, duplicates & spiked tube analysis Instrument calibration with certified gas and liquid standards	Both
14	Methane	AS/NZ 3580.17.2016 Direct reading of gaseous pollutants by cavity ring down spectroscopy Picarro G1301	1	Continuous sampling Precision <1 ppbv Daily zero and calibration measurements with certified gas standards.	Both
15	Radon	ANSTO Dual flow loop 2 filter radon detector	3	Continuous (hourly) sampling Detection limit 0.03–0.04 Bq m^{-3}	North
16	Mercury	Tekran Gaseous Elemental Mercury Analyser	2	Continuous Systematic uncertainty of 10% (Slemr et al. 2015) Stated detection limit <0.1 ng m^{-3}	North

#	Pollutant	Instrument/ method	Tier	Performance characteristics	AQMS North/ South
17	Polycyclic Aromatic Hydrocarbons (PAHs)	NEPM prescribed method- US EPA Compendium Method TO-13A Determination of PAHs in Ambient Air Using GC-MS (USEPA 1999c)	1	Integrated Sampling 24 h samples every 2nd day (12 pm–12 pm)[1] 225 LPM Sampling on SKC sorbent cartridge PUF Calibration with certified liquid standards 20% field blanks	North
18	Meteorology	Ecotech meteorology sensors		Continuous measurement Air temp, RH, Air pressure, wind speed and wind direction	Both

[1] The timing of the integrated sampling may be altered subject to HF activity schedules, site access and other logistical constraints.

3.2.2 Perimeter sites

The instrumentation to be incorporated into the perimeter sites is summarised in

Table 4. Due to their remote location, the perimeter monitoring systems will be solar-battery powered, portable, and weather proof. Each perimeter site will incorporate a Microvol PM_{10} sampler for mass analysis, and an E-sampler for continuous $PM_{2.5}$ concentration measurement and mass analysis.

The Ecotech AQMS will both use Palas Fidas Optical light scattering instruments for continuous PM_{10} and $PM_{2.5}$ measurement. AQMS South will also have a PM_{10} Low Volume sampler for gravimetric mass determination and composition analysis (see Table 3). To establish equivalence in the results obtained from the different AQMS and perimeter site PM instruments, one perimeter unit will be located permanently at the AQMS North site. Following the HF monitoring period, all five perimeter site units will be collocated for comparison across methods.

The perimeter sites will also contain sampling equipment for integrated 12 h sampling of VOCs onto adsorbent tubes (US EPA Compendium method TO-17, US EPA 1999a) and 24 h sampling of aldehydes onto DNPH cartridges (US EPA Method TO-11A, US EPA 1999b). Locating a perimeter site unit at AQMS North site has the additional advantage of providing measurements of VOCs and aldehydes which could not incorporated into the AQMS North instrumentation suite.

It is important to reiterate that the measurement techniques listed in **Error! Not a valid bookmark self-reference.** and 4 for BTEX and formaldehyde can measure many other VOC species. Likewise, the proposed PM_{10} analysis techniques—including elemental analysis, soluble ion analysis, and anhydrous sugars analysis—will provide detailed information on the composition of PM_{10} (see Appendix A.5. for details). Additional species from these analyses will be included in reporting if found to be associated with potential negative impacts on air quality associated with HF at the site, or are useful for characterising the sources of PM, VOCs or other air pollutants at the site.

Table 4 Proposed instrumentation for perimeter sites and performance characteristics of each

#	Pollutant	Instrument/method	Tier	Performance
19	PM_{10} sampling	PM_{10} sampled by Microvol 1100 low volume sampler with PM_{10} size selective inlet		Integrated sampling 1 sample per week (12 pm–12 pm)^1 ~3 LPM onto 47 mm Teflon filter 10% field blanks
20	PM_{10} mass analysis	AS/NZS 3580.9.9:2006 Determination of suspended particulate matter – PM_{10} low volume sampler – Gravimetric method	1	Integrated sampling (see #19) Repeat filter weighing before and after sampling, until three weights within 0.001 mg are obtained. Balance resolution 0.0001 mg.
21	PM_{10} elemental analysis	Ion beam analysis (IBA)	3	Integrated sampling (see #19) Simultaneous IBA techniques as per Table 3 #8
22	PM_{10} soluble ions & anhydrous sugars analysis	Ion chromatography (IC) and anion exchange chromatography (HPAEC)	3	Integrated sampling (see #19) IC and HPAEC analysis as per Table 3 #9
23	$PM_{2.5}$	Met-One E Sampler – Light scattering aerosol monitor with $PM_{2.5}$ size selective inlet	3	Continuous sampling @ 2LPM Validation by comparison with mass of weekly sample collected on inbuilt filter collection
24	BTEX & other VOCs	Sampling by SKC Pocket pumps Compatible with US EPA Compendium method TO17. See Table 2 #10	2	Integrated sampling 2 × 12 h samples per day (12 pm–12 am–12 pm)^1 20 mL min^{-1} on Markes Carbograph 1TD/ Carbopack X sorbent tubes
25	Formaldehyde & other carbonyls	Sampling by TSI SP730 Sampling pump Compatible with NEPM prescribed method – US EPA Compendium Method TO11A. See Table 2 #11	1	Integrated sampling 2 × 12 h samples per day @ 1 LPM
26	Meteorology	Lufft WS 500UMB Weather Sensor	na	Continuous Air temperature, RH, air pressure, wind direction and wind speed, electronic compass.

[1] The timing of the integrated sampling may be altered subject to HF activity schedules, site access and other logistical constraints.

3.3 Proposed sampling schedule

The planned start date for HF injection activities at the study site is August 2017. All measurements of key air pollutants will be undertaken for some period before, during and after hydraulic fracturing activities.

The measurement methods outlined in Table 3 and

Table 4 include a combination of continuous and integrated sampling techniques. Continuous measurements of NO_x, CO, O_3, PM, methane and VOCs by PTR-MS at the AQMS are planned to start in mid-July 2017. Measurements at one of these stations will cease ~20 days after HF completion, and measurements of NO_x, CO, O_3, PM and methane at the other will continue through to late 2017. Passive VOC monitoring at four locations was deployed at the proposed study site in June 2017 and will also continue through to late 2017.

Integrated sampling techniques involve sampling (12-hour, 24-hour, weekly) onto media such as filters, adsorbent tubes, DNPH and PUF cartridges. The collection and analysis of these integrated samples is more costly and labour intensive than many continuous techniques and as such the integrated techniques will be deployed for shorter periods before, during and after HF activities.

The collection of integrated samples onto filters and sampling tubes/cartridges will be performed for the following periods:

- Before HF: minimum of 10 days prior to the commencement of HF injections.
- During HF: integrated sampling is planned to occur over the entire period of HF injection, estimated at ~25 days based on 10 wells schedule to undergo HF at the site with additional time for flow-back and completions to finish at the final well site. On average HF treatments occur over two days per well.
- After HF: minimum of 10 days after well completions are scheduled to finish.

Ten days prior to HF could be considered inadequate to establish baseline for a given site; however, as described in Section 2.3.1, existing air quality measurements have been undertaken in the Miles–Chinchilla–Condamine area of the Surat Basin since 2014 as part of the SBAAQ Study. These existing monitoring programs will provide important information on regional pollutant levels in the Surat Basin at sites not directly impacted by HF activities.

3.4 Project team

Under the leadership of CSIRO Oceans and Atmosphere, seven organisations will be involved in the measurement the measurement and analysis procedures for the proposed study. The organisations carrying out the the measurements or analyses are listed in

Table 5.

Table 5 Organisations responsible for measurement systems

#	Pollutant	Measurement Type	Responsible Organisation
AQMS sampling and analysis			
1	NO_x	Continuous sampling	Ecotech
2	CO	Continuous sampling	Ecotech
3	O_3	Continuous sampling	Ecotech
4	TSP, PM_{10} & $PM_{2.5}$	Continuous sampling	Ecotech
5	$PM_{2.5}$ Black carbon	Continuous sampling	Ecotech
6	PM_{10} sampling	Integrated sampling	CSIRO
7	PM_{10} mass analysis	Analysis of integrated samples (from #6)	ANSTO
8	PM_{10} elemental analysis	Analysis of integrated samples (from #6)	ANSTO
9	PM_{10} analysis for soluble ions & anhydrous sugars	Analysis of integrated samples (from #6)	CSIRO
10	BTEX & other VOCs	Integrated sampling and analysis US EPA Method TO-117	CSIRO
11	Formaldehyde & other carbonyls	Integrated sampling and analysis US EPA Method TO-11A	CSIRO

12	BTEX, formaldehyde & other VOCs	Continuous sampling by PTR-MS	CSIRO
13	BTEX Formaldehyde H_2S	Integrated sampling and analysis by Passive Radiello method	SGS Leeder
14	Methane	Continuous sampling	Ecotech
15	Radon	Continuous sampling	ANSTO
16	Mercury	Continuous sampling	Macquarie University
17	Polycyclic Aromatic Hydrocarbons (PAHs)	Integrated sampling	CSIRO
		Analysis of integrated samples	University of Queensland
18	Meteorology	Continuous measurement	Ecotech
Perimeter monitoring sites sampling and analysis			
19	PM_{10} sampling	Integrated sampling	CSIRO
20	PM_{10} mass analysis	Analysis of integrated samples (from #19)	ANSTO
21	PM_{10} elemental analysis	Analysis of integrated samples (from #19)	ANSTO
22	PM_{10} analysis for soluble ions & anhydrous sugars	Analysis of integrated samples (from #19)	CSIRO
23	$PM_{2.5}$	Continuous sampling	CSIRO
24	BTEX & other VOCs	Integrated sampling and analysis US EPA Method TO-15	CSIRO
25	Formaldehyde & other carbonyls	Integrated sampling and analysis US EPA Method TO-11A	CSIRO
26	Meteorology	Continuous	CSIRO

3.5 Sample and data management

Samples collected from each instrument at each site will have a unique label that includes the specific site, the date, the sampling method, and the sample type (e.g. VOC, PM_{10}). All sample media deployed will be recorded in sample logs including unique sample ID, sample location, date & time on, date & time off, and other relevant sampling information (e.g. pump parameters, total volume sampled). Details of sample media deployment, collection, and all relevant transport, storage, handling steps will be prescribed in work instructions and entered into chain-of-custody (COC) documentation.

All organisations participating in the study will be expected to provide appropriate records and documents including standard operating procedures, field data, chain-of-custody (COC), quality assurance/quality control data for field and laboratory activities, as well as raw data, calibration data and data reports.

All data acquired by continuous monitoring or sampling instruments will be routinely downloaded and securely stored and archived in CSIRO's Bowen Research Cloud.

Data reports will be provided to CSIRO electronically as Excel spreadsheets or Adobe pdfs. All information used to confirm final reported data will be included in data reports. All field and laboratory documentation will provide enough detail to allow for reconstruction of processes, procedures and activities undertaken by each responsible organisation. Field notebooks and organisation-specific data entry forms and field checklists are to be kept by the responsible organisation.

3.6 Other sources of information

In addition to existing air quality measurement data as outlined in Section 2.3, other information will be collected by industry and CSIRO and made available for analysis and reporting in the proposed air quality study. The data from accompanying industry and CSIRO monitoring will provide useful information to assess the potential for surface water, groundwater, HF chemicals and soil/sand at the site to act as local sources of air pollutants. These information sources include but are not limited to the following.

3.6.1 CSIRO Land and Water: Proposed measurements of groundwater, surface water and soil

As described in the preface, CSIRO Land and Water has prepared an accompanying peer-reviewed report describing a suitable measurement program to provide enhanced information on the impacts of HF on surface water, groundwater and soil. Subject to approval by the GISERA Queensland RRAC, both peer-reviewed study designs will be implemented at selected well sites in June 2017 as part of Phase 2 of this project.

The proposed measurements of surface water, groundwater and soil will be overseen by CSIRO Land and Water personnel and will occur at the same time as the proposed air quality measurements described in this report. The proposed measurements of surface water, groundwater and soil will include analysis of the composition of:

- groundwater prior to and after HF treatment at selected well heads and groundwater bores in the vicinity (<2 km) of the HF activities
- injectate from selected well site operations (HF chemicals + frac-water + proppant)
- flow-back fluids at multiple time intervals during storage onsite from selected well site operations
- soil samples taken in the vicinity of selected HF well sites.

3.6.2 Origin Energy: Hydraulic fracturing well completion reports

Under the *Petroleum Regulation 2004*, companies are required to submit well completion reports for each well treated with HF. These reports provide detailed accounts of the well integrity testing, well perforation methods, HF stages (number and depth), the types and volumes of input chemicals, proppants and water used at each stage and HF diagnostic data used to track the HF progress at each stage. The completion reports for the wells that undergo HF at the study site will be provided by Origin Energy to CSIRO as soon as practicable.

3.6.3 Origin Energy: Stimulation impact monitoring

The Department of Environment and Heritage Protection (DEHP) issues Environmental Authorities (EAs) that permit CSG companies to perform petroleum activities including HF. As part the EA, companies are required to provide stimulation impact monitoring plans for each site and undertake the prescribed monitoring and analysis to ensure the HF activity complies with the conditions of the EA. The prescribed monitoring activities include (Origin 2016):

- Baseline: landholder bore water quality and CSG well water quality before HF
- HF operations: HF fluids composition and aquifer connection
- HF well produced fluids: initial flow-back and produced water quality.

Industry monitoring is usually undertaken by third-party providers and the data reported directly to the CSG companies. Historical data from previous Origin Energy HF operations, as well as the prospective monitoring to be undertaken by third-party providers on behalf of Origin at the study site, will be made available for the proposed study.

3.6.4 Origin Energy: Site activity schedules

Origin Energy will provide updated schedules and locations for relevant activities occurring on site prior to and during the measurement period including: pond installation/removal, filling, chemical treatments of water, specialised HF well head installation, well perforation, fluid injections, flow-back and well completions.

3.6.5 Wider industry data

As part of the proposed study CSIRO will seek further engagement from the GISERA industry partners operating in the Surat Basin and nearby Bowen Basin (Origin Energy, QGC and Santos) to request information on the frequency and use of specific practices and chemicals in HF operations by each company, and the relevant stimulation impact monitoring data for each site. Where available, this information will be used to assess the representativeness of the HF activities at the proposed study site in comparison to activities across the Surat and Bowen Basins. This, in turn, will provide information on the applicability of the results observed in this study to improved understanding of the potential impacts of HF on air quality at other sites.

4 Summary

This report presents a proposed methodology for a study of the impacts of HF activities on local air quality. The methodology comprises a suite of measurements of atmospheric gaseous and particle species to be undertaken before, during and after HF at a selected site in the Surat Basin. The aim of the proposed methodology is to address the following study objectives.

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

- simultaneous measurements at other AQMS in the SBAAQ Study network
- measurements taken at the site before and after 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. The data from the proposed methodology 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 air pollutant load. For instance, the aluminum/silicon ratio in elemental composition analysis of PM_{10} can be used to estimate the contribution of soil and sand including proppant to total PM_{10} load. Likewise, that ratio of benzene to CO differs between diesel exhaust and wood smoke emissions; levoglucosan 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 (see 0) if an adequate number of samples of sufficient quality are successfully collected.

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 proposed methodology will be used to address Objective 3 by:

- employing, where possible, Australian Standard measurement techniques (Tier 1) and properly validated Tier 2 and 3 techniques to provide data that are directly comparable to NEPM and Queensland EPP ambient air quality guidelines
- providing compatible data from HF site for comparison measurements taken simultaneously at other AQMS in SBAAQ Study network

- providing compatible data for comparison with measurements taken simultaneously at other locations not impacted by CSG activities, including other areas of Queensland, via data from the Queensland EPA ambient air quality network
- providing compatible data for comparison with historical measurements at other locations, not impacted by CSG activities, where CSIRO has deployed similar instrumentation.

4.1 Timelines and milestones

The GISERA Hydraulic Fracturing Study, comprising the currently underway Phase 1 research and the proposed Phase 2 measurement programs, will provide detailed information on the impact of HF on air, soil and water quality in the vicinity of coal seam gas wells in an Australian gas field. The data and reports generated as part of this project will be made publicly available via the GISERA website for use by individuals, communities, research organisations, governments and industry.

The timeline for the proposed air quality study and reporting are listed below:

- July–October 2017: Measurement Period
- November 2017: Report of data capture and preliminary analysis of VOC radiello data from October 2016 to August 2017 at two sites before, during and after HF.
- October 2018: Draft final report, *The impacts of hydraulic fracturing on air quality in the vicinity of well sites in the Surat Basin, Queensland*, for peer review.
- December 2018: Deliver final report, *The impacts of hydraulic fracturing on air quality in the vicinity of well sites in the Surat Basin, Queensland*.

4.2 Out of scope

Impacts of drilling and well construction: The wells on the proposed study site will be drilled prior to commencement of the measurement period. Assessment of methodologies to determine the potential impact of drilling and well construction activities on air quality are not within the scope of this study design.

Formal risk assessment: Prior to undertaking HF activities as part of their Environmental Authority Permit, companies must update the stimulation risk assessment in their Environmental Management Plan related to hydraulic fracturing “to ensure that stimulation activities are managed to prevent environmental harm and meet the additional requirements within this environmental authority” (Origin Energy DEHP issued Environmental Authority, 2016). The study design described here is not a methodology for a risk assessment.

Impacts on human health: This study design presented here will not determine the impacts of HF on human health. Instead the data collected in this study will be compared with federal, state and other air quality guidelines determined to protect human health and the environment. The data from the proposed study will be made be publicly available for potential use in studies specifically targeting the impact of CSG activities on human health.

Representativeness and scalability: The study design presented here is specific to HF activity being carried out in the well sites identified in this study design in the Surat Basin. The representativeness of this study and the scalability of data to other well sites in the Surat Basin or other locations will depend on a number of factors including the representativeness of the HF processes employed, underlying geology, structure of the coal seams, well depths, etc.

5 References

ACOLA. (2013). Engineering Energy: Unconventional Gas Production- A Study of Shale Gas in Australia, Australian Council of Learned Academies. Available: https://www.acola.org.au/PDF/SAF06FINAL/Final%20Report%20Engineering%20Energy%20June%202013.pdf. Accessed: 3/4/2017.

AECOM. (2016). *APLNG Project Hydraulic Fracturing Risk Assessment, prepared for Origin Energy Resources Ltd.* By AECOM Pty Ltd, Fortitude Valley, Australia. (Not publicly available).

APLNG (2010) Environmental Impact Statement, Volume 2, Gas fields, Australian-Pacific LNG, Available: https://www.aplng.com.au/about-us/compliance/eis.html , Accessed: 20/4/2017.

AMAP/UNEP (2013) Technical Background Report for the Global Mercury Assessment 2013. Arctic Monitoring and Assessment Programme, Oslo, Norway/UNEP Chemicals Branch, Geneva, Switzerland. vi + 263 pp http://www.amap.no/documents/doc/Technical-Background-Report-for-the-Global-Mercury-Assessment-2013/848.

ARPANSA. (2002). Australian Radiation Recommendations for limiting exposure to ionizing radiation (Guidance note [NOHSC:3022(1995)]). Australian Radiation Protection and Nuclear Safety Authority, Yallambie Victoria. Available: http://www.arpansa.gov.au/pubs/rps/rps1.pdf.

Arrow Energy. (2012). Surat Gas Project Environmental Impact Statement. Available: https://www.arrowenergy.com.au/projects/project-assessment-eis/surat-gas-project-eis. Accessed: 5/6/17.

AS (1993). AS 3580.5.1-1993 Determination of oxides of nitrogen – Chemiluminescence method.

AS/NZS 3580.9.9:2006 (2006) Methods for sampling and analysis of ambient air -Determination of suspended particulate matter-PM10 low volume sampler- Gravimetric method.

AS/NZS. (2007). AS/NZS 3580.1.1:2007. Methods for sampling and analysis of ambient air. Part 1.1: Guide to siting air monitoring equipment.

AS/NZS. (2011a). AS/NZS 3580:5.1:2011. Methods of Sampling and Analysis of Ambient Air – Determination of oxides of nitrogen – Direct reading instrumental method.

AS/NZS. (2011b). AS/NZS 3580:6.1:2011. Methods of Sampling and Analysis of Ambient Air – Determination of ozone – Direct reading instrumental method.

AS/NZS. (2011c). AS/NZS 3580:7.1:2011. Methods of Sampling and Analysis of Ambient Air – Determination of carbon monoxide – Direct reading instrumental method.

AS/NZS. (2016). AS/NZS 3580:17.1:2016. Methods of Sampling and Analysis of Ambient Air – Method 17: Determination of gaseous compounds in ambient air – Direct reading cavity ring-down spectroscopy instrumental method.

BS EN (2014) BS EN 12341:2014 Ambient air. Standard gravimetric measurement method for the determination of the PM10 or PM2,5 mass concentration of suspended particulate matter ISBN 978 0 580 78524 5.

Cham, S. T., & Stone, P. (2013). How Can Understanding Community Concerns About Hydraulic Fracturing Help to Address Them? Effective and Sustainable Hydraulic fracturing. (Eds Andrew P. Bunger, John McLennan and Rob Jeffrey), ISBN 978-953-51-1137-5. Available: https://www.intechopen.com/books/effective-and-sustainable-hydraulic-fracturing/how-can-understanding-community-concerns-about-hydraulic-fracturing-help-to-address-them-.

Chan, Y. C., Cohen, D. D., Hawas, O., Stelcer, E., Simpson, R., Denison, L., Wong, N., Hodge, M., Comino, E., & Carswell, S. (2008). Apportionment of sources of fine and coarse particles in four major Australian cities by positive matrix factorisation. *Atmospheric Environment, 42*(2), 374-389.

Cohen, D. D. (1993). Applications of simultaneous IBA techniques to aerosol analysis. *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms, 79*(1-4), 385-388.

Cohen, D. D. (1998). Characterisation of atmospheric fine particles using IBA techniques. *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms, 136*, 14-22.

Cohen, D. D., Bailey, G. M., & Kondepudi, R. (1996). Elemental analysis by PIXE and other IBA techniques and their application to source fingerprinting of atmospheric fine particle pollution. *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms, 109*, 218-226.

Cohen, D. D., Crawford, J., Stelcer, E., & Atanacio, A. J. (2012). Application of positive matrix factorization, multi-linear engine and back trajectory techniques to the quantification of coal-fired power station pollution in metropolitan Sydney. *Atmospheric Environment, 61*, 204-211.

Cohen, D. D., Stelcer, E., Garton, D., & Crawford, J. (2011). Fine particle characterisation, source apportionment and long-range dust transport into the Sydney Basin: a long term study between 1998 and 2009, *Atmospheric Pollution Research, 2*(2), 182-189.

Cope M, Keywood MD, Emmerson K and Galbally IE (2014) Sydney Particle Study - Stage II. Report to the Office of Environment and Heritage NSW, 152p http://www.environment.nsw.gov.au/resources/aqms/SydParticleStudy10-13.pdf.

CSE. (2014). Final Report of the Independent Review of Coal Seam Gas Activities in NSW, NSW Chief Scientist and Engineer, Sydney NSW. Available: http://www.chiefscientist.nsw.gov.au/__data/assets/pdf_file/0005/56912/140930-CSG-Final-Report.pdf.

CSIRO. (2015). What is Hydraulic Fracturing? Available: http://www.csiro.au/en/Research/Energy/Hydraulic-fracturing/a-What-is-hydraulic-fracturing. Accessed 20/4/2017.

Day, S., Ong., C., Rodger, A., Etheridge, D., Hibberd, M., van Gorsel, E., Spencer, D., Krummel, P., Zegelin, S., Fry, R., Dell'Amico, M., Sestak, S., Williams, D., Loh, Z., & Barrett, D. (2015). *Characterisation of Regional Fluxes of Methane in the Surat Basin, Queensland. Phase 2: A pilot study to detect and quantify methane sources.* CSIRO, Australia. 80 pp.

Day, S., Tibbett, A., Sestak, S., Knight, C., Marvig, P., McGarry, S., Weir, S., White, S., Armand, S., van Holst, J., Fry, R., Dell'Amico, M., Halliburton, B., & Azzi, M. (2016). Methane and Volatile Organic Compound Emissions in New South Wales. CSIRO, Australia. Available: http://www.epa.nsw.gov.au/resources/air/methane-volatile-organic-compound-emissions-nsw-3063.pdf. Accessed: 8/6/2017.

DEHP. (2014). Fraccing. Department of Environment and Heritage Protection. Available: http://www.ehp.qld.gov.au/management/non-mining/fraccing.html. Accessed: 4/3/2017.

DPIPWE (2015). Review of Hydraulic fracturing in Tasmania – Final report. Department of Primary Industries, Parks, Water and the Environment, Tasmania. Available: http://dpipwe.tas.gov.au/Documents/Review of hydraulic fracturing in Tasmania - Final Report 25 Feb 15.pdf. Accessed: 4/3/2017.

Dunne E., Galbally I.E., Cheng M., Selleck P.W., Molloy S.B. and S.J. L (2017). Comparison of VOC measurements made by PTR-MS, Adsorbent Tube/GC-FID-MS and DNPH-derivatization/HPLC during the Sydney Particle Study, 2012: a contribution to the assessment of uncertainty in current atmospheric VOC measurements, Manuscript under review *Atmos. Meas. Tech. Discussions*. Available: https://doi.org/10.5194/amt-2016-349. Accessed: 10/3/2017.

EPC. (2015). Inquiry into onshore unconventional gas in Victoria - Final Report, Parliament of Victoria Legislative Council, Environmental Planning Committee, Available: http://www.parliament.vic.gov.au/images/stories/committees/SCEP/GAS/Report/EPC_58-03_Text_WEB.pdf.

EPP. (2008). *Environment Protection (Air) Policy (2008)* https://www.legislation.qld.gov.au/LEGISLTN/CURRENT/E/EnvProtAirPo08.pdf. Accessed 25/4/2017.

Field, R. A., Soltis, J., & Murphy, S. (2014). Air quality concerns of unconventional oil and natural gas production. *Environmental Science-Processes & Impacts, 16*(5), 954-969.

Geoscience Australia. (2016). Australian Energy resources Assessment-Gas, Geoscience Australia, Synmonston ACT. Available: http://www.ga.gov.au/aera/gas. Accessed: 15/6/2017

Gilman, J. B., Lerner, B. M., Kuster, W. C., & de Gouw, J. A. (2013). Source Signature of Volatile Organic Compounds from Oil and Natural Gas Operations in Northeastern Colorado. [Article]. *Environmental Science & Technology, 47*(3), 1297-1305.

Hibberd, M., Keywood, M., Cohen, D., Stelcer, E., Scorgie, Y., & Thompson, S. (2015). *Lower Hunter Particle Characterisation Study (Vol. 4th Progress Report (Summer)).* CSIRO: Prepared for the NSW Environmental Protection Authority.

Hibberd, M., Selleck, P., Keywood, M.D., Cohen, D., Stelcer, E., & Atanacio, A. (2013). Upper Hunter Valley Particle Characterization Study. Report to NSW OEH. 40 pp. Available: http://www.environment.nsw.gov.au/resources/aqms/UHFPCSFinal.pdf.

IESC. (2014). Hydraulic fracturing ('fraccing') techniques, including reporting requirements and governance arrangements, Background review.

ISO. (1995). ISO 6879:1995 Air Quality- Performance Characteristics and related concepts for air quality measruing methods. Geneva, Switzerland: International Organization for Standardization.

SO (2000) ISO16017-1:2000 Indoor, ambient and workplace air -- Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography -- Part 1: Pumped sampling ISO 16017-1:2000(E) Geneva Switzerland: International Organization for Standardization

Katestone Environmental. (2016). Review of Combabula Devlopment Area Air Monitoring Program, Prepared for Origin energy, Katestone Environmental Pty Ltd, Brisbane, Queensland. (Not publicly available).

Keywood M and P S (2016) Advances in technologies for sampling, measuring and monitoring coal dust and related emissions along the rail corridor. Report commissioned for the Office of the NSW Chief Scientist & Engineer http://www.chiefscientist.nsw.gov.au/__data/assets/pdf_file/0009/89865/Dr-Keywoods-Information-Paper.pdf.

Keywood M and Dunne E (2017) State of the knowledge about the potential sources of air pollutants associated with CSG extraction using hydraulic fracturing Report to GISERA Milestone 2.1 of Project W.11 in review.

Lan, X., Talbot, R., Laine, P., Torres, A., Lefer, B., & Flynn, J. (2015). Atmospheric Mercury in the Barnett Shale Area, Texas: Implications for Emissions from Oil and Gas Processing. *Environmental Science & Technology, 49*(17), 10692-10700.

Lawson, S. J., Selleck, P. W., Galbally, I. E., Keywood, M. D., Harvey, M. J., Lerot, C., Helmig, D., & Ristovski, Z. (2015). Seasonal in situ observations of glyoxal and methylglyoxal over the temperate oceans of the Southern Hemisphere. *Atmospheric Chemistry and Physics*, 15(1): 223-240. doi: 10.5194/acp-15-223-2015.

Lawson, S. J., Hibberd, M. F., & Keywood M. (2016). Ambient Air Quality in the Surat Basin - Overview of Study Design, Report for the Gas Industry Social and Environmental Research Alliance (GISERA), Project No G.3. Available: https://gisera.org.au/wp-content/uploads/2016/02/GISERA-AQ-study-design_final.pdf. Accessed: 5/6/2017

Legislative Council of WA (2015) Report 42: Implications for Western Australia of Hydraulic Fracturing for Unconventional Gas, Standing Committee on Environment and Public Affairs, Legislative Council of WA. Available: http://www.dmp.wa.gov.au/Documents/Petroleum/Report42-HydraulicFracturing_UnconventionalGas.pdf. Accessed: 4/3/2017.

Li, L. J., Qi, L., & Cocker, D. R. (2017). Contribution of methyl group to secondary organic aerosol formation from aromatic hydrocarbon photooxidation. *Atmospheric Environment,* 151, 133-139.

Liang, Y. C., Liang, H. D., & Zhu, S. Q. (2014). Mercury emission from coal seam fire at Wuda, Inner Mongolia, China. *Atmospheric Environment, 83*, 176-184.

NEPM. (2011). National Environment Protection (Air Toxics) Measure https://www.legislation.gov.au/Details/F2011C00855. Accessed: 25/4/2107.

NEPM. (2015). National Environment Protection (Ambient Air Quality) Measure http://www.legislation.gov.au/Details/F2016C00215. Accessed: 25/4/2017.

Norris, G., Vedantham, R., & et al. (2008). EPA Positive matrix factorization (PMF) 3.0 - Fundamentals and User Guide. US EAP/600/R-08/108. Available: https://www.epa.gov/air-research/positive-matrix-factorization-model-environmental-data-analyses. Accessed: 15/6/17.

Norris G and Duvall R (2014) EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide https://www.epa.gov/sites/production/files/2015-02/documents/pmf_5.0_user_guide.pdf

NPI (2016) National Pollutant Inventory website. Available: http://www.npi.gov.au/.

NRC. (2016). Inquiry into Unconventional Gas (Fracking) in the South East of South Australia -Final Report, Natural Resources Committee, Parliament of South Australia, Available: http://www.parliament.sa.gov.au/Committees/Pages/Committees.aspx?CTId=5&CId=295.

NTG. (2014). Report of the Independent Inquiry into Hydraulic Fracturing in the Northern Territory, Northern Territory Government. Available: https://frackinginquiry.nt.gov.au/__data/assets/pdf_file/0008/387764/report-inquiry-into-hydraulic-fracturing-nt.pdf.

NTG. (2017). Independent Scientific Inquiry into Hydraulic Fracturing in the Northern Territory (webpage) Available: https://frackinginquiry.nt.gov.au/home.

Origin. (2016). Stimulation Impact Monitoring Plan - Guide for the management, sampling and reporting requirements of stimulation fluids, stimulated well produced fluids and related landholder bores . 22 pp. (Not publicy available).

Paatero, P. (1997). Least squares formulation of robust non-negative factor analysis. *Chemometrics and Intelligent Laboratory Systems,* 37(1), 23-35.

QGC (2010) Environmental Impact Statement, Volume 3 – Environmental Impact of Gas Fields Avaliable: http://www.shell.com.au/about-us/projects-and-locations/qgc/environment/environment-management-assessment.html.

Queensland Globe. (2016). Queensland Government CSG Globe, http://www.business.qld.gov.au/business/support-tools-grants/services/mapping-data-imagery/queensland-globe.

Queensland Government. (2017). Coal Seam Gas Production, Queensland Government Data, Available: https://data.qld.gov.au/dataset/petroleum-gas-production-and-reserve-statistics/resource/63a8a6cc-7fb6-4040-b4e7-9d453b14d3ed. Accessed 24/4/2017.

Radiello (2006) Radiello Manual, http://www.radiello.com/english/Radiello%27s%20manual%2001-06.pdf.

Schinteie, R., Pinetown, K., Douglas, G., & Sestak, S. (2015). Literature review of dissolved hydrocarbons in groundwater with emphasis on the Australian Surat and Bowen basins. CSIRO, Australia. Available: https://gisera.org.au/wp-content/uploads/2016/04/GISERA-Hydrocarbons-Lit-Review-2015.pdf. Accessed: 20/4/2017.

Slemr F, Angot H, Dommergue A, Magand O, Barret M, Weigelt A, Ebinghaus R, Brunke EG, Pfaffhuber KA, Edwards G, Howard D, Powell J, Keywood M and Wang F (2015) Comparison of mercury concentrations measured at several sites in the Southern Hemisphere. Atmospheric Chemistry and Physics 15(6): 3125-3133. doi: 10.5194/acp-15-3125-2015.

Tait DR, Santos IR, Maher DT, Cyronak TJ and Davis RJ (2013) Enrichment of Radon and Carbon Dioxide in the Open Atmosphere of an Australian Coal Seam Gas Field. Environmental Science & Technology 47(7): 3099-3104. doi: 10.1021/es304538g

US EPA (2013). Regional Screening Levels for Chemical Contaminants at Superfund Sites - Resident Ambient Air, Available: http://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables-may-2016. Accessed: 9/6/2017.

US EPA. (1999a). Compendium Method TO-17 Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes. https://www3.epa.gov/ttn/amtic/files/ambient/airtox/to-17r.pdf.

US EPA. (1999b). Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air Second Edition Compendium Method TO-11A Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) [Active Sampling Methodology] https://www3.epa.gov/ttnamti1/files/ambient/airtox/to-11ar.pdf.

US EPA. (1999c). Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air Second Edition Compendium Method TO-13A Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS) https://www3.epa.gov/ttnamti1/files/ambient/airtox/to-13arr.pdf.

Victorian Auditor General (2015). Unconventional Gas: Managing Risks and Impacts - Victorian Auditor General's Report, State Government of Victoria, Available: http://www.audit.vic.gov.au/publications/20150819-Unconventional-gas/20150819-Unconventional-gas.pdf. Accessed: 6/3/2017.

Warneke, C., Veres, P., Murphy, S. M., Soltis, J., Field, R. A., Graus, M. G., Koss, A., Li, S. M., Li, R., Yuan, B., Roberts, J. M., & de Gouw, J. A. (2015). PTR-QMS versus PTR-TOF comparison in a region with oil and natural gas extraction industry in the Uintah Basin in 2013. *Atmospheric Measurement Techniques,* 8(1), 411-420.

Appendix A: Method and instrument descriptions

A.1 Measurement methods: oxides of nitrogen (NOx)

Oxides of nitrogen (NO_x) includes NO and NO_2 and are gases produced by combustion processes. Nitrogen dioxide (NO_2) is one of the six criteria air pollutants identified by the Ambient Air Quality NEPM (NEPM 2015). CSG industry environmental impact statements (EIS) identified NO_2 as an important pollutant (QGC 2010, APLNG 2010) and a review conducted as a prelude to this study design identified exhaust from diesel-powered equipment (mixers, pumps, rigs) and vehicles as the most likely source of NO_x associated with HF activities.

A.1.1 AQMS – Continuous NO_x measurements by chemiluminescence method

At the AQMS oxides of nitrogen will be measured by the chemiluminescence method using an Ecotech EC 9841 analyser (Ecotech, Knoxfield, Victoria, www.ecotech.com.au). This instrument is a Tier 1 method and is compatible with Australian Standard AS 3580.5.1 (1993). The manufacturer stated detection limit of the EC 9841 is 0.5 ppb, which is 60 times the NEPM 1 h standard of 0.03 ppm, and a precision of 0.5 ppb or 1% of reading whichever is greater. Daily instrument zero and span tests will be conducted for the duration of sampling.

A.2 Measurement methods: carbon monoxide (CO)

Carbon monoxide (CO) is a gas formed by combustion processes and is one of the six key pollutants identified by the Ambient Air Quality NEPM (NEPM 2015) and environmental impact statements from the CSG Industry bodies (QGC 2010, APLNG 2010). The NEPM 8 h air quality standard for CO is 9 ppm. The review conducted as a prelude to this study design (Keywood & Dunne 2017) identified exhaust from diesel powered equipment (mixers, pumps, rigs) and vehicles as the most likely source of CO associated with HF activities. NO_x and CO are both emitted in exhaust and ratios of their concentration when measured in parallel can be used to distinguish between sources such as exhaust emissions and smoke from biomass burning.

A.2.1 AQMS – Continuous CO measurements using non-dispersive infra-red photometry

At the AQMS carbon monoxide will be measured by an Ecotech EC 9830 non-disperisve infra-red photometry method (Ecotech, Knoxfield, Victoria, www.ecotech.com.au). This instrument is a Tier 1 method and is compatible with Australian Standard AS 3580.7.1 (AS/NZS 2011c). The manufacturer stated detection limit of the EC 9830 is 0.05 ppm or 0.2% of reading whichever is greater, and is significantly lower than the NEPM 8 h standard of 9 ppm. Stated precision is 0.1 ppm or 1% of reading whichever is greater. Daily instrument zero and span tests will be conducted for the duration of sampling.

A.3 Measurement methods: ozone (O_3)

Ozone is formed in the atmosphere via reactions among other pollutants, specifically VOCs and NO_x, in the presence of sunlight. Ozone is one of the six key pollutants identified by the Ambient Air Quality NEPM (NEPM 2015). A combination of NO_x emissions associated with HF activities and VOCs from HF and non-HF sources may potentially result in ozone production.

A.3.1 AQMS – Continuous O_3 measurements by nondispersive ultraviolet (UV) photometry

At the AQMS ozone will be measured by an Ecotech EC 9810 nondispersive ultraviolet (UV) photometry method (Ecotech, Knoxfield, Victoria, www.ecotech.com.au). This instrument is a Tier 1 method and is compatible with Australian Standard AS 3580.6.1 (AS/NZS 2011b). The manufacturer-stated detection limit of the EC 9810 is 0.5 ppb or 0.2% of reading whichever is greater, and is significantly lower than the NEPM 4 h standard of 0.08 ppm. Stated precision is 0.1 ppm or 1% of reading whichever is greater. Daily instrument zero and span tests will be conducted for the duration of sampling.

A.4 Measurement methods: particle sampling systems

Particulate matter (PM) is one of the six key air pollutants in the Ambient Air Quality NEPM (NEPM 2015) which prescribes limits for particles less than 10 microns in diameter (PM_{10}) and fine particles less than 2.5 microns in diameter ($PM_{2.5}$). PM was identified by CSG industry EIS as an important potential pollutant (QGC 2010, APLNG 2010). HF-related sources include diesel exhaust and dust emissions. In rural areas, emissions from agricultural sources may make a substantial contribution to PM. In addition, PM can be formed as a secondary pollutant in the atmosphere via chemical reactions between gases or between gases and particles in the air. Consequently, the composition of particles can differ depending on their sources and atmospheric aging processes.

A.4.1 AQMS – Fine dust monitoring and ambient air measuring system (FIDAS)

The FIDAS is a Tier 2 method and is compatible with European Standards EN 12341, EN 14907. The FIDAS measures continuously and simultaneously concentrations of PM_1, $PM_{2.5}$, PM_4, PM_{10}, total suspended particles (TSP), as well as the particle number concentration and the particle size distribution in a size range of 180 nm to 18 µm.

Air is sampled via an instrument-specific temperature and humidity controlled inlet at a flow rate of 4.8 LPM. The systems use a polychromatic LED white light source for the optical light scattering of single particles and is equipped with an optical aerosol spectrometer for particle detection. The particles are classified into 64 size bins and each size fraction (bin) is multiplied by a correlation factor to convert particle size and number into mass (range 0–10 000 $\mu g\ m^{-3}$). A mass fraction is achieved by applying an additional separation curve to the determined particle size distribution.

The ability to measure a range of PM size bins with a single instrument at near continuous time resolutions is a major advantage of the FIDAS for measurements over other PM measurement systems. Other particle concentration measurement systems exist that are Tier 1 methods and meet NEPM reporting requirements, including Tapered Element Oscillation Method (TEOM) and Beta Attenuation Method (BAM). Both techniques use size-selective inlets and can only measure one particle size range $PM_{2.5}$ or PM_{10} with a single instrument. The BAM and TEOM time resolution is limited to one sample per hour and both techniques can suffer losses due to evaporation/volatilisation of moisture or semi volatiles from filter media (Keywood & Selleck 2016). These instruments are better suited for longer term sampling in urban/industrial ambient air monitoring applications.

CSIRO is employing a separate Tier 2 method at the AQMS for gravimetric mass determination of PM_{10} from samples collected using the Derenda low volume particle sampler (see A.4.3). A comparison between the Ecotech Fidas 200 data and PM_{10} mass collected using the CSIRO

Derenda low volume particle sampler at the AQMS will be undertaken as part of the proposed study.

A.4.2 AQMS – Black carbon analyzer

For the purposes of this study, black carbon will be used as a tracer for combustion emissions of PM. The Met One Instruments BC 1054 Multispectrum Black Carbon analyser collects particles on to filter tape and measures the transmittance of light across the filter tape at 10 different wavelengths ranging from 370–950 nm. It then calculates in real time the black carbon concentrations for each wavelength at a standard time resolution of 1 minute.

A.4.3 AQMS – Comde-Derenda low volume particle sampler

When coupled with gravimetric mass determination (A.5.1), the Comde-Derenda low volume particle sampler at the AQMS is a Tier 2 method compatible with EN 12341:1998 Air Quality - Determination of the PM_{10} Fraction of Suspended Particulate Matter (BS EN 2014).

Two of these low volume samplers will be located nearby the AQMS site. Two 12-hour samples will be collected each day, one on each sampler. Each sampler will be equipped with a PM_{10} impactor inlet and operate at a flow rate of 2.3 m^3 h^{-1}. The volumetric flow rate is monitored by a measuring orifice and the flow is regulated to an accuracy of better than 2%. The particles will be collected onto a 47 mm teflon filters (Pall teflo 2 µm 47 mm p/n R2PJ047). The sampler is also equipped with ambient temperature, pressure and humidity sensors for standard volume measurements.

The filters will be analysed by total gravimetric mass determination (see A.6.1), ion chromatography for major soluble ions (A.6.2) and ion beam analysis for elemental composition (A.6.3).

A.4.4 Perimeter sites – Microvol 1100 low volume particle sampler

When coupled with gravimetric mass determination (A.5.1.) this is a Tier 1 method and is compatible with AS/NZS 3580.9.9:2006 Methods for sampling and analysis of ambient air - Determination of suspended particulate matter – PM_{10} low volume sampler – Gravimetric method (AS/NZS 2006).

Each perimeter site will house a Microvol 1100 low volume sampler for collecting particles in ambient air. Each sampler is equipped with a PM_{10} inlet and is microprocessor controlled and maintains a constant volumetric flow rate of 3.0 LPM using a mass flow sensor and ambient temperature and pressure sensors. The particles are collected onto 47 mm Teflon filters (Pall p/n R2PJ047).

A.4.5 Perimeter sites – E-Sampler

The E-Sampler (Met-One Instruments Inc. Oregon, USA) continuously measures particle mass concentration through near-forward light scattering. A visible laser light source scatters particles in proportion to the particulate load. The instrument is calibrated using polystyrene latex spheres of known index of refraction and diameter at multiple points to validate linearity. This is a Tier 3 method and validation of its performance will occur by using the E-Sampler's ability to collect a sample on a filter simultaneously, which will be used to determine the sample-period specific mass scattering coefficient. Manufacturer stated sensitivity is 0.001 mg m^{-3}, with accuracy of 8% of NIOSH 0600 and precision of 0.003 mg m^{-3}or 2% of reading whichever is greater.

A.5 Measurement methods: particle mass and composition analysis

A.5.1 Gravimetric mass measurements of particulate samples

Gravimetric mass determination from samples collected using the Derenda low volume particle sampler at the AQMS and the Microvol sampling at the perimeter sites are Tier 1 and 2 methods compatible with AS/NZS 3580.9.9:2006 Methods for sampling and analysis of ambient air - Determination of suspended particulate matter – PM_{10} low volume sampler – Gravimetric method (AS/NZ 2006).

Particle mass less than 10 µm in diameter (PM_{10}) is measured by gravimetric mass determination. PM_{10} samples are collected using the Derenda low volume sampler or Microvol. This draws air at a constant flow rate through a PM_{10} size-selective inlet (which removes particles greater than 10 µm in diameter) and onto a 47 mm stretched Teflon filter (Pall R2PJ047, 2 µm pore size) on which particles less than 10 µm diameter are trapped. Each filter is weighed before and after sampling to determine the mass of particles collected. Gravimetric mass measurements are performed using a Matteke Toledo MX5 microbalance under laboratory conditions at 22 °C and 20% relative humidity. The resolution of the balance is 0.0008 mg (0.8 µg) and the overall uncertainty is 10%.

The precision will be calculated as the % relative standard deviation of samples taken, when sampling systems are co-located at AQMS or at CSIRO's Aspendale laboratories following the field measurement period. Previous studies by CSIRO have reported precisions of 4.6% for summer and 1.9% for winter.

A.5.2 Ion chromatography analysis of particulate samples

Ion chromatography analysis from samples collected using the Derenda low volume particle sampler at the AQMS and the Microvol samplers at the perimeter sites is a Tier 3 method. This method has been used extensively in the past by CSIRO Oceans and Atmosphere to characterise PM composition (e.g. Hibberd et al. 2013, 2015; Cope et al. 2014).

47 mm Teflon filters sampled by Comde-Derenda low volume sampler will be analysed for major water soluble ions by suppressed ion chromatography (IC) and for anhydrous sugars including levoglucosan by high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD). The filters will be extracted in 10 ml of 18.2 mΩ de-ionized water. The sample is then preserved using 1% chloroform.

Anion and cation concentrations are determined with a Dionex ICS-3000 reagent free ion chromatograph. Anions are separated using a Dionex AS17c analytical column (2 × 250 mm), an ASRS-300 suppressor and a gradient eluent of 0.75 mM to 35 mM potassium hydroxide. Cations are separated using a Dionex CS12a column (2 × 250 mm), a CSRS-300 suppressor and an isocratic eluent of 20 mM methanesulfonic acid.

Anhydrous sugar concentrations are determined by HPAEC-PAD with a Dionex ICS-3000 chromatograph with electrochemical detection. The electrochemical detector uses disposable gold electrodes and is operated in the integrating (pulsed) amperometric mode using the carbohydrate (standard quad) waveform. Anhydrous sugars are separated using a Dionex CarboPac MA 1 analytical column (4 × 250mm) with a gradient eluent of 300 mM to 550 mM sodium hydroxide.

The species whose concentrations will be determined are:

- Chloride (Cl^-)
- Nitrate (NO_3^-)
- Sulfate (SO_4^{2-})
- Oxalate ($C_2O_4^-$)
- Formate (HCOO$^-$)
- Acetate (CH_3COO^-)
- Phosphate (PO_4^{3-})
- Methanosulfonate (MSA$^-$)
- Sodium (Na^+)
- Ammonium (NH_4^+)
- Magnesium (Mg^{2+})
- Calcium (Ca^{2+})
- Potassium (K^+)
- Levoglucosan ($C_6H_{10}O_5$, an anhydrous sugar - woodsmoke tracer)
- Mannosan ($C_6H_{10}O_5$, an anhydrous sugar - woodsmoke tracer)

A.5.3 Ion beam analysis of particulate samples by ANSTO

Ion beam analysis of the PM_{10} samples will be conducted by ANSTO personnel at the Lucas Heights Laboratories. Ion beam analysis (IBA) will be used. The Teflon filters will be analysed non-destructively on the ANSTO STAR 2MV accelerator using nuclear IBA techniques to determine what elements are present in the PM_{10} samples. The simultaneous IBA techniques applied are:

- Proton induced X-ray emission (PIXE) – for analysis of elements from aluminium to lead in concentrations from a few ng m^{-3} upwards, as described in Cohen (1993).
- Proton induced gamma-ray emission (PIGE) – for analysis of light elements such as fluorine and sodium in concentrations above 100 ng m^{-3}, as described in Cohen (1998).
- Proton elastic scattering analysis (PESA) – for analysis of hydrogen at levels down to 20 ng ng m^{-3}, as described in Cohen et al. (1996).

The elements that will be determined by IBA are:

- Hydrogen (H)
- Sodium (Na)
- Aluminium (Al)
- Silicon (Si)
- Phosphorous (P)
- Sulfur (S)
- Chlorine (Cl)
- Potassium (K)
- Calcium (Ca)
- Titanium (Ti)
- Vanadium (V)
- Chromium (Cr)
- Manganese (Mn)
- Iron (Fe)
- Cobalt (Co)
- Nickel (Ni)
- Copper (Cu)
- Zinc (Zn)
- Bromine (Br)
- Lead (Pb)

A full description of these methods and how they are used can be found on the ANSTO web page (http://www.ansto.gov.au/ResearchHub/OurResearch/IER/Capabilities/IBA/index.htm).

A.6 Measurement methods: volatile organic compounds

Volatile organic compounds (VOCs) are organic compounds that have boiling points in the range ~50–250 °C that allow them to exist in the gas phase at ambient temperatures. They exist in the atmosphere at concentrations that range from parts per billion to parts per trillion and are emitted from a variety of natural and man-made sources. These minor components of atmospheric composition have important roles in processes affecting the health of humans and the environment.

Four VOCs are listed in the National Environment Protection (NEPM) Ambient Air Toxics Measures: benzene, toluene, xylenes (BTEX) and formaldehyde. The Queensland EPP air objectives include BTEX and formaldehyde plus an additional six VOCs: 1,2-dichloroethane, 1,3-butadiene, dichloromethane, styrene, tetrachloroethylene, and vinyl chloride monomer.

As part of the proposed study design four VOC sampling and analysis, techniques would be deployed that would enable the analysis of a wide range of VOCs including NEPM and some EPP-listed air pollutants at high time resolutions.

A.6.1 Passive radiello sampling

As discussed in Section 2.1.4, sampling for VOCs via the passive Radiello method was initiated at four locations within the proposed study site in October 2016. Radiello passive samplers are deployed by SGS Leeder Chinchilla for a period of two weeks and are analysed by SGS Leeder in Mitcham, Melbourne. Three types of Radiello samplers have been deployed at each site: one for VOCs including BTEX, one for aldehydes including formaldehyde and one for hydrogen sulphide (H_2S).

Samples are chemically extracted from the Radiello cartridges and analysed by GC-FID for VOCs, HPLC method for aldehydes, and spectrophotometric method for H_2S. Detection limits are in the range of 0.01–0.24 ppb dependent on species and sampling duration (CSIRO data, unpublished) and manufacturer-stated measurement uncertainties (2 σ) are 2.5–14.5 % (Radiello, 2006).

HF activities occur on time scales of hours to days. Consequently, higher time resolution measurements are required to capture VOC emissions related to each activity and for comparison with short-term (e.g. 24 h) ambient air quality guidelines designed to protect human health and the environment from acute ambient exposures. Radiello data collected as 2-weekly integrated samples is not comparable with short-term ambient air quality objectives.

A.6.1 AQMS & perimeter sites – Active sampling of VOCs onto adsorbent tubes analysed by GC-FID-MS

The methods of adsorbent tube VOC sampling (AT-VOC) and analysis proposed here are Tier 2 methods and are compatible with ISO16017-1:2000 (ISO 2000) and in accordance with US EPA Compendium method TO-17 Determination of Volatile Organic Compounds in Ambient Air using active sampling onto sorbent tubes (USEPA, 1999a).

For the purposes of this study, as a minimum the AT-VOC method will be used to provide a 24 h integrated measurements of benzene, toluene and xylenes that are directly comparable with the NEPM Air toxics annual and 24 h objectives. In addition to BTEX, this method can be used to measure alkanes >C_4, other aromatics, naphthalene and phenolic compounds that have been identified as potentially present in emissions from flow-back fluids, coal seam gas and in emissions from vehicles and equipment on site.

At the AQMS, ambient air will be drawn through a ~10 m length of 3/8 inch PTFE tubing inlet into a custom designed automated sampler. The automated sampler is a continuous air sampler with two channels allowing for simultaneous extractive sampling onto VOC adsorbent tubes and DNPH cartridges. Two 12 h samples per day will be collected by the automated sampler which actively draws air through two multi-adsorbent tubes in series using a constant flow air sampling pump at a set flow rate of 20 mL min^{-1}.

At the perimeter monitoring sites, ambient air will be drawn through a ~1.5 m length of 1/4 inch silco steel tubing. Two 12 h samples per day will be collected by actively drawing air through two multi-adsorbent tubes in series using a battery-powered constant flow air sampling pump (Pocket pump SKC) at a set flow rate of 20 mL min^{-1}.

The adsorbent tubes from both the AQMS and perimeter sites will be analysed by a gas chromatograph (GC) equipped with flame ionization detection (FID) and a mass spectrometer (MS). Detection limits for this method are typically 0.005–0.010 ppb with a calculated measurement uncertainties of ~10–15% depending on the species under consideration.

Further details of this method can be found in Dunne et al. (2017).

A series of certified gas standards including a: BTEX standard (benzene, toluene, ethylbenzene and xylenes); a TO-15 standard; will be used to calibrate the GC-FID-MS. The calibration will be done via an injection of the calibration gas onto an adsorption tube using a fixed volume temperature stabilised loop for standards with >2 ppm individual VOCs and via sampling a known volume of calibration gas onto an adsorption tube using a calibrated mass flow controller for standards with <2 ppm individual VOCs.

A.6.2 AQMS & perimeter sites – Active sampling and derivatization of aldehydes and ketones onto DNPH cartridges analysed by HPLC

This method of DNPH-HPLC sampling and analysis for aldehydes and ketone is the prescribed NEPM method (Tier 1) for determination of formaldehyde and is compatible with Compendium Method TO 11A- Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) [Active Sampling Methodology](USEPA, 1999b).

For the purposes of this study, as a minimum the DNPH method will be used to provide 24 h integrated measurements of formaldehyde that are directly comparable with the NEPM Air Toxics annual and 24 h objectives. In addition to formaldehyde, this method may be used to measure other C_2–C_6 aldehydes and ketones, possibly including glutaraldehye which is sometimes used in as a biocide in hydraulic fracturing fluids.

At the AQMS, ambient air will be drawn through a ~10 m length of 3/8 inch PTFE tubing inlet into the custom-designed automated sampler. Two 12 h samples per day will be collected by the automated sampler which actively draws air through DNPH-coated solid silica adsorbent cartridges (Supleco LpDNPH S10) using a constant flow air sampling pump at a set flow rate of 1 L min^{-1}.

At the perimeter monitoring sites, ambient air will be drawn through a ~1.5 m length of 1/4 inch teflon tubing. One 24 h sample per day will be collected by actively drawing air through DNPH coated solid silica adsorbent cartridges using a battery powered constant flow air sampling pump (TSI Sidepak) at a set flow rate of 1 L min^{-1}.

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 will be maintained at ~15° C. During sampling at the perimeter sites the DNPH cartridges will be housed in an insulated instrument box and will be collected daily to minimise their exposure to high ambient temperatures. All cartridges will be refrigerated before and after sampling. An ozone scrubber (KI impregnated filter) will placed in front of all DNPH cartridges during sampling to account for known artefact formation due to the presence of ozone.

Following sampling, the aldehyde and ketone derivatives trapped on the DNPH cartridges will be eluted from the cartridge in 2.5 mL of acetonitrile and analysed by ultra-high performance liquid chromatography (UHPLC) consisting of a Thermo Scientific Dionex Ultimate 3000 RS system with diode array (DAD) and mass spectrometry (MS) detection. Compound separation was performed with a RSLC acclaim carbonyl column (2.2 µm, 2.1 mm I.D., 150 mm length, Part No. 077973). The chromatographic conditions will include a flow rate of 0.4 mL min^{-1} and an injection volume of 3.0 µL, and the DAD will be operated in the 220–520 nm wavelength range with 360 nm used for mono-carbonyl quantification and the MS used for carbonyl identification. The peaks will be separated by gradient elution with an initial mobile phase of 52% acetonitrile and 48% deionized water (18.2 ΩM cm, Millipore Milli-Q Advantage) for 8.3 min, followed by a linear gradient to 100% acetonitrile for 8 min, and with a column temperature of 30 °C. A certified liquid standard (Supelco Carb Method 1004 DNPH mix 2 C/N 47651-U) containing 30 µg mL^{-1} of each derivatised carbonyl will be diluted 1:25 in a volumetric flask. This prepared standard will then be used to perform a 4-point calibration (0.15, 0.30, 0.6 and 1.2 µg mL^{-1}).

Detection limits for this method are typically 0.01–0.02 ppb with a calculated measurement uncertainties of ~9–12% depending on the sampling conditions and species under consideration.

Further details of the DNPH method can be found in Dunne et al. (2017).

A.6.3 AQMS – 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 sub-ppb detection of a range of VOCs. For the purposes of this study PTR-MS will be classified as a Tier 3 method and will be validated against Tier 2 methods of VOC adsorbent tube sampling (A.6.1) and DNPH sampling (A.6.2). As part of the proposed study, a commercially built PTR-MS instrument (Ionicon Analytik GmbH, Innsbruck, Austria) will be run continuously in the AQMS.

As a minimum, the PTR-MS employed in this study will be used to provide continuous measurements of BTEX and formaldehyde that, following appropriate validation and calibration procedures, will be directly comparable with the NEPM Air Toxics annual and 24 h objectives for these species. In addition to BTEX and formaldehyde this method can potentially be used to measure:

- C_2–C_6 aldehydes and ketones, C_1–C_3 alcohols, low molecular weight organic acids and other oxygenated VOCs, some of which are known ingredients in hydraulic fracturing fluids, and may also be present in flow-back fluids, CSG and in emissions from vehicles and equipment on site.

- other aromatics (>C_8), naphthalene and phenolic compounds potentially present in emissions from flow-back fluids, CSG, and in emissions from vehicles and equipment on site.

PTR-MS is not suitable for measuring small alkanes (<C_{10}) and alkenes (<C_5).

A flow of 1.5 L min^{-1} of ambient air will be drawn via ~12 m of 3/8 inch O.D. PTFE tubing inlet by a constant flow sampling pump through the PTR-MS auxiliary system and the PTR-MS will sample 300 mL min^{-1} from the auxiliary system. A commercially built PTR-MS (Ionicon Analytik, GmbH, Innsbruck Austria) will be used for continuous VOC measurements.

The drift tube will be operated at 60 °C, and an applied voltage of ~600 V and a pressure of ~2 mbar. The PTR-MS quadrupole will continuously scan 181 masses between 14 and 200 amu with a dwell time for a single mass (m/z) of 1 s, generating a full mass scan approximately every 3 min (20 data points h^{-1} m/z^{-1}).

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 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. This zero air has the same mole fractions of H_2O and CO_2 as the ambient air being sampled, neglecting minor contributions from the oxidation of the VOCs present. All PTR-MS ion signals from calibration and ambient measurements will be background corrected.

The minimum detectable limit for each m/z scanned by the PTR-MS will be determined from the scatter in the zero measurements using the principles of ISO 6879 (ISO 1995). The MDL for a single measurement is set at the 95th percentile of the deviations about the mean zero. The PTR-MS will be calibrated daily for 30 min. For each calibration measurement, a set flow of 10–20 mL min^{-1} of a ~1 ppm calibration standard will diluted in a flow 1500 mL min^{-1} of ambient air that had been passed through the zero furnace. The PTR-MS will be calibrated with three certified gas standards containing >20 VOC species. These certified gas standards are supplied by Apel-Reimer Environmental Inc (Broomfield CO, USA). The stated accuracy for each component in the standards is ±5%.

Detection limits for this method are typically 0.003–0.200 ppb with a calculated measurement uncertainties of ~9–12% depending on the species under consideration.

A.7. Measurement methods: methane, radon, mercury and PAHs

A.7.1 AQMS – Methane by cavity ring-down spectroscopy method

Methane is typically 96–98% of CSG composition but is also present in emissions from livestock. While methane is a powerful greenhouse gas, it is only a concern for human health at very high concentrations where it can act as an asphyxiant and as an explosive gas at concentrations of 5–15%; these concentrations are unlikely to be encountered in ambient air. For the purposes of this study, methane measurements will be used as a tracer for emissions of CSG, the presence of which will be used to infer the levels of other minor components potentially present in CSG such as radon, mercury and VOCs.

At the AQMS, methane will be measured by cavity ring-down method using a Picarro G1301 analyser (Picarro Inc., Santa Clara, California). This instrument is a Tier 1 method and is compatible with Australian Standard AS/NZS 3580.17.2016 (AS/NZS 2016). The manufacturer-stated precision of the Picarro is <1 ppbv. Daily instrument zero and span tests will be conducted for the duration of sampling.

A.7.2 AQMS – Gaseous radon by dual flow loop two-filter radon detector

A previous study in the Surat Basin (Tait et al. 2013) reported enrichment of atmospheric radon concentrations in the Surat Basin and hypothesized that the radon enhancement was a result of radon present in CSG being emitted within gas fields from CSG infrastructure (well heads, pipelines, etc.) and emissions from soil sources resulting from changes in the underlying geology caused by CSG extraction processes.

As part of the proposed study, ANSTO will deploy a dual flow loop, two-filter radon detector at the AQMS that will provide continuous monitoring of ambient radon in air. Limits of detection of 30–40 mBq m^{-3} with a high precision down to very low concentrations typical in background air.

Further details are available at:
http://www.ansto.gov.au/ResearchHub/OurResearch/IER/Facilities/Radonanalyticallabs/index.htm#sthash.ZgcGf9gP.dpuf

A.7.3 AQMS – Gaseous mercury

Mercury is well-established as a toxic global pollutant (AMAP/UNEP 2013). Mercury is ubiquitous in the environment and is the only metal that is in the gaseous phase at ambient temperatures. It is introduced into the atmosphere mainly in the form of gaseous elemental mercury (GEM), which has a typical atmospheric lifetime on the order of six months to two years.

Mercury is a trace element found in coal. The content in coal depends on the coal type, formation, and location. Australian coals are characteristically lower in mercury content compared to other coals. Mercury emissions to the atmosphere from CSG extraction activities have not been quantified. A few measurements have been reported in the literature from CSG extraction and coal seam fires (Liang et al. 2014, Lan et al. 2015) suggesting there may be significant emissions from CSG exploration. The implication is that total gaseous mercury (TGM) emission from CSG can be used as a tracer to unambiguously identify other emissions from CSG activity such as methane. Moreover, the dearth of data on mercury from coal seam exploration is a motivation on its own to quantify these emissions and their impact, if any.

The mercury measurement technique proposed for this study is a Tier 3 method; however, the Macquarie University team is internationally recognised and has played a leading role in development of methods for the measurement of mercury and its speciation which will be applied in this project. Macquarie University will undertake mercury measurements at the AQMS using a Tekran® 2537 unit for TGM/GEM measurement. Manufacturer stated detection limits are 0.1 µg m^{-3} and the unit is capable of autonomous calibration using an in-built permeation source.

A.7.4 AQMS – PAHs

Sampling and analysis will be performed following AS/NZS 3580.16:2014 Methods for sampling and analysis of ambient air. Method 16: Determination of polycyclic aromatic hydrocarbons (PAH). In this method ambient air is drawn at a constant flow rate through a quartz filter (102 mm diameter) and polyurethane foam (PUF) sorbent plug (75 mm long; 65 mm diameter). Sampling is performed using The Flowset High Volume PUF sampler (Lear Siegler, Caringbah, NSW) containing a TSP inlet, filer holder, glass sorbent cartridge, a mass flow sensor and run clock. The sampler complies with US EPA Methods TO-4, TO-9 and TO-13. The sample flow is calibrated using an orifice plate and manometer to measure differential pressure across the orifice.

The sampling method collects aerosol phase species on the filter and gas-phase species on the PUF. Filters and PUFs are individually sealed in cleaned aluminium and are stored at -18°C before and after sampling. Exposed samples and field blanks are stored at <4°C during transport to the laboratory for analysis.

Throughout the campaign, 25 samples, 3 field blanks (1 in 10 samples) and 2 laboratory blanks (1 in 20 samples) will be collected. Sampling is normally of 24h duration at 225 litres to enable the collection of sufficient PAH mass for subsequent laboratory analysis whilst minimising breakthrough of more volatile species. Throughout the campaign, the sampling period will nominally be 48 hours but may be reduced to 24 hours during periods when wells near the site are fracked.

Deuterated PAHs will be added to the pre-cleaned PUFs before sampling to quantify breakthough of PAH species (a requirement for checking breakthrough if sample volumes are greater than 350 m^3). A mixture of 100 ng of D-Naphthalene, D-Acenaphthylene, D-Anthracene, D-Pyrene and D-Dibenzo (a,h) anthracene in isooctane is add to each PUF before sampling.

The collected quartz filter and PUFs are spiked with a solution containing seven deuterated PAHs at different levels as internal standards for quantification purposes. The quartz filter and PUF samples are then extracted in a Dionex ASE 350 Accelerated Solvent Extractor (Thermo Fisher Scientific) using n-hexane and acetone (1:1, v/v). The extracts are cleaned up using silica-ALOX chromatographic cartridges and analysed for 13 PAH compounds including Phe, Ant, Flu, Pyr, BaA, Chr, BbF, BkF, BeP, BaP, I123cdP, DahA and BghiP. Samples are analysed using a Thermo 1310 gas chromatograph coupled to a DFS Magnetic Sector high-resolution mass spectrometer (GC-HRMS). The HRMS is operated in electron impact-multiple ion detection (EI-MID) mode and resolution is set to ≥ 10,000 (10% valley definition).

Appendix B: Proposed HF stimulation treatments for Condabri Site

The initially proposed study site was within Origin Energy's Walloons Appraisal Project Phase 2 (WAP2). The following information of the proposed WAP2 HF treatments was provided by Origin Energy on request from CSIRO project team. The details of the Varidel HF treatments were not available at the time of writing this report.

B.1 Fracture stimulation campaign

The following outlines the stimulation technology required for each of the 18 wells in WAP2:

- Acid stimulation: CNN 212, CNN 204, CNN 215
- Skin removal stimulation: CNN 207, CON 382
- Linear Micro Prop (LMP): CON 386, CNN 210
- Cement & Reconnect (C&R): CON 384, CNN 206, CNN 211
- Standard full fracture stimulation: CNN 203, CNN 205, CNN 209, CNN 216, CNN 218, CON 383, CON 385, CON 387

All wells will be perforated prior to the fracture stimulation using 3-3/8" 34JL SDP shaped charges. It is required to displace the wells with inhibited fluid prior to perforation if the wells are filled with fresh water.

B.2 Treatments

B.2.1 Gel, Straddle Coiled Tubing Assisted Fracture Stimulation

The stimulation treatment will be performed with the use of coil tubing and coil-deployed fracturing cups to provide zonal isolation between stages. The well will be perforated using 3-3/8" shaped charges in the 5-1/2" casing at 6 spf and 60O phasing. Chemical tracers may be also added to the treatment slurry for fracture evaluation. The stimulation treatment will be pumped down the coiled tubing using gelled fluids to place sand. An Injection Falloff Test will be conducted prior to the main treatment to assess the stress, leak-off and permeability. The maximum required downhole pressure is estimated 3000 psi. A frac tree with appropriate pressure rating is required to be installed prior to stimulation. It is expected that up to eight stages are required for this treatment.

B.2.2 Gel, Plug and Perforation Rigless Fracture Stimulation

The stimulation treatment will be performed with the use of a wireline truck to run and shoot the perforation guns, and to set the bridge plug for zonal isolation. The well will be perforated using 3-3/8" shaped charges in the 7" casing at 6 spf and 60O phasing. Chemical tracers may be also added to the treatment slurry for fracture evaluation. The stimulation treatment will be pumped down the 7" casing using gelled fluids to place sand. The maximum required downhole pressure is estimated 3000 psi. A frac tree with appropriate pressure rating is required to be installed prior to stimulation. It is expected that up to eight stages are required for this treatment.

B.2.3 Skin Frac Design

In transitioning areas where a wide range of permeability is encountered within a single well, a smaller stimulation volume may be required for better permeability intervals. An Injection Falloff Test (IFT) will be conducted prior to the main treatment to determine if skin frac is required. The stimulation technology is identical to that of B.2.1.

B.2.4 Acid Stimulation Design

Acid stimulation is capable of dissolving cement filtrate and natural calcite in the formation to improve communication between the wellbore and reservoir. Furthermore, wells with less than optimal cement bond quality do not meet minimum requirements for hydraulic fracture stimulation, but they may still benefit from acid stimulation.

B.2.5 Linear Micro Proppant Stimulation Design

In very low permeability (less than 10 mD) areas, standard fracture stimulation is deemed uneconomic. Therefore, a more cost-effective fluid system such as linear viscous fluid system is required to meet the economic criteria. The stimulation treatment will be performed with the use of coil tubing and coil-deployed fracturing cups to provide zonal isolation between stages. The well will be perforated using 3-3/8" shaped charges in the 5-1/2" casing at 6 spf and 60O phasing. Chemical tracers may be also added to the treatment slurry for fracture evaluation. The stimulation treatment will be pumped down the coiled tubing using gelled fluids to place sand. An Injection Falloff Test will be conducted prior to the main treatment to assess the stress, leak-off and permeability. The maximum required downhole pressure is estimated 3000 psi. A frac tree with appropriate pressure rating is required to be installed prior to stimulation. It is expected that up to eight stages are required for this treatment.

B.2.6 Cement and Reconnect Stimulation Design

In moderate to high permeability (50–150 mD) the optimum and cost-effective completion technology is yet unknown. Pre-perforated liner completion is the most cost-effective technology, however, fines production is a major issue. Therefore, casing and cementing is deemed inevitable to rectify fines production and migration within this permeability range. To identify the most optimum and cost effective completion a step-by-step is deemed beneficial. The following outlines the steps within this approach;

1. Perforate and connect well to reservoir, flow test the well and appraise.
2. Perform acid stimulation as outlined in B.2.4, flow test and appraise.
3. Perform skin removal fracture stimulation as outlined in B.2.3, flow test and appraise.

Appendix C: Receptor modelling

PMF is a multivariate factor analysis tool that decomposes a matrix of speciated sample data into two matrices – factor contributions and factor profiles. These factors are then interpreted to determine what sources are represented by these factors. This is done using measured source profile information, wind direction analysis, and emissions inventories (Norris et al. 2008). The method is described in greater detail by (Paatero 1997).

Sources can be identified based on characteristic combinations of elements. PMF requires large numbers of samples with variations in the relative contributions from each source to produce reliable results. The study will need to collect over 100 samples to satisfy this requirement.

PMF is widely used in air pollution studies for source apportionment, including in Australia (e.g. Chan et al. 2008; Cohen et al. 2011; Cohen et al. 2012; Hibberd et al. 2013). The US EPA has developed a software package to implement this technique, EPA PMF 5.0 (Norris & Duvall 2014).

In practice, there are many potential sources of PM_{10} but PMF does not require or use any a priori information about the chemical composition of possible PM_{10} sources. Rather it uses a mathematical technique to identify the factors. Indeed, an advantage of the PMF over other source apportionment techniques is that it is able to identify the presence of particles which are not directly emitted as particles (primary particles) but which form by chemical reactions in the atmosphere and gas-to-particle conversions (secondary particles).

Once the factors are obtained, further analysis is undertaken to identify the sources in each factor. This uses information about known sources and other knowledge of atmospheric chemistry as well as wind sector and seasonal analysis to identify the most likely source of emissions for each factor and hence the contribution that each source makes to the total PM_{10} concentrations. In many cases, there is a single dominant source in a factor and this has been used to name the factors. However, if sources are co-located or otherwise correlated, they can appear together in a single factor or across several factors.

Appendix D: Alterations to peer-reviewed study design

This report, *Design of a study to assess the potential impacts of hydraulic fracturing on air quality in the vicinity of well sites in the Surat Basin, Queensland,* is a deliverable for Task 4 of the GISERA project. The first draft of this report was submitted for peer review in April 2017 in accordance with the project order. A second draft (Draft 2), which incorporated the response to reviewer's comments, was finalised in June 2017. The selected location for the proposed study described in Draft 1 and 2 of the report became unavailable due to a lack of access to mains power to operate monitoring equipment at the site. Hence, an alternative site was selected.

The main body of this report presents a revised version of the study design adapted for the new site. In terms of its approach and methodology, the revised study design deviates as little as possible from the previous draft incorporating the response to peer-review.

This appendix lists the major revisions to Draft 2 made in preparation of the current report (Draft 3). Sections of the text presented that were significantly changed are underlined in the following table.

Original text from Draft 2	Revised text for Draft 3
Section 2 Study Area The well operators, Origin Energy have granted CSIRO access to development areas addressed in the approved Hydraulic Fracturing Risk Assessment Risk Assessment (AECOM 2016). The proposed study site is within the Miles-Condamine-Chinchilla region in the Condabri project area in which Origin Energy has approval to perform HF operations on 227 wells between 2016 and 2020. The HF treatments planned at the site are referred to by Origin as the Walloons Appraisal Project Phase 2 (WAP2). Descriptions of the planned WAP2 HF treatments was provided by Origin Energy on request from CSIRO project team and this document is provided in Appendix B.	**Section 2 Study Area** Origin Energy has granted CSIRO access to development areas addressed in the approved Origin Energy–APLNG Hydraulic Fracturing Risk Assessment (AECOM 2016). The proposed study site is within the Roma–Yuleba region in the Combabula project area in which Origin Energy has approval to perform HF operations on 545 wells between 2016 and 2020. The HF treatments planned at the site are referred to in the risk assessment under the Varidel campaign. Details of the planned Varidel HF treatments will be provided by Origin Energy and are likely to include the treatment types listed for previous HF activities. Descriptions of previous HF treatments were provided by Origin Energy on request from the CSIRO project team and this document is provided in Appendix B.
Section 2 Study Area The proposed study site was deemed appropriate for the purposes of this study based on: The scope of HF operations planned- injection volumes, pressures and the number of chemical additives to be used are representative of processes to be employed in future Origin Energy well stimulation activities based on the information provided by Origin Energy and presented in Appendix B and the APLNG Hydraulic Fracturing risk assessment (AECOM 2016).	Section 2 Study Area The proposed study site was deemed appropriate for the purposes of this study based on: The scope of HF operations planned–injection volumes, pressures and the number of chemical additives to be used–are representative of processes to be employed in future Origin Energy well stimulation activities based on the information provided by Origin Energy and presented in Appendix B and the APLNG Hydraulic Fracturing risk assessment (AECOM 2016).

The timing of the planned operations are compatible with the timeframes of the proposed for the Phase 2 study. The location of the site within the SBAAQ Study network (See Section 2.1 below)	The timing of the planned operations is compatible with the timeframes of the proposed for the Phase 2 study. Availability of mains power for operation of monitoring equipment.
Section 2 Study Area The proposed study location is a farmland property of approximately 1030 ha located between Miles and Condamine (Figure 2) (26°45’21’’ S, 150°10’49’’E). The property is predominantly flat, semi-arid open grassland with stands of native tree vegetation (Error! Reference source not found.). Dogwood Creek, an ephemeral surface waterway borders the western boundary of the property and the Leichardt Highway borders the eastern boundary. Linked by the Leichhardt Highway, the township of Miles (population < 2000) lies approximately 9 km to the North of the proposed study site and Miles Airport lies approximately 5 km to the south. The area to the west of Dogwood Creek is dominated by farmland with ~ 5 CSG wells within a 5 km radius of the boundary. In contrast, the area to the east of the property, bounded by the Leichhardt Hwy, is dominated by farmland with a high density of CSG wells (grid spaced ~ 600 – 700 m) (Error! Reference source not found.). There is also a feedlot within 5 km of the eastern boundary. The wells in this area are serviced by a network of pipelines and vents, by the Condabri Central Gas Processing Facility which is approximately 5 km to the south of the proposed study site. The property contains 19 CSG wells, grid spaced at ~ 600 – 700 m intervals. The wells are operated Origin Energy Resources Pty Ltd and were drilled and constructed between August and September 2015 with an additional well constructed in August 2016 (Source: Qld Globe). Well depths range from 740 – 860 m and target the Walloon Coal Measures. Eighteen wells are scheduled to undergo HF in June – July 2017 after which they will be brought on-line and connected to the gas and water pipeline network (Source: AECOM 2016, not publicly available).	**Section 2 Study Area** The proposed study location is 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. The Combabula State Forest borders the western boundary of the property and Horse Creek Road borders the eastern boundary. Linked by Horse Creek Road, the township of Yuleba (population <200) lies approximately 35 km to the SSW of the proposed study site. The area to the north of the property is dominated by farmland with a high density of CSG wells (grid spaced ~600–800 m) (**Error! Reference source not found.**). The wells in this area are serviced by a gathering network connecting to the Reedy Creek Gas Processing Facility (GPF) which is approximately 12 km to the WSW. The areas to the east, west and south of the property is state forest and open farmland with a low density (<5) of CSG wells. The property contains 10 CSG 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 and target the Walloon Coal Measures. All 10 wells are scheduled to undergo HF in sometime between August and September 2017 after which they will be brought online and gathering system (AECOM 2016). Revised Figure 2 showing new Combabula site inserted
Section 2 Study Area Subsection headings: 2.1 Existing Air Quality Measurements 2.2 Meteorology	Revised section 2 Study Area Subsection headings: 2.1 Proposed Study Location, 2.2 Meteorology, 2.3 Existing Air Quality Measurements
Section 2.2 Meteorology The results of this analysis indicate predominant winds during the scheduled period for HF activities at the site	**Section 2.2 Meteorology** The results of this analysis indicate predominant winds during the scheduled period for HF activities at the site

of June – August are likely to be south westerly with an equivalent east/north-easterly component. These model outputs compare well with observed wind data from the Miles Airport AQMS (see Figure 3) in June 2016 (Ecotech, 2016).	in August and September are likely to be south-westerly with an equivalent east/north-easterly component. In 2015 Origin Energy commissioned Katestone Environmental Pty Ltd to review the results of an ambient air monitoring program, including meteorological data that was undertaken in July–November 2015 in the Combabula Development Area (CDA) (Katestone Environmental 2016). The scope of this study is discussed further in Section 2.3.3. Meteorological observations were undertaken at an air quality monitoring station (AQMS) in the CDA, located ~12 km to the WSW of the site proposed for the study presented here as shown in Figure 2. A wind rose of the observed 1-hour average wind speed and direction at the CDA AQMS is presented in Figure 3 alongside the outputs of the TAPM modelling by Day et al (2015). Winds measured at the CDA monitoring station were predominantly north-easterly, with an equivalent proportion of southerly winds. The frequency of observed wind speeds at the CDA AQMS by time of day is shown in Table 2. Moderate winds (2–4 $m\ s^{-1}$) were measured for approximately 58% of the monitoring period with ~20% light winds (<2 $m\ s^{-1}$), ~20% moderate to strong winds (4–6 $m\ s^{-1}$) and <5% strong winds (>6 $m\ s^{-1}$) were observed. Inserted Table 3 Measured wind speed frequency at the CDA ambient air monitoring station (% of total for period) Revised Figure 3 - removed Miles windrose and replaced with CDA AQMS windrose. Revised months of TAPM data included.
Section 2.1 Existing Air Quality Measurements A major advantage of the proposed study site is its location within the air quality monitoring network operating as part of the current GISERA SBAAQ Study (see Error! Reference source not found.). The network comprises 5 ambient air quality monitoring stations (indicated in yellow in Error! Reference source not found. right panel) and 10 sites at which volatile organic compounds (VOCs) are being monitored by passive samplers (indicated in red in Error! Reference source not found. left panel). The data from these monitoring programs will be made available to the HF Study. The data from the HF study will be compared to the SBAAQ study areas which are not directly impacted by HF activities in order to quantify enhancements in air pollutant levels above background that occur during HF operations.	**Section 2.3 Existing Air Quality Measurements** 2.3.1 Surat Basin Ambient Air Quality Study CSIRO is leading the GISERA Surat Basin Ambient Air Quality (SBAAQ) Study (Lawson et al. 2016) which is currently underway in the Miles–Chinchilla–Condamine region of the Surat Basin, approximately 100 km to the ESE of the proposed study site (Figure 1). The SBAAQ Study comprises a network of five ambient air quality monitoring stations and 10 sites at which volatile organic compounds (VOCs) are being monitored. This network includes two sites outside of areas of concentrated gas infrastructure and under appropriate wind conditions will provide regional background measurements of air pollutants. Both the SBAAQ Study area and the area under consideration in this study share similar geography, intensity of CSG infrastructure (Queensland Globe 2016)

In October 2016 Origin Energy with advice from CSIRO initiated an additional program VOC monitoring at 4 locations within the proposed study site, and at 3 locations in the neighbouring field directly to the east that contains 5 wells that underwent HF in November 2016. This VOC monitoring is planned to end in late 2017 and the data will be incorporated into reporting for this HF study, providing critical longer term information on the levels of VOCs before, during and after HF activities in the proposed study site.	and meteorology (see Section 2.2). Given the similarity, the data from the SBAAQ Study can reasonably be considered representative of the wider region, including the proposed study site, and the data can be used as a comparison of regional air pollutant levels against which local enhancements in air pollutants associated with HF activities can be assessed. 2.3.2 VOC monitoring In June 2017, Origin Energy, with advice from CSIRO, initiated an additional program of VOC monitoring at three locations within the proposed study site, and at one location in a neighbouring field 7 km directly to the east. This location contains CSG infrastructure but will not be undergoing HF activities in the near future. This VOC monitoring is planned to end in late 2017 and the data will be incorporated into reporting for this HF study, providing critical longer term information on the levels of VOCs before, during and after HF activities in the proposed study site. Additional VOC data will be reported from VOC monitoring that began in October 2015 at two properties in the Miles region of the Surat Basin. Over 20 wells on these properties were subject to HF treatments in November 2015 and June–July 2016. VOC monitoring was conducted at seven sites across the two properties and is planned to end in late 2017. The data will be incorporated into reporting for this HF study, providing a second set of long-term data on the levels of VOCs before, during and after HF activities. 2.3.3 Combabula Development Area Air Monitoring Program As described in Section 2.2, Katestone Environmental Pty Ltd was engaged by Origin Energy in 2015 to review the results of an ambient air monitoring program, that was undertaken in the Combabula Development Area (CDA) (Katestone Environmental 2016). The air monitoring program comprised an air quality monitoring station (AQMS) the located ~12km to the WSW of the site proposed for the for the present study as shown in Figure 2. Air pollutants measured as part of the CDA program included carbon monoxide, oxides of nitrogen (NO, NO_2, NO_x) and ozone for the period July–November 2015.These observations will provide useful historical data from the Combabula region against which local air pollutant levels during HF activities can be compared.
Section 3 Methodology The proposed measurement methodology will be presented as two parts - a fixed air quality monitoring	**Section 3 Methodology** The proposed measurement methodology will be presented as two parts: two fixed air quality monitoring

station (AQMS) located within the HF field and four battery powered perimeter monitoring stations located around the boundary of the property (perimeter monitoring sites).	stations (AQMS) located within the HF field and five solar-battery-powered monitoring stations located around the boundary of the property (perimeter monitoring sites).
Section 3.1 Proposed Measurement Locations	**Section 3.1 Proposed measurement locations**
AQMS - The proposed location of the AQMS is at the southern end of the HF field (Figure 4) and was determined following consideration of a number of factors. The dominant factor considered was access to power at the site, which was limited to locations near existing power lines within the property. The proposed location was determined following consultations between the landholder, Origin and CSIRO with consideration given to:	AQMS - The proposed locations of the two AQMS are at the northern and southern ends of the HF field (Figure 4). The dominant factor considered in determining their location was access to power at the site, which was limited to locations near existing substations that form part of the CSG infrastructure within the property. The proposed location was determined following consultations between Origin and CSIRO with consideration given to:
Proximity to wells to undergo HF treatment- there are ~10 wells within ~20 m – 1200 m of the AQMS (Figure 5).	proximity to wells scheduled to undergo HF treatment: all 10 wells are within 1200 m of an AQMS (Figure 4).
Meteorology- as described in Section 2.2, the south westerly and east/north-easterly wind directions are expected to dominate when HF operations are underway in June – July 2017.	meteorology: as described in Section 2.2, winds from the south and east/north-east sectors are expected to dominate when HF operations are underway in August–September 2017.
Compliance with AS/NZS 3580.1.1:2007: Guide to siting air monitoring equipment (AS/NZS 2007) in terms of distance from trees, proximity to nearby roads and clear sky angle.	compliance with AS/NZS 3580.1.1:2007: Guide to siting air monitoring equipment (AS/NZS 2007) in terms of distance from trees, proximity to nearby roads and clear sky angle.
Perimeter Monitoring Sites - The proposed locations of the four battery powered perimeter monitoring sites will be determined in the field following similar criteria as outlined above. Likely areas in which perimeter sites will be located are shown in Figure 4. When determining these locations consideration will also be given to:	Perimeter monitoring sites - The proposed locations of the five solar-battery-powered perimeter monitoring sites will be determined in the field following similar criteria as outlined above. Likely areas in which perimeter sites will be located are shown in Figure 4. When determining these locations consideration will also be given to:
Areas located in the vicinity of the land-holders home so that the impact of HF activities on the air quality experienced by residents can be assessed.	locating sites on the eastern and western side of the property to provide measurements upwind and downwind of HF operations when ENE winds prevail.
Areas located on the eastern side of the property bounded by the Leichardt highway so the impact of traffic emissions, as well as HF activity, on local air quality can be assessed.	locating sites on the northern and southern ends of the property to provide measurements upwind and downwind of HF operations when southerly winds prevail.
Areas located at the SW end of the property and another at the NE end so that one site is usually upwind providing a measurement of air quality without the influence of HF activities; and one site is usually downwind to allow any enhancement in air pollutant levels downwind of the HF activities to be detected.	locating one site adjacent to the AQMS in the southern end of the field to provide validation of perimeter site instrumentation against high-quality AQMS instrumentation.
	locating sites in proximity to wells where possible to enhance probability of capturing impacts on air quality of HF operations which normally occur over ~2–4 days per well.
The location of the AQMS within the HF field and perimeter monitoring sites will provide a measurement of the potentially complex, integrated mix of air	The location of the AQMS and perimeter monitoring sites within the HF field is designed to capture the

pollutants from multiple HF and non-HF related sources across the site.	potentially complex, spatially and temporally dynamic mixture of air pollutants from multiple HF and non-HF-related sources across the site. Figure 4 Replaced with map of Combabula site
Section 3.2.1 Air Quality Monitoring Station (AQMS) The AQMS will be comprised of two separate air conditioned mobile laboratories (Figure 5) provided by Ecotech Pty Ltd (Brisbane Queensland, Australia). These enclosures are purpose built for housing high quality, sensitive measurement systems and come complete with masts, inlets and require mains 240V power supply. One enclosure will house a suite of Ecotech owned and operated instrumentation to measure carbon monoxide (CO), Nitrogen dioxide (NO_2), ozone (O_3), methane (CH_4), particulates (PM_{10} & $PM_{2.5}$), and black carbon. The proposed instrumentation to be installed in the AQMS is summarised in Table 3. For measurements of gas phase species at the AQMS, ambient air will be drawn through a glass inlet height ~ 3.5 m into a common manifold via an inlet fan that provides ~20 LPM of constant flow at low pressure from which instruments draw their sampling flows via Teflon tubing by way of individual vacuum pumps. The data from each instrument will be analysed by Ecotech Pty Ltd, and the data will provided to CSIRO for Quality Assurance and reporting. A second enclosure located at the site will house CSIRO instrumentation including a proton transfer reaction mass spectrometer (PTR-MS) for continuous VOC measurements, systems for integrated sampling of VOCs onto adsorbent tubes and DNPH cartridges and collection of particulate samples onto filters, as well as instrumentation for measurements of gaseous mercury, radon and PAHs.	**Section 3.2.1 AQMS** The AQMS are air-conditioned mobile laboratories (Figure 5) provided by Ecotech Pty Ltd (Brisbane, Queensland, Australia). 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 proposed instrumentation to be installed in the AQMS at both the northern and southern sites is summarised in Table 3. The AQMS in the south of the field (AQMS South) will be comprised of two separate but co-located enclosures. One enclosure will house a suite of Ecotech owned and operated instrumentation to measure carbon monoxide (CO), Nitrogen dioxide (NO_2), ozone (O_3), methane (CH_4), particulates (PM_{10} & $PM_{2.5}$) and black carbon. For measurements of gas phase species at this AQMS, ambient air will be drawn through a glass inlet height ~3.5 m into a common manifold via an inlet fan that provides ~20 LPM of constant flow at low pressure from which instruments draw their sampling flows via Teflon tubing by way of individual vacuum pumps. The data from each instrument will be analysed by Ecotech Pty Ltd, and the data will be provided to CSIRO for quality assurance and reporting. A second enclosure located at the site will house CSIRO instrumentation including a proton transfer reaction mass spectrometer (PTR-MS) for continuous VOC measurements, systems for integrated sampling of VOCs onto adsorbent tubes and DNPH cartridges, and a collection of particulate samples onto filters. The AQMS in the north of the field (AQMS North) will be comprised of a single AQMS enclosure housing a matching suite of Ecotech owned and operated instrumentation to measure carbon monoxide (CO), nitrogen dioxide (NO_2), ozone (O_3), methane (CH_4), particulates (PM_{10} & $PM_{2.5}$) as well as instrumentation for measurements of gaseous mercury, radon and PAHs provided by CSIRO and project partners Macquarie University and the Australian Nuclear Science and Technology Organisation (ANSTO). Table 2 has been re-numbered to Table 3.

	Table 3 has been revised to include a column indicating which instruments will be deployed in the AQMS north and south sites.
Section 3.2.2 Perimeter sites Due to their remote location the perimeter monitoring systems will be battery/solar powered, portable, and weather proof. Each perimeter site will incorporate an AS510 remote air quality monitor (Atmospheric Sensors, Bedforshire UK) which utilises a series of electrochemical sensors to continuously measure CO, NO, NO_x, O_3 and light scattering sensors to measure particulates (PM_{10}, $PM_{2.5}$). These monitors are small (257 x 105 x 210 mm), low power (12 V), low cost, weather-proof systems well suited to deployment in the remote perimeter sites in the proposed study. The AS510 monitors are Tier 3 methods and their performance is highly dependent on operating conditions (temperature, RH), and the monitors have the potential for artefact formation due to ozone, and drift in zero and span. However with appropriate set-up, validation procedures, post-processing and artefact removal these sensors can provide quantitative measurements of selected air pollutants (Mead et al., 2013). This requires specialist knowledge of the sensor performance, field conditions and the applied data processing algorithms. Data from these sensors will be sent via telemetry directly to Atmospheric Sensors for processing. As part of this study CSIRO have engaged an expert in electrochemical sensor systems, Dr Mead, from Cranfield University, Bedforshire UK, who took the lead in quantifying the performance of autonomous electrochemical sensors via comparison to research-quality instrumentation during the NASA-led DISCOVER-AQ field campaigns. Six AS510 units will be deployed as part of the study: one unit will be permanently located at the AQMS for comparison with Tier 1 and 2 methods; one each will be located at the four perimeter sites; and the remaining one will be a mobile transfer standard that will be operated at each perimeter site for a period of one week, and the AQMS for three weeks during monitoring in order to characterise the performance of each of the sensors deployed with minimal instrument downtime. Following the HF monitoring period, all six AS510 sensors will be collocated at an AQMS for comparison with NEPM methods. Likewise, five perimeter site units will be deployed as part of the study each containing a Microvol for PM_{10} mass and composition measurement and an Esampler for $PM_{2.5}$ mass and composition measurement.	Section 3.2.2 Perimeter sites Due to their remote location, the perimeter monitoring systems will be solar-battery powered, portable, and weather proof. Each perimeter site will incorporate a Microvol for PM_{10} sampling and mass analysis, an E-sampler for continuous $PM_{2.5}$ concentration measurement. The Ecotech AQMS will both use Palas Fidas Optical light scattering instruments for continuous PM_{10} and $PM_{2.5}$ measurement. AQMS South will also have a PM_{10} Low Volume sampler for gravimetric mass determination (see Table 3). The Ecotech AQMS will both use Palas Fidas Optical light scattering instruments for continuous PM_{10} and $PM_{2.5}$ measurement. AQMS South will also have a PM_{10} Low Volume sampler for gravimetric mass determination and composition analysis (see Table 3). To establish equivalence in the results obtained from the different AQMS and perimeter site PM instruments one perimeter unit will be located permanently at the AQMS North site. Following the HF monitoring period, all five perimeter site units will be collocated at an AQMS for comparison across methods. The perimeter sites will also contain sampling equipment for integrated 12-hour sampling of VOCs onto adsorbent tubes (US EPA Compendium method TO-17, US EPA 1999) and 24 h sampling of aldehydes onto DNPH cartridges (US EPA Method TO-11A, US EPA 1999). Locating a perimeter site unit at AQMS North site has the additional advantage of providing measurements of VOCs and aldehydes which could not incorporated into the AQMS North instrumentation suite.

Different PM measurement techniques will be employed at the AQMS a Palas Fidas Optical light scattering instrument (PM$_{10}$ and PM$_{2.5}$) and a PM$_{10}$ Low Volume sampler for gravimetric mass determination (see Table 2). In order to establish equivalence in the results obtained from the different AQMS and perimeter site particle instruments one perimeter unit will be a mobile transfer standard that will be operated at each perimeter site for a period of one week, and the AQMS for three weeks during monitoring in order to characterise the performance of each of the sensors deployed with minimal instrument downtime. Following the HF monitoring period, all five perimeter Site Units will be collocated at an AQMS for comparison with NEPM methods.

The perimeter sites will also contain sampling equipment for integrated 12 h sampling of VOCs onto adsorbent tubes, 24 h sampling onto DNPH cartridges, 7 day integrated samples of PM$_{10}$ mass on filters and continuous PM$_{2.5}$ concentration with 7 day PM$_{2.5}$ mass on filters. The instrumentation to be installed at the perimeter sites are summarised in The instrumentation **to be incorporated into the perimeter sites is summarised in**

Table 4. Due to their remote location, the perimeter monitoring systems will be solar-battery powered, portable, and weather proof. Each perimeter site will incorporate a Microvol PM$_{10}$ sampler for mass analysis, and an E-sampler for continuous PM$_{2.5}$ concentration measurement and mass analysis.

The Ecotech AQMS will both use Palas Fidas Optical light scattering instruments for continuous PM$_{10}$ and PM$_{2.5}$ measurement. AQMS South will also have a PM$_{10}$ Low Volume sampler for gravimetric mass determination and composition analysis (see Table 3). To establish equivalence in the results obtained from the different AQMS and perimeter site PM instruments, one perimeter unit will be located permanently at the AQMS North site. Following the HF

monitoring period, all five perimeter site units will be collocated for comparison across methods.

The perimeter sites will also contain sampling equipment for integrated 12 h sampling of VOCs onto adsorbent tubes (US EPA Compendium method TO-17, US EPA 1999a) and 24 h sampling of aldehydes onto DNPH cartridges (US EPA Method TO-11A, US EPA 1999b). Locating a perimeter site unit at AQMS North site has the additional advantage of providing measurements of VOCs and aldehydes which could not incorporated into the AQMS North instrumentation suite.

It is important to reiterate that the measurement techniques listed in Error! Not a valid bookmark self-reference. **and 4 for BTEX and formaldehyde can measure many other VOC species. Likewise, the proposed PM_{10} analysis techniques—including elemental analysis, soluble ion analysis, and anhydrous sugars analysis—will provide detailed information on the composition of PM_{10} (see Appendix A.5. for details). Additional species from these analyses will be included in reporting if found to be associated with potential negative impacts on air quality associated with HF at the site, or are useful for characterising the sources of PM, VOCs or other air pollutants at the site.**

Table 4.

Section 3.3 Proposed Sampling Schedule	Section 3.3 Proposed sampling schedule
3.3.1 Baseline and Post-HF measurements	Merged subsections 3.3.1 and 3.3.2
The planned start date for HF injection activities at the study site is 1 June 2017. The planned sampling schedule will comprise 5 days of sampling prior to the commencement of HF injections, and 5 days after well	The planned start date for HF injection activities at the study site is August 2017. All measurements of key air

completions are scheduled to finish. Usually 5 days prior to HF would not be considered an adequate sampling period to establish baseline for a given site however, as described in Section 2.3, significant existing air quality measurements have been undertaken in this area since 2014 as part of the SBAAQ Study in this area of the Surat Basin including 5 AQMS (measuring NO_x, CO, O_3, $PM_{2.5}$ and PM_{10} and at some locations Methane) along with 10 passive Radiello VOC monitoring sites. Combined these existing monitoring programs will provide important baseline information on pollutant levels in the Surat Basin. Furthermore, the data reported for the proposed HF study will be compared with measurements taken simultaneously at SBAAQ Study sites not directly impacted by HF activities.

Additional passive VOC monitoring at 7 locations was deployed at the proposed study site and a neighbouring property in October 2016 and will continue through to late 2017. Some measurements at the AQMS including NO_x, CO, O_3, PM, and Methane will also continue at the site after HF operations until the end of 2017. Overall these ongoing monitoring programs will provide important information on air quality at the site before and after HF.

Section 3.3.2 Air Quality Monitoring During HF Operations

The measurement methods outlined in Table 3 and The instrumentation **to be incorporated into the perimeter sites is summarised in**

Table 4. Due to their remote location, the perimeter monitoring systems will be solar-battery powered, portable, and weather proof. Each perimeter site will incorporate a Microvol PM_{10} sampler for mass analysis, and an E-sampler for continuous $PM_{2.5}$ concentration measurement and mass analysis.

The Ecotech AQMS will both use Palas Fidas Optical light scattering instruments for continuous PM_{10} and $PM_{2.5}$ measurement. AQMS South will also have a PM_{10} Low Volume sampler for gravimetric mass determination and composition analysis (see

pollutants will be undertaken for some period before, during and after hydraulic fracturing activities.

The measurement methods outlined in Tables 3 and 4 include a combination of continuous and integrated sampling techniques. Continuous measurements of NO_x, CO, O_3, PM, methane and VOCs by PTR-MS (Table 3) at the AQMS, are planned to start in mid-July 2017. Measurements at one of these stations will cease ~20 days after HF completion, and measurements of NO_x, CO, O_3, PM and methane at the other will continue through to late 2017. Passive VOC monitoring at four locations was deployed at the proposed study site in June 2017 and will also continue through to late 2017.

Integrated sampling techniques involve sampling (12-hour, 24-hour, weekly) onto media such as filters, adsorbent tubes, DNPH cartridges. The collection and analysis of these integrated samples is more costly and labour intensive than many continuous techniques and as such the integrated techniques will be deployed for shorter periods before, during and after hydraulic fracturing activities.

The collection of integrated samples onto filters and sampling tubes/cartridges will be performed for the following periods:

Before HF: minimum of 10 days prior to the commencement of HF injections.

During HF: integrated sampling is planned to occur over the entire period of HF injection estimated at ~25 days based on 10 wells schedule to undergo HF at the site with additional time for flow-back and completions to finish at the final well site. On average HF treatments occur over two days per well.

After HF: minimum of 10 days after well completions are scheduled to finish.

Ten days prior to HF could be considered inadequate to establish baseline for a given site; however, as described in Section 2.3.1, existing air quality measurements have been undertaken in the Miles–Chinchilla–Condamine area of the Surat Basin since 2014 as part of the SBAAQ Study. These existing monitoring programs will provide important information on regional pollutant levels in the Surat Basin at sites not directly impacted by HF activities.

Deleted previous Table 4 Proposed sampling schedule

Table 3). To establish equivalence in the results obtained from the different AQMS and perimeter site PM instruments, one perimeter unit will be located permanently at the AQMS North site. Following the HF monitoring period, all five perimeter site units will be collocated for comparison across methods.

The perimeter sites will also contain sampling equipment for integrated 12 h sampling of VOCs onto adsorbent tubes (US EPA Compendium method TO-17, US EPA 1999a) and 24 h sampling of aldehydes onto DNPH cartridges (US EPA Method TO-11A, US EPA 1999b). Locating a perimeter site unit at AQMS North site has the additional advantage of providing measurements of VOCs and aldehydes which could not incorporated into the AQMS North instrumentation suite.

It is important to reiterate that the measurement techniques listed in Error! Not a valid bookmark self-reference. **and 4 for BTEX and formaldehyde can measure many other VOC species. Likewise, the proposed PM$_{10}$ analysis techniques—including elemental analysis, soluble ion analysis, and anhydrous sugars analysis—will provide detailed information on the composition of PM$_{10}$ (see Appendix A.5. for details). Additional species from these analyses will be included in reporting if found to be associated with potential negative impacts on air quality associated with HF at the site, or are useful for characterising the sources of PM, VOCs or other air pollutants at the site.**

Table 4 include a combination of continuous and integrated sampling techniques. All measurements of key air pollutants will be undertaken for some period before, during and after hydraulic fracturing activities. Continuous methods will be operated before, during and after the HF period estimated at ~50 days. Integrated sampling techniques involve sampling (12h, 24h, weekly) onto media such as filters, adsorbent tubes, DNPH cartridges. The collection and analysis of these integrated samples are more costly and labour intensive than many continuous techniques and as such the integrated techniques will be deployed for ~ 36 days including periods before, during and after hydraulic fracturing activities. The sampling schedule is designed to:

Capture pre- and post HF periods

Target periods when wells in the southern half of the field, in proximity (< 2km) to the AQMS are undergoing HF treatment.

Cover periods when different types of HF injection processes are in use.

The different HF stimulation process planned for each well at the study are listed in Table 4. Origin Energy have provided brief descriptions of each these processes and they are provided in Appendix B.

A proposed sampling schedule for the continuous and integrated sampling methods is listed in The planned **start date for HF injection activities at the study site is August 2017. All measurements of key air pollutants will be undertaken for some period before, during and after hydraulic fracturing activities.**

The measurement methods outlined in Table 3 and

Table 4 include a combination of continuous and integrated sampling techniques. Continuous measurements of NO_x, CO, O_3, PM, methane and VOCs by PTR-MS at the AQMS are planned to start in mid-July 2017. Measurements at one of these stations will cease ~20 days after HF completion, and measurements of NO_x, CO, O_3, PM and methane at the other will continue through to late 2017. Passive VOC monitoring at four locations was deployed at the proposed study

site in June 2017 and will also continue through to late 2017.

Integrated sampling techniques involve sampling (12-hour, 24-hour, weekly) onto media such as filters, adsorbent tubes, DNPH and PUF cartridges. The collection and analysis of these integrated samples is more costly and labour intensive than many continuous techniques and as such the integrated techniques will be deployed for shorter periods before, during and after HF activities.

The collection of integrated samples onto filters and sampling tubes/cartridges will be performed for the following periods:

- **Before HF: minimum of 10 days prior to the commencement of HF injections.**
- **During HF: integrated sampling is planned to occur over the entire period of HF injection, estimated at ~25 days based on 10 wells schedule to undergo HF at the site with additional time for flow-back and completions to finish at the final well site. On average HF treatments occur over two days per well.**
- **After HF: minimum of 10 days after well completions are scheduled to finish.**

Ten days prior to HF could be considered inadequate to establish baseline for a given site; however, as described in Section 2.3.1, existing air quality measurements have been undertaken in the Miles–Chinchilla–Condamine area of the Surat Basin since 2014 as part of the SBAAQ Study. These existing monitoring programs will provide important information on regional pollutant levels in the Surat Basin at sites not directly impacted by HF activities.

. The schedule is arranged in order that each well will undergo HF (wells identified by their unique ID No, see Figure 5 for locations). The dates for the start of HF to

the end of well completion are listed along with the HF process planned for each well. The location of the wells and the number order in which they will undergo HF are also shown in the map in Figure 4 in relation to their location to the proposed perimeter and AQMS sites.	
Section 3.6 Other sources of information The following sections provide a brief description of the monitoring data and information that will be collected by industry and CSIRO and made available for analysis and reporting in the proposed air quality study. The data from accompanying industry and CSIRO monitoring will provide useful information to assess the potential for surface water, groundwater, HF chemicals and soil/sand at the site to act as local sources of air pollutants. **Section 3.6.1 GISERA Surat Basin Ambient Air Quality (SBAAQ) Study** The previously mentioned SBAAQ Study (Lawson et al 2016) comprises 5 ambient air quality monitoring stations and 10 sites at which volatile organic compounds (VOCs) are being monitored by passive samplers. Measurements commenced in 2015 and the data provides critical longer term information on the levels of air pollutants across the Surat Basin. This data will provide a longer term regional measurement of air pollutant levels against which any local enhancements in VOCs observed during HF activities in this study can be compared.	**Section 3.6 Other sources of information** In addition to existing air quality measurement data as outlined in Section 2.3, other information will be collected by industry and CSIRO and made available for analysis and reporting in the proposed air quality study. The data from accompanying industry and CSIRO monitoring will provide useful information to assess the potential for surface water, groundwater, HF chemicals and soil/sand at the site to act as local sources of air pollutants. These information sources include but are not limited to the following. Deleted 3.6.1 repetitive - info previously discussed in section 2.3
Section 4 Summary This report presents a proposed methodology for an air quality study of the impacts of hydraulic fracturing activities on local air quality. The methodology comprises a suite of measurements of atmospheric gaseous and particle species to be undertaken before, during and after hydraulic fracturing at a selected site in the Surat Basin. The aim of the proposed methodology is to address the study objectives as outlined below: Objective 1 - Quantify enhancements in air pollutant levels above background that occur during HF operations. The data from the proposed methodology will be used to address objective 1 by: Comparison of data from HF site with simultaneous measurements at nearby Miles Airport and other AQMS in SBAAQ study network. Comparison of data from HF site with measurements taken at the site prior to HF operations Objective 2 - Provide information on the contribution of HF and non-HF related sources of air pollutants to local	**Section 4 Summary** This report presents a proposed methodology for a study of the impacts of HF activities on local air quality. The methodology comprises a suite of measurements of atmospheric gaseous and particle species to be undertaken before, during and after HF at a selected site in the Surat Basin. The aim of the proposed methodology is to address the following study objectives. Objective 1: Quantify enhancements in air pollutant levels above background that occur during HF operations. The data from the proposed methodology will be used to address Objective 1 by comparison of data from the HF site with: simultaneous measurements at other AQMS in SBAAQ Study network. measurements taken at the site before and after 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. The data from the proposed methodology will be used to address objective 2 by:	air quality at the selected study site. The data from the proposed methodology 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.	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 air pollutant load. For instance, the Al/Si ratio in elemental composition analysis of PM_{10} can be used to estimate contribution of soil (Al) and sand (Si) including proppant to total PM_{10} load. Likewise, that ratio of benzene to CO differs between diesel exhaust and wood smoke emissions; levoglucosan can also be used as a tracer for woodsmoke.	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 air pollutant load. For instance, the Al/Si ratio in elemental composition analysis of PM_{10} can be used to estimate contribution of soil (Al) and sand (Si) including proppant to total PM_{10} load. Likewise, that ratio of benzene to CO differs between diesel exhaust and wood smoke emissions; levoglucosan can also be used as a tracer for woodsmoke.
Statistical analysis methods will be applied to the whole dataset to investigate pollutant sources. This may include analyses such as positive matrix factorisation (see 0) if an adequate number of samples of sufficient quality are successfully collected.	statistical analysis methods, which will be applied to the whole dataset to investigate pollutant sources. This may include analyses such as positive matrix factorisation (see 0) if an adequate number of samples of sufficient quality are successfully collected.
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 proposed methodology will be used to address objective 3 by:	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 proposed methodology will be used to address Objective 3 by:
Employing where possible, Australian Standard measurement techniques (Tier 1) and properly validated Tier 2 and 3 techniques to provide data that are directly comparable to NEPM and Qld EPP ambient air quality guidelines.	employing where possible, Australian Standard measurement techniques (Tier 1) and properly validated Tier 2 and 3 techniques to provide data that are directly comparable to NEPM and Queensland EPP ambient air quality guidelines
Providing compatible data from HF site for comparison measurements taken simultaneously nearby at Miles Airport and other AQMS in SBAAQ study network.	providing compatible data from HF site for comparison measurements taken simultaneously at other AQMS in SBAAQ Study network
Providing compatible data for comparison with measurements taken simultaneously at other locations not impacted by CSG activities, including other areas of Queensland via data from the Qld EPA ambient air quality network.	providing compatible data for comparison with measurements taken simultaneously at other locations not impacted by CSG activities, including other areas of Queensland via data from the Queensland EPA ambient air quality network
Providing compatible data for comparison with historical measurements at other locations, not impacted by CSG activities, where CSIRO has deployed similar instrumentation.	providing compatible data for comparison with historical measurements at other locations, not impacted by CSG activities, where CSIRO has deployed similar instrumentation.

Section 4.1 Timelines and milestones	**Section 4.1 Timelines and milestones**
The GISERA Hydraulic Fracturing Study, comprising the currently underway Phase 1 research and the proposed Phase 2 measurement programs will provide detailed information on the impact of HF on air, soil and water quality in the vicinity of coal seam gas wells in an Australian gas field. The data and reports generated as part of this project will be made publicly available via the GISERA website for use by individuals, communities, research organisations, governments and industry.	The GISERA Hydraulic Fracturing Study, comprising the currently underway Phase 1 research and the proposed Phase 2 measurement programs, will provide detailed information on the impact of HF on air, soil and water quality in the vicinity of coal seam gas wells in an Australian gas field. The data and reports generated as part of this project will be made publicly available via the GISERA website for use by individuals, communities, research organisations, governments and industry.
The timeline for the proposed air quality study and reporting are listed below:	The timeline for the proposed air quality study and reporting are listed below:
June – July 2017- Measurement Period	July– September 2017: Measurement Period
October 2017 - Report of Data Capture and preliminary analysis of VOC radiello data from October 2016 to August 2017 at two sites before, during and after hydraulic fracturing.	November 2017: Report of Data Capture and preliminary analysis of VOC radiello data from October 2016 to August 2017 at two sites before, during and after HF.
October 2018 - Draft final "The impacts of hydraulic fracturing on air quality in the vicinity of well sites in the Surat Basin, Queensland" for peer review.	October 2018: Draft final report, *The impacts of hydraulic fracturing on air quality in the vicinity of well sites in the Surat Basin, Queensland* for peer review.
December 2018 – Final report "The impacts of hydraulic fracturing on air quality in the vicinity of well sites in the Surat Basin, Queensland"	December 2018: Deliver final report, *The impacts of hydraulic fracturing on air quality in the vicinity of well sites in the Surat Basin, Queensland*.
	Appendix A – reference to AS510 monitors removed.

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